

ACKNOWLEDGMENTS

Chapter

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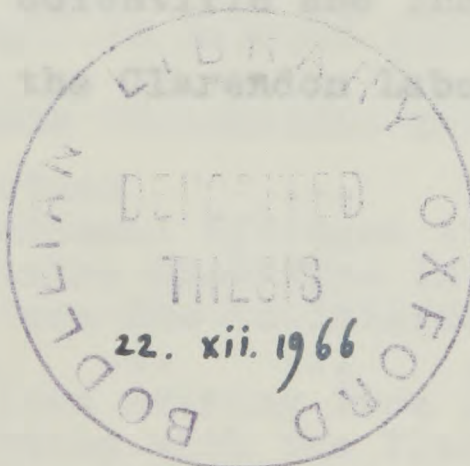
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A thesis submitted for the degree of
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Chapter

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CONTENTS

<u>Chapter</u>		<u>Page</u>
1	INTRODUCTORY	1.1
2	EXPERIMENTAL APPARATUS	
	2.1 Spectrometers	2.1
	2.2 The N.M.R. System	2.3
	2.3 Cavities	2.5
	2.4 Cryogenics	2.7
3	DIVALENT THULIUM IN CALCIUM FLUORIDE	
	3.1 Introduction	3.1
	3.2 Simple Crystal Field Theory	3.6
	3.3 Second Order Corrections	3.13
	3.4 Thulium E.P.R. Measurements	3.20
	3.5 Thulium ENDOR Measurements	3.21
	3.6 Possible Corrections to Observed ENDOR Frequencies	3.23
	3.7 Evaluation of the Nuclear Moment	3.26
	3.8 Discussion	3.27
4	FLUORINE ENDOR OF $\text{CaF}_2:\text{Tm}$	
	4.1 ENDOR Frequencies	4.1
	4.2 Determination of Hyperfine Parameters	4.4
	4.3 Nearest Neighbour Parameters	4.6
	4.4 Discussion	4.7
	4.5 ENDOR Linewidths	4.14
	Addendum to Chapter 4	4.19
5	BONDING OF Tm^{2+} IN CALCIUM FLUORIDE	5.1
6	ATOMIC HYDROGEN IN ALKALINE EARTH FLUORIDES	
	6.1 Introduction	6.1
	6.2 Substitutional Hydrogen Atoms in CaF_2	6.5
	6.3 The Fluorine Hyperfine Interaction	6.9
	6.4 Corrections Due to Interaction with the Proton	6.16
	6.5 Corrections Arising from Second Order Interaction with the Fluorine System	6.17
	6.6 Evaluation of E.P.R. Parameters	6.21
	6.7 Annealing of the Spectrum of Substitutional Hydrogen in CaF_2	6.23
	6.8 Hydrogen in Strontium Fluoride	6.24
	6.9 Annealing of the $\text{SrF}_2:\text{H}$ Substitutional Spectrum	6.26

<u>Chapter</u>		<u>Page</u>
	6.10 Hydrogen in BaF_2	6.27
	6.11 The Forbidden Transitions	6.29
	6.12 Formation and Annealing Mechanisms .	6.33
	6.13 The E.P.R. Parameters	6.41
7	FLUORINE ENDOR OF SUBSTITUTIONAL HYDROGEN ATOMS IN CALCIUM FLUORIDE	
	7.1 Introduction... ..	7.1
	7.2 ENDOR of Distant Fluorine Shells ...	7.2
	7.3 Angular Characteristics of ENDOR Spectra	7.5
	7.4 (110) Plane Angular Plot	7.8
	7.5 Discussion of (110) Plane Angular Plot	7.9
	7.6 Angular Plot in the (111) Plane ...	7.11
	7.7 Hyperfine Parameters for Distant Shells	7.13
	7.8 Discussion of Hyperfine Parameters of Distant Shells	7.16
	7.9 Interstitial Fluorine Ions	7.19
	7.10 Associated F Centres	7.20
	7.11 ENDOR of Interstitial Hydrogen Atoms	7.20
	7.12 Nearest Neighbour Fluorine ENDOR ...	7.21
	7.13 Magnetic Field Dependence	7.24
	7.14 Second Order Fluorine Hyperfine Inter- action	7.25
	7.15 Effect of Using Different EPR Lines	7.26
	7.16 ENDOR Determination of A_1	7.27
	7.17 Nearest Neighbour Angular Variation	7.28
	7.18 Conclusion	7.29
8	EXPERIMENTAL TECHNIQUES	
	8.1 More Accurate Determination of g value	8.1
	8.2 Measurement of ENDOR lines... ..	8.5
	8.3 Measurement of E.P.R. Multiplets ...	8.6
	APPENDIX	
	Angular Characteristic of Ligand Hyper- fine Structure in Cubic Crystals..	A.1

Abstract

An ENDOR spectrometer has been designed and constructed which is capable of operating at 9000 Mc/s or 23,000 Mc/s. Simple 115 kc/s field modulation detection is used and the nuclear resonance power is frequency modulated. Nuclear transitions are detected as a change in the dispersive component of the E.P.R. signal. Apart from conventional cryogenics allowing the use of temperature down to that of pumped helium a second system allows X-irradiation of the sample at similar temperatures while actually in the X or K band microwave cavity.

Detailed E.P.R. and ENDOR measurements have been made of $^{169}\text{Tm}^{2+}$ ions and hydrogen atoms in CaF_2 .

Tm^{2+} ions on interstitial sites with eightfold cubic co-ordination are produced by X-irradiation of $\text{CaF}_2:\text{Tm}^{3+}$ at room temperature. The E.P.R. spectrum observed at 20°K has two lines, showing poorly resolved fluorine structure, about 30 G wide whose positions are described by

$$\mathcal{K} = g\beta\mathbf{H}\cdot\mathbf{S} + A\mathbf{I}\cdot\mathbf{S}$$

with $S = \frac{1}{2}$, $I = \frac{1}{2}$, $g = 3.452 \pm 0.003$ and $|A| = (368 \pm 2) \times 10^{-4} \text{ cm.}^{-1}$

The ground configuration of Tm^{2+} is $4f^{13}$, ^2F . The spin orbit coupling splits the ground term by $\frac{7}{2} \zeta$ into $J = \frac{7}{2}$ and $J = \frac{5}{2}$ with $J = \frac{7}{2}$ lowest. $\zeta = 2513 \text{ cm.}^{-1}$ in CaF_2 . The cubic field splits $J = \frac{7}{2}$ into two doublets, Γ_6 , Γ_7 , and a quartet,

Γ_8 , with Γ_7 lowest. $J = \frac{5}{2}$ is split into a doublet, Γ_7' , and a quartet Γ_8' . Kiss (1962) has measured directly by optical fluorescence the energies of Γ_8 , Γ_7' and Γ_8' . Second order crystal field effects admix to the Γ_7 groundstate an amplitude $\alpha = 0.0487$ of the Γ_7' doublet. The g value calculated for this groundstate is 0.022 greater than the experimental value because of covalency. The values are reconciled by introducing an orbital reduction factor $k = 0.991 \pm 0.001$.

The experimental hyperfine parameter is corrected for the core polarisation contribution, estimated at + 13.7 Mc/s, and for the orbital reduction factor, leading to an estimate of the hyperfine parameter of a free Tm^{2+} ion of 382.4 Mc/s. Comparison with Ritter's (1962) atomic beam measurements on the Tm atom indicates a value of $\langle r^{-3} \rangle$ for Tm^{2+} greater by 2% than for the atom. This is consistent with Judd and Lindgren's (1961) calculations of 10.51 a.u. for Tm^0 and 10.95 a.u. for Tm^{3+} .

Thulium ENDOR measurements give a much more precise value for the hyperfine parameter of 1101.376 ± 0.004 Mc/s. An apparent nuclear g value for ^{169}Tm is derived of 0.756 ± 0.005 (n.m.). A correction of -0.288 due to second order perturbation via the magnetic field and hyperfine interaction is calculated from Kiss' results for the positions of excited states. The resulting nuclear moment

$\mu_n = -0.234 \pm 0.003$ n.m. is close to Ritter's atomic beam value of -0.229 ± 0.003 n.m.

Fluorine ENDOR of $\text{CaF}_2:\text{Tm}^{2+}$ was used to measure the hyperfine interaction with fluorine shells 1, 2, 3 and 4. Only the first shell differs significantly from a classical magnetic point dipolar interaction. The first shell parameters are $A_s = 2.584 \pm 0.01$ Mc/s and $A_p = 12.283 \pm 0.01$ Mc/s, both with the same sign. The classical point dipolar interaction is $+9.809$ Mc/s, indicating the choice of positive sign for A_p and a contribution due to bonding of 2.474 Mc/s. This is contrary to Watson and Freeman (1961) who predict a polarisation spin density at the extremity of a rare earth ion which is antiparallel to that of the 4f electrons.

The measured first shell parameters are adequate to explain the EPR line structure as a superposition of forbidden transitions in which first shell fluorine nuclei are flipped.

The thulium and fluorine ENDOR linewidths behave as if inhomogeneously broadened and those for fluorine ENDOR agree with van Vleck's (1948) calculations for N.M.R. in CaF_2 .

The bonding of the Tm^{2+} ion to its ligands is described in terms of the molecular orbital picture. The Tm^{2+} ground state is expressed in terms of single f electron functions. These are augmented by combinations of ligand orbitals transforming according to the same representations of the cubic group. For Tm^{2+} both π and σ bonding occurs. Using the

independent bonding model, the one-electron hyperfine operator is applied to that part of the molecular orbital is centred on one ligand to give expressions for the isotropic and anisotropic hyperfine interactions. These are functions of the π , σ and s bonding parameters: f_π , f_σ , f_s and $(f_\sigma f_\pi)^{\frac{1}{2}}$. The experimental results do not give sufficient information to determine the bonding parameters separately.

X-irradiation at room temperature of hydrogenated CaF_2 produces interstitial hydrogen atoms (Hall and Schumacher 1962). X-irradiation below 100°K is found to produce hydrogen atoms on substitutional fluorine sites whose E.P.R. spectrum shows a resolved interaction with the six nearest fluorine nuclei. This is described by

$$\mathcal{H}^F = \sum_{n=1}^6 \left[\underline{S} \cdot \underline{A}_n^F \cdot \underline{I}_n^F - g_F \beta_n \underline{H} \cdot \underline{I}_n^F \right]$$

where $\underline{A}_n^F$ is axial. The solution of this Hamiltonian and derivation of the E.P.R. parameters are discussed.

At 145°K the hydrogen atoms move irreversibly to interstitial sites with perfect eightfold co-ordination.

Similar results are found for $\text{SrF}_2:\text{H}$ but $\text{BaF}_2:\text{H}$ gives rise only to a very weak substitutional spectrum.

All the hydrogen spectra in alkaline earth fluorides have g values greater than that of free hydrogen and it is suggested that this is due to charge transfer being important.

agree well with calculation.

The proton hyperfine interactions are all larger by up to 40 Mc/s than that for free hydrogen (1420 Mc/s) but this is only about 10% of the increase calculated if the fluorine hyperfine interaction is assigned only to overlap effects. Charge transfer is again suggested to account for the small size of the increases.

Fluorine ENDOR measurements on substitutional hydrogen in CaF_2 give spectra in principal crystal directions which cannot readily be interpreted. Angular plots were made ⁱⁿ (110) and (111) planes to enable the ENDOR lines to be identified. It emerges that the third and fourth shell fluorines have values of A_p equal to twice the classical point dipolar values and values of A_s of 1.371 ± 0.01 Mc/s and 0.806 ± 0.02 Mc/s respectively. This is explained as a transferred interaction via first shell fluorine 2p orbitals for the fourth shell and via nearest neighbour Ca^{2+} ions for the third shell. The second shell fluorines have A_p equal to 0.09 Mc/s less than the classical point dipolar value and A_s equals -0.020 ± 0.01 Mc/s. Overlap with excited π states on the first shell fluorines, admixed by spin-orbit coupling, is proposed to account for the effective negative bonding contribution.

ENDOR lines due to first shell fluorines confirm the E.P.R. parameters. Small shifts due to the proton and splitting due to indirect nuclear-nuclear interaction are observed and agree well with calculation.

References

- Hall, J.L. and Schumacher, R.T., 1962. Phys. Rev., 127, 1892.
- Judd, B.R. and Lindgren, I.P.K., 1961. Phys. Rev., 122, 1802.
- Kiss, Z.J., 1962. Phys. Rev., 127, 718.
- Ritter, G.J., 1962. Phys. Rev., 128, 2238.
- van Vleck, J.H., 1948. Phys. Rev., 74, 1168.
- Watson, R.E. and Freeman, A.J., 1961. Phys. Rev. Lett., 6, 277.

used in view of the following advantages:

(i) Much higher sensitivity than R.F.E. Nuclear transitions occur between levels with approximately the population difference appropriate to the electronic Boltzmann factor. The nuclear transition is detected by the absorption of a microwave photon rather than a V.M.F. photon. Measurements are, therefore, possible on dilute samples containing perhaps only 0.01% of nuclei of interest.

(ii) Higher resolution than R.F.E. In all the systems studied the R.F.E. lines were inhomogeneously broadened. By selecting only a narrow range of spin packets and looking at a nuclear rather than an electronic moment the NMR technique produced inhomogeneously broadened lines only 20-30 kc/s wide.

(iii) Selection of host lattice nuclei near to the paramagnetic centres. This allows measurement of hyperfine interactions with nuclei which form only a small fraction of the

Chapter I

INTRODUCTORY

The ENDOR principle was proposed and first demonstrated by Fehér (1956b, 1959) as a sequel to work on nuclear polarisation (1956a). It is now established alongside E.P.R. and N.M.R. as a standard spectroscopic technique.

This thesis reports ENDOR measurements on two impurities in CaF_2 , Tm^{2+} ions and hydrogen atoms. The ENDOR method was used in view of the following advantages:

(i) Much higher sensitivity than N.M.R. Nuclear transitions occur between levels with approximately the population difference appropriate to the electronic Boltzmann factor. The nuclear transition is detected by the absorption of a microwave photon rather than a V.H.F. photon. Measurements are, therefore, possible on dilute samples containing perhaps only 0.01% of nuclei of interest.

(ii) Higher resolution than E.P.R. In all the systems studied the E.P.R. lines were inhomogeneously broadened. By selecting only a narrow range of spin packets and looking at a nuclear rather than an electronic moment the ENDOR technique produced inhomogeneously broadened lines only 20-30 kc/s wide.

(iii) Selection of host lattice nuclei near to the paramagnetic centres. This allows measurement of hyperfine interactions with nuclei which form only a small fraction of the

total number of that species in the crystal.

The ENDOR principle was used without great concern over the mechanisms involved but we give here notes on techniques which have been successful. Feker's (1959) measurements on donors in silicon were made using the transient "packet shifting" method. The spectrometer was tuned to dispersion. The magnetic field was set to the centre of the inhomogeneously broadened line and a small high frequency field modulation applied. As the unmodulated N.M.R. oscillator was tuned through a nuclear transition frequency a transient change in E.P.R. signal level occurred.

Feker derives an expression for the magnetisation in phase with the microwave field (x') for an inhomogeneous line consisting of a distribution of spin packets $h(H_1 - H_0)$ as

$$M_x(H) = \pm M_0 \int_{-\infty}^{+\infty} \frac{h(H_1 - H_0) \cdot dH_1}{[1 + (H_1 - H)^2 / H_1^2]^{\frac{1}{2}}} \quad (1)$$

where M_0 is the static magnetisation; H_1 the circularly polarised microwave field amplitude and H_0 the field at the line centre. If the magnetic field is set on a spin packet at H_1 , of initial magnetisation M_1 , and field modulation $H_m \sin \omega_m t$, much larger than the spin packet width, is applied then, provided ω_m is high enough, repetitive adiabatic fast passage of the spin packets within $\pm H_m$ of H_1 will occur. In the intervals between reversals of the magnetisation of

each spin packet it will tend to relax towards its initial value. After many cycles of H_m the magnetisation of spin packets within the saturated part of the line, although alternating at ω_m , will reach an equilibrium amplitude. This amplitude depends on the distance of the spin packet from H_i and varies between zero at H_i and the initial value at $H_i \pm H_m$. Since lock-in detection is being used the detected signal is proportional to the component of x' varying at ω_m . Feker gives this as $(8/\pi^2)M_i \cos \omega_m t$. The chart recording of a slow sweep of the EPR line, therefore, follows the shape of M_x given by (1). This is very similar to the absorption lineshape, $h(H_i - H_0)$ and not the derivative of a dispersion curve. This agrees with the EPR lineshapes observed for $\text{CaF}_2:\text{Tm}^{2+}$ and $\text{CaF}_2:\text{H}$ in the present work.

Since $1/\omega_m$ is much shorter than T_1 a large number of cycles of field modulation is needed before the magnetisation of a spin packet falls to its equilibrium saturated value. During this period the detected signal at ω_m is larger than the final value and at the beginning of the saturation of each spin packet is proportional to $(4/\pi)M_i$. This is the basis of the ENDOR effect in this system. The induced nuclear transitions shift off-resonance, unsaturated spin packets into the saturated part of the EPR line. Similarly spin packets are removed from the saturated region to "cool off". There is a consequent transient increase in the detected EPR signal

which decays with characteristic time T_1 .

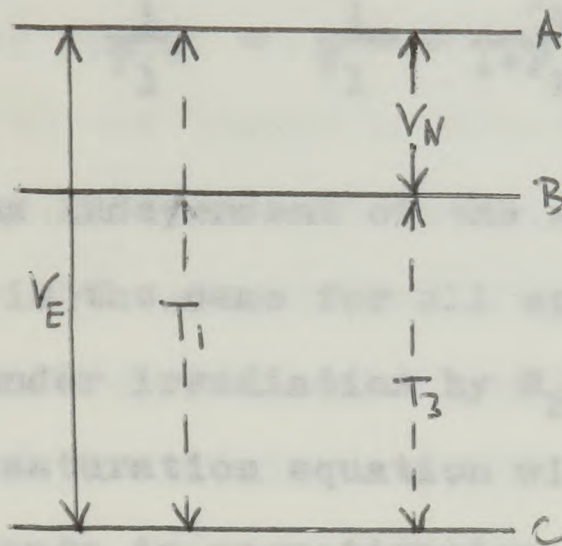
In Feker's sample T_1 was so long (many minutes) that there was no possibility of observing other than a transient ENDOR effect. However, in many other situations T_1 is much shorter; in the present work it is in the millisecond region. The packet shifting may then be performed repetitively by modulating the N.M.R. oscillator, giving much greater sensitivity. Spin packets are continuously shifted into and out of the saturated part of the EPR line. While off resonance they relax and are available for use on the next modulation cycle. Clearly the cycle time must be long enough for the saturated spin packets taken off resonance to relax but short enough that the transient change in EPR level occupies an appreciable part of the cycle. The NMR oscillator may be amplitude or frequency modulated with lock-in detection of the ENDOR signal. Frequency modulation makes adiabatic fast passage of the nuclear resonance possible. Both systems should reproduce the NMR lineshape either directly or differentiated.⁽⁶¹⁾ and Doyle (1962) used "adiabatic" ENDOR

Feker observed that with ENDOR of ligands the nearest neighbours gave an increase in EPR signal while more distant nuclei gave a decrease. We found the same effect for both Tm^{2+} and hydrogen in CaF_2 . It is shown strikingly in Fig. 4.1. For $H \parallel [100]$ the nearest neighbour fluorine hyperfine E.P.R. components are separated by only 2.6 Mc/s and the corresponding

ENDOR transitions (lines 1a) have the same phase as more distant fluorines. However, for $H \parallel [110]$ the EPR separations are 10 Mc/s and the corresponding ENDOR lines have reversed phase. This might be explained as follows. When the hyperfine interaction is large the nuclear transition brings a fresh spin packet into the saturated part of the EPR line giving an increase in EPR signal. If the hyperfine interaction is so small that the spin packet in question is actually in the saturated part of the line then the nuclear transition merely causes an interchange of partly saturated spin packets. Being in contact with the microwave field they should have a definite phase relationship. The nuclear transition upsets this, leading to a reduction in magnetisation and EPR signal. It was found that such ENDOR signals were considerably stronger than those from nearest neighbours. McIrvine, et. al. (1964) give evidence that the ENDOR effect for large hyperfine interaction is not due to dephasing of spin packets.

Seidel (1961) and Doyle (1962) used "stationary" ENDOR in the investigation of alkali halide F centres. In this method the EPR absorption signal is monitored and excitation of nuclear transitions causes a steady state change in EPR signal. No field modulation is used and the ENDOR signal is detected at the frequency of amplitude modulation of the N.M.R. oscillator. Seidel obtains good agreement with

experiment for a model in which the nuclear transitions effectively reduce the electronic relaxation time T_1 .



The saturated electronic transition is between levels A and C. Relaxation between the nuclear levels A and B is assumed non-existent or very slow. Levels B and C are coupled by a relaxation process characterised by $T_3 \gg T_1$. This may occur through cross relaxation or by uncorrelated electronic and nuclear relaxation processes. Inducing the nuclear transition $A \leftrightarrow B$ puts a second relaxation path $A \rightarrow B \rightarrow C$ in parallel with T_1 and increases the EPR absorption. For a short T_3 a large ENDOR signal may be obtained provided a large enough NMR field, H_2 , is available. Seidel found for alkali halide F centres that an amplitude of several gauss could be used.

For the nuclear transition $A \leftrightarrow B$ the spin lattice relaxation time is effectively T_3 . For a nuclear transition

probability P_N induced by the N.M.R. field the effective electronic spin lattice relaxation time T_1^* is given by

$$\frac{1}{T_1^*} = \frac{1}{T_1} + \frac{P_N}{1 + P_N T_3} \quad (2)$$

T_1^* is thus independent of the saturation of the EPR transition and is the same for all spin packets. The magnetisation under irradiation by H_2 can be described by Portis' (1953) saturation equation with T_1^* in place of T_1 . The relative change in magnetisation due to the irradiation, the ENDOR signal, is shown to vary with H_2 and the microwave field H_1 according to

$$\frac{\Delta \chi''}{\chi''_{\max}} = \frac{\frac{1}{8} \gamma_e^3 H_1^3 T_1^3}{\left(1 + \frac{1}{4} \gamma_e^2 H_1^2 T_1^2\right)^{3/2}} \cdot \frac{\frac{1}{4} \gamma_N^2 H_2^2 T_1 T_{2N}}{\left(1 + \frac{1}{4} \gamma_N^2 H_2^2 T_3 T_{2N}\right)} \quad (3)$$

The increase of ENDOR signal with H_1 or H_2 levels off as each becomes large. The maximum ENDOR signal is

$$\frac{\Delta \chi''_{\max}}{\chi''_{\max}} = \frac{T_1}{T_3} \quad (4)$$

showing the dependence on T_3 as a relaxation path in parallel with T_1 . For small H_2 the ENDOR signal is independent of T_3 since the relaxation bottle-neck is between levels A and B. For large H_2 T_3 is the limiting factor.

An ingenious ENDOR technique has been used by Mims (1965)

using spin echo detection of the EPR signal. A 90° microwave pulse turns the spins into the equatorial plane where they precess for a time τ with a distribution of phases relative to the microwave field. A second 90° pulse has an effect, which varies with the phases of the individual precessing spins, from turning them back to their original alignment to turning them to the antiparallel alignment. The overall effect is to leave a sinusoidal spectral pattern of periodicity $2\pi/\tau$ in place of the original smooth lineshape. A third 90° pulse turns this M_z pattern into the equatorial plane where phase convergence leads to emission of a stimulated echo signal a time τ later. The ENDOR effect is obtained by applying a pulse of N.M.R. power between microwave pulses 2 and 3. When the frequency is such as to induce transitions of nuclei coupled to the precessing spins the population difference between the two spin states is altered leading to a reduction in the periodic component of the magnetisation pattern M_z . The spin echo following the third pulse is thus reduced.

Since it does not depend on the balancing of relaxation times this ENDOR technique should be very sensitive in any system in which spin echoes are obtainable. N.M.R. frequencies as low as 200 kc/s have been used without difficulty. One disadvantage is that for small hyperfine interactions there are blind spots in the detection of nuclear transitions but these can be shifted in frequency by altering τ .

References to Chapter I

- Doyle, W.T., 1962. Phys. Rev., 126, 1421.
- Feker, G., 1956a. Phys. Rev., 103, 500.
- Feker, G., 1956b. Phys. Rev., 103, 834.
- Feker, G., 1959. Phys. Rev., 114, 1219.
- McIrvine, E.C., Lambe, J. and Laurance, N., 1964. Phys. Rev., 136, A467.
- Mims, W.B., 1965. Proc. Phys. Soc., 283, 452.
- Portis, A.M., 1953. Phys. Rev., 91, 1071.
- Seidel, H., 1961. Zeits. f. Phys., 165, 239.

Chapter 2

EXPERIMENTAL APPARATUS

2.1 Spectrometers

The ENDOR spectrometer was very similar in conception to that of Williams (1961 and Baker and Williams (1962)) and was designed in terms of a high sensitivity X-band E.P.R. spectrometer using 115 kc/s field modulation detection. (Bowers, Kamper and Knight (1957); Llewellyn (1957)). A detailed discussion of sensitivity considerations has been given by Feher (1957) and a rather shorter treatment of the salient points by Goldsborough and Mandel (1960). The nuclear resonance part of the equipment was designed initially to be used with the X-band spectrometer but could readily be coupled into a complementary K band E.P.R. spectrometer constructed by Mr. J.R. Pilbrow (1965). In fact much of the work reported here was carried out at K band.

Both spectrometers were designed for use with reflection cavities and used magic-T bridge detection, enabling the E.P.R. dispersion or absorption signals to be displayed. More than usual stability of microwave frequency is required for ENDOR to avoid unhelpful changes of E.P.R. saturation conditions during lengthy measurements. The X band source, by L.F.E., Boston, U.S.A., consisted of a Varian V58 klystron stabilised by reference to a tunable

discriminator cavity of invar. The nominal instability was not greater than 5 in 10^8 . The K band source was a Mullard R9602^c klystron stabilised to a reference cavity using a 0.5 Mc/s F.M. stabilisation system (George and Teaney (1960)). The measured instability was $1:10^5$ over one hour. This type of klystron is rather sensitive to magnetic interference which causes a high level of F.M. noise, so the cooling fan had to be mounted some three feet away. This also reduced mechanical noise from air turbulence. The complete answer, which would also have produced greater frequency stability, is to immerse the klystron in a thermostatted oil bath.

Fig. 2.1 shows the block diagram of the ENDOR spectrometer, applicable to both frequencies. The N.M.R. oscillator is frequency modulated at some low audio frequency over a fraction of the ENDOR linewidth. When a nuclear transition frequency is traversed this causes a modulation at the audio frequency of the D.C. output from the 115 kc/s phase-sensitive E.P.R. detector. After passing through a narrow band tuned audio amplifier (General Radio Type 1232A) and phase adjusting network this audio signal is phase-sensitively detected and displayed on the chart recorder with a suitable time constant of up to ten seconds.

Magnetic field was measured by a Newport Instruments

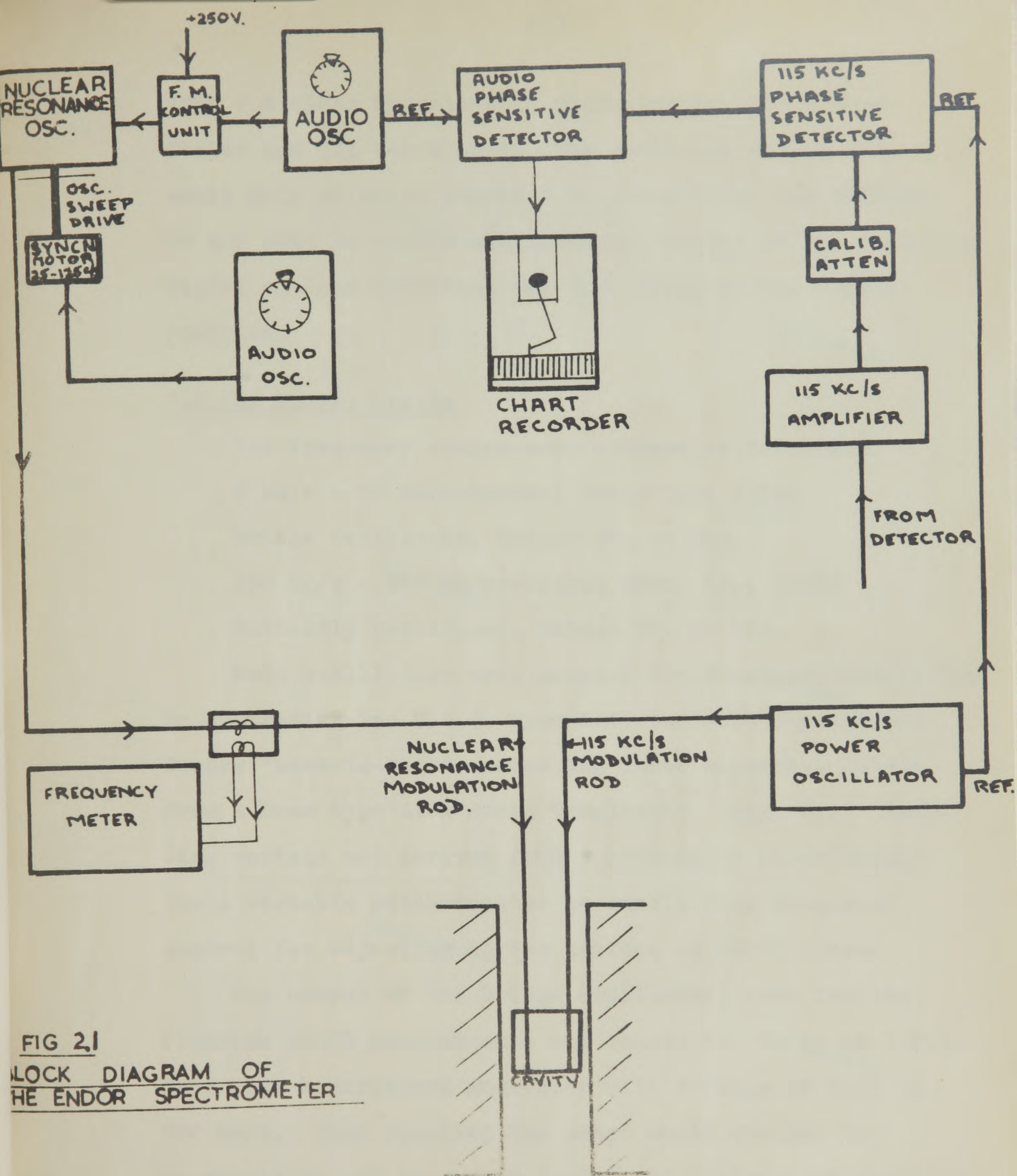


FIG 2.1

BLOCK DIAGRAM OF
THE ENDOR SPECTROMETER

Type P Nuclear Magnetometer using protons for X band fields and ^7Li for K band. The probe was fitted with a small pair of coils supplied by a variable, low voltage, 50 c/s unit to enable oscilloscope display of the resonance signal without affecting the D.C. field at the sample position.

2.2 The N.M.R. System

Two frequency ranges were covered as follows:-

5 kc/s - 50 Mc/s: General Radio Type 1330A

Bridge Oscillator. Output $\frac{3}{4}$ W. at 50 Ω .

250 Mc/s - 960 Mc/s: General Radio Type 1209B

Butterfly Oscillator. Output $\frac{1}{4}$ W. at 50 Ω .

Both oscillators were adapted for frequency modulation by connecting two G.E.C. Type SVC3 Variable Capacitance Diodes "back-to-back" across the tuned circuits, driven from a Dawe Type 440A Audio Oscillator. (Fig. 2.2) Biasing voltage was derived from a stabilised power supply via a variable potentiometer to enable fine frequency control for adjusting to the centres of ENDOR lines.

The output of the Bridge Oscillator, used for the fluorine ENDOR measurements was raised to 3W. by an I.F.I. Type 500A Distributed amplifier with a range of 0.22 to 220 Mc/s. When required the power could further be increased to 14W by an E.M.I. Type 2C Distributed amplifier

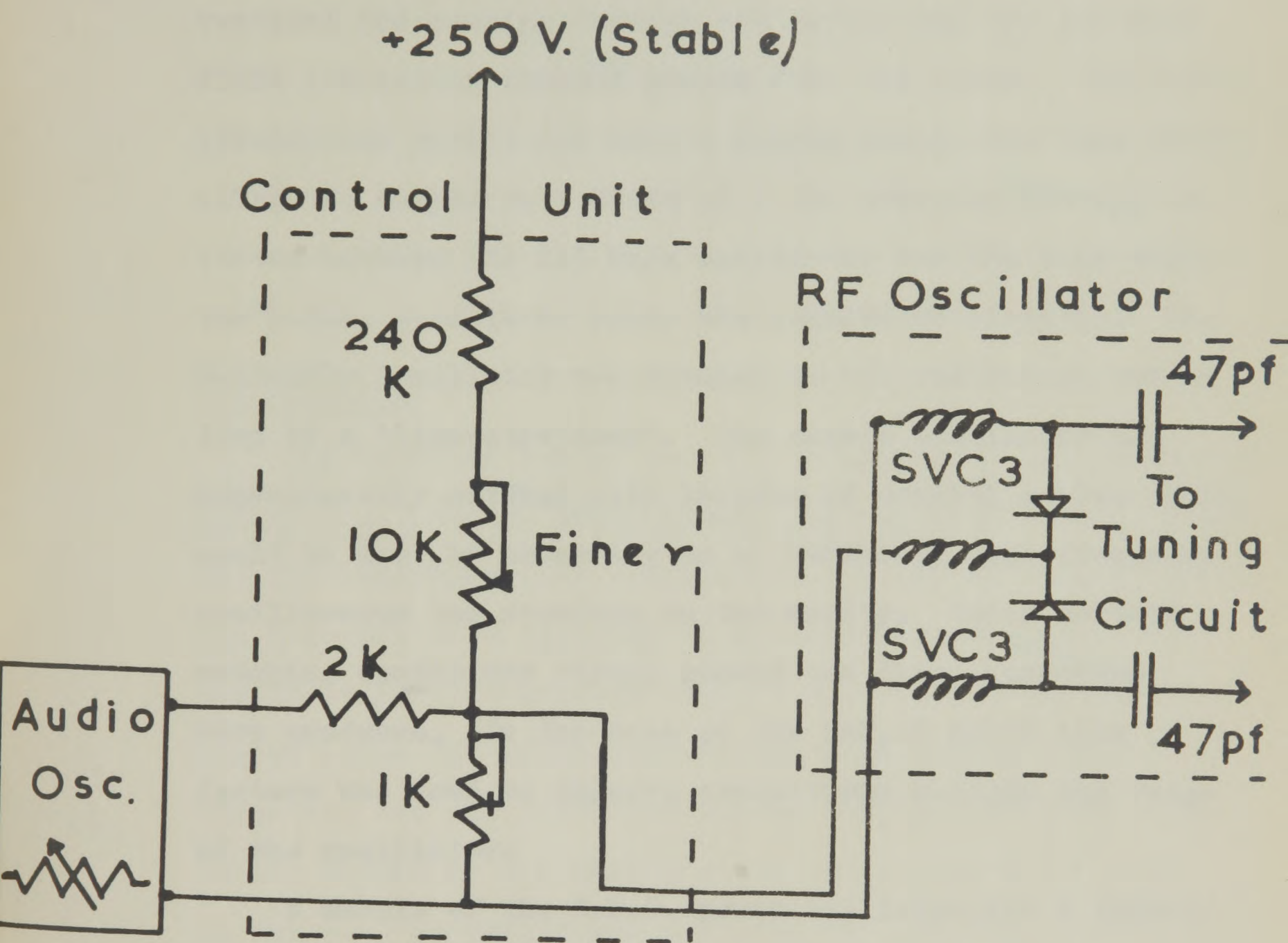


Fig 2.2 Frequency Modulation Circuit.

covering the range up to 100 Mc/s, with a resistive load. With the X band cavities the N.M.R. power was fed down one vertical rod passing through the cavity and the 115 kc/s field modulation current passed down the other. The K band irradiation cavity had only a single modulation loop encircling the sample so a choke of a few microhenries was inserted between the 115 kc/s oscillator and the loop while the N.M.R. oscillator power was coupled on directly. The Butterfly Oscillator was matched to the modulation rod or loop by a "line-stretcher". The Bridge Oscillator was approximately matched with lengths of coaxial cable. This could be done by observing on a Tektronix high frequency oscilloscope the waveform in the cavity. Under certain matching conditions strong second and third harmonics were produced. In the case of the $\text{CaF}_2\text{:H}$ ENDOR this feature was used to observe transitions outside the range of the oscillator.

A sample of the N.M.R. power was taken via a loosely coupled transformer for frequency measurement on a Rohde and Schwarz Type W.I.K. frequency meter. This could indicate on a meter beat frequencies of up to 330 kc/s with its own internally generated signal. The meter operated off a pulse-count circuit and, therefore, read the mean modulus of the deviation of a frequency modulated signal after adjustment for zero beat with the carrier. This

gave a quick indication of the depth of frequency modulation on the N.M.R. oscillators.

The N.M.R. oscillator was swept by driving its tuning mechanism with a Venner synchronous motor. These motors are available in a wide range of output speeds and, after starting, will run on frequencies between about 30 c/s and 150 c/s. They were driven by a variable frequency power oscillator to give a choice of sweep speeds.

2.3 Cavities

The standard X-band cavity was identical to the quartz-filled TE_{011} design of Williams, and was fitted with vacuum cap for immersion into refrigerant. A second X-band cavity and cryostat were designed to allow X-irradiation of the sample at low temperature (Fig. 2.3). The cavity was suspended below the helium can in the main vacuum space of the cryostat, and the radiation passed through the 3 mm. hole in the bottom of the cavity which had negligible effect on the Q. The cavity was unfilled and the TE_{011} cylindrical mode was chosen because of its high Q. It had to be made rather longer than optimum (diameter = length) to bring to a minimum the diameter of this rather large mode which cuts off at 3.9 cms. diameter at 9.5 kMc/s. Initial tuning at room temperature was effected by screwing the cavity body on the thread at the top. The cavity was silver plated inside and protected from oxydation by a

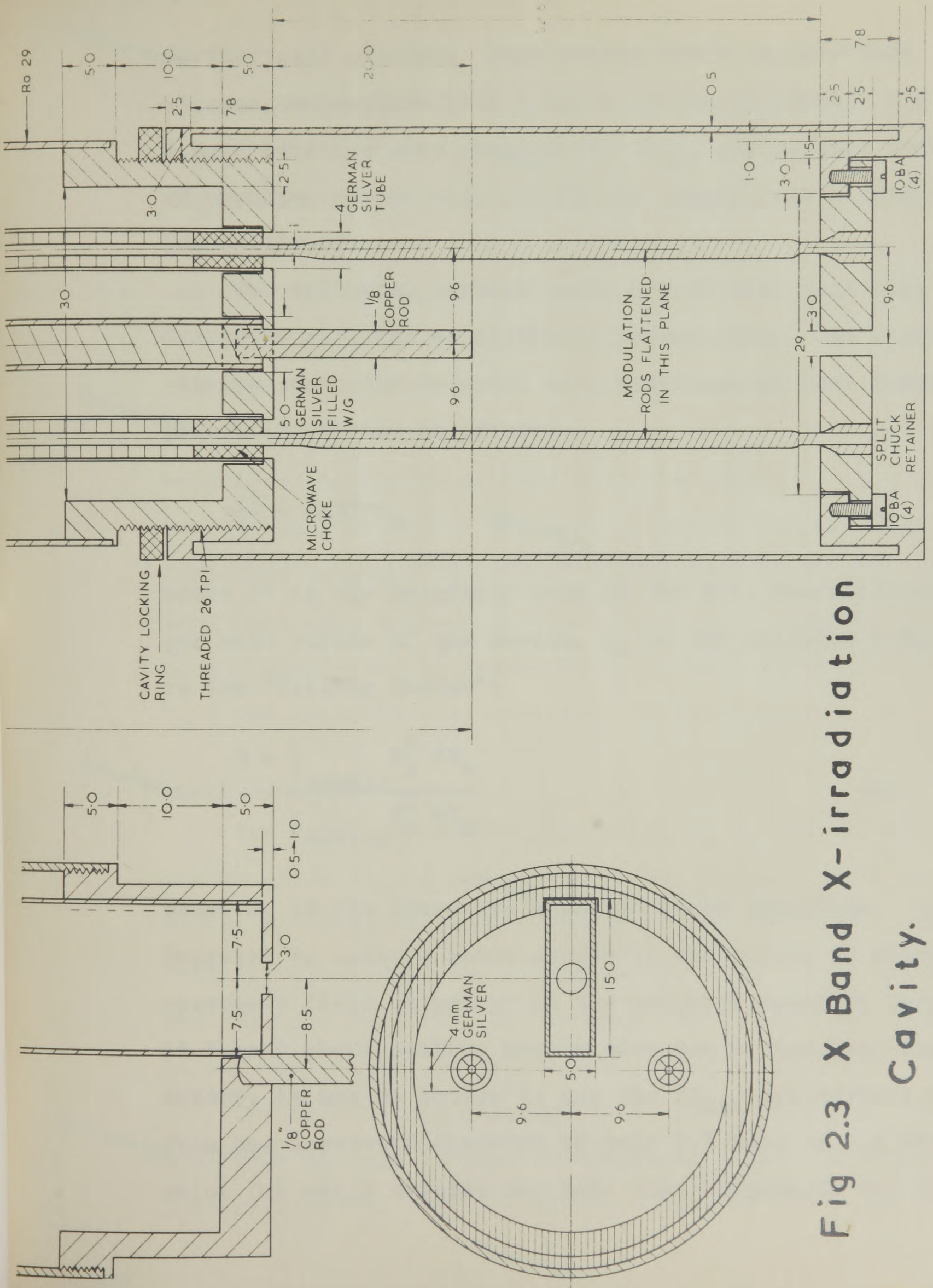


Fig 2.3 X Band X-irradiation
 Cavity.

further gold plating. This raised the Q to over 5000 at room temperature with a large sample in place. The K band cavities were also of the TE_{011} cylindrical mode of unplated copper with a Q at low temperature of about 5000 (Pilbrow).

The following general point may be made regarding design of cavities at different frequencies. The signal obtained from the detector of a spectrometer when tuned to absorption varies as (Feher)

$$\frac{\Delta V}{V} \sim 4\pi\eta X'' Q_0 \quad (1)$$

where X'' is the imaginary part of the R.F. susceptibility length is also reduced to about half per unit volume of the sample, Q_0 is the unloaded Q and η is the "filling factor":

$$\eta = \frac{\int_{\text{sample}} H_1^2 dV_s}{\int_{\text{cavity}} H_1^2 dV_c} \quad (2)$$

where H_1 is the microwave magnetic field amplitude. η is improved by using a large sample in the region of highest microwave field intensity in the smallest possible cavity. At X band where maximum sample size can be the limiting factor, it may be better to use the TE_{111} cylindrical mode. This has a cut-off diameter of only 2.7 cms. at 9.6 kMc/s which for small samples may more than compensate for the

rather lower Q . This argument is particularly strong for X irradiation induced centres, such as $\text{CaF}_2:\text{H}$ where only part of the crystal is liable to contain centres. The TE_{111} mode has the added advantage that the maximum microwave magnetic field runs across the bottom of the cavity allowing the sample to be nearer the X ray source.

On the other hand, at Q band frequencies dielectric loss in the sample becomes important and, unless needle-like, a normal sample in a TE_{011} mode cavity will extend well into the region of high electric field, causing unacceptable loss of Q . However, if the cavity diameter is increased to about twice that which gives maximum Q , the length is also reduced to about half and a conveniently-shaped sample can be accommodated without excessive loss of Q and probably with improved filling factor.

2.4 Cryogenics

Two metal cryostats were designed and constructed, one to allow simple immersion of the standard X-band cavity system in refrigerant, and the other to allow low temperature irradiation of the sample insitu. The opportunity was taken to make some improvements on designs currently in use and salient points of design are given below.

The irradiation cryostat is shown in Fig. 2.4. X-rays are fired upwards through an aluminium window in the outer can and directly into the cavity suspended below the helium

Common
Outer.

2 Inner's,
X-band,
K-band.

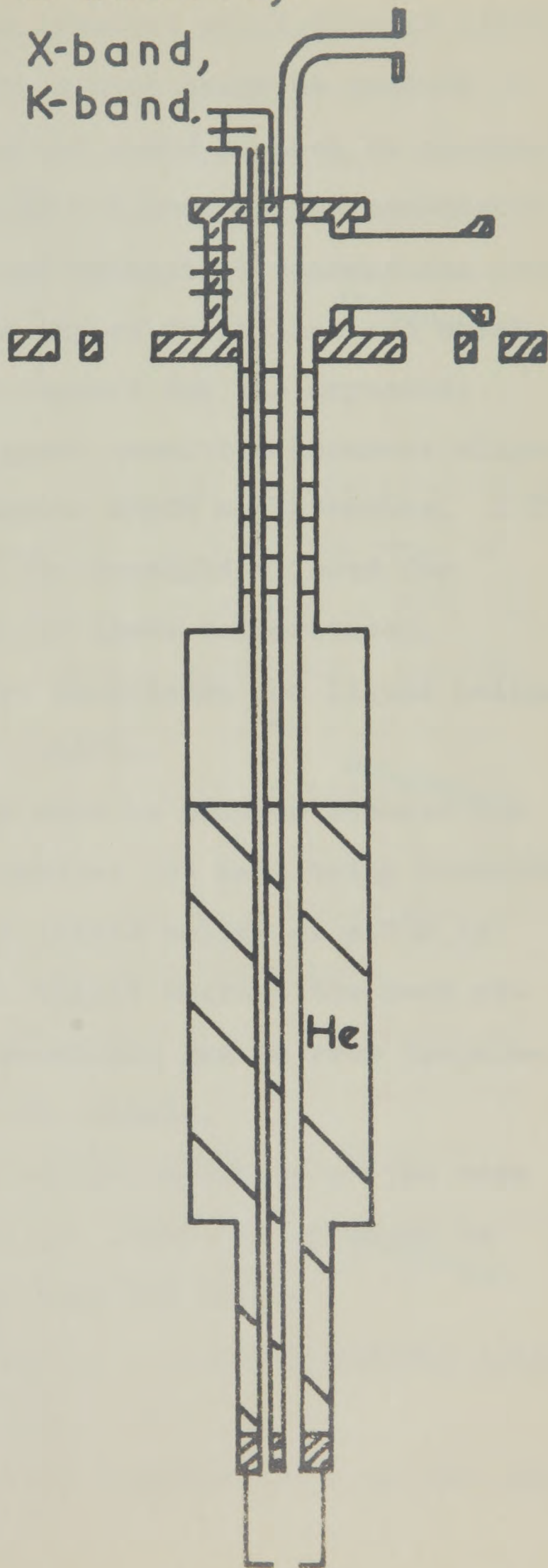
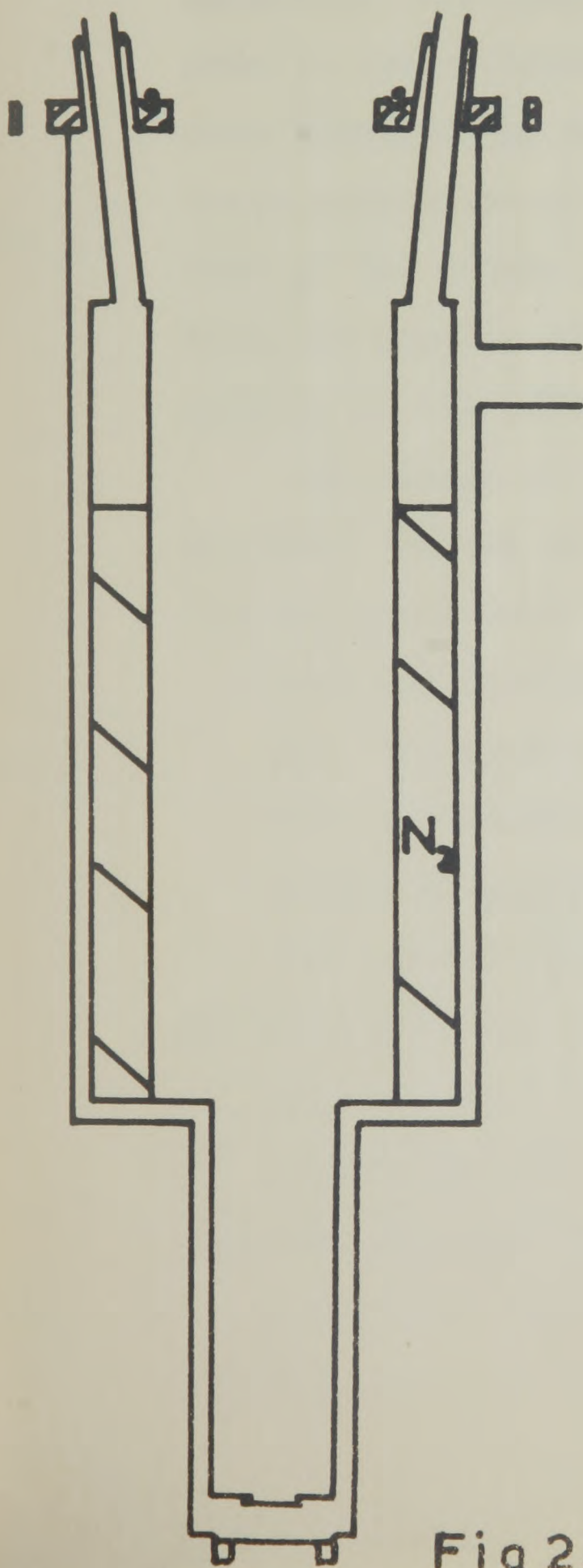


Fig 2.4. X-Irradiation Cryostat.

can. The outer part of the cryostat consisting of nitrogen annulus and outer vacuum jacket could be removed at the O-ring joint at the top and could be used in conjunction with either an X band or a K band helium can-cavity assembly. All electrical and mechanical connections were made to the manifold at the top of the helium can which also provided the point of support for the cryostat. Screw adjustment of the support permitted accurate alignment of the sample for fluorine ENDOR measurements. A 2" diameter pumping line from the manifold allowed for pumping on the refrigerant for lower temperatures.

The design of efficient containers for liquid helium has been treated by Wexler (1957).

- (a) Efficient heat exchange must be ensured between the cold gas leaving the cryostat and heat being conducted in. The latent heat of liquid helium at 4.2°K is only 2.7 Joules per cc. liquid whereas the heat absorbed in raising the resulting gas to room temperature is 210 Joules per cc. liquid.
- (b) Heat radiated into the helium should be of the same order as heat conducted in. There is no point in making one much smaller than the other.
- (c) Radiated heat can be greatly reduced by careful preparation of metal surfaces.
- (d) The effect of finite thermal conductivity on the tem-

perature of radiation shields etc. in contact with refrigerant at only one end can be important.

A size for the helium can is fixed and heat radiated from the nitrogen can and radiation shields at 77°K is estimated. It is good enough to use the approximation

$$\frac{dH}{dt} = A\sigma e[T_o^4 - T_i^4] \quad (3)$$

where σ is Stefan's constant, e is the emissivity of the surface with the least emissivity and A is the area of helium can surface. Wexler found for copper at 77°K that e can be reduced to 0.02 by careful polishing. However, in normal use it will rapidly tarnish to an e of 0.15. This effect can be much reduced by gold plating, giving an initial e of about 0.03 which does not rise very rapidly with time. For the cryostat in Fig. 2.4, using this value, radiated heat should be 7-10 mW into the helium.

Wexler considered the calculation of the length of exit tube from the helium can to give a particular rate of heat conduction into the helium, assuming perfect thermal contact between the emerging gas and the tube walls and a thermal conductivity for the material of the tube of $(a + bT)$ at temperature $T^\circ K$.

The required length is given by

$$l = \left(\frac{A}{nC_p} \right) \left[\{a + b(T_1 - g)\} \ln \left(1 + \frac{T_2 - T_1}{g} \right) + b(T_2 - T_1) \right] \quad (4)$$

Where A is the cross sectional area of the tube walls; nC_p is the thermal capacity per degree K. of the gas emerging per second (equals $3.11 \times 10^{-3} \text{ J sec}^{-1} (^{\circ}\text{K})^{-1}$ for a total heat input of 14 mW); g is the heat conducted in multiplied by $(nC_p)^{-1}$; T_1 and T_2 are the temperatures of the top and bottom of the tube respectively.

If conducted heat is set equal to radiated heat of 7 mW; $T_2 = 77^{\circ}\text{K}$ and $T_1 = 4^{\circ}\text{K}$; the exit tube and waveguide etc., are treated as a total cross section of stainless steel of 0.75 cm^2 and the thermal conductivity of stainless steel is taken as $-2.28 + 1.21T \text{ mW.cm}^{-1} (^{\circ}\text{K})^{-1}$ then the length required is about 50 cms. Due to the nitrogen annulus of the irradiation cryostat being removable it was not possible to tie the helium tube to 77°K at any point, which to some extent reduced the cryostat performance. Efficient heat exchange was secured by a series of baffle plates on the waveguide designed to encourage turbulence. They also prevented the helium seeing the room temperature radiation from the top of the cryostat.

The volume of the nitrogen can must be adequate to outlast the helium. The radiation input was calculated as 3 W., taking e as 0.03. A surprisingly large amount of

heat is conducted down the nitrogen filling tubes. Four stainless steel tubes one cm. in diameter, 0.03" wall thickness and 20 cms. long will conduct 6 W due to the rather large thermal conductivity of stainless steel as it approaches room temperature. At 80°K it is $80 \text{ mW cm}^{-1} (^{\circ}\text{K})^{-1}$ and $400 \text{ mW cm}^{-1} (^{\circ}\text{K})^{-1}$ at room temperature. The latent heat of nitrogen is 160 J. (cc)^{-1} .

If radiation falls uniformly at a rate q per unit length on a cylindrical radiation shield of thermal conductivity K and one end of which is at the refrigerant temperature T_0 , the temperature of the other end will rise to

$$T = \frac{ql^2}{2KA} + T_0 \quad (5)$$

where l is the length and A the cross sectional area of the walls. The dependence on l^2 should be noted. This is of significance in the tail of the cryostat where the cavity is surrounded only by radiation shield. At 77°K no trouble is caused by using normal commercial copper but for a radiation shield at helium temperature only high purity copper should be used because of the large fall in the thermal conductivity of normally pure copper.

REFERENCES TO CHAPTER 2

- Baker, J.M., & Williams, F.I.B., 1962, Proc.Roy.Soc. A267
283
- Bowers, K.D., Kamper, R.A., & Knight, R.B.D., 1957, J.Sci.
Instrum. 34, 49.
- Feher, G., 1957, Bell Syst.Tech.J. 36, 449.
- George, A.J., & Teaney, D.T., 1960, Rev.Sci.Instrum. 31
997.
- Goldsborough, J.P., & Mandel, M., 1960, Rev.Sci.,Instrum.
31, 1044.
- Llewellyn, P.M., 1957, J.Sci.Instrum, 34, 236.
- Pilbrow, J.R., 1965, Thesis, Oxford.
- Wexler, A., 1957, J.App.Phys. 22, 1463.
- Williams, F.I.B., 1961, Thesis, Oxford.

Chapter 3

DIVALENT THULIUM IN CALCIUM FLUORIDE

3.1. Introduction

The paramagnetic resonance spectrum of $^{169}\text{Tm}^{2+}$ in CaF_2 was reported by Hayes and Twidell (1961). Single crystals of CaF_2 containing 0.05% diamagnetic Tm^{3+} ions were grown by the Stockbarger method. X-irradiation for a few hours at room temperature converted a proportion of the Tm^{3+} ions to Tm^{2+} whose paramagnetic resonance spectrum could be observed at temperatures of 77°K and below. The main features of this spectrum were described by the isotropic spin Hamiltonian:

$$\mathcal{H} = g\beta\mathbf{H}\cdot\mathbf{S}' + A\mathbf{I}\cdot\mathbf{S}' \quad (1)$$

with $\mathbf{I}$, the nuclear spin of the 100% abundant ^{169}Tm , equal to $\frac{1}{2}$, $\mathbf{S}' = \frac{1}{2}$, $g = 3.453 \pm 0.003$ and $|A| = (368 \pm 2) \times 10^{-4} \text{ cm.}^{-1}$.

The crystal structure of CaF_2 (Fig. 3.1) consists of two interleaved face-centred-cubic lattices of F^- ions and one of Ca^{2+} ions, each with a lattice constant of $5.451 \text{ \AA}$. This may be visualised as a single cubic array of F^- ions with every other body-centre occupied by a Ca^{2+} ion. The Tm^{2+} ions are located substitutionally at Ca^{2+} sites and the nature of the E.P.R. spectrum indicates that the

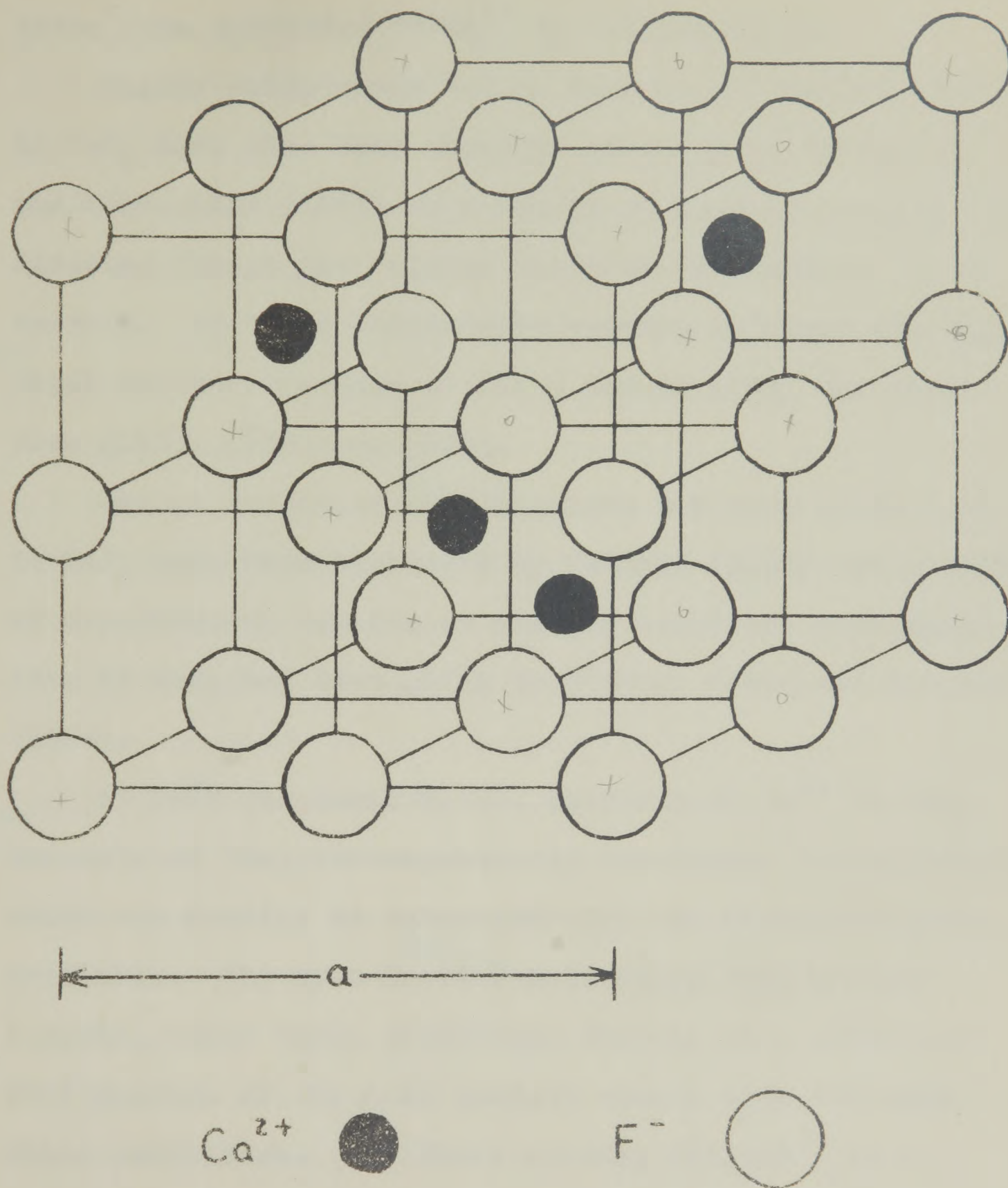


Fig. 3.1 Fluorite Lattice.

charge compensating defects necessary are remote from those ions converted to Tm^{2+} by X-irradiation.

Highly anisotropic E.P.R. spectra of thulium ions in CaF_2 have also been observed recently by Forrester and McLaughlan (1965) as a result of special growing conditions, though the valence state of the thulium is uncertain. Of three anisotropic spectra obtained the principal one has the axes of its g tensor along the direction $[110]$, $[\bar{1}10]$ and $[001]$.

Charge compensation mechanisms for rare earth ions in CaF_2 have been discussed by Twidell (1963) and a review of experimental results on all the trivalent rare earth ions in CaF_2 has been given by Bierig, Weber and Warshaw (1964).

At 20°K the cubic E.P.R. spectrum of Tm^{2+} in CaF_2 consists of two, inhomogeneously broadened, strong lines which can readily be saturated with the microwave power available. The spin-lattice relaxation time of about 1 m.sec. under these conditions ensures that adiabatic fast passage of the spin packets occurs with 115-kc/s field modulation. For these reasons $\text{CaF}_2:\text{Tm}^{2+}$ is a suitable system on which to attempt an ENDOR investigation. The choice is supported by the following considerations:-

- 1) Accurate atomic beam measurements of the hyperfine interaction for the ^{169}Tm atom have been made by Ritter

(1962). Since Tm^{2+} differs from the atom only in the loss of two 6s electrons it will have the same ground state in a magnetic field and its properties may be compared directly. An accurate determination of the Tm^{2+} A value will show the effect of the 6s electrons on the 4f wavefunctions. The hyperfine constant and the nuclear moment can be measured separately in an ENDOR experiment, enabling information to be obtained on the value of $\langle r^{-3} \rangle$ for the divalent ion. Broad, partly resolved structure on the EPR lines reduces the accuracy of determination of the A value to only 0.5% but an ENDOR measurement will give more than sufficient accuracy. The positions of excited crystal field states of Tm^{2+} in CaF_2 are available from the optical fluorescence measurements of Kiss (1962). These enable corrections to the hyperfine interaction due to the crystal field to be calculated, rather than estimated from the apparent shift in g-value, which could lead to incorrect results. (See sect. 3.3(i) and Hayes and Twidell).

2) There are features of the EPR spectrum not included in the spin Hamiltonian (1). When the magnetic field is along [100] or [110] crystal directions a partly resolved anisotropic superstructure is observed which is markedly different at K band from X band (Fig. 3.2). This is due to interaction of the Tm^{2+} ion with the eight nearest-

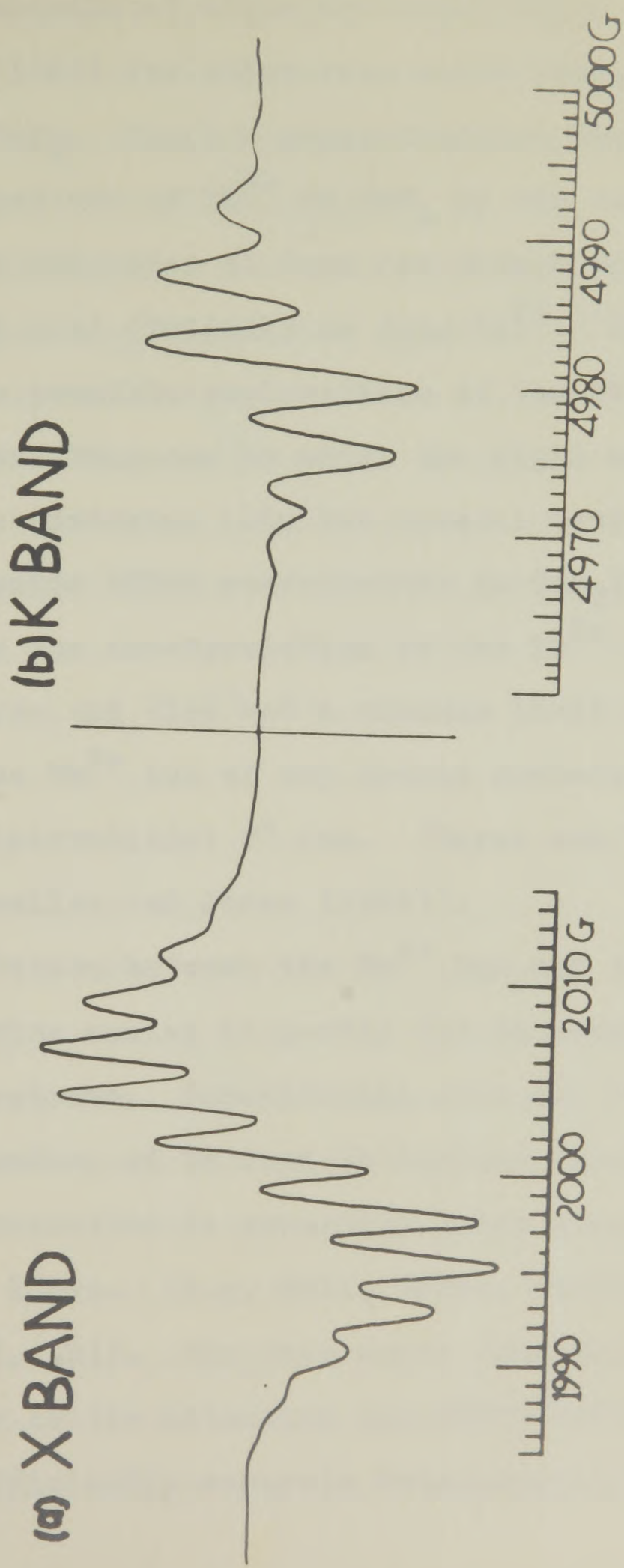


Fig 3.2 $\text{CaF}_2:\text{Tm}^{2+}$ High Field EPR Line, $H\parallel[100]$

neighbour fluorine nuclei at a distance of $2.36 \text{ \AA}$ but is unlike the "satellite" structure reported by Baker, Hayes and O'Brien (1960) for other rare earth ions, Ce^{3+} , Eu^{2+} and Gd^{3+} in CaF_2 . Similar superstructure was observed in the X band spectrum of Yb^{3+} in CaF_2 by Low and Ranon (1963) but in this case it does not change significantly on going to K band (Twidell) as does Tm^{2+} . Low and Ranon suggest three possible explanations of the Yb^{3+} superstructure, favouring one in which the eight nearest fluorines are distorted into two unequal tetrahedra. Accurate fluorine ENDOR measurements on $\text{CaF}_2:\text{Tm}^{2+}$ would shed light on the interpretation of the Tm^{2+} and Yb^{3+} superstructures and also set a minimum limit to the distance from the Tm^{2+} ion of any charge compensating defect, if it is an interstitial F^- ion. (Hayes and Twidell, Bleaney, Llewellyn and Jones (1956)).

3) The interaction between the Tm^{2+} ion and the eight nearest fluorine nuclei is partly due to covalent bonding of the 4f electrons. Considerable work has been carried out on the bonding of 3d ions in various fluoride crystals where the interaction is generally large enough to give resolved EPR lines. (e.g. Hall, Hayes, Stevenson and Wilkins (1963,a,b)). The rare earth ions have received comparatively little attention and ENDOR methods are needed to give a sufficiently accurate determination of the rather

small interactions. Since the electronic configuration of Tm^{2+} consists of one hole in the 4f shell which may be treated fairly simply, one might hope to interpret the measured parameters in terms of a bonding theory similar to that applied to the 3d group.

4) Another term omitted from the spin Hamiltonian of Hayes and Twidell was $-g_n \beta_n \underline{H} \cdot \underline{I}$ where g_n is the ^{169}Tm nuclear g factor. They were able to deduce the nuclear moment as $|\mu_n| = 0.24 \pm 0.01 \text{ mm.}$ but had to use a value of $\langle r^{-3} \rangle$ interpolated from values given by Judd and Lindgren (1961) for Tm^0 and Tm^{3+} . By measuring the nuclear Zeeman energy by inducing a nuclear transition the nuclear moment may be deduced directly. $^{169}\text{Tm}^{2+}$ provides an exacting test of the ENDOR technique for doing this since the hyperfine energy is approximately 1000 Mc/s while the nuclear Zeeman energy at K band is only 2.8 Mc/s.

(1) The Tm^{2+} crystal field ground manifold gives rise to an apparent $\underline{H} \cdot \underline{I}$ term as suggested by Baker and Bleaney (1958), arising from the combined effect of the hyperfine interaction and the magnetic field. The magnitude of this term may be calculated, using the energies of the excited states given by Kiss, to give experimental test of theory and the final result may be compared with Ritter's atomic beam measurement of the nuclear moment of ^{169}Tm .

3.2 Simple Crystal Field Theory

The electronic configuration, $4f^{13}$, of the Tm^{2+} ion may be treated conveniently as a single $4f$ hole. Spin-orbit coupling gives rise to two manifolds, $\underline{J} = \frac{5}{2}$ and $\underline{J} = \frac{7}{2}$ with $\underline{J} = \frac{7}{2}$ lowest and separated by $\frac{7}{2}\zeta$ where ζ is the effective spin-orbit coupling parameter. As with all rare earth ions the effect of the crystal field, relative to spin-orbit coupling, is smaller than is typical of the iron group. It has been suggested that this is due to partial screening of the crystal field by the closed $5s^2$ and $5p^6$ shells. However, Burns (1962) has calculated the effect and shown that if the crystal field is written as $V_c = \sum B_n^m r_{4f}^n Y_n^m$ then the effect at the $4f$ electrons of distortion of the $5s$ and $5p$ distribution is equivalent to a reduction in r_{4f}^n of not more than 12%. He explains the rare earth situation under the following points:

- (1) The lattice sums (B_n^m) for typical crystals which will accept $3d$ ions are up to ten times larger than for crystals which accept rare earth impurities.
- (2) The larger covalent bonding of $3d$ ions to the ligands increases the cubic crystal field splitting, $10 Dq$.
- (3) $\langle r^n \rangle$ for $3d$ ions are about twice those for $4f$ ions.
- (4) The spin-orbit coupling parameters for $4f$ ions are twice those for $3d$ ions.

Thus, to first order, the effect of the crystal field

may be computed within the two $\underline{J}$ -manifolds separately. The point symmetry of the Tm^{2+} ion site in CaF_2 is O_h and the crystal field eigenstates will form bases of irreducible representations of this group, the two dimensional Γ_6 and Γ_7 , and the four dimensional Γ_8 for $\underline{J} = \frac{7}{2}$ and Γ_7 and Γ_8 only for $\underline{J} = \frac{5}{2}$ (Statz and Koster 1959).

Since the number of electrons is odd Kramer's degeneracy will remain. The doublets are split only by a magnetic field and are unaffected by random variations of crystal field. E.P.R. transitions between components of a doublet will have symmetrical lineshape and maximum intensity with the microwave magnetic field perpendicular to the D.C. field in contrast to the asymptotic low field "tail" and highly anisotropic g value ($g_x = g_y = 0$) typical of a non-Kramers doublet (Baker and Bleaney).

The crystal field eigenstates and eigenvalues may be calculated by using the cubic field operator equivalent (Elliott and Stevens (1953, a,b)).

$$V_c = B_4(O_4^0 + 5 O_4^4) + B_6(O_6^0 - 21 O_6^4) \quad (2)$$

Matrix elements of O_4^0 and O_6^0 are given by Stevens (1952) and of O_6^4 and O_4^4 by Baker, Bleaney and Hayes (1958).

The resulting eigenstates will be referred to the 4-fold cubic crystal axes.

The parameters B_4 and B_6 are based on the concept of

an electrostatic point charge model for the crystal field. Twidell gives an a priori calculation of B_4 and B_6 for Tm^{2+} in CaF_2 involving the quantities $\langle r^4 \rangle$ and $\langle r^6 \rangle$ respectively for the 4f shells. These quantities may be interpolated from the calculations of Freeman and Watson (1962) but are not entirely reliable. Furthermore published values of crystal field parameters for rare earth ions in various host lattices show considerable disagreement between experimental and calculated values. Burns (1965) has investigated these discrepancies in some detail and suggests they may arise from effects of shielding by 5s and 5p electrons, radial expansion of 4f charge density due to overlap with the ligands, and the extended nature of induced moments on neighbouring ions. No conclusive support for any one mechanism is found. Hutchings and Ray (1963) included effects of induced dipole and quadrupole moments in a detailed crystal field calculation for $PrCl_3$ but found poor agreement with experiment. However, no account of bonding in any orbitals was taken. Jorgensen, Pappalardo and Schmidtke (1963) pointed out that experimental values of the crystal field parameters, $A_n^m \langle r^n \rangle$ were not consistent with any reasonable picture of an electrostatic integral. They suggest that the $A_n^m \langle r^n \rangle$ have no independent physical significance but merely serve to keep track of energy differences between the seven f

orbitals. The energy differences arise largely from weak covalent bonding. The parameters B_4 and B_6 are therefore, left to be determined, along with G from the experimental results.

For Tm^{2+} the crystal field calculation may be carried out in terms of the two J manifolds or in terms of $L = 3$. The latter method requires the spin-orbit eigenstates to be determined first and each crystal field eigenstate has in general four components. This lengthens the process of finding matrix elements required in making second order corrections. Since most matrix elements required between manifolds J and $J \pm 1$ may readily be found from the tables of Elliott and Stevens (1953a) we work in terms of $J = \frac{5}{2}$ and $\frac{7}{2}$.

Lea, Leask and Wolf (1962) give complete tables and diagrams of the effect of the cubic field on different J manifolds from $J = 2$ to $J = 8$ for ratios of B_4 to B_6 from 0 to $\pm \infty$. For $J = \frac{7}{2}$ the ground state will be Γ_6 for $B_4/B_6 = -\infty$ to $\frac{21}{4}$ and Γ_7 for $B_4/B_6 = \frac{21}{4}$ to $+\infty$. Γ_8 cannot be the ground state. The cubic field eigenvectors in terms of $|J_z\rangle$ are given in Table 3.1 for $J = \frac{7}{2}$ and $J = \frac{5}{2}$. Since there are no repeated representations within either manifold the eigenvectors are independent of the ratio B_4/B_6 . This enables second order corrections to be calculated with confidence in the accuracy of the eigenvectors.

Table 3.1 Cubic Crystal Field Eigenvectors in Terms of $|J_z\rangle$ Referred to the Fourfold Crystal Axes (Lea, Leask and Wolf 1962), Eigenvalues and Observed Energies for $\text{CaF}_2:\text{Tm}^{2+}$ (Kiss 1962)

Representation	Eigenvectors	Eigenvalue	Observed Energy (cm^{-1})
$J = \frac{5}{2}$ Γ_8	$\sqrt{\frac{5}{6}} +\frac{5}{2}\rangle + \sqrt{\frac{1}{6}} +\frac{3}{2}\rangle$ $ +\frac{1}{2}\rangle$	$\frac{7\zeta}{2} + \frac{22b_4}{7}$	$9376.6 = W_5$
Γ_7	$\sqrt{\frac{1}{6}} +\frac{5}{2}\rangle - \sqrt{\frac{5}{6}} +\frac{3}{2}\rangle$	$\frac{7\zeta}{2} - \frac{44b_4}{7}$	$8966.2 = W_4$
$J = \frac{7}{2}$ Γ_6	$\sqrt{\frac{5}{12}} +\frac{7}{2}\rangle + \sqrt{\frac{7}{12}} +\frac{1}{2}\rangle$	$6b_4 - 20b_6$	
Γ_8	$\sqrt{\frac{7}{12}} +\frac{7}{2}\rangle - \sqrt{\frac{5}{12}} +\frac{1}{2}\rangle$	$\frac{6b_4}{7} + 16b_6$	$555.8 = W_2$
	$\frac{1}{2} +\frac{5}{2}\rangle + \sqrt{\frac{3}{4}} +\frac{3}{2}\rangle$		
Γ_7	$\sqrt{\frac{3}{4}} +\frac{5}{2}\rangle - \frac{1}{2} +\frac{3}{2}\rangle$	$\frac{-54b_4}{7} - 12b_6$	$0 = W_1$

No Account has been taken of crystal field admixing of the two J manifolds.

These eigenvectors were checked by applying the cubic field operator (2), giving the energies in terms of B_4 and B_6 . It should be noted that B_4 and B_6 as defined by (2) depend on the manifold of total angular momentum within which the operator equivalents are calculated since, from the point charge model (Bleaney (1964)):

$$B_4 = \left(\frac{e^2}{hc} \right) \frac{\langle r^4 \rangle}{a^5} \langle J11\theta11J \rangle (x_1 + x_2 + x_3 + x_4) \quad (3)$$

$$B_6 = \left(\frac{e^2}{hc} \right) \frac{\langle r^6 \rangle}{a^7} \langle J11\gamma11J \rangle (y_1 + y_2 + y_3 + y_4)$$

where $2a$ is the size of the unit cubic cell (5.451 Å for CaF_2); x_i, y_i are numerical factors appropriate to CaF_2 , representing the contributions of successive shells of ions; $\langle J11\theta11J \rangle$ and $\langle J11\gamma11J \rangle$ are multiplying factors appropriate to the total angular momentum as given by Stevens. From these factors we find:-

$$B_4^{J=\frac{7}{2}} = \frac{3}{7} B_4^{L=3}$$

$$B_4^{J=\frac{5}{2}} = \frac{11}{7} B_4^{L=3}$$

$$B_6^{J=\frac{7}{2}} = \frac{1}{7} B_6^{L=3}$$

$$B_6^{J=\frac{5}{2}} = 0$$

(4)

The eigenvalues in Table 3.1 are given in terms of the more convenient quantities used by Bleaney and Twidell:

$$\begin{aligned} b_4 &= 60 B_4^{L=3} \\ b_6 &= 180 B_6^{L=3} \end{aligned} \quad (5)$$

Kiss has identified $\underline{J} = \frac{7}{2}$, Γ_7 as the ground state and measured directly the positions of $\underline{J} = \frac{7}{2}$, Γ_8 and $\underline{J} = \frac{5}{2}$, Γ_7, Γ_8 from optical fluorescence. These energies are given in Table 3.1. After allowing for second order corrections to the crystal field energies Bleaney has used these values to find:

$$\begin{aligned} \zeta &= 2513 \text{ cm}^{-1} \\ b_4 &= 45.8 \text{ cm}^{-1} \\ b_6 &= 5.05 \text{ cm}^{-1} \end{aligned} \quad (6)$$

which would place the Γ_6 state at 588 cm^{-1} above the ground state Γ_7 .

In deriving the spin Hamiltonian (1) the Γ_7 doublet ground state has been regarded as the two components of a fictitious spin, $\underline{S}' = \frac{1}{2}$. The g value is obtained from equating the operator $\beta \underline{H} \cdot \underline{g} \cdot \underline{S}'$ within $\underline{S}' = \frac{1}{2}$ to the Zeeman operator $\beta \underline{H} \cdot (\underline{L} + g_e \underline{S})$ within the Γ_7 ground state. The

latter is readily evaluated using operator equivalents with the result (using $g_e = 2$)

$$g_x = g_y = g_z = g_o = \frac{24}{7} \quad (7)$$

The Zeeman operator for the thulium atom in a magnetic field is written as

$$H_z = g_j \underline{H} \cdot \underline{J} \quad (8)$$

where g_j is simply the Landé factor of the $\underline{J} = \frac{7}{2}$ state, $\frac{8}{7}$. Thus

$$g_o = 3g_j \quad (9)$$

The hyperfine constant A in the spin Hamiltonian (1) is evaluated by equating $\underline{S}' \cdot \underline{A} \cdot \underline{I}$ within $\underline{S}' = \frac{1}{2}$ to $2\beta\beta_n g_n \langle r^{-3} \rangle \underline{N} \cdot \underline{I}$ within Γ_7 where

$$\underline{N} = \sum_{\text{electrons}} \left(\underline{1}_i - \underline{S}_i + \frac{3(\underline{r}_i \cdot \underline{S}_i) \underline{r}_i}{r_i^2} \right) \quad (10)$$

(Elliott and Stevens (1953a)) and no allowance is made for any S-electron character of the wavefunctions. Again using operator equivalents we obtain

$$A_x = A_y = A_z = A_o = \frac{16}{7} 2\beta\beta_n g_n \langle r^{-3} \rangle_{\text{ion}} \quad (11)$$

For the thulium atom the hyperfine operator is written

$$H_{\text{HF}} = a \underline{J} \cdot \underline{I} \quad (12)$$

and we find

$$a = \frac{16}{21} 2\beta\beta_n g_n \langle r^{-3} \rangle_{\text{atom}} \quad (13)$$

Thus, assuming no S-contact interaction

$$A_0 \langle r^{-3} \rangle_{\text{atom}} = 3a \langle r^{-3} \rangle_{\text{ion}} \quad (14)$$

3.3 Second Order Corrections

The eigenfunctions and eigenvectors of Table 3.1 are not sufficiently accurate for our purposes and higher order corrections must be considered due to the following:

- (i) The crystal field.
- (ii) The magnetic field.
- (iii) The hyperfine interaction.
- (iv) Combinations of these.

(i) The Crystal Field

This is the most important effect and it couples separately the two Γ_7 states and the two Γ_8 states. The effect of the crystal field on the ground state wavefunctions causes each half of the Kramers doublet to become

$$\psi_{\text{G.S.}} = [1 + \alpha^2]^{-\frac{1}{2}} \{ \Gamma_7(\frac{7}{2}) + \alpha \Gamma_7(\frac{5}{2}) \} \quad (15)$$

$$\text{where } \alpha = \frac{-\langle \Gamma_7(\frac{5}{2}) | \text{CRYSTAL FIELD} | \Gamma_7(\frac{7}{2}) \rangle}{W_4 - W_1}$$

From the measurements of Kiss $W_4 - W_1$ is equal to 8966.2 cm^{-1} leading to $\alpha = +0.0487$ for each half of the Kramers doublet.

Applying the Zeeman operator to the new ground state (15), taking care to use the correct multiplying factors for the $\underline{J} = \frac{7}{2}$ and $\underline{J} = \frac{5}{2}$ components, gives in place of eqn. (9)

$$g = 3g_J + \frac{16\alpha}{7\sqrt{3}} - \frac{34}{7}\alpha^2 \quad (17)$$

to order α^2 .

Using the hyperfine operator equation (11) is converted to

$$A = \left(\frac{16}{7} - \frac{8\alpha^2}{7\sqrt{3}} - \frac{32\alpha^2}{7} \right) \cdot 288 g_n \langle r^{-3} \rangle_{\text{ion}} \quad (18)$$

$$\text{that is } A = A_0 \left(1 - \frac{\alpha}{2\sqrt{3}} - 2\alpha^2 \right) \quad (19)$$

The cross terms in the matrix elements between the ground state $|J\rangle$ or $|J+1\rangle$ and first excited state $|J+1\rangle$ or $|J\rangle$ required in deriving (17) and (18) are given for all rare earth trivalent ions by Elliott and Stevens (1953a). The data for Yb^{3+} are appropriate for Tm^{2+} .

The crystal field matrix elements between the two $\underline{J}$ manifolds also give small second order changes to the positions of the two Γ_7 doublets and Γ_8 quartets. These do not, of course, affect the E.P.R. results in the ground-

state but have to be allowed for when calculating b_4 , b_6 and ζ from the optical data. The energy shifts are

$$\delta W = \pm \frac{|\langle \frac{5}{2} | \text{CRYSTAL FIELD} | \frac{7}{2} \rangle|^2}{W(\frac{5}{2}) - W(\frac{7}{2})} \quad (20)$$

being negative for the $J = \frac{7}{2}$ states. Evaluating the matrix elements we find, in agreement with Bleaney,

$$\delta W(\Gamma_7) = 21.4 \text{ cm.}^{-1}$$

$$\delta W(\Gamma_8) = 0.2 \text{ cm.}^{-1}$$

(ii) The Magnetic Field

The mixing of states by the magnetic field will cause a second order shift in energies leading to a term in the dependence of energy on field which is quadratic in H . Such states could not be described by a simple, linear g value. However, in the present case where all states are Kramers doublets, each half of the Γ_7 ground state will be affected in the same way and have its energy shifted in the same direction. If the shift of each half is the same the separation will be described by the original g value. On the other hand if the first order effect of the magnetic field is to cause a significant difference between the separations of each half of the ground Γ_7 doublet from the appropriate half of the doublet to which it is coupled then the energy shift of each half will be

different and a quadratic term will be observed in the ground state splitting.

The states which are coupled by the magnetic field in the present case can be found by group theory (Statz and Koster). It follows from the orthogonality relations between group characters of irreducible representations that an operator which transforms according to an irreducible representation of the group, Γ_γ , has non-zero matrix elements between two other irreducible representations of the group, Γ_α and Γ_β , only if the direct product $\Gamma_\alpha^* \times \Gamma_\beta$ contains Γ_γ . The components of the Zeeman operator, $L_x + 2S_x$, $L_y + 2S_y$, $L_z + 2S_z$, form bases of the three dimensional irreducible representation Γ_4 of the cubic group. The following direct products given by Statz and Koster are relevant to our problem:

$$\Gamma_6^* \times \Gamma_6 = \Gamma_1 + \Gamma_4$$

$$\Gamma_7^* \times \Gamma_7 = \Gamma_1 + \Gamma_4$$

$$\Gamma_8^* \times \Gamma_8 = \Gamma_1 + \Gamma_2 + \Gamma_3 + 2\Gamma_4 + 2\Gamma_5$$

$$\Gamma_6^* \times \Gamma_7 = \Gamma_2 + \Gamma_5$$

$$\Gamma_6^* \times \Gamma_8 = \Gamma_3 + \Gamma_4 + \Gamma_5$$

$$\Gamma_7^* \times \Gamma_8 = \Gamma_3 + \Gamma_4 + \Gamma_5$$

Thus the magnetic field will connect the Γ_7 ground state to the Γ_8 states and the other Γ_7 state but not to the Γ_6

state. Due to the large spin orbit energy the $\underline{J} = \frac{5}{2}$ states clearly have negligible effect so we have only to consider the effects of the $\underline{J} = \frac{7}{2}$, Γ_8 state at 555.8 cm.^{-1} above the ground state. A quick estimate with H along the Z axis, for K band quantum size shows that the Γ_7 doublet will be shifted by $6 \times 10^{-4} \text{ cm.}^{-1}$ and that the difference in the shifts of the two components of the doublet is 0.26% of this amount which is quite negligible.

(iii) The Hyperfine Interaction

Writing in terms of the operator equivalent, $\underline{J}$, the second order energy shift due to the hyperfine interaction will be of the form

$$\delta = - \frac{\sum A.}{9} \frac{2 |\langle \underline{J} \dots \dots | \underline{J} \cdot \underline{I} | \underline{J} \dots \dots \rangle|^2}{\Delta W} \quad (21)$$

We may separate the operator into three components since they couple different states to the ground state:- $J_z I_z$, $\frac{1}{2} J^+ I^-$, $\frac{1}{2} J^- I^+$. $J_z I_z$ clearly leads to an energy shift which depends on m^2 , the nuclear magnetic quantum number. For $\underline{I} = \frac{1}{2}$ this produces a pseudo quadrupole interaction. In the case of ^{169}Tm $\underline{I} = \frac{1}{2}$ so all nuclear states are shifted equally and this cannot be detected by any transition within the ground state. $J^+ I^-$ and $J^- I^+$ produce a further effect. Consider a groundstate which is a doublet characterised by $\langle J, J_z = \pm M |$ and an excited doublet described by $\langle J, J_z = \pm (M+1) |$. $J^+ I^-$ will couple only $|-(M+1)\rangle |m+1\rangle$ to

$| -M \rangle | m \rangle$ with energy shift proportional to $[J(J+1) - (M+1)M]$
 $[I(I+1) - m^2 - m]$. $J^- I^+$ will couple only $| + M+1 \rangle | m-1 \rangle$ to
 $| M \rangle | m \rangle$ with energy shift proportional to $[J(J+1) - (M+1)M]$
 $[I(I+1) - m^2 + m]$. Thus the energy shift of the level $| \pm M \rangle | m \rangle$
 is

$$\delta | \pm M \rangle | m \rangle \propto [I(I+1) - m^2 \pm m] \quad (22)$$

The second term contributes again to the pseudo quadrupole effect but the last term has an effect very like that of $A S_z I_z$ in the spin Hamiltonian and is experimentally inseparable from it. The Tm^{2+} electronic states have some features of this simple scheme considered above and a virtual $S_z I_z$ term is produced. Again the symmetry properties show that the hyperfine interaction does not couple the Γ_6 and Γ_7 states. The calculated change in measured hyperfine parameter due to coupling to the $\underline{J} = \frac{7}{2}$, Γ_8 state is 20 kc/s (in about 1100 Mc/s). The effect of $J = \frac{5}{2}$ states is negligible.

(iv) Combined Effect of Magnetic Field and Hyperfine Interaction

The importance of the contribution from this source to the measured nuclear g value was pointed out by Baker and Bleaney. In terms of the operator equivalent $\underline{J}$ the second order energy shift of the ground state due to other $\underline{J} = \frac{7}{2}$ states is

$$\delta = -2 \sum_n \frac{1}{\Delta W_n} \langle \varphi_0 | \frac{8}{7} \beta \underline{H} \cdot \underline{J} | \varphi_n \rangle \langle \varphi_n | \frac{A}{3} \underline{J} \cdot \underline{I} | \varphi_0 \rangle \quad (23)$$

The factor 2 arises from the equivalent term with the magnetic field and hyperfine interaction interchanged. Expanding, we find the ground state energy shift

$$\begin{aligned} \delta W_0 = & -2 \cdot \frac{8}{7} \beta \cdot \frac{A}{3} \sum_n \frac{1}{\Delta W_n} \left[H_z I_z |\langle \varphi_0 | J_z | \varphi_n \rangle|^2 \right. \\ & + H_x I_x |\langle \varphi_0 | J_x | \varphi_n \rangle|^2 + H_y I_y |\langle \varphi_0 | J_y | \varphi_n \rangle|^2 \\ & \left. + (H_x I_y + H_y I_x) \langle \varphi_0 | J_x | \varphi_n \rangle \langle \varphi_0 | J_y | \varphi_n \rangle \right] \quad (24) \end{aligned}$$

Thus the energy is of the form $-\beta \underline{H} \cdot \underline{g}_n' \cdot \underline{I}$, where $\underline{g}_n'$ is a tensor and is of the same form as the term in the spin Hamiltonian, $-g_n \beta \underline{H} \cdot \underline{I}$, which represents the effect of the magnetic field on the real nuclear magnetic moment. Experimentally the two are indistinguishable and the sum is measured.

Accurate thulium ENDOR measurements were made with $\underline{H}$ along the Z direction in which case the value of g_n' due to coupling to the $\underline{J} = \frac{7}{2}$, Γ_8 state is found to be -0.288. Its importance may be judged from comparison with the real nuclear g factor of -0.458. This correction may be regarded as the interaction of the real nuclear moment with the electronic moment induced by the magnetic field.

3.4 Thulium E.P.R. Measurements

The spin Hamiltonian

$$\mathcal{H} = g\beta\mathbf{H}\cdot\mathbf{S} + A\mathbf{I}\cdot\mathbf{S} - g_n\beta_n\mathbf{H}\cdot\mathbf{I} \quad (25)$$

with $\mathbf{S} = \frac{1}{2}$, $\mathbf{I} = \frac{1}{2}$

is used to describe the EPR and thulium ENDOR spectra.

The crystal of CaF_2 containing nominally 0.1% Tm^{3+} ions was X-irradiated in air at 50 kV, 50mA for ten hours at 4 cms. from the target.

The appearance of the absorption derivative of the high field line of the two line EPR spectrum at 20°K for both X and K band is shown in Fig. 3.2 where it can be seen that the overall extent of the line is about 27G. The magnetic field is parallel to [100], the direction in which the fluorine structure is best resolved, due to all eight nearest neighbour fluorine being equivalent. Structure is also resolved in the [110] direction but not in the [111] direction.

The g and A values were measured at 20°K to enable approximate calculation of the thulium ENDOR frequencies to be made, and for use in evaluating the nuclear moment. The magnetic field was in the [100] direction and the dispersion signal was used to enable the peak of the central component of the E.P.R. line to be located as accurately as possible. We obtain $g = 3.452 \pm 0.002$ and

$A = 228.4 \pm 0.5\text{G}$ which is in good agreement with previous workers. No direct determination of g_n is possible from the E.P.R. spectrum.

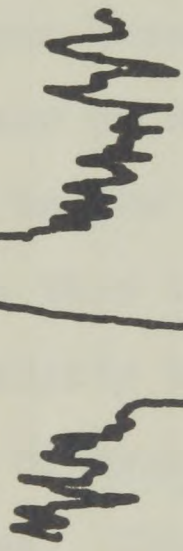
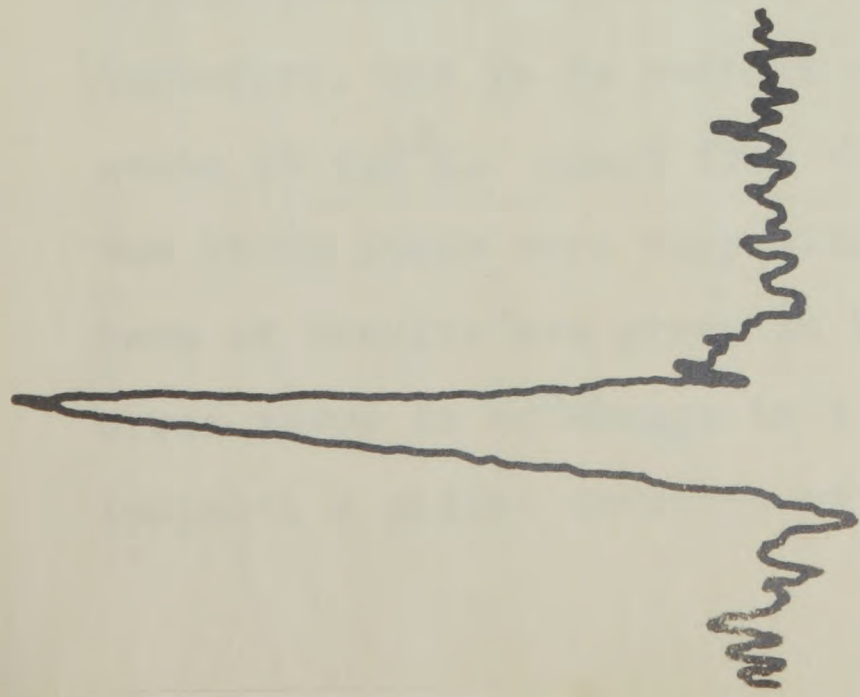
3.5 Thulium ENDOR Measurements

The four energy levels of the spin Hamiltonian (25) are given by the usual Breit-Rabi formula. For a given magnetic field the two nuclear transition frequencies are given by

$$\begin{aligned} \nu(S_z = +\frac{1}{2}) &= \left| \frac{1}{2h} (G-F) + \frac{A}{2} - \frac{1}{2} \left[\frac{1}{h^2} (G+F)^2 + A^2 \right]^{\frac{1}{2}} \right| \\ \nu(S_z = -\frac{1}{2}) &= \left| -\frac{1}{2h} (G-F) + \frac{A}{2} + \frac{1}{2} \left[\frac{1}{h^2} (G+F)^2 + A^2 \right]^{\frac{1}{2}} \right| \end{aligned} \quad (26)$$

where $G = g\beta H$, $F = g_n \beta_n H$ and A is in frequency units. Thus provided the field is kept constant, the A value is given directly in frequency units as the sum of the two ENDOR frequencies, independently of any other parameters.

The X band thulium ENDOR measurements were carried out using the quartz filled cavity. The magnetic field was aligned to within 5° of $[100]$ by using the resolution of the fluorine structure as a monitor. No ENDOR signals were observed at 20°K but by pumping on the refrigerant with a rotary vacuum pump quite strong signals were produced. The cavity temperature was estimated at 15°K on a carbon resistance thermometer. The ENDOR lines were unexpectedly



500kc/s

K Band

75kc/s

Fig 3.3 T_m ENDOR Lines at 15°K.

Time Constant 10 sec.

broad, being about 500 kc/s between points of maximum slope so a mean F.M. deviation of some 75 kc/s was needed to give good intensity. The optimum modulating frequency, so far as could be determined in the face of random variation of line intensity, was about 80 c/s and the 115 kc/s field modulation amplitude was about 0.1G. The ENDOR lineshape varied with cavity tuning from a perfectly anti-symmetric derivative of an absorption line to an entirely unsymmetrical shape (Fig. 3.3). The level of microwave saturation required for most intense ENDOR lines was very low. The optimum level was found to be when noise just started to appear on the peak of the E.P.R. dispersion signal as seen on the oscilloscope. Doubling the microwave power from this level was sufficient to reduce the ENDOR line intensity below noise level.

Variation of hyperfine parameter with temperature was investigated. Ideally such an investigation should be taken at least to 77°K but the nature of the $\text{CaF}_2:\text{Tm}^{2+}$ system prevented measurements above about 15°K. We, therefore, had to be content with repeating the measurements at 4.2°K. Apart from a slight increase in intensity the ENDOR lines were very similar to those at 15°K. Both sets of results are given in Table 3.2. Within experimental error there is no change in A value but the results could indicate a slight increase at 4.2°K of 0.005%.

Table 3.2 $\text{CaF}_2:\text{Tm}^{2+}$ Thulium ENDOR Frequencies, Hyperfine Parameter and, Nuclear g-value

	Field (G)	ENDOR Frequencies (Mc/s)		A value (Mc/s) ($=\nu_1 + \nu_2$)	g_n (n.m.)
		ν_1	ν_2		
(a) X Band 15°K	1757.7	516.30 ± 0.05	585.11 ± 0.05	1101.41 ± 0.1	
	1987.4	520.48 ± 0.05	580.82 ± 0.01	1101.30 ± 0.15	
(b) X Band 4.2°K	1756.2	516.276 ± 0.020	585.140 ± 0.027	1101.416 ± 0.05	
	1985.7	520.470 ± 0.025	580.993 ± 0.025	1101.463 ± 0.05	
(c) K Band 15°K	4717.8	540.1226 ± 0.002	561.2537 ± 0.002	1101.376 ± 0.004	0.757 ± 0.005
	4953.8	540.8714 ± 0.002	560.5051 ± 0.003	1101.376 ± 0.004	0.754 ± 0.005

In order to give a more accurate value for the nuclear moment the measurements were repeated at K band where the nuclear Zeeman energy is two and a half times greater. However, the accuracy of measurement of the ENDOR frequencies themselves was also considerably improved by two factors:

- 1) The ENDOR linewidth between points of maximum slope fell to about 120 Kc/s.
- 2) The ENDOR line intensity was appreciably greater (Fig. 3.3) due to higher EPR intensity and also to the modulation rods in the standard K band cavity being nearer the sample giving an increased NMR field.

The four ENDOR frequencies were measured with the magnetic field monitored throughout to fulfil the condition that both ENDOR frequencies on a given E.P.R. line should have the same magnetic field. The results are also given in Table 3.2 and it will be noticed how closely the sums of ENDOR frequencies on the two E.P.R. lines agree.

3.6 Possible Corrections to Observed ENDOR Frequencies

Baker and Hurrell (1963) have considered what shift in the ENDOR frequencies of the impurity ion nucleus may be expected from hyperfine interaction with ligand nuclei. We may summarise their results as they apply to the present case by reference to Fig. 3.4. which represents the energy levels of the thulium nucleus and one fluorine

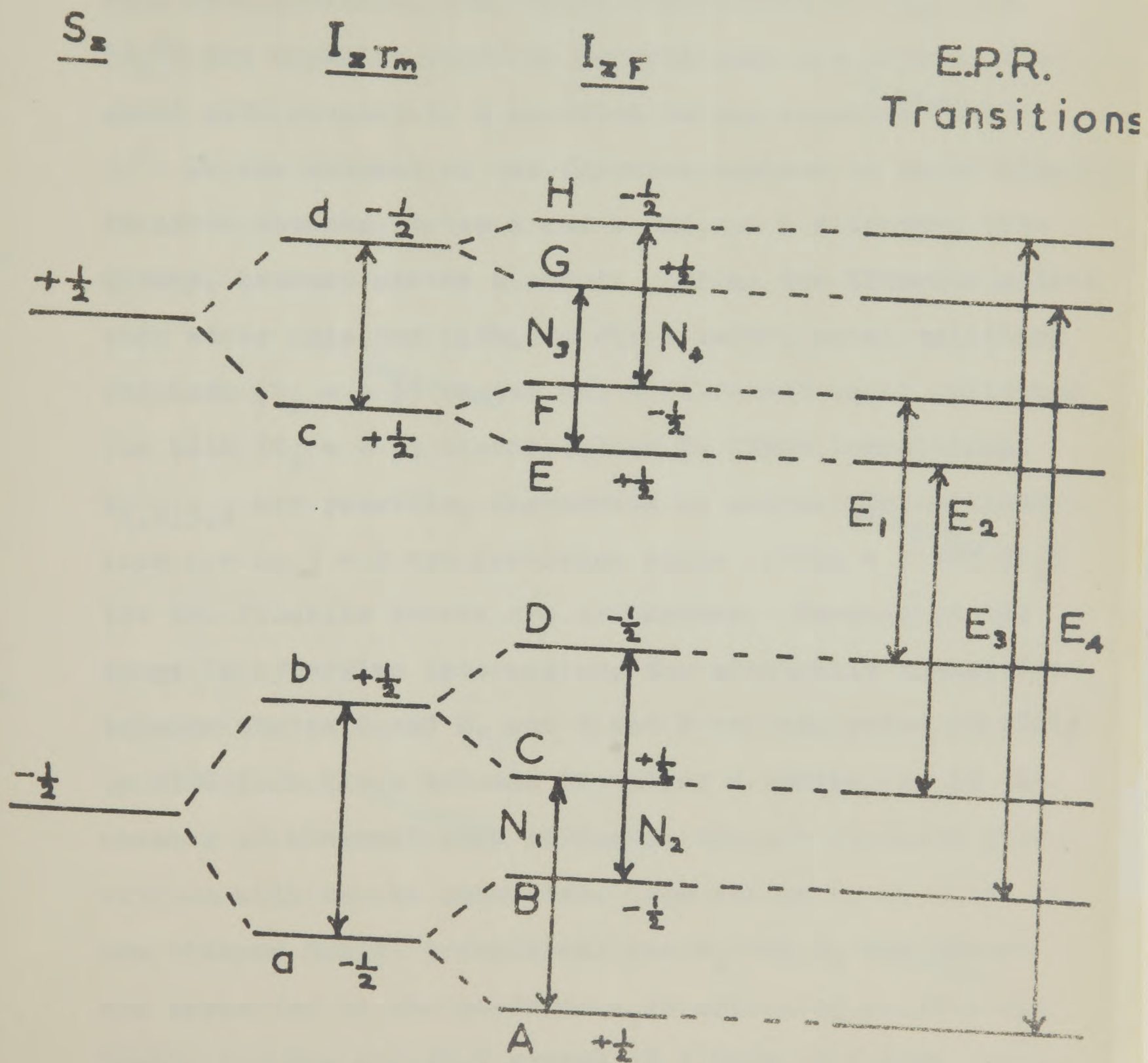


Fig 3.4. Energy Levels of Tm^{3+} Ion and

One F^{19} Nucleus

nucleus ($I = \frac{1}{2}$), interacting with the electron at constant field. The order of levels may be different from that shown as it depends on the sign and magnitude of the hyperfine interactions. The states represented by " I_z " and " I_z^F " are symbolic since in general none are exactly diagonal with respect to z parallel to the magnetic field.

In the absence of the fluorine nucleus we would observe Tm ENDOR between states a and b and, at a different frequency, between states c and d. Adding the fluorine splits each state into two with, to first order, equal splitting for both $|S_z = +\frac{1}{2}\rangle$ states and a different equal splitting for both $|S_z = -\frac{1}{2}\rangle$ states. Four Tm ENDOR transitions, $N_{1,2,3,4}$ are possible, degenerate in pairs. Transitions like $A \leftrightarrow D$, $B \leftrightarrow C$ are forbidden since within a given $|S_z\rangle$ the two-fluorine states are orthogonal. Because of the large Tm hyperfine interaction, the electronic transition between states C and D, and E and F are separated in field by 230G from those between the other 4 states, so in the absence of abnormal spin diffusion the non resonant transitions will not be saturated. For states C, D, E and F the allowed E.P.R. transitions are E_1 and E_2 and these are separated by the difference in splitting of fluorine levels for the two $|S_z\rangle$ states (2.5 Mc/s at K band for $H//[100]$).

If some perturbation removes the equality of the

splittings of the two pairs of fluorine states on a given $|S_z\rangle$ the ENDOR transitions N_3, N_4 and N_1, N_2 will be split about the unperturbed frequency. If both E_1 and E_2 are equally saturated N_3 and N_4 will be observed together, causing a broadening of the Tm ENDOR lines but very little shift in its centre. This is probably the case for CaF_2 : Tm^{2+} since E_1 and E_2 are so close together and spin diffusion appears to be occurring. If E_1 only were saturated N_1 and N_3 would not be observed and the Tm ENDOR frequencies would appear slightly shifted. Similarly for saturation of E_2 alone.

A difference in splitting of the pairs of fluorine levels for a given $|S_z\rangle$ is caused by the thulium hyperfine interaction. This admixes some of $|S_z = -\frac{1}{2}, I_{z_{\text{Tm}}} = +\frac{1}{2}\rangle$ to $|+\frac{1}{2}, -\frac{1}{2}\rangle$ while leaving $|+,+\rangle$ and $|--\rangle$ unchanged. The change in fluorine spacings can be estimated by using the expectation value of $\langle S_z \rangle$ within the mixed states rather than $\pm \frac{1}{2}$. For the present case at K band the change is about 1.5 kc/s which may be neglected.

A second shift comes from terms in the full spin (27) Hamiltonian coupling different electron spin states via the fluorine ligand hyperfine interaction. However, the shift is independent of I_z and so causes no change in the Tm ENDOR frequency.

A final correction comes from indirect fluorine-fluorine

interaction via the electron when all eight nearest neighbour fluorines are considered. This raises the degeneracy of different nuclear states corresponding to $\sum_{n=1}^8 I_{zn}^f = K$ and Λ is available to high accuracy as the ν_{12} and ν_{13} ($K = -4 \rightarrow +4$) for any particular K .

Baker and Hurrell find that if the centre of the E.P.R. line is saturated this leads to no change in the Tm ENDOR frequency. Saturating the side of the E.P.R. line will give a shift of a very few kilocycles at X band. Our measurements were made at K band with the magnetic field near the centre of the E.P.R. line so we disregard this effect.

There are thus no corrections of significance to be made to the four measured Tm ENDOR frequencies.

3.7 Evaluation of the Nuclear Moment

Expanding the square root in (26) to the accuracy of the ENDOR frequency measurement (a few kilocycles at K band) gives

$$\begin{aligned} \nu(S_z = +\frac{1}{2}) &= \left| \frac{A}{2} - \frac{F}{h} - \frac{1}{4} \frac{hA^2}{(G+F)} + \frac{1}{16} \frac{h^3 A^4}{(G+F)^3} \right| = |\Lambda_{\frac{1}{2}}| \\ \nu(S_z = -\frac{1}{2}) &= \left| \frac{A}{2} + \frac{F}{h} + \frac{1}{4} \frac{hA^2}{(G+F)} - \frac{1}{16} \frac{h^3 A^4}{(G+F)^3} \right| = |\Lambda_{-\frac{1}{2}}| \end{aligned} \quad (27)$$

Thus, providing the magnetic field is the same for both measurements.

$$\frac{2F}{h} = \left| \Delta_{-\frac{1}{2}} - \Delta_{+\frac{1}{2}} \right| - \frac{1}{2} \frac{hA^2}{(G+F)} + \frac{1}{8} \frac{h^3 A^4}{(G+F)^3} \quad (28)$$

and A is available to high accuracy as the sum of $\nu_{-\frac{1}{2}}$ and $\nu_{+\frac{1}{2}}$. The second term of (28) is almost equal to $\nu_{-\frac{1}{2}} - \nu_{+\frac{1}{2}}$, 20 Mc/s at K band, 60 Mc/s at X band and is potentially the largest source of error, due to its dependence on $g\beta H$. Since $(\nu_{-\frac{1}{2}} - \nu_{+\frac{1}{2}})$ is accurate to about 10 kc/s at K band we would require $g\beta H$ to be accurate to a few parts in 10^4 to make full use of the accuracy of the ENDOR measurement. In fact the accuracy is limited by the accuracy of the g value, 3.452 ± 0.002 rather than by magnetic field measurement. The values of g_n derived from measurements on each E.P.R. line at K band are given in Table 3.2. This is satisfactory and justifies the calculated

3.8 Discussion

(a) Nuclear Moment

The two values of the apparent nuclear moment g_n obtained from the K band measurements agree rather better than the expected limits of error. This is not surprising since the main source of error in the Tm^{2+} g value would affect both measurements in the same way. The mean value is, therefore, $|g_n| = 0.756 \pm 0.005$ (nuclear magnetons).

It can be shown that the sign of $\frac{2F}{h}$ given by (28) is independent of the sign assumed for the Tm A value provided

$|\Delta_{-\frac{1}{2}} - \Delta_{+\frac{1}{2}}|$ is taken always as the positive difference between the two frequencies. The K band measurements then show that g_n'' is negative. Applying the correction calculated in Section 3.3(iv), due to coupling to excited states gives

$$g_n = g_n'' - (-0.288) = -0.468.$$

Since the spin of the ^{169}Tm nucleus is $\frac{1}{2}$ this gives a nuclear moment of

$$\mu_n = -0.234 \pm 0.003 \text{ n.m.}$$

Ritter, using atomic beam methods has measured the ^{169}Tm nuclear moment as

$$\mu_n = -0.229 \pm 0.003 \text{ n.m.}$$

The agreement is satisfactory and justifies the calculated correction from the excited states. Also illustrated is the power of the ENDOR technique in minute investigation of the ground state of the paramagnetic ion.

(b) Hyperfine Constant

(1) Core Polarisation

In deriving the expressions (11) and (18) for the hyperfine interaction account was taken only of the contribution of the 4f electrons and any s-contact interaction was specifically excluded. However, for the Tm^{2+} ion there is likely to be a contribution from s electrons to the

measured hyperfine parameter. These electrons are in closed shells and should, therefore, give no field at the nucleus. Abragam, Horowitz and Pryce (1955) in considering this effect for the iron group suggested it could be caused by admixing of higher configurations in which a 3s electron had been promoted to a higher s-state. However, their calculation could only account for 10% of the experimentally observed value. They pointed out the important experimental result that for iron group ions the field at the nucleus due to core polarisation was proportional to the unpaired electronic spin.

More detailed calculations were made by Patson and Freeman (1961) starting from the point of view that exchange interaction between the unpaired electrons and s electrons in closed shells caused the latter to have different spatial functions depending on spin orientation relative to the unpaired electrons. They calculated the contributions to field per unit spin at the nucleus from 1s, 2s and 3s shells separately and found shells inside the 3d gave negative contributions and these outside a positive one. For these purposes the 3s shell appears to be "outside". The total effect was negative and approximately constant for the ions considered and rather larger than the experimental value. For iron group atoms the extra positive contribution from the 4s electrons should reduce

the total effect to a very small value.

For rare earth ions in CaF_2 Freeman and Watson (1962) suggested that following the iron group results the core polarisation could be taken as proportional to the projection of $\underline{S}$ along $\underline{J}$. In the iron group the core polarisation effect was found to reduce with increasing covalency of the ligands. For rare earth ions the bonding is smaller and fluorine ions are one of the least covalent ligands so that core polarisation is more likely to be determined by the ion.

Baker and Williams (1962) give for $^{151}\text{Eu}^{2+}$, $A_c = -83 \text{ Mc/s}$ and $g_I = -7.50 \times 10^{-4}$ Bohr magnetons, leading to a value of 60 Mc/s per unit nuclear magneton per unit $\langle S_z \rangle$. We compute $\langle S_z \rangle$ within the ground state of Tm^{2+} , including the contribution from $J = \frac{5}{2}$ using $S_z = (L_z + 2S_z) - J_z$ and find for the change in $\langle S_z \rangle$ due to transition between the two halves of the ground doublet.

$$\Delta \langle S_z \rangle = 2 \langle + | S_z | + \rangle = \frac{3}{7} + \frac{16\alpha}{7\sqrt{3}} - \frac{4\alpha^2}{21} \quad (29)$$

The core polarisation correction to the Tm^{2+} hyperfine interaction is then

$$A_c = -60 g_n \left(\frac{3}{7} + \frac{16\alpha}{7\sqrt{3}} - \frac{4\alpha^2}{21} \right) \quad (30)$$

Using the measured value of $g_n = -0.468$ gives an estimate of A_c as +13.7 Mc/s.

(ii) Orbital Reduction Factor

Covalent bonding occurs between the Tm^{2+} 4f electrons and the ligand fluorines. The effect of this on the central ion properties may be described empirically (Stevens (1953)) by replacing the angular momentum operator by $k\mathbf{L}$; $k < 1$. The need for the orbital reduction factor in the case of Tm^{2+} in CaF_2 is shown by comparing its g value with that expected from eqn. (17). Judd and Lindgren have calculated the diamagnetic and relativistic corrections to g_j for rare earth atoms and trivalent ions and also allowed for breakdown of Russell-Saunders coupling. They conclude that the corrections for Tm are less than 0.2%. However, we may allow for them by using $g_j = 1.141$ measured by Ritter for the Tm atom rather than the Landé g factor. The calculated g value for Tm^{2+} in CaF_2 is then 3.474 as compared with the experimental value of 3.452. This is well outside the experimental error so we use the difference to estimate the value of k by replacing the Zeeman operator with $k\mathbf{L} + 2\mathbf{S}$. Operating within the $\Gamma_7(\frac{7}{2}) + \alpha\Gamma_7(\frac{5}{2})$ ground state leads to

$$g = 3g_j - \frac{18}{8}(1 - k) + \frac{16\alpha}{7\sqrt{3}}(2 - k) - \frac{34}{7}\alpha^2 \quad (31)$$

from which the required value of k is found to be 0.991 ± 0.001 .

This value of k may now be used to continue discussion

of the measured A value. Since the hyperfine interaction in Tm^{2+} derives mainly from the orbital momentum the value calculated from (19) may simply be multiplied by k . Putting this equal to the measured hyperfine interaction less core polarisation:

$$-1101.4 - 13.7 = kA_0 \left(1 - \frac{\alpha}{2\sqrt{\beta}} - 2\alpha^2\right) \quad (32)$$

Thus for the free Tm^{2+} ion $a_{\text{III}} = \frac{A_0}{3} = -382.4 \text{ Mc/s}$. A discussion of the Tm^{2+} A value similar to the above and based on these ENDOR measurements was given by Bleaney (1964).

Freeman and Watson state (footnote, ref. 52) that in the case of the Eu atom as compared to the Eu^{2+} ion the contribution to core polarization from the 6s shell, being opposite in sign, reduces the total effect to a very small value. This is similar to their calculated effect for iron group atoms. We, therefore, neglect any core polarization correction for the Tm atom and take Ritter's value for the hyperfine interaction, -374.14 Mc/s as being due to the 4f electrons alone. Comparison with the estimated value for the free Tm^{2+} ion shows that removal of the two 6s electrons leads to an increase of $\langle r^{-3} \rangle$ for the 4f shell of about 2% (depending on the correctness of the core polarisation correction). This is consistent with the calculations of Freeman and Watson (1962) who find the amplitude of the 6s radial function to be very small over the region of the

4f maximum. Bleaney points out that the $\text{CaF}_2:\text{Tm}^{2+}$ optical and E.P.R. measurements would lead to a spin-orbit coupling parameter for the Tm^{2+} ion (which also depends on $\langle r^{-3} \rangle$) of 2536 cm.^{-1} . This is 1.2% larger than for atomic thulium.

The importance of atomic beam and ENDOR measurements for rare earths lies in the direct determination of nuclear moment and hyperfine interaction separately, giving an experimental value of $\langle r^{-3} \rangle$ for the electrons in the ground state. This can be used as one test of any theoretically derived wavefunctions as, for example, the Hartree-Fock calculations of Freeman and Watson for trivalent rare earths. Various estimates of $\langle r^{-3} \rangle$ for the Tm atom have been discussed by Ritter in the light of his atomic beam measurements. He finds Lindgren's value of 10.73 a.u. based on a modified hydrogenic function to be in best agreement with experiment. Similar calculations by Judd and Lindgren give $\langle r^{-3} \rangle$ for the Tm atom as 10.51 a.u. and for Tm^{3+} 10.95. Our result that for Tm^{2+} $\langle r^{-3} \rangle$ should be 2% larger than for the atom, fits into this range quite well.

Baker, Bleaney & Hayes (1958).

Buckmaster, H.A., 1967, *Canad. J. Phys.* 45, 2875.

Jones, D.S., Baker, J.D., & Jones, E.F., 1956, *Proc. Phys. Soc.*, 74, 749.

Judd, B.R., 1953, *Proc. Roy. Soc.* 221, 199.

Stevens (1952).

REFERENCES TO CHAPTER 3

- Baker, J.M., & Williams, F.I.B., 1961, Proc. Roy. Soc. A230, 169.
- Abragam, A., Horowitz, J., & Pryce, M.H.L., 1955, Proc. Roy. Soc. A230, 169.
- Baker, J.M., & Bleaney, B., 1958, Proc. Roy. Soc. A245, 156.
- Baker, J.M., Bleaney, B., & Hayes, W., 1958, Proc. Roy. Soc., A247, 141.
- Baker, J.M., Hayes, W., & O'Brien, M.C.M., 1960, Proc. Roy. Soc. A254, 273.
- Baker, J.M., & Hurrell, J.P., 1963, Proc. Phys. Soc. 82, 742.
- Baker, J.M. & Williams, F.I.B., 1962, Proc. Roy. Soc. A267, 283.
- Bierig, R.W., Weber, M.J., & Warshaw, S.J., 1964, Phys. Rev. 134, A1492, A1504.
- Bleaney, B., 1964, Proc. Roy. Soc. A277, 289.
- Bleaney, B., Llewellyn, P.M., & Jones, D.A., 1956, Proc. Phys. Soc., B69, 858.
- Burns, G., 1962, Phys. Rev. 128, 2121.
- Burns, G., 1965, J. Chem. Phys. 42, 377.
- Elliott, R.J., & Stevens, K.W.H., 1953, (a) Proc. Roy. Soc. A218, 553. (b) Ibid, A219, 387.
- Other authors giving matrix elements of crystal field operators are:-
- Baker, Bleaney & Hayes (1958).
- Buckmaster, H.A., 1962, Canad. J. Phys. 40, 1670.
- Jones, D.A., Baker, J.M., & Pope, D.F.D., 1959, Proc. Phys. Soc., 74, 249.
- Judd, B.R., 1955, Proc. Roy. Soc. A227, 552.
- Stevens (1952).

Transformation properties of the operators are given by:-

Baker, J.M., & Williams, F.I.B., 1961, Proc.Phys.Soc. 78, 1340.

Buckmaster, H.A., 1964, Canad.J.Phys. 42, 386.

Weiler, M.H., & Wylie, D.W., 1965, Proc.Phys.Soc. 85, 608.

Forrester, P.A., & McLaughton, B.D., 1965, Conference on Solid State Physics, Bristol.

Freeman, A.J., & Watson, R.E., 1962, Phys.Rev. 127, 2058.

Hall, T.P.P., Hayes, W., Stevenson, R.W.H., & Wilkens, J., 1961, (a) J.Chem.Phys. 38, 1977. (b) Ibid, 39, 35.

Hayes, W., & Twidell, J.W., 1961, J.Chem.Phys., 35, 1521.

Hutchings, M.T., & Ray, D.K., 1963, Proc.Phys.Soc. 81, 522.

Jorgensen, C.K., Pappalardo, R., & Schmidtke, H.H., 1963, J.Chem.Phys. 39, 1422.

Judd, B.R., & Lindgren, I.P.K., 1961, Phys.Rev. 122, 1802.

Kiss, Z.J., 1962, Phys.Rev. 127, 718.

Lea, K.R., Leask, M.J.M., & Wolf, W.P., 1962, J.Phys.Chem. Solids 23, 1381.

Low, W., & Ranon, V., 1963, Ed.W.Low, Paramagnetic Resonance, Vol. I, p. 167, Academic Press.

Ritter, G.J., 1962, Phys.Rev. 128, 2238.

Statz, H., & Koster, G.F., 1959, Phys.Rev. 115, 1568.

Stevens, K.W.H., 1952, Proc.Phys.Soc. 65, 209.

Stevens, K.W.H., 1953, Proc.Roy.Soc. A219, 542.

Twidell, J.W., 1963, Thesis, Oxford.

Watson, R.E., & Freeman, A.J., 1961, Phys.Rev. 123, 2027.

axial symmetry about Chapter 4rins nuclei. FLUORINE ENDOR OF $\text{CaF}_2:\text{Tm}$ 4.1 ENDOR Frequencies

The E.P.R. line shows the partly resolved interaction between the hole on the Tm^{2+} ion and the nearby fluorine nuclei. This consists mainly of the dipolar interaction with the nuclear magnetic moments but, for the nearest neighbour fluorines, there is also an appreciable contribution from covalent bonding.

To describe the fluorine ENDOR spectrum we use the spin Hamiltonian

$$\mathcal{H}_F = g\beta\mathbf{H}\cdot\mathbf{S} + \sum_n (\mathbf{S} \cdot \mathbf{A}_n \cdot \mathbf{I}_n^F - g_F\beta_n \mathbf{H} \cdot \mathbf{I}_n^F) \quad (1)$$

where the sum is over all interacting fluorine nuclei, $\mathbf{I}_n^F$ is the fluorine nuclear spin, $\frac{1}{2}$, and g_F is the fluorine nuclear g factor, 5.2546. Any direct interaction between the nuclei has been omitted as being very small. Interaction between the electron spin and thulium nucleus is also omitted since it does not change during a fluorine ENDOR transition and its effect on the spacing of the fluorine levels is very small.

For second and more distant fluorine shells we take the hyperfine interaction to have an isotropic part, A_s , and a dipole-like anisotropic part, A_p , with approximately

axial symmetry about the line joining the thulium and fluorine nuclei. Implicit in (1) is an indirect interaction between different fluorines leading to energy shifts of order $|A_n|^2/\nu_e$ where ν_e is the microwave frequency. Since this is very small we neglect it and treat separately the interaction of each fluorine nucleus with the electronic system. When the magnetic field is at an arbitrary angle, θ , to the bond direction these assumptions lead to the spin Hamiltonian for each fluorine nucleus.

$$\begin{aligned} \mathcal{H}_F = & [A_S + A_P(3\cos^2\theta - 1)]S_z I_z^F \\ & + 3A_P \sin\theta \cos\theta S_z I_x^F - g_F \beta_n H_z I_z^F \end{aligned} \quad (2)$$

where we have omitted terms which couple the two electronic spin states only through the small fluorine hyperfine parameters. The exact solution of this Hamiltonian gives the two fluorine ENDOR frequencies in a field H for $\underline{S} = \frac{1}{2}$

$$\begin{aligned} \nu(S_z) = & \left[\left\{ g_F \beta_n \frac{H}{\hbar} - S_z [A_S + A_P(3\cos^2\theta - 1)] \right\}^2 \right. \\ & \left. + \frac{9}{4} A_P^2 \sin^2\theta \cos^2\theta \right]^{\frac{1}{2}} \end{aligned} \quad (3)$$

with ν , A_S and A_P in Mc/s. For the second and more distant fluorine shells a second order expansion of (3) is sufficiently accurate giving

$$\begin{aligned}
 \nu(S_z) = & g_F \beta_n \frac{H}{h} - S_z [A_S + A_P(3\cos^2\theta - 1)] \\
 & + \frac{9hA_P^2 \sin^2\theta \cos^2\theta}{8g_F \beta_n H}
 \end{aligned}
 \tag{4}$$

$(S_z = \frac{1}{2})$

The nuclear Zeeman term (approx. 20 Mc/s at K band) is the largest in (4) and this defines the centre of the ENDOR spectrum. The hyperfine interaction may be thought of as representing a small additional field at the fluorine nucleus due to the electron, which is roughly parallel or antiparallel to the static field depending on the (fictitious) spin state. Each fluorine nucleus, therefore, produces two ENDOR lines, approximately symmetrically placed about the fluorine N.M.R. frequency. The separation of the pair is $A_S + A_P(3\cos^2\theta - 1)$ causing lines from the more distant shells to be grouped in an unresolved superposition at the centre of the spectrum. Under the assumptions made all fluorines in a given shell with the same value of $\cos^2\theta$ will produce ENDOR lines at the same frequencies and the fluorines are always degenerate at least in pairs. When the magnetic field is along high symmetry crystal directions the degeneracy is quite high. Table 4.1 gives the appropriate values of $\cos^2\theta$ and the degeneracy for shells 1-4, for $\underline{H}$ along the three principal crystal directions.

Table 4.1 Fluorine Equivalencies for the Cation Site in Calcium Fluoride

	1st Shell		2nd Shell		3rd Shell		4th Shell	
	$\cos^2\theta$	No. of Fluorines	$\cos^2\theta$	No. of Fluorines	$\cos^2\theta$	No. of Fluorines	$\cos^2\theta$	No. of Fluorines
$\underline{H}/[100]$	1/3	8	9/11 1/11	8 16	1/19 9/19	8 16	1/3 25/27 1/27	8 8 16
	2/3 0	4 4	8/11 2/11 0	8 12 4	18/19 8/19 2/19 0	4 8 8 4	2/3 8/27 2/27 0	12 8 4 8
	1 1/9	2 6	25/33 3/11 1/33	6 12 6	49/57 25/57 1/57	6 6 12	1 49/81 25/81 1/9	2 6 12 12
$\underline{H}/[111]$								

The positions of fluorines in the various shells relative to the cation site as origin, in units of half the $[100]$ F-F separation, are given by vectors constructed from all permutations of the following components:-

1st Shell $\left(\begin{smallmatrix} \pm 1, \\ \pm 1, \\ \pm 1, \end{smallmatrix} \begin{smallmatrix} \pm 1, \\ \pm 1, \\ \pm 1, \end{smallmatrix}\right)$.
 2nd Shell $\left(\begin{smallmatrix} \pm 1, \\ \pm 1, \\ \pm 1, \end{smallmatrix} \begin{smallmatrix} \pm 3, \\ \pm 3, \\ \pm 3, \end{smallmatrix}\right)$.
 3rd Shell $\left(\begin{smallmatrix} \pm 1, \\ \pm 1, \\ \pm 1, \end{smallmatrix} \begin{smallmatrix} \pm 3, \\ \pm 3, \\ \pm 3, \end{smallmatrix}\right)$.
 4th Shell $\left(\begin{smallmatrix} \pm 3, \\ \pm 3, \\ \pm 3, \end{smallmatrix} \begin{smallmatrix} \pm 1, \\ \pm 1, \\ \pm 1, \end{smallmatrix}\right)$, and $\left(\begin{smallmatrix} \pm 1, \\ \pm 1, \\ \pm 1, \end{smallmatrix} \begin{smallmatrix} \pm 5, \\ \pm 5, \\ \pm 5, \end{smallmatrix}\right)$.

4.2 Determination of Hyperfine Parameters

The crystal was mounted as accurately as possible in the K-band cavity to have a (110)-type plane horizontal. The magnetic field could then be rotated into directions [100], [011] and [111] as required. The fluorine ENDOR spectra were produced as described in sec. 8.2 using the E.P.R. dispersion signal at the same temperature (15°K) as proved optimum for the thulium ENDOR. Accurate alignment of the magnetic field along each of the three principal directions was achieved by using the degeneracy of the extreme lines as a monitor. Since these lines split very rapidly with mis-alignment an accuracy of about 0.1° was possible, though not without considerable time and patience.

The resulting three K band ENDOR spectra on the high field E.P.R. line are shown in fig. 4.1. They have the expected symmetry about the fluorine N.M.R. frequency which is the reverse phase line at 19.87 Mc/s. (The fact that the [100] spectrum has opposite phase to the other two is simply due to opposite phase of the reference signal on the detector in this instance.) It is interesting that the first shell ENDOR lines have the same phase as the main spectrum for $H//[100]$ but opposite phase for the other two directions. The figures above the lines refer to the fluorine shells concerned and the letters distinguish different equivalent sets within each shell for that direc-

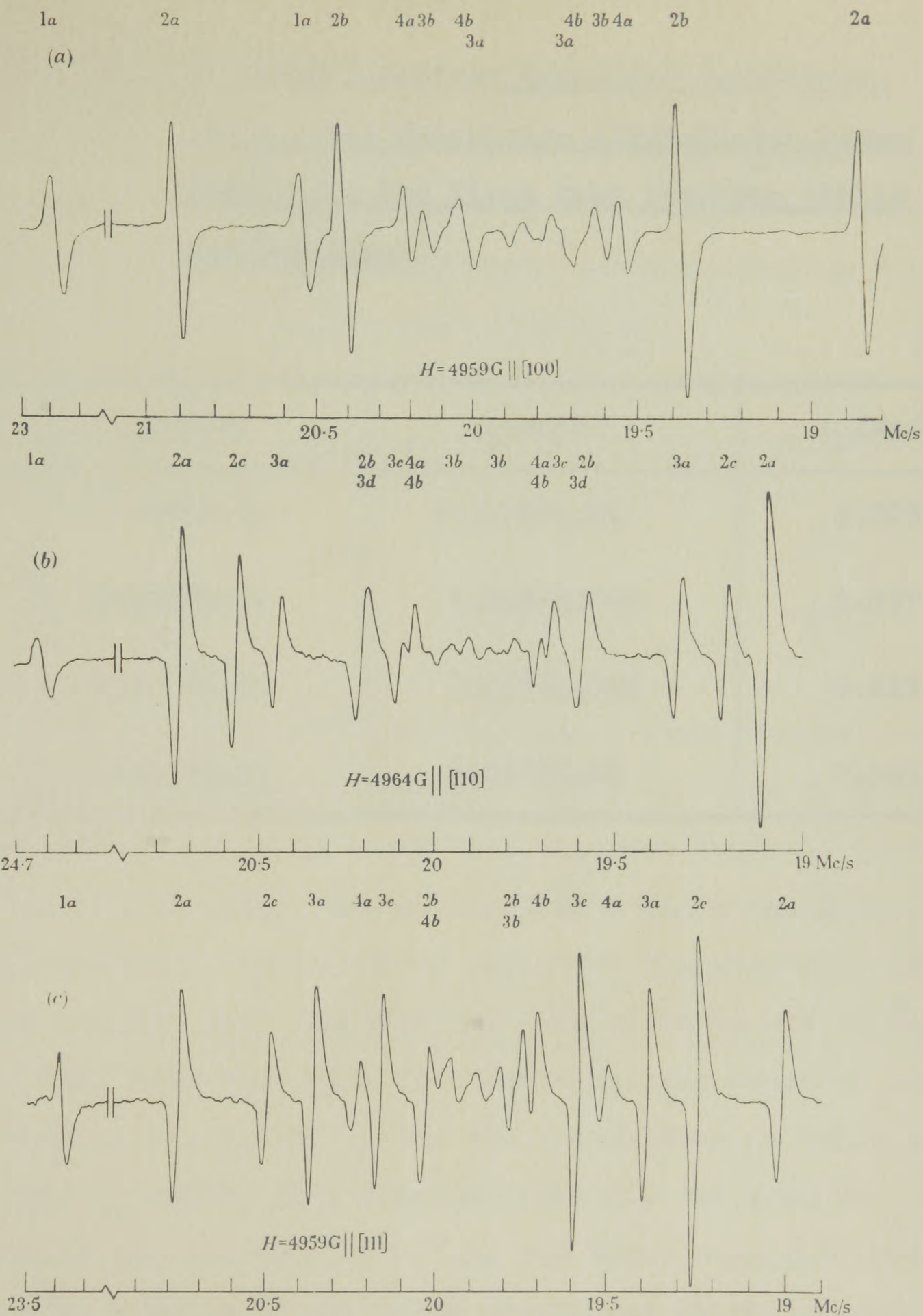


FIGURE 4.1 K-band fluorine endor spectra with the external magnetic field in the (a) [100], (b) [110], and (c) [111], directions. The ordinate represents $\delta^2\chi'/\delta\nu\delta H$, the derivative with respect to nuclear frequency of the derivative, $\delta\chi'/\delta H$, of the e.p.r. dispersion line. The lines labelled 1, 2, 3, 4 arise from interaction with fluorines in the first, second, third and fourth fluorine shells.

Table 4.2 Measured Fluorines Hyperfine Parameters,
 A_S , A_P , and Calculated Point-Dipole Para-
meter, A_D , For First Four Fluorine Shells
For $\text{CaF}_2\text{:Tm}$.

Shell	A_S (Mc/s)	A_P (Mc/s)	A_D (Mc/s)
1	2.584 ± 0.01	12.283 ± 0.01	9.809
2	0.010 ± 0.01	1.386 ± 0.005	1.397
3	0.00 ± 0.01	0.612 ± 0.005	0.615
4	0.00 ± 0.01	0.367 ± 0.01	0.363

tion of $\underline{H}$.

All the stronger lines were measured four times and some weaker ones at the centres of the spectra were measured by interpolation. The frequencies were corrected to a common magnetic field for each direction.

To identify the lines for shells 2-4 the dipolar hyperfine constant was calculated on the basis of classical point dipoles.

$$A_D = \frac{g_S g_N \mu_N \mu_B}{h R^3} \quad (5)$$

where R is the distance from thulium to fluorine nucleus. The values are given in Table 4.2. Using the fact that the separation of pairs of lines is $A_S + A_P(3\cos^2\theta - 1)$ the lines in the simpler [100] spectrum were identified approximately and confirmed or corrected by the other two spectra. All the measurable pair spacings for each shell in all three directions were then used in a least squares computer fit to evaluate the A_S and A_P and these are given in Table 4.2.

The A_S and A_P were also put into (4) and used to calculate the frequencies of all the lines expected from shells 2, 3 and 4 in the three directions at the appropriate standard fields. Table 4.3 compares the results with the corrected measured frequencies.

Table 4.3 Comparison of Calculated and Observed
Fluorine Endor Frequencies for Second,
Third and Fourth Fluorine Shells for
the High Field $\Delta M_I = 0$ Thulium Hyper-
fine Line at K Band.

(a) [100] direction		H = 4958.8G	
line (see figure 4.1 (a))	$\cos^2 \theta$	$\nu_{\text{calc.}}$ (Mc/s)	$\nu_{\text{obs.}}$ (Mc/s)
2a	$\frac{9}{11}$	20.887 18.869	20.903 18.863
2b	$\frac{1}{11}$	19.371 20.371	19.374 20.377
3a	$\frac{9}{19}$	19.995* 19.739*	20.010 19.717
3b	$\frac{1}{19}$	19.605 20.121	19.604 20.126
4a	$\frac{25}{27}$	20.190 19.543	20.190 19.538
4b	$\frac{1}{27}$	20.025* 19.699*	20.010 19.717

Table 4.3 (Continued)

(b) [110] direction		H = 4963.8G	
line (see figure 4.1 (b))	$\cos^2 \theta$	$\nu_{\text{calc.}}$ (Mc/s)	$\nu_{\text{obs.}}$ (Mc/s)
2a	$\frac{8}{11}$	20.719 19.073	20.731 19.087
2b	$\frac{2}{11}$	19.588* 20.208*	19.588 20.203
2c	0	19.194 20.570	19.197 20.565
3a	$\frac{18}{19}$	20.447 19.319	20.446 19.323
3b	$\frac{8}{19}$	19.967 19.807	(too weak to measure)
3c	$\frac{2}{19}$	19.674 20.094	19.675 20.095
3d	0	19.576* 20.188*	19.588 20.203
4a	0	20.066* 19.698*	20.071 19.702
4b	$\frac{2}{3}$	20.069* 19.701*	20.071 19.702

* These lines appear in spectra of the pure components. The observed frequencies quoted are those of the composite lines.

Table 4.3 (Continued)

(c) [111] direction		H = 4959.3G	
line (see figure 4.1 (c))	$\cos^2 \theta$	$\nu_{\text{calc.}}$ (Mc/s)	$\nu_{\text{obs.}}$ (Mc/s)
2a	$\frac{25}{33}$	20.771 18.998	20.769 19.007
2b	$\frac{3}{11}$	19.764* 20.007*	19.768 20.022
2c	$\frac{1}{33}$	19.241 20.493	19.242 20.494
3a	$\frac{49}{57}$	20.350 19.383	20.350 19.388
3b	$\frac{25}{57}$	19.965 19.773*	(too weak to measure) 19.768
3c	$\frac{1}{57}$	19.574 20.154	19.575 20.156
4a	1	20.235 19.501	20.222 19.504
4b	$\frac{49}{81}$	20.017* 19.717	20.022 19.717

* These lines appear in unresolved pairs (see figure 4.1); the observed frequencies quoted are those of the centres of the composite lines.

4.3 Nearest Neighbour Parameters

The bond axes for the eight nearest neighbour fluorines are 3-fold axes of the crystal. The hyperfine tensors will therefore have axial symmetry about these directions with principal values $A_{//}$, $A_{\perp}$ and $A_{\perp}$. So far as they go the experimental results support this assumption and we again use the expression (3) to describe the ENDOR spectrum. It is not possible to give a general expansion of (3) for nearest neighbours since A_p is about equal to $g_F \beta_n H$ so the hyperfine interaction may be greater or less than $g_F \beta_n H$ depending on the value of $\cos^2 \theta$. For all the nearest neighbour lines actually observed $g_F \beta_n H$ was the larger, allowing the use of (4). This introduces errors of the order of 100 kc/s at K band but is adequate for correcting the measured frequencies to a common field and for obtaining approximate values of A_s and A_p . Not all the expected nearest neighbour lines were observed so those that were were measured on both EPR lines and corrected to one magnetic field value for each line. A_s and A_p were obtained from a least squares fit of the eight frequencies to the exact expression (3). The calculated and observed frequencies are compared in Table 4.4.

Table 4.4 Comparison of Calculated and Observed
Nearest-Neighbour Fluorine ENDOR Fre-
quencies for Both $\Delta m_I = 0$ Thulium EPR
Lines at K Band.

Field Direction	$\cos^2 \theta$	High Field EPR line (4961.6G)		Low Field EPR line (4734.6G)	
		$\nu_{\text{calc.}}$ (Mc/s)	$\nu_{\text{obs.}}$ (Mc/s)	$\nu_{\text{calc.}}$ (Mc/s)	$\nu_{\text{obs.}}$ (Mc/s)
[100]	$\frac{1}{3}$	22.870 20.503	22.876 20.514	22.032 19.683	22.042 19.688
[110]	0	24.706	24.707	23.796	23.785
[111]	$\frac{1}{9}$	23.391	23.388	22.510	22.504

Table 4.5 $\text{CaF}_2:\text{Tm}$ ENDOR Linewidths at 15°K

	X Band (kc/s)	K band (kc/s)
Thulium ENDOR	500 ± 50	75 ± 5
Fluorine ENDOR [100]	19.8 ± 3	33.7 ± 4
Fluorine ENDOR [110]		27.1 ± 3
Fluorine ENDOR [111]		18.8 ± 4

Thulium ENDOR linewidth was isotropic within experimental error.

Errors on Fluorine ENDOR linewidth make no allowance for residual mis-alignment.

In contrast to the Tm ENDOR all the fluorine ENDOR lines were symmetrical absorption derivatives under all conditions and a modulating frequency of about 80 c/s was used. The nearest neighbour lines were more difficult to produce at best intensity especially for H//[011] or [111]; they depended rather critically on microwave power level.

Most measurements were made at K band since the lines were stronger but the main spectrum was also remeasured at X band and gave substantially the same parameters for shells 2, 3 and 4. Nearest neighbour lines were not observed.

4.4. Discussion

(a) Distant Shells

The errors quoted for the hyperfine parameters for shells 2, 3 and 4 are those obtained from the least squares fits and Table 4.3 shows how closely the frequencies calculated from these values agree with those observed. The wide range of values of $\cos^2 \theta$ for each shell for which lines were observed establishes well the dipolar form of the anisotropic interactions and confirms the site of the Tm²⁺ ion. The difference from the calculated point dipole value for shell 2 could be accounted for by an expansion of the shell by only 0.2%. Since the least squares fit requires a small, if uncertain, amount of isotropic interaction which can only come from bonding it is possible that

part of this reduction could be due to slight bonding to the fluorine 2p orbitals. A third possibility is that these are manifestations of the failure of the axial approximation or of the point dipole approximation for the Tm^{2+} ion.

Shells 3 and 4 parameters are, within the experimental error, equal to the calculated point dipole values. This indicates that the lattice is undistorted from the second fluorine shell outwards and would seem to place any charge compensating fluorine ion outside the fourth shell at least. An interstitial fluorine would have the largest interaction with $\text{H} // [100]$ and, if inside the fourth shell, would produce a pair of lines separated by more than 0.8 Mc/s. Fig 4.1 (a) shows that, unless they are accidentally degenerate with lines 2b, no such lines are produced.

(b) Nearest Neighbours

Table 4.4 shows that an axial hyperfine tensor can be fitted to within 10 kc/s to the measured frequencies at both values of magnetic field. Three different values of $\cos^2\theta$ were observed to define the angular variation, though two of them were not very different from each other. The accuracy with which the frequencies could be measured was sufficient to substantiate to within a few percent the axial symmetry. Any axial hyperfine tensor

may be decomposed into a traceless tensor (dipolar variation) and a constant tensor (isotropic interaction). For nearest neighbours bonding is appreciable but the contribution to the anisotropic hyperfine interaction from this cause is not necessarily dipolar. Any deviation will be accommodated by a change in the apparent value of A_s so the experimental A_s and A'_p should not be assigned too closely to distinct types of bonding.

The frequencies given by (3) depend explicitly on the relative signs of A_s and A_p . The observed frequencies can only be fitted with A_s and A_p of the same sign. The absolute signs are unknown since it cannot be determined which observed frequency corresponds to which electron spin state. However, the comparison of A_p with the classical point dipole value of +9.809 Mc/s suggests the positive sign may be more reasonable. The contribution, A'_p , to A_p from bonding would then be +2.474 Mc/s. If A_p were taken as negative the bonding contribution would need to be -22.92 Mc/s which seems rather large.

On the other hand a positive value for A_s is in conflict with the calculations of Watson and Freeman (1961) who show that exchange polarisation of 5s and 5p shells of rare earth ions by the 4f shell can lead to a net spin density in the outer reaches of the ion which is anti-parallel to the 4f spin. For Gd^{3+} in GdF_3 where the ligand

distance is $2.2 \text{ \AA}$ they calculate an A_S due to 5s polarisation of -4 Mc/s which is ten times larger than and opposite in sign to that due to the 4f shell. Baker and Hurrell (1963) have used the data of Watson and Freeman to estimate that for Eu^{2+} in CaF_2 $A_S = -8.2 \text{ Mc/s}$. Their ENDOR measurements on this system gives $A_S = -2.23 \pm 0.01 \text{ Mc/s}$. Furthermore their A_P of $+4.01 \pm 0.01 \text{ Mc/s}$ is 1.6 Mc/s less than the classical dipolar value, indicating a negative contribution, A_P' , from anisotropic bonding. It would clearly be interesting to have measurement of nearest neighbour parameters for other rare earth ions in CaF_2 to investigate the exchange polarisation effect in the outer shells.

It should be noted that the fluorine hyperfine parameters for Tm^{2+} are given in terms of the fictitious spin of $\frac{1}{2}$. The real spin $\langle S_z \rangle$, of the Γ_7 groundstate is $\frac{3}{7} \times \frac{1}{2}$ so the parameters should be multiplied by $\frac{7}{3}$ for comparison with other systems.

(c) E.P.R. Line Structure

With the accurate knowledge of the fluorine hyperfine parameters it should be possible to reconstruct the structure on the E.P.R. lines. With $H//[100]$ a fluorine multiplet will consist of nine lines of intensity ratio $1:8:28:56:70:56$ etc., separated from each other by the hyperfine interaction, which in this case is approximately A_S , 2.584 Mc/s . This leads to a separation between the extreme components of

3.5G. From Fig. 3.2 it can be seen that this is equal to the width of each component of the observed line structure. Above and below each allowed transition would be two forbidden ones in which a nearest neighbour fluorine may be thought of as "flipping" with the electron. These transitions are separated from the allowed by the ENDOR frequencies for $S_z = +\frac{1}{2}$ or $-\frac{1}{2}$ as appropriate. For the present case the separations are 22.876 and 20.514 Mc/s. (see Table 4.4) so they would not be separately resolved. However, their average corresponds very closely to the measured separation of 4.2G between the centres of adjacent components, of the E.P.R. structure. In Fig 4.2 an integration of the E.P.R. line at K band shows slightly poorer resolution on the low field side corresponding to smaller spacing of components. This would be expected from the reduction in the nuclear Zeeman term which represents the largest contribution to the fluorine ENDOR frequencies. Furthermore the X band E.P.R. line shows a much closer spacing of components as expected. This is perhaps the strongest evidence that the structure is not a straightforward hyperfine interaction.

To estimate the intensity of the forbidden transitions, contributions to the total forbidden line must be summed from all nine unresolved allowed transitions in the central component. This is easily done when it is realised that

the forbidden transition requires one of the "up" fluorines to be turned "down" during the electronic transition (or vice versa for the forbidden line on the other side of the centre). The number of ways this can be done for each of the nine allowed transitions is weighted by the intensity of that transition and summed to give the total forbidden intensity. The intensity of double forbidden transitions in which two fluorines are flipped and which occur at twice the ENDOR frequency from the centre are similarly found by turning over two fluorines at a time. If α is the ratio of forbidden to allowed transition intensity for one fluorine interacting with the electron then, relative to the total intensity of the central allowed component, the forbidden transitions have intensity $\frac{1104}{256}\alpha$, the double forbidden intensity is $\frac{1792}{256}\alpha^2$ and the treble forbidden intensity is $\frac{1792}{256}\alpha^3$.

The eigenstates of one nearest neighbour fluorine with $H//[100]$ at K band in terms of $|S_z = \pm\frac{1}{2}, I_z^F = \pm\frac{1}{2}\rangle$ are approximately

$$\frac{5}{\sqrt{26}} \left| \pm\frac{1}{2}, +\frac{1}{2} \right\rangle \pm \frac{1}{\sqrt{26}} \left| \pm\frac{1}{2}, -\frac{1}{2} \right\rangle \quad (6)$$

$$\frac{5}{\sqrt{26}} \left| \pm\frac{1}{2}, -\frac{1}{2} \right\rangle \mp \frac{1}{\sqrt{26}} \left| \pm\frac{1}{2}, +\frac{1}{2} \right\rangle$$

giving α approximately equal to 0.16. It should be noted

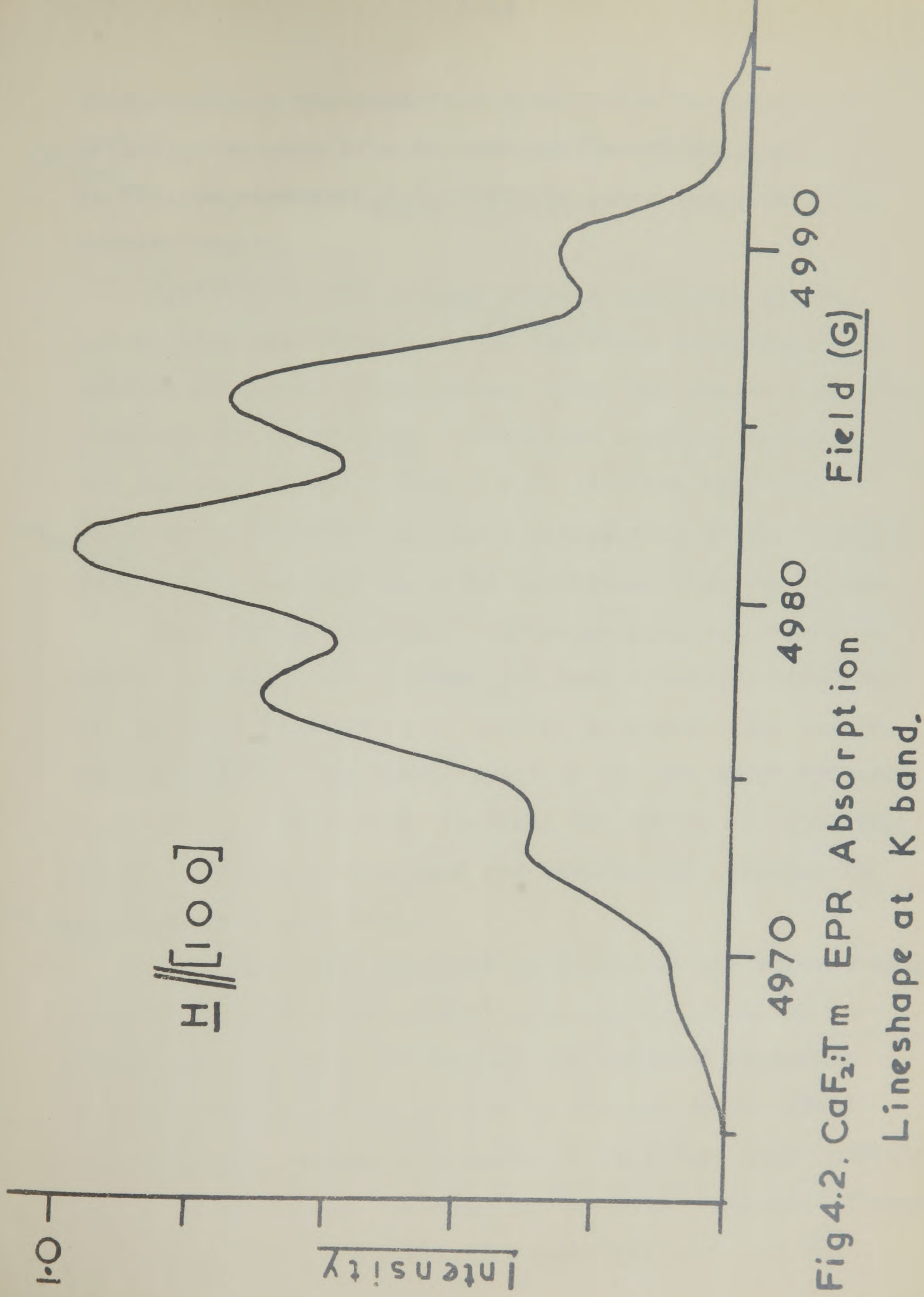


Fig 4.2. $\text{CaF}_2:\text{Tm}$ EPR Absorption

Lineshape at K band.

that, although the hyperfine interaction is small with $H/[100]$, the size of α depends on the off-diagonal term in (2), $3A_P \sin \theta \cos \theta S_z I_x^P$, which is quite large at intermediate angles.

4.2 ENDOR linewidths
Relative to the central allowed component of the E.P.R. line the intensities of the first forbidden transitions should be approximately 0.65, the second forbidden 0.18 and the third 0.03. A detailed computer analysis with behaviour at A and X bands. Computations were not made of the K band E.P.R. line but Fig. 4.2, which is an accurate numerical integration of the recorded derivative, can be seen to be consistent with the values.

The fact that the Yb^{3+} structure does not appear to align on the fluorine ENDOR. The results are given in change on going from X band to K band (Twidell, 1963) may Table 4.5.

be explained by suggesting that A_S is appreciably larger than for Tm^{2+} . This would split up the two ENDOR frequencies for $S_z = +\frac{1}{2}$ and $-\frac{1}{2}$, doubling the number of forbidden

as a superposition of spin packets, each corresponding to E.P.R. components at K band and causing the spectrum to a particular local field. In carrying out an ENDOR experiment one spin packet near the centre of the E.P.R. line is selected with the magnetic field and, if spin diffusion is negligible, only spins within this packet are saturated; equivalent and also the size of the measured hyperfine the ENDOR linewidth will vary as the size of the spin packet width. The spin packet width varies as the square root of the microwave field. The linewidths observed are much more satisfactory and is consistent with all the

The lack of any observed splitting of the nearest neighbour ENDOR lines from $H/[100]$ when all eight should be is negligible, only spins within this packet are saturated; equivalent and also the size of the measured hyperfine the ENDOR linewidth will vary as the size of the spin packet width. The spin packet width varies as the square root of the microwave field. The linewidths observed are much more satisfactory and is consistent with all the

The above discussion in terms of forbidden transitions seems the magnetic ions and reflects the fact that the microwave field. The linewidths observed are much more satisfactory and is consistent with all the

experimental evidence in the case of Tm^{2+} . Confirmation with regard to Yb^{3+} must await accurate determination of the nearest neighbour parameters.

4.5 ENDOR Linewidths

The significant reduction in Tm ENDOR linewidth on changing to K band has already been mentioned. This inspired a quick investigation of Tm and fluorine ENDOR linewidth behaviour at X and K bands. Accurate measurements were not attempted since this would have required considerable work to overcome the effects of poor lineshape on the Tm ENDOR, (with weak lines at X band) and residual misalignment on the fluorine ENDOR. The results are given in Table 4.5.

(i) Thulium ENDOR linewidth

An inhomogeneously broadened line may be considered as a superposition of spin packets, each corresponding to a particular local field. In carrying out an ENDOR experiment one spin packet near the centre of the E.P.R. line is selected with the magnetic field and, if spin diffusion is negligible, only spins within this packet are saturated; the ENDOR linewidth will then be the same as the spin packet width. The spin packet width arises from homogeneous broadening due to spin-spin interaction between the magnetic ions and radiation broadening due to the microwave field. The linewidths observed are considerably

larger than this because of inhomogeneous broadening.

0.19 If the general expression for an ENDOR transition frequency between states $|S_z, I_z - 1\rangle$ and $|S_z, I_z\rangle$, as found by second order perturbation theory, is differentiated with respect to the magnetic field, H , the line width of an inhomogeneously broadened ENDOR line is readily found to be

$$\delta\nu = \frac{g_n \beta_n \Delta H}{h} - \frac{A^2}{2g\beta h} [S_z(S_z + 1) - S(S + 1) - 2I_z S_z] \frac{\Delta H}{H^2} \quad (7)$$

where ΔH is the width of the portion of the E.P.R. line saturated by the microwave field. When spin diffusion occurs E.P.R. transitions in Tm^{2+} ions which are non-resonant, due to the ion being in a slightly different local field, can also be saturated. The ENDOR frequency observed will be appropriate to that local field causing broadening of the line. The value of ΔH to be inserted in (7) is then the total width of the E.P.R. line saturated by the spin diffusion mechanism. For Tm ENDOR the first term in (7) is negligible, leading to a linewidth varying as H^{-2} . Inserting the measured linewidths into (7) we find $\Delta H = 32 \pm 3G$ at X-band and $29 \pm 2G$ at K band. and the agreement of these values supports the suggestion of inhomogeneous broadening. The very large value of ΔH indicates that rapid spin diffusion is occurring. It cannot be due to dipole-dipole interaction between the Tm^{2+} ions in the dilute $CaF_2:Tm$

system; the linewidth from this cause is estimated at 0.1G. A possible explanation is that fluorine ions in shells near the Tm^{2+} ion relax at a rate comparable with that of the Tm^{2+} ion itself and the inhomogeneous broadening due to hyperfine interactions with these fluorines is not static. This is consistent with the large transition probability calculated for the forbidden transitions involving nearest neighbour fluorines.

These results are in contrast to those of Baker and Williams (1962) who find ENDOR linewidths at X band of 7 kc/s and 8 kc/s for $^{153}\text{Eu}^{2+}$ and $^{151}\text{Eu}^{2+}$ in CaF_2 . In this case the inhomogeneous contribution to the linewidth is very small due to the rather small hyperfine interaction ($A^{153} = -45.7$ Mc/s; $A^{151} = -102.9$ Mc/s) and because of negligible spin diffusion.

(ii) Fluorine ENDOR Linewidth

The fluorine ENDOR linewidths of transitions in the second, third and fourth fluorine shells are expected to arise predominantly from fluorine nuclear dipole-dipole interactions. Even if the microwave energy saturated only Tm^{2+} ions of one particular value of local field this does not prevent their being a wide variety of local fields at the fluorine nuclei coupled to these ions. Van Vleck (1948) has calculated the fluorine nuclear resonance linewidths in CaF_2 arising from fluorine dipole-dipole

interactions and finds the linewidths between points of maximum slope to be 28.8 kc/s for $H/[100]$, 20.0 kc/s, $H/[110]$ and 12.2 kc/s, $H/[111]$. These results were confirmed by the nuclear resonance experiments of Pake and Purcell (1948). Table 4.5 shows that within the somewhat large experimental errors the fluorine ENDOR linewidths agree with these values at both X and K band. If we assume inhomogeneous broadening, examination of (7) shows that for fluorine ENDOR where A is only of the order of 10 Mc/s the second, field dependent term is negligible, leading to the same linewidth at X and K bands as observed. The corresponding value of ΔH is 5.7G.

Baker and Hurrell have considered sources of broadening of ENDOR lines and pointed out the indirect fluorine-fluorine interaction for nearest neighbour fluorines due to coupling via the electron. The interaction of the form $\langle |A_i^F S_{+i}^F -| \rangle \langle |A_j^F S_{-j}^F +| \rangle$ raises the degeneracy of the energy levels of nearest neighbour fluorines by an amount of the order of $(A^F)^2 / \nu_e$ where ν_e is the microwave frequency. This is of the order of 6 kc/s max. at K band and 15 kc/s max. at X band. Accordingly, nearest neighbour ENDOR lines will be broadened largely by the fluorine nuclear dipole fields and will have similar linewidths to the more distant shells as is observed.

REFERENCES TO CHAPTER 4

Baker, J.M., & Hurrell, J.P., 1963, Proc.Phys.Soc. 82, 742.

Baker, J.M., & Williams, F.I.B., 1962, Proc.Roy.Soc., A267, 283.

Low, W., & Ranon, U., 1963, Ed. W. Low, Paramagnetic Resonance, Vol. I, p. 167. Academic Press.

Pake, G.E., & Purcell, E.M., 1948, Phys.Rev. 74, 1184.

Twidell, J.W., 1963, Thesis, Oxford.

Van Vleck, J.H., 1948, Phys. Rev. 74, 1168.

Watson, R.E., & Freeman, A.J., 1961, Phys.Rev.Lett. 6, 277.

As with Tm^{2+} Addendum to Chapter 4 same sign, which

cannot be determined. Similar arguments to those used for Tm^{2+} again indicate that the positive sign should be chosen. Since the writing of this chapter there has come to hand a preprint reporting ENDOR measurements on the nearest neighbour fluorines of the isoelectronic Yb^{3+} on cubic sites in CaF_2 (Ranon and Hyde, 1966). The hyperfine interaction between the Yb^{3+} ion and fluorine nucleus was found to be axial as expected with

$$|A_{\parallel}| = 36.8 \pm 0.1 \text{ Mc/s}$$

$$|A_{\perp}| = 15.9 \pm 0.05 \text{ Mc/s}$$

$A_{\parallel}$ and $A_{\perp}$ have opposite signs. These values correspond to

$$A_s = 1.67 \pm 0.05 \text{ Mc/s}$$

$$A_p = 17.57 \pm 0.05 \text{ Mc/s}$$

which are similar to the values obtained for Tm^{2+} with a smaller A_s and an A_p larger than the point dipole value by nearly 80%. Ranon and Hyde point out that it is reasonable to assume that the electronic cloud of Yb^{3+} would be more localised than that of Tm^{2+} because of the higher nuclear charge, resulting in a smaller contact interaction, A_s , with the ligands. On the other hand the extra positive charge of the Yb^{3+} would cause the lobes of the fluorine p orbitals to penetrate deeper into the Yb^{3+} electronic cloud, increasing A_p .

As with Tm^{2+} A_s and A_p are of the same sign, which cannot be determined. Similar arguments to those used for Tm^{2+} again indicate that the positive sign should be chosen.

Ranon and Hyde find that in fact the superhyperfine structure on the E.P.R. line for $H \parallel [100]$ is field dependent in a similar way to Tm^{2+} . At X band there are 17 components separated by 3.03 ± 0.05 G. and at Q band there are at least 7 components separated by 6.65 ± 0.10 G. From the measured hyperfine parameters Ranon and Hyde made a detailed calculation of this structure at both frequencies and obtained good agreement with experiment. The basis of the calculation was the same as suggested for the Tm^{2+} case (see sect. 4.4(c)), namely that, since the hyperfine and Zeeman energies of the ligand nuclei are comparable, there is a high probability of $\Delta M_s = \pm 1$, $\Delta M_I^F = \pm 1$ transitions. The resulting E.P.R. line structure is the superposition of all the forbidden transitions.

Ranon and Hyde did not observe all the ENDOR lines expected from the 8 nearest neighbours. All the lines associated with the electronic state $|+\frac{1}{2}\rangle$ (taking A_s , A_p positive) were observed but those for $|-\frac{1}{2}\rangle$ were either extremely weak or missing. This may be compared with the Tm^{2+} case where both lines were observed at equal intensity for $H \parallel [100]$ but only one line appeared for each of the $[110]$ and $[111]$ directions.

Reference

Ranon, U. and Hyde, J.S., 1966. Phys. Rev., 141, 259.

The effect of a small amount of covalent bonding between the 3d electrons of transition metal ions and their ligands has been recognized in the appearance of resolved hyperfine interaction with ligand nuclei in E.P.R. spectra and shift of the E.O.R. frequency in concentrated crystals (e.g. 10^3 in CuF_2 , Thomsen and Jørgensen (1964)). The theory has been developed by Stevens (1953), Gützlaff (1955), Abragam and Pryor (1957) and others in terms of the molecular orbital approach. This has been used by Kugel, Jørgensen, Pryor and others (1965) to calculate the hyperfine shift in Cu^{2+} and by Ball, Pryor, Jørgensen and Abragam (1967a, b) for a wide range of 3d transition metal ions in various lattices.

Stimulus for the work on 3d transition metal ions came from the fact that the interaction of the 3d electrons with the ligands often leads to a large change in the magnetic properties of the ions. The work was done in the context of the study of the properties of the 3d transition metal ions in various lattices. However, since the 3d transition metal ions have been given a detailed account in the literature, the work on the 3d transition metal ions and the hyperfine interaction has been given a detailed account in the literature.

it seemed worthwhile to Chapter 5 experimental application of the BONDING OF Tm^{2+} IN CALCIUM FLUORIDE system.

The molecular orbital is constructed from a central ion. The effect of a small amount of covalent bonding between the 3d electrons of iron group ions in ionic crystals and their ligands has been recognized in the appearance of resolved hyperfine interaction with ligand nuclei in E.P.R. spectra and shift of the N.M.R. frequency in concentrated crystals (e.g. ^{19}F in MnF_2 , Shulman and Jaccarino (1956)). The theory has been developed by Stevens (1953), Owen (1955), Marshall and Stuart (1961) and others in terms of the molecular orbital approach. This has been used by Clogston, Jaccarino, Peter and Walker (1960) in discussing the spherical Mn^{2+} in ZnF_2 and by Hall, Hayes, Stevenson and Wilkins (1963a, b) for a wide range of iron group impurities in various fluoride lattices.

Stimulus for the work on iron group ions has come from the fact that the interaction with ligand nuclei is often large enough to be measured by conventional E.P.R. techniques. For rare earth ions this is not the case so little work on the application of bonding theory has been done. However, since the ENDOR measurements on $CaF_2:TM^{2+}$ have given a detailed account of the interaction between the Tm^{2+} ion and the nearest neighbour fluorine nuclei,

it seemed worthwhile to make a somewhat experimental application of the molecular orbital method to this system.

The molecular orbital is constructed from a central ion single-electron orbital which transforms according to an irreducible representation of the symmetry group of the complex and the appropriate linear combination of ligand orbitals which transforms according to the same irreducible representation. To simplify the problem by way of illustration, if we consider one central ion orbital bonding with one ligand orbital two molecular orbitals are formed. The lower energy, bonding orbital consists mainly of ligand function and the other, antibonding orbital consists mainly of central ion function:

$$\psi_B = M(\phi + B\psi)$$

(1)

$$\psi_A = N(\psi - A\phi).$$

where ϕ represents the ligand function and ψ is the central ion function. M and N are normalising constants.

ψ_A and ψ_B are required to be orthogonal; thus

$$A = \frac{B + \langle \phi | \psi \rangle}{1 + B \langle \phi | \psi \rangle}$$

(2)

In the extreme case (Heitler-London) of no electron transfer from ligand to central ion $B = 0$ and thus $A = \langle \phi | \psi \rangle$.

The "antibonding orbital" then simply represents the

orthogonalisation of the central ion orbital to the ligand orbital, required by the Pauli exclusion principle.

In this simplified example three electrons have to be accommodated in the molecular orbitals, two from the ligand and one from the central ion. Two will be paired off with opposite spins in the bonding orbital and one will be in the antibonding orbital. The magnetic properties of the complex will thus derive from the antibonding orbital. When the orbitals of all the ligands are considered, sufficient linear combinations consistent with the symmetry of the complex can be constructed to accommodate all the ligand electrons. Those linear combinations which find one-electron functions of the same symmetry properties represented in the central ion ground state wavefunction will form bonding and antibonding orbitals. The rest will be non-bonding. All the bonding and non-bonding orbitals will be doubly occupied by paired-off electrons and will not contribute to the magnetic properties of the complex (but see Watson and Freeman (1964)).

To derive the hyperfine interaction with one ligand the independent bonding model is used which assumes no overlap between different ligands and that all ligands are equivalent. The ground state of the central ion is expressed in terms of one-electron functions which are then augmented by the appropriate combinations of ligand

orbitals to form the antibonding orbitals. Any one ligand is selected and the hyperfine operator is applied to those parts of the ground state function, in terms of the antibonding orbitals, which represent contributions from this ligand. (1963)

The Tm^{2+} ground state in terms of $|J, J_z\rangle$ is an unsuitable starting point so we use the expressions given by Twidell (1963) in terms of $|L_z, S_z\rangle$ single f-electron functions within manifolds of $L = 3$, $S = \frac{1}{2}$:

$$|+\frac{1}{2}\rangle = \sqrt{\frac{3 \cdot 6}{4 \cdot 7}} |2+\rangle - \sqrt{\frac{1 \cdot 2}{4 \cdot 7}} |-2+\rangle + \sqrt{\frac{3 \cdot 1}{4 \cdot 7}} |3-\rangle - \sqrt{\frac{1 \cdot 5}{4 \cdot 7}} |-1-\rangle \quad (3)$$

$$|-\frac{1}{2}\rangle = -\left[\sqrt{\frac{3 \cdot 6}{4 \cdot 7}} |-2-\rangle - \sqrt{\frac{1 \cdot 2}{4 \cdot 7}} |2-\rangle + \sqrt{\frac{3 \cdot 1}{4 \cdot 7}} |-3+\rangle - \sqrt{\frac{1 \cdot 5}{4 \cdot 7}} |1+\rangle \right]$$

The negative sign for the expression for $|-\frac{1}{2}\rangle$ has been introduced in order that the g value shall be isotropic. Without it $g_x = g_y = -g_z$ (see Pryce (1959)). Expressing these functions in cartesian form relative to the crystal axes X, Y, Z in terms of functions appropriate to the cubic symmetry gives

$$\begin{aligned} |+\frac{1}{2}\rangle &= \frac{1}{\sqrt{7}} \left[\{2i|xyz\rangle + |z(x^2 - y^2)\rangle\} |+\rangle \right. \\ &\quad \left. + \{i|y(z^2 - x^2)\rangle + |x(y^2 - z^2)\rangle\} |-\rangle \right] \\ |-\frac{1}{2}\rangle &= \frac{1}{\sqrt{7}} \left[\{2i|xyz\rangle - |z(x^2 - y^2)\rangle\} |-\rangle \right. \\ &\quad \left. - \{i|y(z^2 - x^2)\rangle - |x(y^2 - z^2)\rangle\} |+\rangle \right] \end{aligned} \quad (4)$$

where all the functions are normalised.

The appropriate combinations of ligand orbitals for eightfold co-ordination with the same symmetry properties as each of the single-electron functions have been given by Hall (1963) and Baker and Hurrell (1963). They are reproduced in Table 5.1. It will be noticed that the $|x(y^2 - z^2)\rangle$ type of orbital forms only π bonds while the $|xyz\rangle$ orbital forms only σ bonds. To avoid undue complexity we treat bonding to fluorine 2p orbitals separately from bonding to s orbitals. We write the antibonding orbitals as

$$\begin{aligned}\psi_{A\pi i} &= N_{\pi}(\psi_i - A_{\pi} \varpi_{\pi i}) \\ \psi_{A\sigma i} &= N_{\sigma}(\psi_i - A_{\sigma} \varpi_{\sigma i})\end{aligned}\tag{5}$$

where ϖ_i are the properly normalised combinations of ligand orbitals and we define $-N_{\pi} A_{\pi} = \pi$ and $-N_{\sigma} A_{\sigma} = \sigma$

Concentrating on ligand 1 and referring to the antibonding orbitals by their f-electron components, Table 5.1 shows

$$|x(y^2 - z^2)\rangle \quad \text{includes} \quad \frac{\pi}{4\sqrt{2}} (-|P_x'\rangle + \sqrt{3}|P_y'\rangle)$$

$$|y(z^2 - x^2)\rangle \quad \text{includes} \quad \frac{\pi}{2\sqrt{2}} |P_x'\rangle$$

$$|z(x^2 - y^2)\rangle \quad \text{includes} \quad \frac{\pi}{4\sqrt{2}} (-|P_x'\rangle - \sqrt{3}|P_y'\rangle)$$

$$|xyz\rangle \quad \text{includes} \quad \frac{\sigma}{2\sqrt{2}} |P_z'\rangle$$

(6)

The augmented functions are substituted into the Tm^{2+} groundstate function and only those portions relating to ligand orbitals are retained. The ligand p functions are rewritten in terms of $|L = 1, L_z\rangle$ using

$$|P_x'\rangle = \frac{1}{\sqrt{2}} (|-1\rangle - |+1\rangle)$$

$$|P_y'\rangle = \frac{i}{\sqrt{2}} (|-1\rangle + |+1\rangle)$$

(7)

$$|P_z'\rangle = |0\rangle$$

all referred to ligand l axes. Thus

$$\begin{aligned} "|+\frac{1}{2}\rangle" &= \frac{1}{\sqrt{7}} \left[\frac{\pi}{8} [(1-\sqrt{3}i)|+1\rangle + (-1-\sqrt{3}i)|-1\rangle] \right. \\ &\quad + \frac{i\sigma}{\sqrt{2}} |0\rangle |+\rangle + \frac{\pi}{8} \{ [1+(\sqrt{3}-1)i] |+1\rangle \\ &\quad \left. + [-1+(\sqrt{3}+1)i] |-1\rangle \} |-\rangle \right] \end{aligned} \quad (8)$$

Table 5.2. Transformation of Axes of Spin Functions.

The transformation represents a rotation of the right-handed coordinate axes from the cubic axes of the crystal, XYZ, to the axes used for ligand 1 (see Table 5.1):

$$\underline{x} = (1, 0, \bar{1}); \quad \underline{y} = (1, \bar{2}, 1); \quad \underline{z} = (\bar{1}, \bar{1}, \bar{1}).$$

The rotation is composed of: α about the Z axis; β about the transformed Y axis; γ about the transformed Z axis in that order. A positive rotation is defined as one which would advance a right-handed screw along the positive direction of the rotation axis.

$$\begin{aligned} |+\frac{1}{2}\rangle_{XYZ} \rightarrow & \cos\beta/2 \exp((\gamma+\alpha)1/2) |+\frac{1}{2}\rangle_{xyz} \\ & -\sin\beta/2 \exp(-(\gamma-\alpha)1/2) |-\frac{1}{2}\rangle_{xyz} \end{aligned}$$

$$\begin{aligned} |-\frac{1}{2}\rangle_{XYZ} \rightarrow & \cos\beta/2 \exp(-(\gamma+\alpha)1/2) |-\frac{1}{2}\rangle_{xyz} \\ & +\sin\beta/2 \exp((\gamma-\alpha)1/2) |+\frac{1}{2}\rangle_{xyz} \end{aligned}$$

The magnitudes of the rotations are:

$$\alpha = +5\pi/4; \quad \beta = +\pi/2 + \cos^{-1}(2/3)^{1/2}; \quad \gamma = +\cos^{-1}(3/4)^{1/2}.$$

and there is a similar form of expression for " $|- \frac{1}{2}\rangle$ ".

It is important at this point to realise that the orbital functions are referred to the axes of ligand 1 whereas the spin functions, $|+\rangle$ and $|-\rangle$, are still referred to the fourfold crystal axes. The axes of the spins must, therefore, be transformed from the crystal axes to those of ligand 1. The corresponding transformations of the spin functions are defined in Table 5.2. Care must be taken in defining the Euler angles, α, β, γ , representing the transformation and ensuring that it represents a rotation of the axes, the functions remaining fixed in space. A careful discussion of these points is given by Tinkham (1964). The final forms of the ligand orbitals in so far as they concern ligand 1 are then obtained by replacing $|+\rangle$ and $|-\rangle$ in (8) and its conjugate by the transformed spin functions.

To evaluate the hyperfine interaction with the fluorine nucleus the hyperfine operator for p electrons is used (Abragam and Pryce 1951)

$$W_{np} = 2g_n\beta\beta_n\langle r^{-3} \rangle (\underline{1} \cdot \underline{I} - k\underline{s} \cdot \underline{I} + \frac{3}{2} \underline{a} \cdot \underline{I}) = \underline{A_1} \cdot \underline{I} \quad (9)$$

where $\underline{a} = \frac{4}{3} \underline{s} - \underline{1}(\underline{1} \cdot \underline{s}) - \underline{1} \cdot \underline{s}) \underline{1}$; $s = \frac{1}{2}$; $I = \frac{1}{2}$; g_n is the fluorine nuclear g factor and $\langle r^{-3} \rangle$ refers to fluorine 2p electrons. The term in k covers the contribution to hyperfine interaction in the fluorine ion from polarisation of

Hyperfine Interaction. (Thornley, 1962)

$$\underline{a} = 4/3 \underline{s} - \underline{1}(\underline{1}.\underline{s}) - (\underline{1}.\underline{s})\underline{1}$$

a_x	$ +I+\rangle$	$ +I-\rangle$	$ 0+\rangle$	$ 0-\rangle$	$ -I+\rangle$	$ -I-\rangle$
$\langle +I+ $		$\frac{1}{6}$	$\frac{-1}{2\sqrt{2}}$			
$\langle +I- $		$\frac{1}{6}$		$\frac{1}{2\sqrt{2}}$	-1	
$\langle 0+ $		$\frac{-1}{2\sqrt{2}}$		$\frac{-1}{3}$	$\frac{1}{2\sqrt{2}}$	
$\langle 0- $		$\frac{1}{2\sqrt{2}}$	$\frac{-1}{3}$			$\frac{-1}{2\sqrt{2}}$
$\langle -I+ $		-1	$\frac{1}{2\sqrt{2}}$			$\frac{1}{6}$
$\langle -I- $				$\frac{-1}{2\sqrt{2}}$	$\frac{1}{6}$	

a_y	$ +I+\rangle$	$ +I-\rangle$	$ 0+\rangle$	$ 0-\rangle$	$ -I+\rangle$	$ -I-\rangle$
$\langle +I+ $		$-\frac{i}{6}$	$\frac{i}{2\sqrt{2}}$			
$\langle +I- $	$\frac{i}{6}$			$\frac{-i}{2\sqrt{2}}$	i	
$\langle 0+ $	$\frac{-i}{2\sqrt{2}}$			$\frac{i}{3}$	$\frac{-i}{2\sqrt{2}}$	
$\langle 0- $		$\frac{i}{2\sqrt{2}}$	$-\frac{i}{3}$			$\frac{i}{2\sqrt{2}}$
$\langle -I+ $		$-i$	$\frac{i}{2\sqrt{2}}$			$-\frac{i}{6}$
$\langle -I- $				$\frac{-i}{2\sqrt{2}}$	$\frac{i}{6}$	

a_z	$ +I+\rangle$	$ +I-\rangle$	$ 0+\rangle$	$ 0-\rangle$	$ -I+\rangle$	$ -I-\rangle$
$\langle +I+ $	$\frac{1}{3}$					
$\langle +I- $		$\frac{1}{3}$	$\frac{1}{\sqrt{2}}$			
$\langle 0+ $		$\frac{1}{\sqrt{2}}$	$\frac{2}{3}$			
$\langle 0- $				$\frac{2}{3}$	$\frac{1}{\sqrt{2}}$	
$\langle -I+ $				$\frac{1}{\sqrt{2}}$	$\frac{1}{3}$	
$\langle -I- $						$\frac{1}{3}$

the s shells by unpaired spins in the 2p orbitals. Hall was able to measure k for the $3d^3$ configuration in KMgF_3 and found k to be 0.04 ± 0.01 . He discussed why it was reasonable in the absence of other information to take k to be a property of the fluorine ion and of this order for all the iron group configurations examined.

The matrix elements " $\langle +\frac{1}{2} | "A_{1z}" | +\frac{1}{2} \rangle$ " and " $\langle -\frac{1}{2} | "A_{1x}" | +\frac{1}{2} \rangle$ " are evaluated for the ligand orbital states, giving the components of the hyperfine tensor in terms of the properties of the fluorine nucleus, the admixture parameters π and σ , and k and $\langle r^{-3} \rangle$ for the fluorine 2p electrons. Matrix elements of $\underline{a}$ for p electrons are given by Thornley (1962) and are reproduced for convenience in Table 5.3. It should be noted that a_z has off-diagonal elements.

After inserting the numerical values for the functions of the Euler angles we obtain for p electrons

$$\begin{aligned} \langle +\frac{1}{2} | "A_{1z}" | +\frac{1}{2} \rangle = & \left[\frac{\pi^2}{7} \cdot \frac{\sqrt{3}}{8} \left(\frac{6}{5} + \frac{k}{2} \right) - \frac{\sigma^2}{7} \cdot \frac{1}{2\sqrt{3}} \left(\frac{2}{5} - \frac{k}{2} \right) \right. \\ & \left. + \frac{\sigma\pi}{7} \cdot \frac{3}{10/2} \right] 2g_n\beta\beta_n \langle r^{-3} \rangle. \end{aligned} \quad (10)$$

$$\begin{aligned} \langle -\frac{1}{2} | "A_{1x}" | +\frac{1}{2} \rangle = & \left[\frac{\pi^2}{7} \cdot \frac{9}{40\sqrt{2}} - \frac{\sigma^2}{7} \cdot \frac{1}{2\sqrt{2}} \left(\frac{1}{5} + \frac{k}{2} \right) \right. \\ & \left. + \frac{\sigma\pi}{7} \cdot \frac{13\sqrt{3}}{40} \right] 2g_n\beta\beta_n \langle r^{-3} \rangle. \end{aligned} \quad (11)$$

For comparison with the measured parameters (10) and (11)

must be equated to the matrix elements within the fictitious $s = \frac{1}{2}$ groundstate, $\langle +\frac{1}{2} | A_{//} S_z | +\frac{1}{2} \rangle$ and $\langle -\frac{1}{2} | A_{\perp} S_x | +\frac{1}{2} \rangle$ respectively. Once again $A_{//}$ and $A_{\perp}$ refer to the axes defined for ligand 1 so the fictitious spin states must be transformed to these axes using Table 5.2 before evaluating the matrix elements. Thus

$$\langle +\frac{1}{2} | A_{//} S_z | +\frac{1}{2} \rangle = \frac{A_{//}}{2} \cos \beta = -A_{//} \frac{1}{2\sqrt{3}} \quad (12)$$

$$\langle -\frac{1}{2} | A_{\perp} S_x | +\frac{1}{2} \rangle = \frac{A_{\perp}}{2} \cos \alpha \cos \beta \cos \gamma - \sin \alpha \sin \gamma = \frac{A_{\perp}}{2\sqrt{2}} \quad (13)$$

Equating (12) and (13) to (10) and (11) gives for the bonding to p orbitals

$$A_{//p} = \left[\frac{3\pi^2}{4} \left(\frac{6}{5} + \frac{k}{2} \right) + \sigma^2 \left(\frac{2}{5} - \frac{k}{2} \right) - \sigma \pi \frac{3/6}{5} \frac{2g_n \beta \beta_n \langle r^{-3} \rangle}{7} \right] \quad (14)$$

$$A_{\perp p} = \left[-\frac{9\pi^2}{20} - \sigma^2 \left(\frac{1}{5} + \frac{k}{2} \right) + \sigma \pi \frac{13\sqrt{6}}{20} \frac{2g_n \beta \beta_n \langle r^{-3} \rangle}{7} \right] \quad (15)$$

Molecular orbitals of fluorine s orbitals have the

same symmetries as p_O orbitals. The calculation follows through as before, except that the s electron hyperfine operator is used

$$\underline{A}_s = (8\pi/3) \cdot 2g_n \beta \beta_n |\phi_s(0)|^2 \underline{s} \quad (16)$$

The resulting hyperfine parameters for bonding to fluorine $2s$ electrons only are

$$A_{//s} = A_{\perp s} = \frac{s^2}{4} \cdot (8\pi/3) \cdot 2g_n \beta \beta_n |\phi_{2s}(0)|^2 \quad (17)$$

The definition of S is analogous to that of σ (see (5) and (6)).

After subtracting the direct dipolar contribution the experimental results show the hyperfine parameters due to bonding to be $A_{//p+s} = 7.53$ Mc/s; $A_{\perp p+s} = 0.11$ Mc/s. The quantities of interest are the unpaired spin densities in the $2p_O$, $2p_\pi$, and $2s$ fluorine orbitals, f_O , f_π and f_s . These are related to the parameters σ , π and s by $f_O = \sigma^2/8$, $f_\pi = \pi^2/8$ and $f_s = s^2/8$. Two relationships for determining the three parameters come from the hyperfine parameters $A_{//p+s}$ and $A_{\perp p+s}$. In principle the third relationship is obtained from the measured g value and resulting orbital reduction factor (Stevens). The orbital reduction factor obtained in sect 3.8 is an average based on the assumption that the reduction of orbital contribution to the magnetic

moment through covalency is the same for all orbitals of Γ_7 ground state. Eqn. (4) and Table 5.1 show that this is not so but that the reduction is the same for all orbitals of the ground state belonging to the same irreducible representation. For the pure Γ_7 ground state (4) the contribution to g value from spin is $6/7$ and from orbit is $18/7$. Following Stevens' definition of orbital reduction factor we denote by k_{TT} the reduction factor for matrix elements of $\underline{L}$ within the T_{2u} representation and by k_{TA} the reduction factor for matrix elements of $\underline{L}$ between T_{2u} and A_{2u} . The experimental g value of the Γ_7 ground state (after correction for the admixture of the $J = 5/2$ Γ'_7 state) is

$$g = 6/7 + (16/7) k_{AT} + (2/7) k_{TT} \quad (18)$$

Since the k 's are functions of f_G , f_K , and f_S , a third relationship between these three parameters is thus obtained.

In principle the expressions for the k 's can be obtained by using the appropriate molecular orbitals constructed from Table 5.1 but the process is lengthy and complications are introduced in translating the axis of angular momentum to the ligands (see Stevens) in an eight-fold complex, so this was not done in the present case.

The lobes of the σ bonding $|xyz\rangle$ orbital point directly towards the eight ligands and this orbital occurs with an amplitude 2 in the ground state, suggesting that σ bonding

will predominate over π bonding. For the extreme case of zero π bonding the measured hyperfine parameters give $f_o = 0.79\%$ and $f_s = 0.01\%$, where we have taken $k = 0.04$, $(8\pi/3) \cdot 2g_n \beta \beta_n |\phi_{2s}(0)|^2 = 1.57 \text{ cm}^{-1}$ and $2g_n \beta \beta_n \langle r^{-3} \rangle = 0.044 \text{ cm}^{-1}$ (Hall et al 1963a). If $\sigma = 10\pi$ then $f_o = 1.6\%$, $f_\pi = 0.016\%$ and $f_s = 0.006\%$. For a smaller ratio of σ to π bonding there are difficulties in obtaining a real solution for f_s . The alternative of taking the hyperfine parameters as negative (see sect 4.4(b)) gives $A_{//p+s} = -46.77 \text{ Mc/s}$ and $A_{\perp p+s} = +19.51 \text{ Mc/s}$ whence, if $\sigma = \pi$, $f_o = f_\pi = 4.0\%$. This is too large to be consistent with the measured average orbital reduction factor when compared with results for iron group ions (Hall et al). Probable results, therefore, are $f_o \approx 1\%$ and $f_s \approx 0.01\%$ with f_π about an order of magnitude less than f_o .

No account has been taken of the effect of crystal field admixture of the excited Γ_7^1 state nor of bonding to fluorine 1s orbitals (Marshall and Stuart). An uncertainty in applying this calculation is the importance of exchange polarisation of 5s and 5p orbitals in contributing to the measured hyperfine parameters (Watson and Freeman 1961). The original calculation of this effect was for an S-state ion with $S = 7/2$. In the present case with the much smaller spin it may well be of minor importance.

REFERENCES TO CHAPTER 5

- Abragam, A. and Pryce, M.H.L. 1951. Proc Roy Soc A205, 135.
- Baker, J.M. and Hurrell, J.P. 1963. Proc Phys Soc 82, 742.
- Clogston, A.M., Gordon, J.P., Jaccarino, V., Peter, M. and Walker, L.R. 1960. Phys Rev 117, 1222.
- Hall, T.P.P. 1963. Thesis, Oxford.
- Hall, T.P.P., Hayes, W., Stevenson, R.W.H. and Wilkens, J. 1963a. J Chem Phys 38, 1977.
- 1963b. J Chem Phys 39, 35.
- Marshall, W. and Stuart, R. 1961. Phys Rev 123, 2048.
- Owen, J. 1955. Proc Roy Soc A227, 183.
- Pryce, M.H.L. 1959. Phys Rev Lett 3, 375.
- Shulman, R.G. and Jaccarino, V. 1956. Phys Rev 103, 1126.
- Stevens, K.W.H. 1953. Proc Roy Soc A219, 542.
- Thornley, J.M.H. 1962. Thesis, Oxford.
- Tinkham, M. 1964. "Group Theory and Quantum Mechanics." McGraw-Hill. p 111.
- Twidell, J.W. 1963. Thesis, Oxford.
- Watson, R.E. and Freeman, A.J. 1962. Phys Rev Lett 6, 277.
- Watson, R.E. and Freeman, A.J. 1964. Phys Rev 134, A1526.

Chapter 6

ATOMIC HYDROGEN IN ALKALINE EARTH FLUORIDES

6.1 Introduction

Alkali halides containing hydrogen impurity have been a subject of investigation for many years (Seitz (1954)). The presence of hydrogen gives rise to a characteristic U.V. absorption band called the U band (e.g. in KCl at 212 $m\mu$) which was identified by Hilsch and Pohl (1938) as due to a hydride ion on a halide site. They also found that irradiation into the U band at temperatures above about -100°C produced F centres and bleached the band. Delbecq, Smaller and Yuster (1956) irradiated into the U band of KCl at 77°K and produced a broad band, called U_1 , on its long wavelength side, together with anion vacancies indicated by the growth of the α band. Prolonged irradiation with light in the whole U band region caused the slow growth of a new band, U_2 , at 236 $m\mu$ together with the F band at 540 $m\mu$. Irradiation in the U_1 band alone caused, for a short time, a rapid growth of the U_2 and F bands together and a decrease of the U_1 band. They assigned the U_1 band to the presence of interstitial H^- ions and the U_2 band to interstitial hydrogen atoms. The latter was prompted by the observation of an E.P.R. spectrum of two lines each 68G wide at a g value of 2 and separated by $500 \pm 10\text{G}$; the hyperfine separation

for the free hydrogen atom would be 506G. The maximum rate of annealing of this spectrum occurred at the same temperature, 108°K , as for the U_2 band. Delbecq and Yuster (1956) proposed a mechanism for conversion of U centres to F centres below 90°K based on the results. Irradiation into the U band ejects a hydride ion into an interstitial position and leaves an anion vacancy. Irradiation into the U_1 band excites the hydride ion, enabling its electron to tunnel to the nearest anion vacancy, provided it is sufficiently near, forming an F centre and a hydrogen atom. However, if the F centre and hydrogen atom are too close to one another the reverse tunnelling process will occur and destroy the F centre. Thus only a certain range of separation between interstitial ion and vacancy will give rise to F centre and hydrogen atom creation.

Fritz (1962) confirmed and extended this work by looking at the effect of U band irradiation at 20°K on the infra red localised mode at 22.5μ of substitutional hydride ions in KBr. He found new triplets of lines were produced around 12.5μ (at the expense of the 22.5μ absorption) which annealed out in three stages. These were identified as interstitial H^- ions at different distances from anion vacancies and it was estimated that the separation for the most stable type, producing a single line at 12.5μ , was at least ten anion-cation distances. For the least stable

type the anion vacancy could be as close as the point $(\frac{3}{2}, 0, 0)$ to the interstitial H^- at $(0, 0, 0)$ in terms of the anion-cation distance.

Kerkhoff, Martienssen and Sander (1963) obtained much more detailed E.P.R. results than Delbecq et al. for atomic hydrogen in KCl, KBr and NaCl. They irradiated crystals doped with hydroxyl ions which led to a much higher concentration of U_2 centres. Their E.P.R. spectra showed a resolved interaction with four halide ions and confirmed the interstitial site for the hydrogen atom. The interaction with the proton was slightly less than would be expected for a free hydrogen atom and was different in each material.

In view of these detailed results on the alkali halides it is of interest to investigate some of the effects of hydrogen impurity in the alkaline earth fluorides. A parallel investigation on further properties of KCl:H was carried out by J.W. Hodby (1965). Magnetic resonance techniques are very suitable for detecting hydrogen atoms through the large and characteristic hyperfine interaction with the proton. Resolved interaction would also be expected with the large nuclear moment of nearby fluoride ions, giving information on the site occupied by the hydrogen atom and possibly of any associated lattice defects. Furthermore, in view of the close connection between hydrogen

atom formation and F centre formation in alkali halides, there might appear information on the elusive CaF_2 F centre. (Arends (1964)).

From another point of view it is also of interest to observe the effect of different environments on the magnetic properties of the hydrogen atom itself.

Magnetic resonance of atomic hydrogen in CaF_2 was first reported by Hall and Schumacher (1962). Their samples were prepared by heating pure CaF_2 crystals to 900°C in hydrogen gas in the presence of aluminium metal. No magnetic resonance spectrum was observed until the crystals were X-irradiated for a few hours at room temperature. This produced a spectrum identified as due to hydrogen atoms, which was stable up to 50°C . Well resolved interaction with fluorine nuclei identified the hydrogen atom site as interstitial, being the body centre of vacant cubes of the fluoride sublattice (See fig. 3.1).

Jones ((1964), Hayes, Jones, Macdonald, Sennett and Elliott (1965)) has carried out infra red measurements in the region $3\text{-}14\mu$ on CaF_2 , SrF_2 and BaF_2 crystals (which all have the same fluorite structure) prepared in the same way as by Hall and Schumacher but not X-irradiated. In each case localised vibrations due to H^- ions are observed. In addition to the fundamental localised mode second and, in the case of CaF_2 , third harmonics are also observed.

The appearance of the second harmonic absorption is conclusive evidence that the H^- ion is in a potential well of tetrahedral symmetry, T_d . A potential of cubic symmetry, O_h , would allow only first and third harmonics. Figure 3.1 shows that each F^- ion in the fluorite lattice is in the tetrahedral field of the four nearest neighbour cations while the cation sites and interstitial sites have O_h symmetry. Thus Hayes et al. conclude that the hydrogenation process introduces H^- ions substitutionally onto F^- sites in alkaline earth fluorides. At some stage in the room temperature X-irradiation the proton must move into the interstitial position. X-irradiation at sufficiently low temperature should show whether the alkaline earth fluorides behave similarly to the alkali halides, producing interstitial H^- ions or whether hydrogen atoms can be trapped on fluoride sites. The fate of the anion vacancy created when the proton finally moves to an interstitial site is also of interest.

6.2 Substitutional Hydrogen Atoms in CaF_2

A crystal of CaF_2 doped with hydrogen by the method of Hall and Schumacher was shown by infra red absorption measurements (G.D. Jones - private communication) to contain a large amount of substitutional H^- ions. The pure crystals, grown by the Stockbarger method and purified by repeated recrystallisation, were supplied by Mervyn Instru-

ments Ltd. Oxygen impurity was removed from the melt by adding 5% wt. PbF_2 . The hydrogen doped crystal was heated to about 200°C to remove any atomic or molecular hydrogen and reform it as substitutional H^- ions. The crystal was X-irradiated in the irradiation cryostat at low temperature using a Matchless X-ray gun running at 50kV, 50mA, at 4 cms. from the target. As well as strong spectra due to self-trapped hole centres (Hayes and Twidell (1962), Sierro (1965)) a new spectrum was observed consisting of two groups of lines symmetrically placed about $g = 2$. This spectrum was strongly saturated at 20°K but at 77°K was easily visible on the oscilloscope where the anisotropy of the multiplet structure was apparent.

For x-irradiation at 20°K the intensity of the spectrum increased with irradiation time up to 35 hours, the longest irradiation carried out. Irradiation at 77°K gave a fairly rapid initial build-up which levelled off after about 12 hours.

The appearance of one of the groups of lines at K band with H parallel to each of the three principal crystal directions is shown in Fig. 6.1(a), (b), (c). It is assigned to hydrogen atoms on fluorine sites in CaF_2 . For comparison Fig. 6.1(d) shows the spectrum at K band of the interstitial hydrogen atom in CaF_2 with $\text{H} \parallel [100]$. In the interstitial case interaction with the eight nearest neigh-

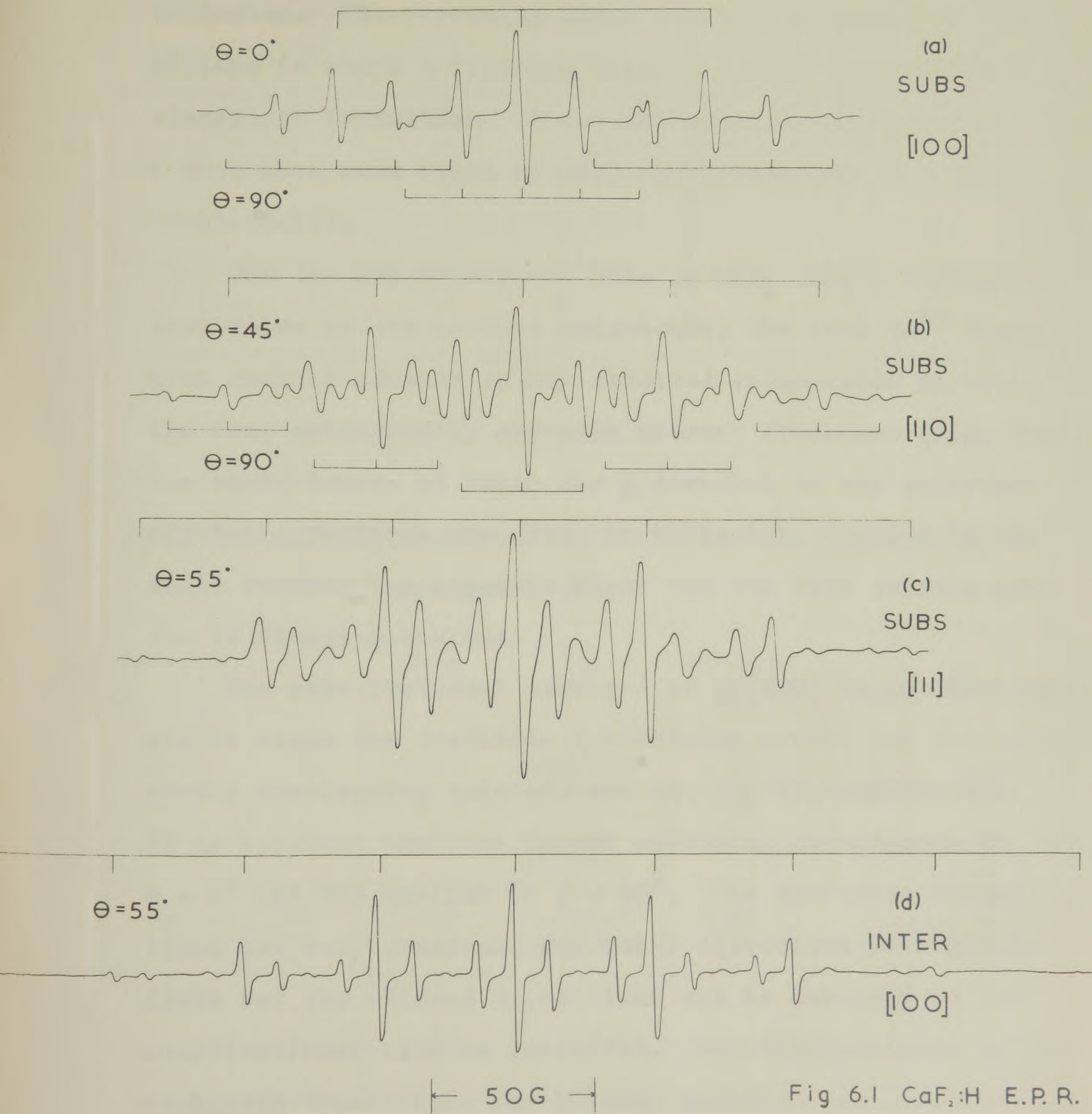


Fig 6.1 $\text{CaF}_2:\text{H}$ E.P.R.

six fluorines which are equivalent in this direction splits each of the two hydrogen lines into nine components as indicated. The remaining lines are due to forbidden transitions in which a fluorine nucleus "flips" during the electronic transition. These are considerably stronger at K band than were found by Hall and Schumacher at X band. (Sect. 6.11).

For the substitutional site in CaF_2 only a negligible proportion of the nearest neighbours, the four Ca^{2+} ions, have nuclear moments so any resolved interaction is with the six, octahedrally arranged nearest fluorines (Fig. 3.1). The equivalences of these for $\underline{H}$ parallel to the principal crystal directions are given in Table 6.1, where θ is the angle between the magnetic field and the line joining proton to fluorine nucleus.

The substitutional spectrum of $\underline{H} \parallel [100]$ is particularly simple since the forbidden transitions vanish and the three, partly overlapping quintets are clearly distinguishable. It is apparent that the larger splitting corresponds to $\theta = 0^\circ$ and the smaller to $\theta = 90^\circ$. The forbidden transitions are very prominent for other directions of magnetic field but the allowed transitions can be assigned to the substitutional site as indicated. The disappearance of the forbidden transitions for $\underline{H} \parallel [100]$ supports the substitutional assignment since it indicates that $\theta = 0^\circ$ or 90° (Sect. 6.11)

Table 6.1. Equivalencies of Nearest Neighbour Fluorines
for Substitutional Site in CaF_2

Direction of H	$\cos^2 \theta$	Number of Fluorines
[100]	$\frac{1}{0}$	$\frac{2}{4}$
[110]	$\frac{\frac{1}{2}}{0}$	$\frac{4}{2}$
[111]	$\frac{1}{3}$	6

Table 6.2 EPR Parameters for Atomic Hydrogen in Alkaline
Earth Fluorides.

Lattice	Temp. °K.	Site	g	A_{proton} Mc/s	$A_{//}$ Mc/s	$A_{\perp}$ Mc/s
CaF_2	77	Subst	2.00235 ± 0.00006	1439.44 ± 0.3	168.11 ± 0.5	52.76 ± 0.3
SrF_2	77	Subst	2.0029 ± 0.0001	1437.83 ± 0.5	$^a 100.959 \pm 0.2$	$23.486^a \pm 0.2$
BaF_2	300	Inter	$2.00232^b \pm 0.00006$	$1424.5^b \pm 0.10$	$^a 83.445 \pm 0.2$	$20.347^a \pm 0.2$

^a Hodby (1965)

^b Welber (1964)

Other entries are from the present work.

The width of each component line of about 3.2G is mainly due to inhomogeneous broadening by more distant fluorine nuclei. The success in describing the interstitial and substitutional spectra in terms of eight and six regularly placed nearest fluorines indicates that in both cases the lattice is locally perfect.

The complete substitutional spectrum may be described by the spin Hamiltonian

$$\begin{aligned} \mathcal{H} = & g\beta\mathbf{H}\cdot\mathbf{S} + A\mathbf{S}\cdot\mathbf{I} - g_p\beta_n\mathbf{H}\cdot\mathbf{I} \\ & + \sum_{n=1}^6 [\mathbf{S}\cdot\mathbf{A}_n^F\cdot\mathbf{I}_n^F - g_F\beta_n\mathbf{H}\cdot\mathbf{I}_n^F] \end{aligned} \quad (1)$$

with $S = \frac{1}{2}$, I , the proton spin, $= \frac{1}{2}$, I_n^F the spin of the n th nearest fluorine nucleus $= \frac{1}{2}$, g_p and g_F are the proton and fluorine nuclear g values respectively. The sum is over the six nearest fluorine nuclei. The first three terms in (1) describe the hydrogen atom itself and the sum describes the resolved interaction with the six nearest fluorines.

Part of the interest in this spectrum lies in the size and sign of the small deviation of the g value from that of a free hydrogen atom. In order to obtain the g value as accurately as possible the position of the centre line of each of the two groups was measured with the klystron frequency stabilised as described in Section 8.1.

For the most accurate determination of the fluorine hyperfine parameters from the E.P.R. spectrum a crystal was mounted on a cleavage (111) plane on the accurately horizontal bottom of the K band X-irradiation cavity. The magnetic field could then be aligned along any of three different [110]-type directions at 60° intervals. The final alignment along one of these directions was made using the fluorine ENDOR spectrum as a sensitive indicator. The position of each of the allowed fluorine hyperfine components was measured separately with the klystron frequency stabilised. Each multiplet was also measured up for the three principal directions using the field marker system. (Sect. 8.3). The experimental values of the spin Hamiltonian parameters are given in Table 6.2.

Because of the large interaction between the electron and the nearest fluorines small corrections must be introduced to obtain the best values for the parameters of the hydrogen atom. For this reason, as well as to obtain the components of the tensors A_n^F , the fluorine hyperfine interaction must be considered in detail.

6.3 The Fluorine Hyperfine Interaction

As a first approximation we consider the interaction between the hydrogen electron and one nearest fluorine nucleus and ignore the effect of interaction with the proton and the other five fluorines.

$$\mathcal{H}^F = g\beta\mathbf{H}\cdot\mathbf{S} + \mathbf{S}\cdot\mathbf{A}^F\cdot\mathbf{I} - g_F\beta_n\mathbf{H}\cdot\mathbf{I} \quad (2)$$

where we have dropped the subscript "n" and superscript "F" on " $\mathbf{I}$ ".

The hydrogen site symmetry is tetrahedral and the line joining proton to nearest fluorine is only a twofold axis. Strictly speaking, therefore, we cannot assume axial symmetry about the bond axis for the tensors $\mathbf{A}_n^F$. However, the E.P.R. spectrum does not have sufficient resolution to indicate departure from axial symmetry so we assume that it is exactly so. We take the principal axes as Z' , parallel to the bond axis, and x' and y' , defined below, which make up the mutually perpendicular right-handed set. The tensors for all six fluorines are identical numerically but with appropriate orientations of their principal axes. In principal axis form each hyperfine tensor is written

$$\mathbf{A}_n^F = \begin{bmatrix} A_{\perp} & 0 & 0 \\ 0 & A_{\perp} & 0 \\ 0 & 0 & A_{\parallel} \end{bmatrix} \quad (3)$$

For convenience we wish to work in a frame such that the Z direction is always parallel to the magnetic field. We transform the axes by a single rotation of the Z' axis through an angle θ which brings it parallel to $\mathbf{H}$, the Z axis. The axis of this rotation defines the $y' \equiv y$ axis.

The hyperfine tensor is expressed in terms of the new axes by the appropriate similarity transformation corresponding to the rotation θ .

$$A^F = R(\theta) A^F R(\theta)^{-1} \quad (4)$$

We obtain

$$A^F = \begin{bmatrix} A_{\perp} \cos^2 \theta + A_{\parallel} \sin^2 \theta & 0 & (A_{\parallel} - A_{\perp}) \sin \theta \cos \theta \\ 0 & A_{\perp} & 0 \\ (A_{\parallel} - A_{\perp}) \sin \theta \cos \theta & 0 & A_{\perp} \sin^2 \theta + A_{\parallel} \cos^2 \theta \end{bmatrix} \quad (5)$$

where θ is the angle between the bond axis and magnetic field.

The four energy levels as a function of H and θ may now be obtained within the stated assumptions by substituting (5) into (2) and diagonalizing. However, it is more illuminating to follow Hall and Schumacher and consider the "local field" at the fluorine nucleus due to the electron.

We equate

$$\underline{S} \cdot \underline{A} \cdot \underline{F} \underline{I} = -g_F \beta_N \underline{H}_L \cdot \underline{I} \quad (6)$$

where $\underline{H}_L$ is the "local field". Thus, from (5)

nucleus as a function of θ , is simply obtained by substituting the nuclear state along $\underline{H}_L$.

$$A_F(\theta) = -g_F \beta_N A_{\perp}(\theta) \cdot \underline{I} = -g_F \beta_N [A_{\perp} \sin^2 \theta + A_{\parallel} \cos^2 \theta] \cdot \underline{I}$$

$$H_{Lx} = - \frac{1}{g_F \beta_n} [S_x (A_{\underline{1}} \cos^2 \theta + A_{11} \sin^2 \theta) + S_z (A_{11} - A_{\underline{1}}) \sin \theta \cos \theta]$$

$$H_{Ly} = - \frac{1}{g_F \beta_n} S_y A_{\underline{1}} \quad (7)$$

$$H_{Lz} = - \frac{1}{g_F \beta_n} [S_x (A_{11} - A_{\underline{1}}) \sin \theta \cos \theta + S_z (A_{\underline{1}} \sin^2 \theta + A_{11} \cos^2 \theta)]$$

The terms off-diagonal in $\underline{S}$ represent coupling between the two electron spin states (separated by 23 kMc/s at K band) via the small fluorine interaction (~ 100 Mc/s). For the moment we neglect these terms and obtain the "total field", $\underline{H}_T$, at the fluorine nucleus by adding the term $+H_0$, representing the magnitude of the external field, to H_{Lz}

$$H_{Tx} = - \frac{1}{g_F \beta_n} \cdot S_z (A_{11} - A_{\underline{1}}) \sin \theta \cos \theta$$

$$H_{Ty} = 0 \quad (8)$$

$$H_{Tz} = - \frac{1}{g_F \beta_n} \cdot S_z (A_{\underline{1}} \sin^2 \theta + A_{11} \cos^2 \theta) + H_0$$

The contribution to the energy of the system by the fluorine nucleus as a function of S_z , is simply obtained by quantizing the nuclear states along $\underline{H}_T$.

$$E_F(S_z) = - g_F \beta_n \underline{H}_T(S_z) \cdot \underline{I} = - g_F \beta_n |H_T(S_z)| \cdot \left(\pm \frac{1}{2}\right) \quad (9)$$

Substituting for $|H_T|$

$$E_F(S_z) = \pm \frac{1}{2} [S_z^2 (A_{11}^2 \cos^2 \theta + A_{\perp}^2 \sin^2 \theta) - 2g_F \beta_n H_o S_z (A_{11} \cos^2 \theta + A_{\perp} \sin^2 \theta) + (g_F \beta_n H_o)^2]^{1/2} \quad (10)$$

and the fluorine nuclear transition energy is given by the square root in (10).

Since terms off-diagonal in S in the spin Hamiltonian have so far been neglected, to this approximation the electronic state is unaffected by the quantum state of any particular fluorine nucleus. Thus the total contribution to fluorine hyperfine energy is simply the sum of appropriate expressions (10) for each of the six nearest fluorines.

At this point Hall and Schumacher approximate by quantizing the fluorine nucleus along H_L rather than H_T giving

$$E_F(S_z) = \pm \frac{1}{2} [S_z (A_{11}^2 \cos^2 \theta + A_{\perp}^2 \sin^2 \theta)^{1/2} - g_F \beta_n H_o \cos \theta] \quad (11)$$

where θ is the acute angle between the external field H and H_L . From this the field separation between two E.P.R. lines corresponding to the allowed transitions $\Delta S_z = 1$, $I_z = +\frac{1}{2}$ and $\Delta S_z = 1$, $I_z = -\frac{1}{2}$ is simply

$$\Delta_{FH} = \frac{1}{8\pi} (A_{11}^2 \cos^2 \theta + A_{\perp}^2 \sin^2 \theta)^{\frac{1}{2}} \quad (12)$$

This approximation is satisfactory for the interstitial hydrogen atom in CaF_2 at X band since $\underline{H_L}$ ($\sim 12\text{kG}$) is considerably larger than the external field (3kG) and so the angle between $\underline{H_L}$ and $\underline{H_T}$ is small. However, for substitutional hydrogen in CaF_2 at K band $\underline{H_L}$ and $\underline{H_O}$ are about the same size and the angle between $\underline{H_L}$ and $\underline{H_T}$ is large (typically 20°). The off-diagonal nuclear Zeeman term neglected in quantising along $\underline{H_L}$ thus becomes three times as large. The relationships between the various fields acting on the fluorine are approximately as shown in Fig. 6.2. Equn. (12) then leads to errors of up to 5% for θ not close to 0° or 90° . The correct interval, Δ_{FH} , for intermediate values of θ is obtained by computing, at the appropriate field, the fluorine energy separations given by (10) for the two electronic states and adding (since the hyperfine energy is greater than the nuclear Zeeman energy). For $\theta = 0^\circ$ or 90° $\underline{H_{Lx}}$ is zero (neglecting the term in S_x) so $\underline{H_L}$ and $\underline{H_T}$ are both parallel to $\underline{H}$. Equn. (12) then leads to the correct result that at $\theta = 0^\circ$ the E.P.R. lines are separated by A_{11} and at $\theta = 90^\circ$ by $A_{\perp}$.

For the substitutional hydrogen A_{11} and $A_{\perp}$ can both be measured directly from the $[100]$ spectrum. The values obtained were used to calculate the separations expected

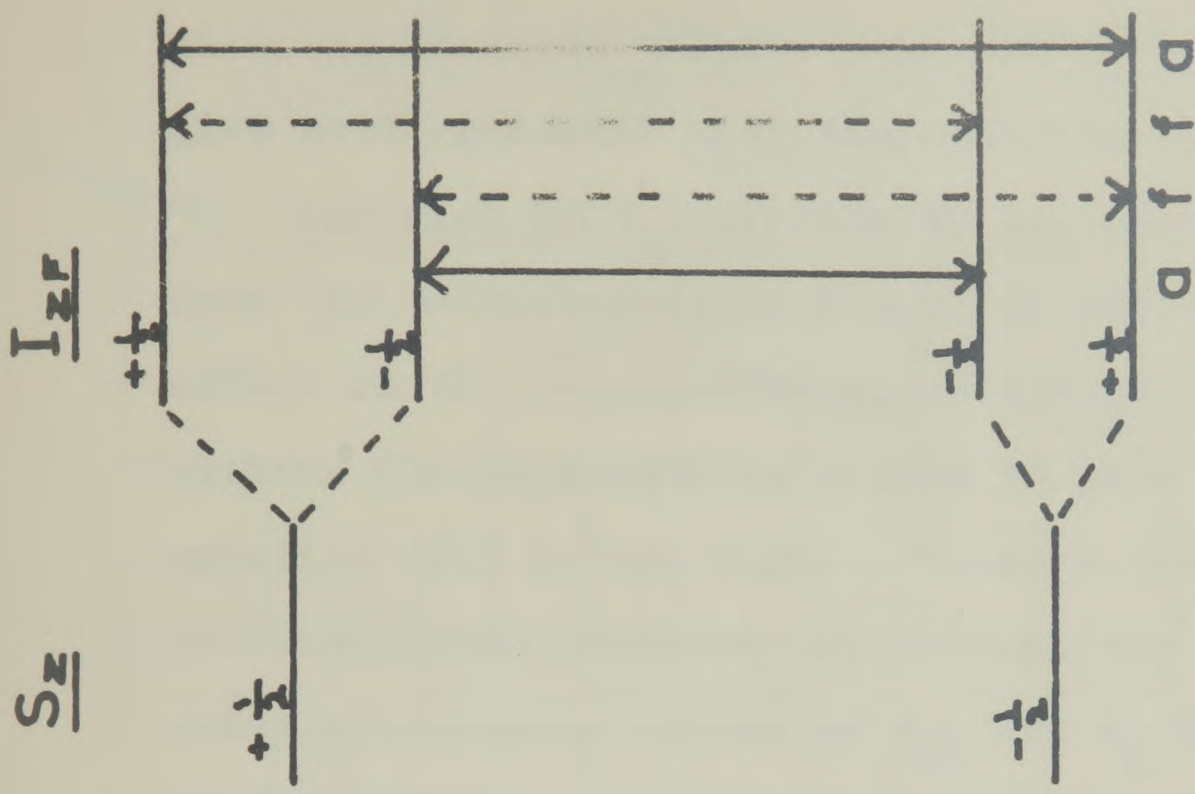


Fig. 6.3 Allowed (a) and

Forbidden (f) EPR Transitions

Involving One F Nucleus.

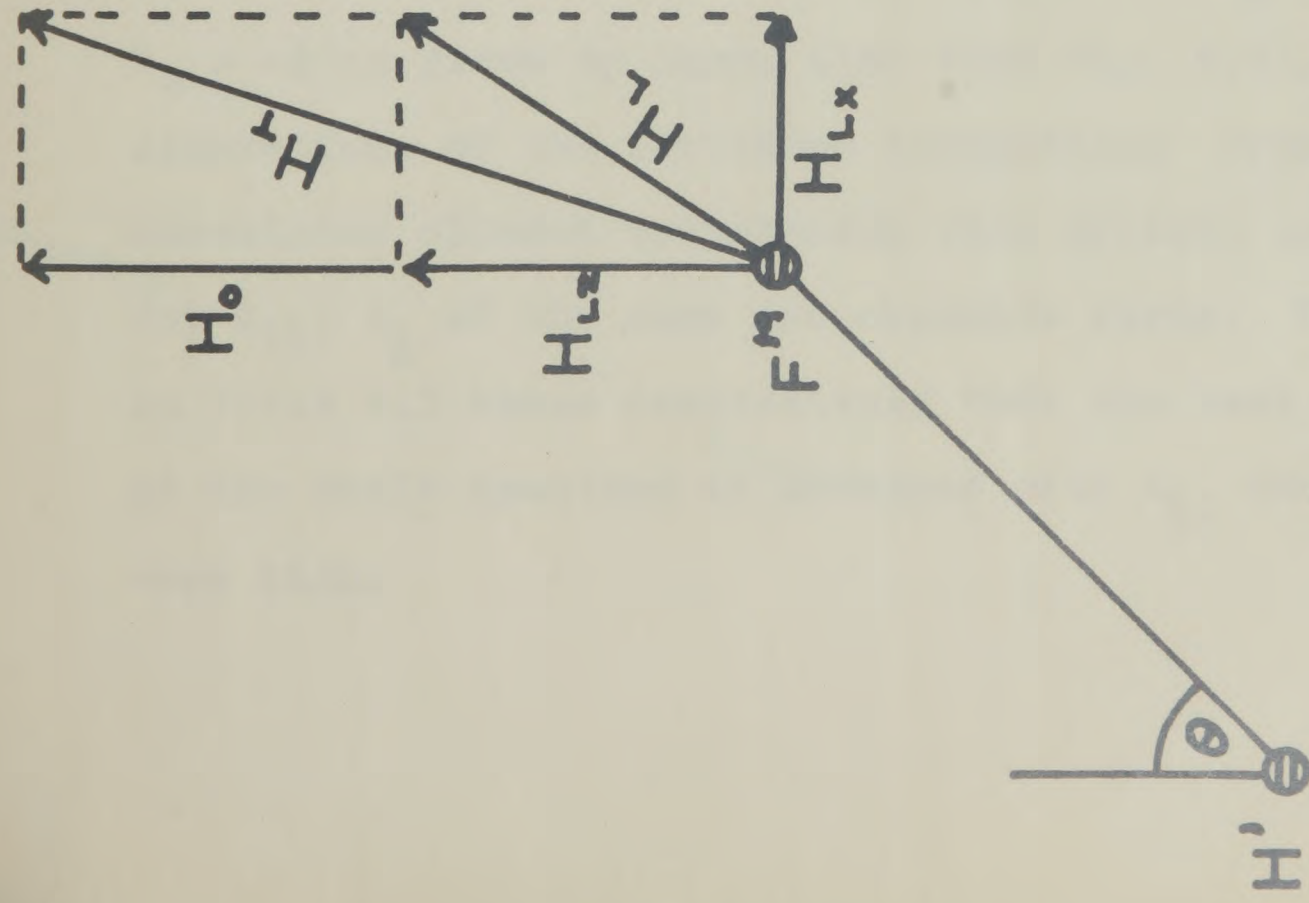


Fig 6.2. Fields Acting

on Ligand F Nucleus.

for the other directions according to (10) and compared with the measured values. A_{11} and $A_{\underline{1}}$ were adjusted to give best agreement with the accurate [110] measurements.

The sign of $A_{\underline{1}}$ relative to A_{11} cannot be determined from the measurements at $\theta = 0^\circ$ or 90° but has a small effect on the calculated separation of the allowed transitions for intermediate angles to just the extent that equation (11) is not valid. Table 6.3(a) compares the calculated and observed separations for the two alternatives using approximate values of A_{11} and $A_{\underline{1}}$ from the [100] spectrum. However, the positions of the two forbidden transitions which occur between each pair of allowed transitions are much more sensitive to the relative signs of A_{11} and $A_{\underline{1}}$. The separation of these transitions from the corresponding allowed transition is equal to the separation of the fluorine nuclear levels either for $S_z = +\frac{1}{2}$ or $S_z = -\frac{1}{2}$ as given by Eqn. (10) (See Fig. 6.3). The expected separations of the forbidden transitions from their associated allowed transitions with $H/[110]$ were calculated for A_{11} , $A_{\underline{1}}$ of the same and opposite signs. The results in Table 6.3 shows conclusively that the best description of the whole spectrum is obtained with A_{11} and $A_{\underline{1}}$ of the same sign.

Table 6.3. Calculated and Observed Spacings of Fluorine Hyperfine Components for Substitutional Hydrogen in CaF_2 at K Bond with $A_{//}$, $A_{\perp}$ of the Same and of Opposite Signs

	$\cos^2 \theta$	Calc. Sep.(G) $A_{//}$, $A_{\perp}$ Same Sign	Calc. Sep.(G) $A_{//}$, $A_{\perp}$ Opposite Sign	Observed Separation (G)
(a) Allowed Transitions	$\frac{1}{2}$	45.88	49.14	45.84
	$\frac{1}{3}$	40.64	45.13	40.79
(b) Forbidden Transitions	$\frac{1}{2}$	12.95	19.69	13.10
	$\frac{1}{3}$	10.31	20.51	10.38

6.4 Corrections Due to Interaction with the Proton

The derivation so far has assumed the electronic quantum state to be described exactly as $|S_z = \pm \frac{1}{2}\rangle$. In fact the hyperfine interaction with the proton is large (~ 1400 Mc/s) and causes appreciable mixing of the hydrogen atom states $|S_z = +\frac{1}{2}, I_{pz} = -\frac{1}{2}\rangle$ and $|S_z = -\frac{1}{2}, I_{pz} = +\frac{1}{2}\rangle$ where I_p is the proton spin. The states $|+\frac{1}{2}, +\frac{1}{2}\rangle$ and $|-\frac{1}{2}, -\frac{1}{2}\rangle$ are unmixed and the expression for the fluorine level separations, (10), simply requires S_z replacing by $\pm\frac{1}{2}$ as appropriate. The correct eigenfunctions of the states " $|+\frac{1}{2}, -\frac{1}{2}\rangle$ " and " $|-\frac{1}{2}, +\frac{1}{2}\rangle$ " in a magnetic field H are given by the Briet-Rabi expressions:

$$|+\frac{1}{2}, -\frac{1}{2}\rangle = \left(1 - \frac{1}{8x^2}\right) |+\frac{1}{2}, -\frac{1}{2}\rangle + \frac{1}{2x} |-\frac{1}{2}, +\frac{1}{2}\rangle \quad (13)$$

$$|-\frac{1}{2}, +\frac{1}{2}\rangle = \left(1 - \frac{1}{8x^2}\right) |-\frac{1}{2}, +\frac{1}{2}\rangle - \frac{1}{2x} |+\frac{1}{2}, -\frac{1}{2}\rangle$$

6.5 Corrections arising from the interaction of the fluorine nuclear spin with the magnetic field

$$\text{where } x = (g^2 + g_p^2) \frac{H}{A}$$

We now take account of the interaction of the fluorine nuclear spin with the magnetic field. Using these expressions to evaluate the projection of $\underline{S}$ along $\underline{H}$ the energies of one fluorine coupled to the states " $|+\frac{1}{2}, -\frac{1}{2}\rangle$ " or " $|-\frac{1}{2}, +\frac{1}{2}\rangle$ " are

nuclear spin functions are

ferent sets of eigenfunctions

I_z being along $\underline{H}$ is easy to

ments of a perturbation theory

$$\begin{aligned}
E_F(S_z') &= \mp \frac{1}{2} \left[\left(\frac{1}{4} - \frac{1}{8x^2} \right) (A_{11}^2 \cos^2 \theta + A_{\perp}^2 \sin^2 \theta) \right. \\
&\quad - 2g_F^8 n H_O S_z' \left(1 - \frac{1}{4x^2} \right) \\
&\quad \times (A_{11} \cos^2 \theta + A_{\perp} \sin^2 \theta) \\
&\quad \left. + (g_F^8 n H_O)^2 \right]^{1/2}
\end{aligned} \tag{14}$$

where S_z' operates on the appropriate approximate quantum state.

At the K band fields used this correction amounts to a reduction in the spacing of adjacent fluorine components of the E.P.R. spectrum by 0.05%. This ranges from 0.008G for $\theta = 90^\circ$ to 0.027G for $\theta = 0^\circ$. While this correction is of little importance for the E.P.R. measurements, the corresponding frequency decreases of 47 kc/s to 151 kc/s could readily be detected by an ENDOR measurement.

6.5 Corrections arising from Second Order Interaction with the Fluorine System.

We now take account of terms in the fluorine Hamiltonian off-diagonal in S which have been omitted so far. The exact diagonalisation of the approximate one fluorine Hamiltonian, represented in equn. (10), indicates that the fluorine nuclear spin functions are diagonal with respect to different sets of co-ordinate axes for $S_z = +\frac{1}{2}$ and $S_z = -\frac{1}{2}$, I_z being along $\underline{H_T}$ in each case. For evaluating matrix elements of a perturbation between the two electron spin states

this is inconvenient so we now quantise the nuclear spin states along $\underline{H}_L$. The approximation involved is sufficiently good in this case where a small correction is being evaluated. The terms omitted from the Hamiltonian earlier now correspond to the perturbing Hamiltonian

$$\mathcal{H}_1^F = \frac{S_x I_x' A_{11}}{A(\theta)} + \frac{S_x I_z' (A_{11}^2 - A_1^2) \sin\theta \cos\theta}{A(\theta)} + S_y I_y' A_1 \quad (15)$$

$$\text{where } A(\theta) = (A_{11}^2 \cos^2\theta + A_1^2 \sin^2\theta)^{\frac{1}{2}}$$

The primes relate to the nuclear co-ordinate axes just defined and the electron is still referred to the axes with $Z//H$.

$\mathcal{H}_1^F$ causes a slight mixing of the electron spin states which depends on the quantum state of the fluorine (similar to the mixing caused by the proton). Because of this other fluorine nuclei coupled to the electron are able to "see" indirectly the state of the first nucleus. The result is to produce a pseudo-dipolar coupling between the nearest neighbour fluorines which is approximately 100 times larger than the direct nuclear dipole-dipole interaction of about 10 kc/s. This has the effect of raising the degeneracy of the various EPR transitions corresponding to $\sum_{n=1}^6 I_{zn} = 0$ (i.e. the central lines of each fluorine multiplet) and shifts the centre of gravity of the composite E.P.R. lines.

To obtain correct values for the hydrogen g value this shift must be estimated.

The accurate EPR measurements were made for $H// [110]$ in which case the nearest fluorines fall into two sets, one set with two fluorines at $\theta = 90^\circ$ and the other with four at $\theta = 45^\circ$. A complete treatment of second order fluorine hyperfine effects in this situation is difficult. However, the correction expected is of the order of the experimental error in measuring the EPR line positions so an approximate treatment is sufficient.

We consider the second order effects for a pair of spin $\frac{1}{2}$ equivalent nuclei related by inversion in the hydrogen. The effect of coupling via the electron is for the nuclei to be better described in terms of eigenstates of total nuclear angular momentum. For a pair of equivalent nuclei these eigenstates belong to a triplet $I = 1$ and a singlet $I = 0$. In terms of the single nucleus functions $|I_z = \pm \frac{1}{2}\rangle_n$ these states are

Triplet:

$$|I = 1, I_z = +1\rangle = |+\frac{1}{2}\rangle_1 |+\frac{1}{2}\rangle_2$$

$$|1, 0\rangle = \frac{1}{\sqrt{2}} [|+\frac{1}{2}\rangle_1 |-\frac{1}{2}\rangle_2 + |-\frac{1}{2}\rangle_2 |+\frac{1}{2}\rangle_1]$$

$$|1, -1\rangle = |-\frac{1}{2}\rangle_1 |-\frac{1}{2}\rangle_2 \quad (16)$$

Singlet:

$$|0, 0\rangle = \frac{1}{\sqrt{2}} [|+\frac{1}{2}\rangle_1 |-\frac{1}{2}\rangle_2 - |+\frac{1}{2}\rangle_2 |-\frac{1}{2}\rangle_1]$$

The total nuclear angular momentum I to which these functions belong may be checked by operating with

$$I^2 = I_1^2 + I_2^2 + I_1^+ I_2^- + I_1^- I_2^+ + 2I_{1z} I_{2z} \quad (17)$$

and equating the result to $I(I+1)|I, I_z\rangle$.

The total perturbation for the pair is the sum of perturbations H_1 for each fluorine. The operators for the two nuclei can be summed without difficulty since they are related to the same set of axes. The total perturbation is an expression identical to (15) but with the spin operators operating within manifolds of total I rather than on single nuclei. This is more conveniently written in terms of the raising and lowering operators

$$H_1^T = S^+ [A_1 I^+ + B_1 I^- + C_1 I_z] \\ + S^- [A_1 I^- + B_1 I^+ + C_1 I_z]$$

$$\text{where } A_1 = \frac{1}{4} \left[\frac{A_{11} A_1}{A(\theta)} - A_1 \right] \quad (18)$$

$$B_1 = \frac{1}{4} \left[\frac{A_{11} A_1}{A(\theta)} + A_1 \right]$$

$$C_1 = \frac{(A_{11}^2 - A_1^2) \sin \theta \cos \theta}{2 A(\theta)}$$

The perturbation H_1^T does not connect levels of different I nor does it affect the singlet $|0,0\rangle$. However, it does connect the states $|I=1, I_z\rangle$ belonging to different electron

spin states. We wish to calculate the consequent splitting of the previously degenerate levels $|1, 0\rangle$ and $|0, 0\rangle$. Since we know these to be correct zero order eigenstates the energy shifts may be found by ordinary non-degenerate perturbation theory. The levels $|S_z\rangle |1, 0\rangle$ are shifted relative to the levels $|S_z\rangle |0, 0\rangle$ by $\frac{2}{V_e} (A_1^2 + B_1^2)$ where V_e is the microwave frequency. The EPR transition $|+\frac{1}{2}\rangle |1, 0\rangle - |-\frac{1}{2}\rangle |1, 0\rangle$ is then shifted to lower field by an amount corresponding to $\frac{4}{V_e} (A_1^2 + B_1^2)$ which at K band for $\theta = 90^\circ$ is equal to 650 Kc/s. For $H \parallel [110]$ the two EPR transitions considered are in first order each six-fold degenerate because of the other set of four equivalent fluorines with $\theta = 45^\circ$. This causes further splitting of the twelve

$$\sum_{n=1}^6 I_{zn} = 0$$

EPR transitions. Treating the quartet in a similar manner to the pair leads to a final shift to lower field of the centre of gravity of the central EPR transition by 0.18 G. In view of its small size the approximations involved in estimating the shift are good enough for the purpose.

6.6 Evaluation of EPR Parameters

Though the measured transition fields depend on the

proton and ^{19}F nuclear moments, g_p and g_F , the dependence is too small to make it sensible to attempt to derive these parameters. The published values for the N.M.R. frequencies were used:

$$\nu_{^{19}\text{F}} = 4.0055 \text{ Mc/s/KG}, \quad \nu_p = 4.2577 \text{ Mc/s/kG}.$$

(a) A_{11} and A_1 were derived as described at the end of section 6.3.

(b) These values were used to correct the measured positions of the central E.P.R. lines of each multiplet for second order fluorine interaction.

(c) The proton hyperfine interaction in Gauss is given by the separation between the two corrected lines. A first approximation to the g value is obtained from the expression to order A^2/g^3H for the E.P.R. transition energy, giving

$$g = \frac{h\nu}{\beta \left[H_1 + \frac{A}{2} + \frac{g\beta A^2}{4H_1(g\beta + g_p\beta_n)} \right]} \quad (19)$$

where A is in Gauss and the free hydrogen g value, 2.0023, is used in the denominator. H_1 is the field for the low field line. Using the value of g obtained A is converted to frequency units and g and A are put into the exact Breit-Rabi expression for the transition frequency at the fields of the two E.P.R. lines, which was known exactly (see Sect. 8.1). The two parameters were then varied to give the measured

klystron frequency for both transitions.

(d) A_{11} and A_1 were converted to frequency units using the accurate g value and slight correction made for mixing of the electronic spin states.

6.7 Annealing of the Spectrum of Substitutional Hydrogen in CaF_2

The substitutional spectrum was stable at 77°K and during subsequent ENDOR measurements a crystal was kept at 77°K for five weeks with no significant decrease in intensity of E.P.R. spectrum. However, since this spectrum is produced only by low temperature irradiation it seemed very likely that it would become unstable at some temperature below room temperature.

A crystal containing the substitutional spectrum was allowed to warm up slowly until an abrupt change in the spectrum was observed, when it was immediately cooled again to 77°K . The new spectrum was that of hydrogen on an interstitial site. Moreover the environment of the hydrogen was perfect as shown by the interaction with eight regularly placed fluorines. The spectrum also confirmed the assignment of crystal directions made for the substitutional spectrum. Due to the intensity of the forbidden transitions it was not possible to say that the substitutional spectrum had disappeared entirely but this seemed very probable. The intensity of the interstitial spectrum produced by annealing

was similar to that of the substitutional and approaching an order of magnitude less than for the same crystal irradiated for a few hours at room temperature. After the anneal the trapped hole centres had also disappeared.

A crystal was irradiated at 77°K for 8 hours and allowed to warm up and give the interstitial spectrum. It was then irradiated at 77°K for a further eight hours. This left the interstitial spectrum at about the original intensity but also formed a comparable intensity of substitutional spectrum. The two spectra were readily distinguishable because of the relative shift caused by the different proton hyperfine interactions as well as the different fluorine multiplet structure. Allowing the crystal to warm up again annealed the new substitutional spectrum and augmented the interstitial. The conclusion is that the second irradiation formed new hydrogen atoms rather than returning interstitial ones to substitutional sites.

The apparatus was not suitable for pulse annealing techniques and accurate determination of sample temperature but J.W. Hodby ((1965) private communication) has studied the annealing process in detail and finds that it occurs according to first order kinetics with a maximum rate at 145°K .

6.8 Hydrogen in Strontium Fluoride

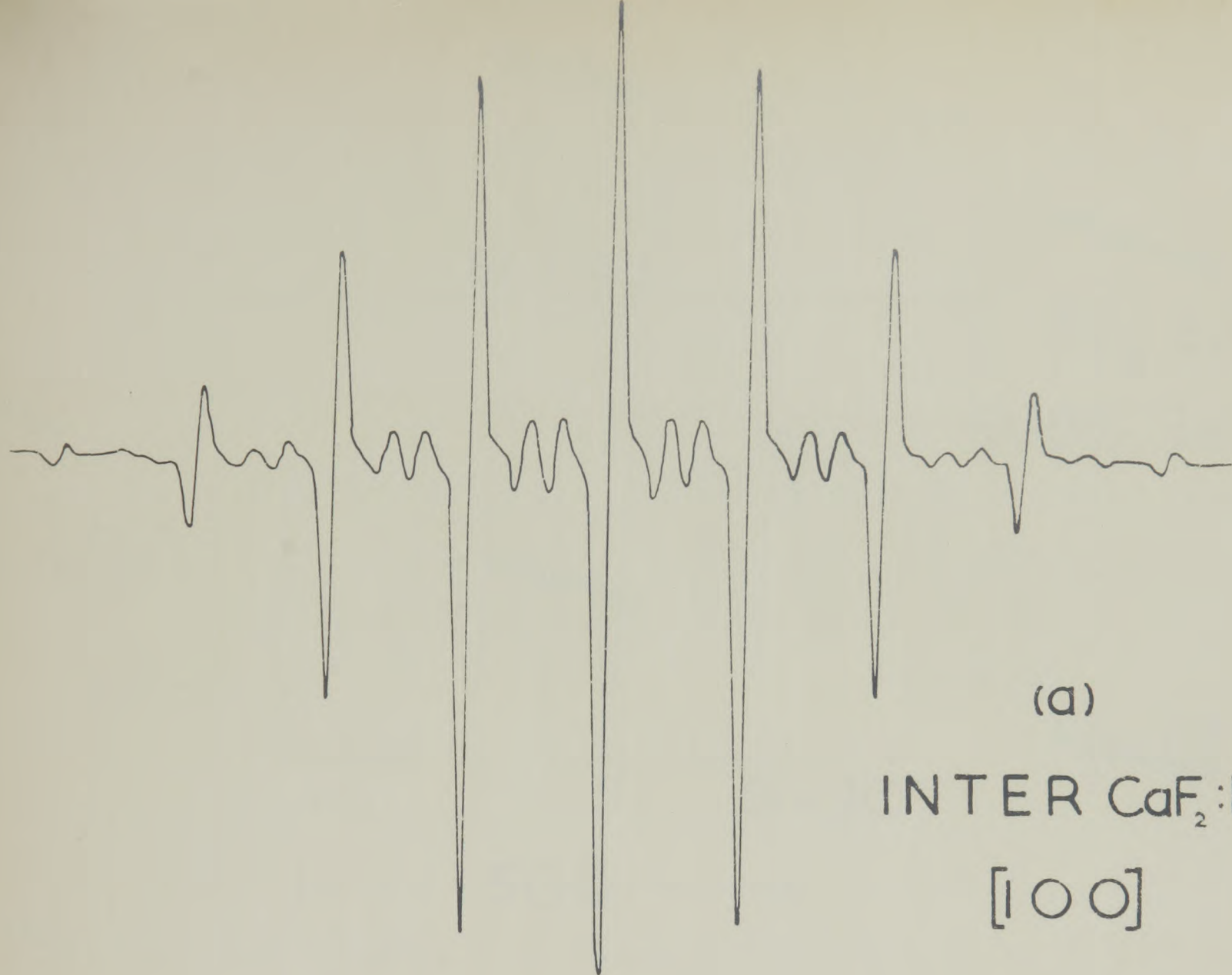
Since it had been shown possible to trap hydrogen atoms

on substitutional sites during low temperature X-irradiation it was of interest to check that this mechanism was not confined to CaF_2 . Accordingly preliminary investigations were carried out on strontium and barium fluorides.

Room temperature X-irradiation of SrF_2 single crystals, hydrogenated by the method of Hall and Schumacher gives rise to the E.P.R. spectrum of interstitial hydrogen atoms (Welber (1964)). The spectrum is qualitatively very similar to that of $\text{CaF}_2\text{:H}$ and the interaction with the eight nearest fluorines is well resolved. These fluorines are $2.54\text{\AA}$ from the hydrogen as compared to $2.36\text{\AA}$ in CaF_2 and, as expected, the fluorine hyperfine parameters are somewhat smaller. The two spectra at X band are compared in Fig. 6.4(a), (b), for $\text{H} // [100]$.

A single hydrogenated crystal of SrF_2 , shown by its infra red spectrum to contain a large quantity of substitutional H^- ions was irradiated at 20°K for periods of 12, 24, and 50 hours at 50 kV, 50 mA tube current, at 4 cms from the target. The E.P.R. spectrum produced saturated strongly at 20°K but was readily visible on the oscilloscope at 77°K . One of the fluorine multiplets is shown in Fig. 6.4(c) for $\text{H} // [110]$. The different irradiation times indicated a fairly rapid build-up at the beginning followed by a tailing off in production efficiency over the long irradiation periods.

By analogy with CaF_2 the spectrum of Fig. 6.4(c) is



← 100 G →

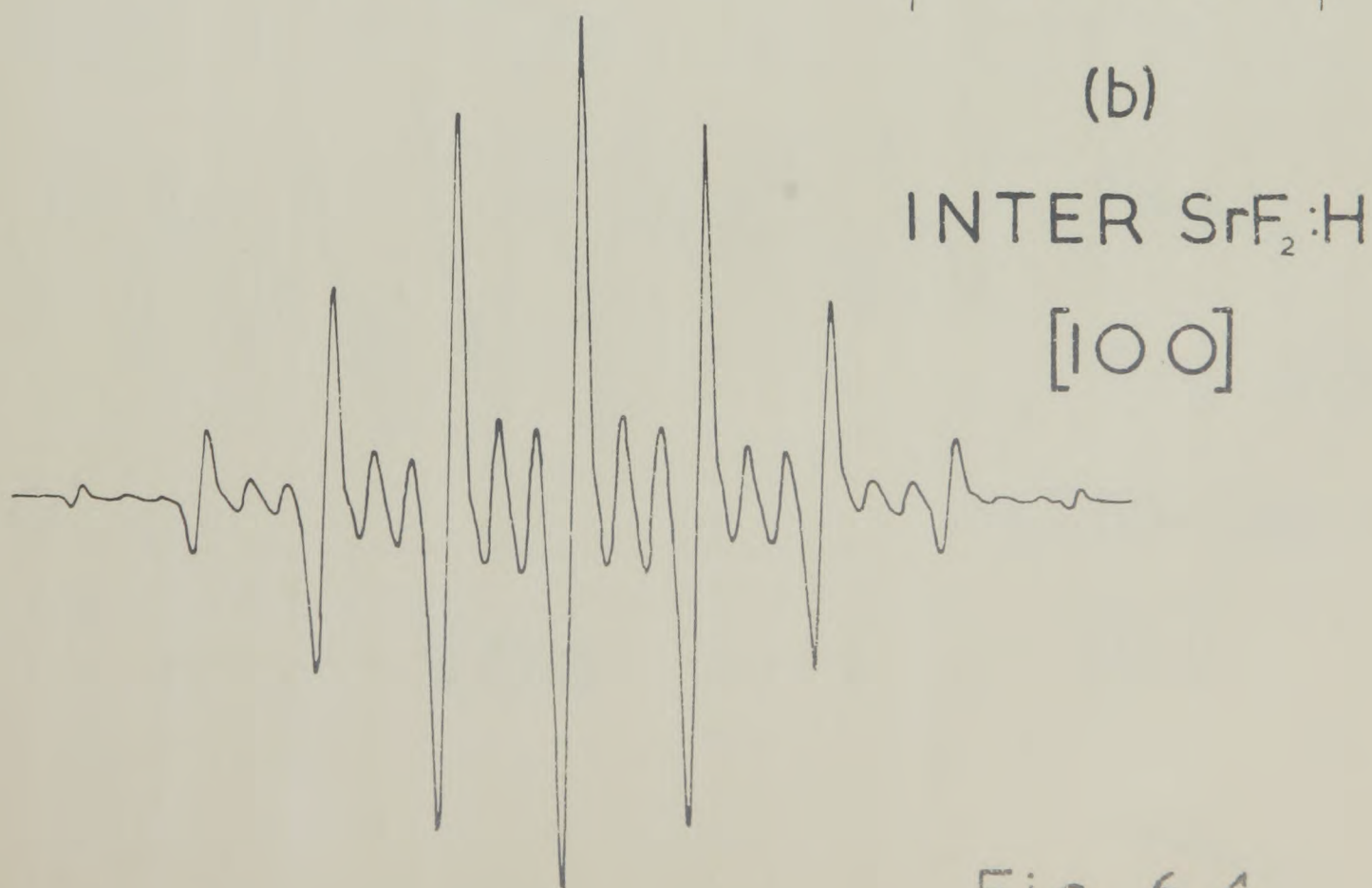
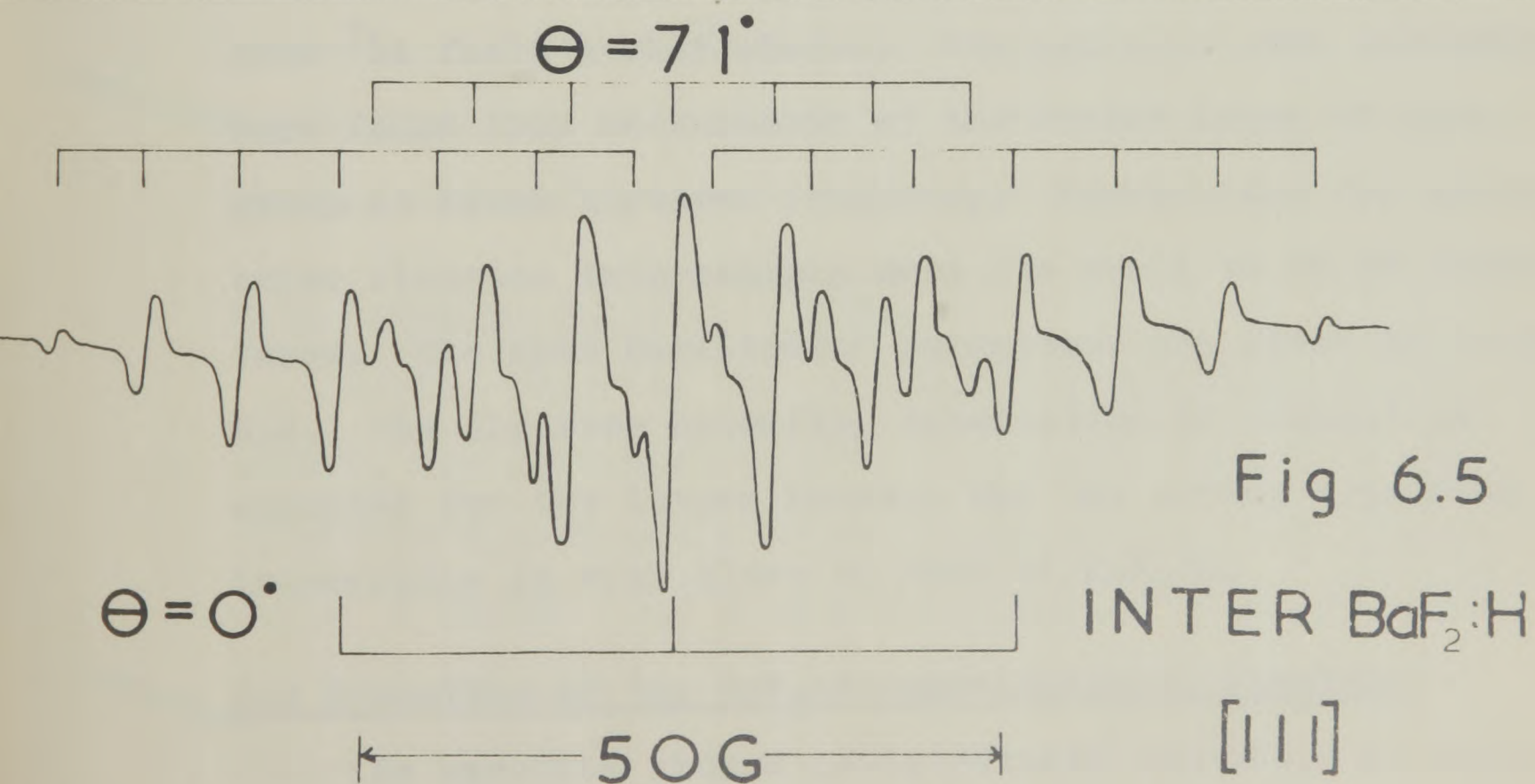
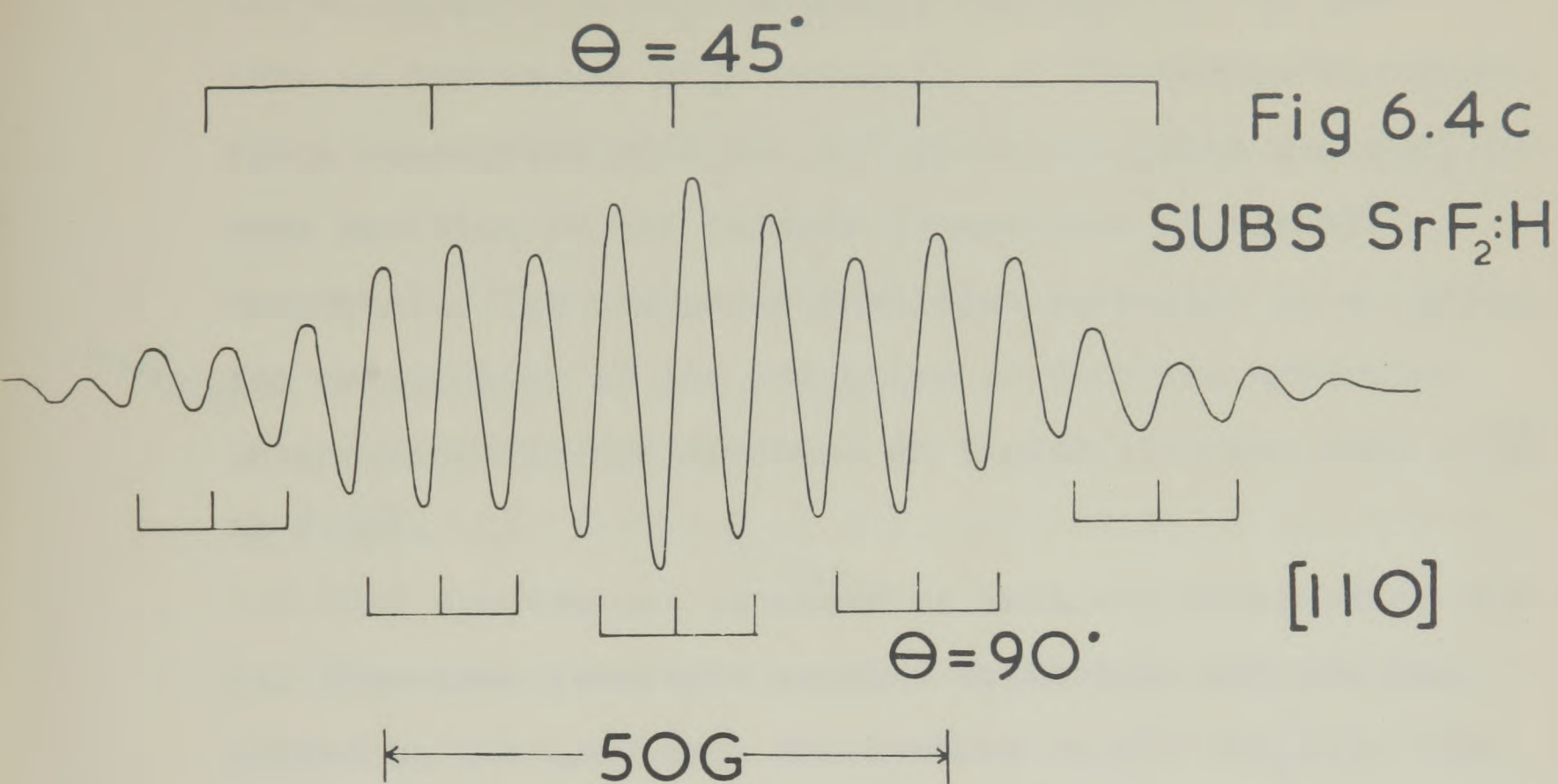


Fig 6.4



assigned to substitutional hydrogen atoms. At first glance the similarity to the $\text{CaF}_2[110]$ spectrum is not great but this is due to the high intensity of the forbidden transitions associated with the 45° fluorines which occur at the same position as the allowed transitions of the 90° fluorines. The increased forbidden intensity is an expected consequence of the reduction of fluorine hyperfine interaction through increase of ligand distance from $2.73\text{\AA}$ to $2.93\text{\AA}$.

The spectra can be shown to indicate interaction with six fluorines forming a regular octahedron and are described by the same spin Hamiltonian as for $\text{CaF}_2(1)$. The components of the fluorine hyperfine tensors were obtained from ^7Li field marker charts. The hydrogen atom parameters were found from measurement of the centre lines of each group at known klystron frequency. Corrections for second order fluorine interactions were too small to be of importance. The spin Hamiltonian parameters are given in Table 6.2. The fluorine hyperfine interaction is reduced as expected for the larger lattice but the proton hyperfine interaction is very close to that of $\text{CaF}_2:\text{H}$.

6.9 Annealing of the $\text{SrF}_2:\text{H}$ Substitutional Spectrum

The spectrum showed no detectable reduction in intensity through being kept at 77°K for one week. However, as expected, slowly warming the crystal produced the change

to the interstitial spectrum. A spectrum similar to that of the self-trapped hole in CaF_2 disappeared at the same time. Immediately cooling again to 77°K showed the environment of the hydrogen to be locally perfect. The intensity was an order of magnitude less than that of the interstitial spectrum produced by room temperature irradiation.

The crystal was further X-irradiated for eleven hours at 20°K . This resulted in the reformation of the substitutional spectrum at the original intensity when observed at 77°K . However, unlike the CaF_2 case, the interstitial spectrum seemed to have disappeared though a weak interstitial spectrum could have been obscured by the closely spaced structure of the substitutional spectrum. It would appear that the reirradiation at 20°K converted the interstitial hydrogen atoms to substitutional.

6.10 Hydrogen In BaF_2

Welber reported the interstitial spectrum of hydrogen in BaF_2 and obtained at 77°K . $A = 1426.1 \pm 0.1 \text{ Mc/s}$ and g , to within experimental error, equal to the free hydrogen value, 2.00226. Due to the large intensity of the forbidden transitions at x band he was able to determine the fluorine hyperfine interaction only for $H//[100]$ and could not make separate determinations of $A_{//}$ and $A_{\perp}$.

Present attempts to produce the substitutional spectrum

were not as successful as for CaF_2 or SrF_2 . A strongly doped crystal was X-irradiated at 20°K , 4 cms from the X-ray tube target at 50 kV, 50 mA for a total of 89 hours. As a result two groups of very weak lines were visible at 77°K with a separation of about 500G. at $g = 2$, bracketed by a particularly strong spectrum of the self-trapped hole type. The structure within each of the two groups of weak lines was anisotropic but no definite alignment could be determined or useful measurements made. X-irradiation at 77°K was even less productive. After warming the weak spectrum to room temperature and cooling to 77°K again there had been a definite change and gross features of the new spectrum were consistent with its being due to the interstitial hydrogen in BaF_2 . The indication is that BaF_2 behaves similarly to CaF_2 and SrF_2 but that formation of hydrogen atoms at low temperature is a much less efficient process.

After X-irradiation for $3\frac{1}{2}$ hours at room temperature the same crystal produced the spectrum of interstitial hydrogen comparable in intensity to that of CaF_2 or SrF_2 when irradiated at room temperature. At K band the fluorine hyperfine structure could clearly be resolved into the three septets for $H/[111]$, due to reduction in intensity of the forbidden transitions (Fig. 6.5). The fluorine hyperfine parameters were derived from field

marker charts of the spectrum at room temperature and are given in Table 6.2.

As observed by Welber the interstitial spectrum in B_aF_2 is unstable at room temperature and disappears after a few days.

6.11 The Forbidden Transitions

Fig. These transitions are shown dotted in Fig. 6.3. Referring to nearest neighbour fluorines only, they correspond to transitions $\Delta M_S = 1$, $\Delta M_F = 1$. As mentioned in section 6.5 the fluorine nuclear eigenstates are quantised along different axes for the two electron spin states. A nuclear eigenstate, $|\pm \frac{1}{2}\rangle$, for one electronic spin state is no longer orthogonal to the opposite nuclear eigenstate $|\mp \frac{1}{2}\rangle^1$ for the other spin state. The extent of non-orthogonality is found by expressing a nuclear eigenstate $|\pm \frac{1}{2}\rangle^1$ in terms of the eigenstates $|\pm \frac{1}{2}\rangle$ by simple rotation of axes about the y direction. If the angle between the axes of nuclear quantisation for the two electronic spin states is ϕ then we obtain

$$\begin{aligned} |+\frac{1}{2}\rangle^1 &= \cos \phi/2 |+\frac{1}{2}\rangle + \sin \phi/2 |-\frac{1}{2}\rangle \\ |-\frac{1}{2}\rangle^1 &= \cos \phi/2 |-\frac{1}{2}\rangle - \sin \phi/2 |+\frac{1}{2}\rangle \end{aligned} \quad (20)$$

The "allowed" transition probability is proportional to the square of the matrix element between $|+\frac{1}{2}\rangle$ and $|+\frac{1}{2}\rangle^1$

and the "forbidden" probability to the square of that between $| + \frac{1}{2} \rangle$ and $| - \frac{1}{2} \rangle^1$. Thus

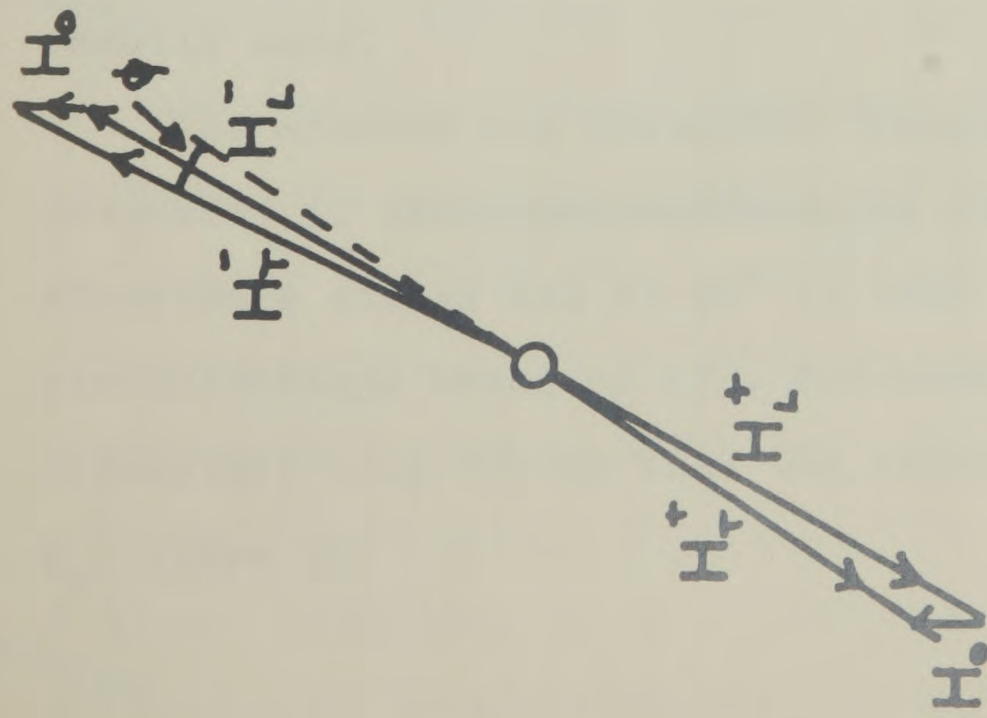
$$P_A \sim \cos^2 \phi/2$$

$$P_F \sim \sin^2 \phi/2$$

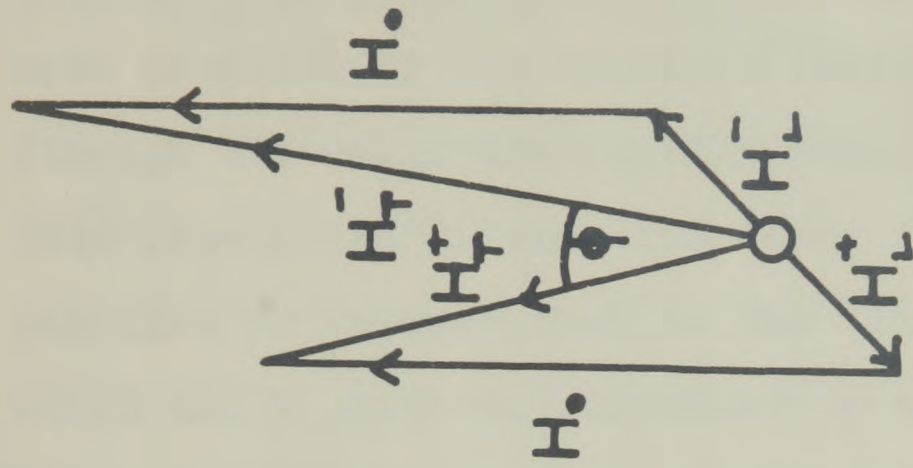
(21)

Fig. 6.6 illustrates the way in which the axis of nuclear quantisation changes direction as a result of an electronic transition. For a hyperfine interaction large compared with the nuclear Zeeman energy the transition almost reverses the quantisation axis (Fig. 6.6(a)). If the hyperfine interaction is very small (Fig. 6.6(b)) the axis only slightly alters its direction. For hyperfine interactions of the order of the nuclear Zeeman energy the two orientations of the nuclear axis are neither closely parallel nor antiparallel and "forbidden" transitions are strong.

Some care is required in defining "allowed" and "forbidden". In the limiting case of zero nuclear Zeeman energy the electronic transition exactly reverses the nuclear quantisation direction but putting $\phi = 180^\circ$ in (21) gives an "allowed" transition probability of zero and a "forbidden" probability of unity. This is a result of quantising along the total field at the fluorine nucleus which leads to a relabelling of the unchanged nuclear quantum states as a result of the electronic transition. The more usual definition



(a) Large Hyperfine Field.



(b) Small Hyperfine Field.

Fig 6.6. Effect of Electronic Transition on Direction of H_T .

of an "allowed" transition is that $\Delta M_S = 1$, $\Delta M_I = 0$ where M_I represents an approximate quantisation along the magnetic field, i.e. on the vector model the component of nuclear spin parallel to the magnetic field does not change sign (though its magnitude usually does change). To conform to this convention we quantise along that direction, either parallel or antiparallel to the total field, $\underline{H}_T$, as required, which has a positive component in the direction of the magnetic field. If ϕ is then taken as the acute angle between the quantisation axes so defined for the two electronic spin states the expressions (21) will conform with the usual ideas of "allowed" and forbidden" intensities.

For $\theta = 0^\circ$ or 90° the two quantisation directions are exactly parallel to each other and to $\underline{H}$ since the component of hyperfine field perpendicular to $\underline{H}$, $S_z(A_{11} - A_{\underline{1}}) \sin \theta \cos \theta$, (Sect. 6.3) is zero. The forbidden intensity is then exactly zero.

The allowed and forbidden transitions have equal intensity if ~~the angle between the~~ total fields for the two electronic states are at 90° to each other. Simple geometrical considerations based on Fig. 6.6 show that for given hyperfine parameters this occurs when the external field has a value, H_c , given by

5 times) resulting in the clear spectrum obtained (Fig. 6.7) which can be interpreted without difficulty.

$$\left(\frac{g_F^3 n H_c}{10^6 h} \right)^2 = \frac{1}{4} (A_{11}^2 \cos^2 \theta + A_{\perp}^2 \sin^2 \theta) \quad (22)$$

with A_{11} , $A_{\perp}$ in Mc/s.

If H is different from H_c the forbidden transitions are less intense than the allowed. Thus, if H is less than H_c in a particular situation, increasing H will make the forbidden transitions more intense while, if H is greater than H_c they will diminish. Table 6.4 gives the values of H_c for both hydrogen sites in the three alkaline earth fluorides for H along principal directions. For convenience H_c is given as the fluorine n.m.r. frequency in Mc/s in a field H_c . In these terms the fields at the central e.p.r. lines for each proton spin state are about 33 and 35 Mc/s respectively at K band and about 11 and 13 Mc/s respectively at X band.

The table makes some interesting points. In most cases H_c is greater than the external field even at K band resulting in considerably stronger forbidden transitions at K band. However, for interstitial hydrogen in BaF_2 with $H \parallel [111]$ H_c is only slightly above the X band field giving very strong forbidden transitions as observed by Welber and making the spectrum very hard to decipher. Going to K band fields reduces the forbidden intensity (the calculated factor being 5 times) resulting in the clear spectrum obtained (Fig. 6.5) which can be interpreted without difficulty.

Table 6.4. Critical Fields for Equal Allowed and Forbidden Intensities

In E.P.R. Spectra

Field Direction	Site	$\cos^2 \theta$	$\text{CaF}_2(^{19}\text{F Mc/s})$	$\text{SrF}_2(^{19}\text{F Mc/s})$	$\text{BaF}_2(^{19}\text{F Mc/s})$
[100]	INTER	1/3	57	43	25
	SUBS	1	No forbidden transitions	No forbidden transitions	
		0	No forbidden transitions	No forbidden transitions	
[110]	INTER	2/3	74	56	38
	SUBS	0	No forbidden transitions	No forbidden transitions	
		1/2	62	37	-
[111]	INTER	0	No forbidden transitions	No forbidden transitions	
		1/9	44	31	17
	SUBS	1	No forbidden transitions	No forbidden transitions	
		1/3	53	31	-

At k bond the fields for the central e.p.r. line for each proton spin state correspond to fluorine N.M.R. frequencies of approx. 33 and 35 Mc/s respectively. At X bond the frequencies are about 11 and 13 Mc/s respectively.

The reverse is the case for substitutional hydrogen in SrF_2 where, for $\underline{H} \parallel [111]$ or $[110]$, H_c is close to the fields used at K band giving rise to the rather unhelpful spectrum observed (Fig. 6.4 (b)). At X band the forbidden intensity is very small. Fortunately, for the substitutional site, the forbidden transitions can be removed at any field by setting $\underline{H}$ along $[100]$.

For both hydrogen sites in CaF_2 H_c is always high enough for the spectra to be dominated by the allowed transitions even at K band.

6.12 Formation and Annealing Mechanisms

The experimental results of this chapter may be summarised as follows:

- (1) X-irradiation at 77°K or below of hydrogenated alkaline earth fluoride crystals produces hydrogen atoms trapped on fluorine sites whose immediate environment is undistorted.
- (2) There is a rapid formation of a small initial concentration of substitutional hydrogen atoms followed by a slower constant growth.
- (3) The formation process for substitutional hydrogenations at 77°K is at least an order of magnitude less efficient than that producing interstitial hydrogen atoms at room temperature in CaF_2 and SrF_2 . At 20°K the process is less efficient still. In BaF_2 the low temperature process is 20-50 times less

efficient than for CaF_2 or SrF_2 whereas at room temperature the efficiency for production of interstitial hydrogen is of the same order for all three crystals. However the interstitial spectrum in BaF_2 anneals out at room temperature in a few days.

(4) In the region of 140°K at least 80% of the substitutional hydrogen atoms move irreversibly to locally perfect interstitial sites in CaF_2 and SrF_2 and probably also in BaF_2 . Under no circumstances could a spectrum be obtained which was not due to hydrogen atoms at the centres of perfect cubes of eight fluorines.

(5) After the change of site further X-irradiation at 77°K of $\text{CaF}_2:\text{H}$ or $\text{SrF}_2:\text{H}$ produces more substitutional hydrogen atoms at an enhanced initial rate.

(6) Further x-irradiation of $\text{SrF}_2:\text{H}$ at 20°K returns a large proportion of the interstitial hydrogen atoms to substitutional sites.

Hodby (1965) has made a thorough investigation of the formation and annealing processes for substitutional hydrogen or deuterium atoms in CaF_2 , SrF_2 and BaF_2 using e.p.r., infrared and optical techniques and has also studied the annealing above 100°C of the interstitial spectra in CaF_2 and SrF_2 . He should be consulted for the detailed observations but we report here some results which supplement those given above:

- (a) Sufficiently long irradiation at 77°K converts at least 80% of the H^{-} ions in the crystals to substitutional hydrogen atoms.
- (b) The formation of hydrogen atoms is accompanied by the formation of F centres. At low temperatures the ratio is about 1:1 while at room temperature there are about 20 hydrogen atoms for every F centre. Due to their large line-width ($\sim 60\text{G}$ for each component) the F centre spectra are easily overlooked when using a field modulation spectrometer adjusted to detect the 3G wide hydrogen lines. The F centre intensity does not change as the hydrogen atoms move to the interstitial sites. F centres are not produced by X-irradiation of the unhydrogenated crystals.
- (c) The transition from substitutional to interstitial site for hydrogen or deuterium in all three crystals obeys first order kinetics. The activation energy is $0.368 \pm 0.02 \text{ eV}$ for $\text{CaF}_2:\text{H}$. The energy falls as the lattice parameter increases and the deuterium energies are always slightly higher than those for hydrogen.
- (d) The annealing of the interstitial spectrum obeys kinetics higher than first order and occurs in two stages. In the first the predominant process is identified as reaction of H atoms to form molecules at about 150°C . In the second stage the hydrogen molecules react with F centres or F aggregate centres to reform the substitutional H^{-} ions.

The alkaline earth fluorides, therefore, differ from the alkali halides in that the hydrogen ions are ionised by X-irradiation at low temperature without leaving their substitutional sites and interstitial H^- ions are not formed. The rate of formation of hydrogen atoms in otherwise pure alkaline earth fluorides appears to be limited by the ability of the host lattice to trap the liberated electrons. This was tested by X-irradiating at $77^{\circ}K$ a hydrogenated crystal of CaF_2 containing 0.1% Er^{3+} ions, which are good electron traps. The rate of formation of substitutional hydrogen atoms increased by at least an order of magnitude.

Ure (1957) has shown that the predominant defect in CaF_2 above $600^{\circ}C$ is of the anti-Frenkel type (equal concentrations of negative ion vacancies and interstitials). However, his measurements for the energy of formation and mobilities of interstitials and vacancies show that at $77^{\circ}K$ the number of vacancies would be orders of magnitude less than the number of hydrogen atoms formed. Thus simple explanation of the approximately 1:1 formation of H atoms and F centres at low temperature by trapping of electrons at intrinsic fluorine vacancies is unlikely to be correct. We suggest instead that fluorine vacancies are created by an inefficient process and trap electrons during the X-irradiation at low temperature. This accounts for the continuous slow growth of the substitutional hydrogen atom concentration

until virtually all the H^- ions have been converted.

Franklin (1964) has calculated the energy of formation of an interstitial-vacancy pair in CaF_2 as 2.8 eV and this is confirmed by Ure's results. The fast initial rate of growth is accounted for by there being a limited number of electron trapping sites already in the crystal, probably associated with impurities. The creation of a weak concentration of trapped hole centres by X-irradiation of nominally pure CaF_2 at 77°K (Twidell (1963)) supports this.

The initial increase in rate of formation of substitutional hydrogen after warming above the transition temperature and cooling to 77°K is consistent with the suggested mechanism. On warming, the hydrogen atoms already formed leave an equal number of vacancies as they move to interstitial sites. Some of these can act as electron traps for the initial rapid formation of more substitutional hydrogen atoms. With room temperature irradiation a constant high rate of formation would be expected since each atom, ending in an interstitial site, leaves behind one fluorine vacancy. No subsidiary mechanism is required to maintain the supply of electron traps. The low ratio of F centres to interstitial hydrogen atoms observed for room temperature irradiation may well be due to aggregation of the F centres. Hodby did in fact observe other e.p.r. spectra near $g = 2$ which were not due to the simple F centre. The most likely, M-type,

aggregate centre is not paramagnetic.

On the basis of his e.p.r. results only, Hodby has proposed mechanisms for the low temperature formation of substitutional hydrogen atoms and their transition at 140°K to perfect interstitial sites: the X-irradiation excites one electron of the hydrogen ion into a state extending over a number of lattice spacings. Meanwhile a fluorine interstitial-vacancy pair is created nearby with the components a number of lattice spacings apart. If the vacancy is sufficiently near the hydrogen there is a chance that the excited electron will be trapped to form an F centre, leaving a substitutional H atom and an interstitial fluorine ion. In support of this mechanism an accompanying optical band at $3910\text{\AA}$ is proposed as being due to an F centre-perturbed by a nearby F^- interstitial. The motion of interstitial H atoms in SrF_2 to substitutional sites under further X-irradiation at 20°K is explained by the ejection of a nearest fluorine ion into a site some lattice spacings away. Because of its small mass the hydrogen atom immediately occupies the vacancy leaving the interstitial F^- ion. It was not clear why this should not apply to CaF_2 as well.

For the transition from substitutional to interstitial site at 140°K a mechanism is required which will transfer 100% of the hydrogen atoms to perfect sites. It is unlikely to be correct to suggest that the atoms become mobile at 140°K .

since the annealing of the interstitial spectrum at 150°C indicates that they would then form H_2 molecules which are stable up to 200°C . Furthermore, although the H atom can readily move to the nearest interstitial site, further motion would be seriously hindered by the repulsive potential of the Ca ions immediately beyond the centre of each face of the fluorine cube.

The Hobbby's mechanism uses the interstitial fluorine ion produced during formation of the H atom. The hydrogen moves under thermal excitation into one of the nearest interstitial sites (a distance $\frac{\sqrt{3}a}{4}$ along 4 of the 8 $[111]$ type directions). The combined effect of bonding with the hydrogen and the lattice distortion produced by the interstitial fluorine causes one of the nearest fluorines to occupy the vacancy, completing the cube round the hydrogen. The new vacancy is then occupied by the interstitial which is required to be immediately adjacent, i.e. in a second nearest interstitial site relative to the original position of the substitutional H atom.

These proposed mechanisms are not entirely in accord with the ENDOR results now available and reported in the next chapter. The relevant points are:

- (1) Any interstitial fluorines were at least as far from the substitutional H atom as the third nearest site.
- (2) There was no non-spherical distortion of the hydrogen

environment on either site within a distance of at least two F-F spacings.

(3) No F centres were nearer than about 7 F-F spacings to either substitutional or interstitial hydrogen atom, whether the latter was produced by room temperature irradiation or by low temperature irradiation and warming.

The distance of the F centre is the main difficulty for the mechanisms proposed. If the interstitial fluorine is closely associated then it is too far away to assist in the transition of the H atom to a perfect interstitial site. If the fluorine is not closely associated with the F centre why should it be near a substitutional H atom as would be required for the transition of all the H atoms to perfect interstitial sites?

Hodby's mechanism would seem to be too localised so we suggest the following modifications as possibilities.

Electrons from the hydride ions are excited into the conduction band and travel through the crystal until they meet hydrogen atoms, other impurity electron traps or anion vacancies formed by the irradiation and not too close to their complementary interstitials. If an F centre is formed too near a hydrogen atom then, following the mechanism of Delbecq and Yuster the electron tunnels back to reform a hydride ion. Thus stable substitutional H atoms are observed not closer than a certain distance to F centres and not intimately

associated with fluorine interstitials.

The transition to the interstitial site is a property of the host lattice rather than the hydrogen atom. Fluorine vacancies and interstitials are not mobile (Ure) but a [100] collision sequence may be a method of removing the vacancy from the neighbourhood of the H atom. Such a collision sequence in a perfect lattice, giving rise to a separated interstitial and vacancy, would require several eV of energy for its initiation. However, since the H atom is very light relative to the fluorine ions and uncharged it would require very little energy for a fluorine ion to knock it into the nearest interstitial site along a [111] direction. The fluorine ion would occupy the vacated hydrogen site and the collision sequence would remove the vacancy several lattice spacings away.

6.13 The E.P.R. Parameters

The e.p.r. spectrum of atomic hydrogen has been observed in a variety of inorganic crystals. The results together with those of the present work are collected in Table 6.5. In addition measurements have been reported for a wide range of phosphate host lattices (Atkins, et. al. (1963)) and for inert gas matrices (Foner, et. al. (1960)). The proton hyperfine parameters vary over a wide range, being greater than that of free hydrogen (1420.4 Mc/s; Anderson, Pipkin and

Table 6.5. EPR Parameters of Atomic Hydrogen in Various Host Lattices.

Lattice	Temp. °K	Site	Nearest Halide Å	g	A _{proton} Mc/s	A _{//} Mc/s	A _⊥ Mc/s
^a CaF ₂	300 ^e	Inter	2.360	2.002468 ±0.00002	1460.26 ±0.10	173.826 ±0.300	69.025 ±0.300
^b CaF ₂	300	Inter	2.360	2.00302 ±0.00006	1460.3 ±0.10		
^b SrF ₂	300	Inter	2.54	2.00248 ±0.00006	1443.6	133.0 ±0.3	46.0 ±0.3
BaF ₂	300	Inter	2.677	2.00232 ^b ±0.00006	1424.5 ^b ±0.10	83.445 ^c	20.347 ^c
CaF ₂	77	Subst	2.725	2.00235 ±0.00006	1439.44 ±0.3	168.11 ±0.5	52.76 ±0.3
SrF ₂	77	Subst	2.93	2.0029 ±0.0001	1437.883 ±0.5	100.959 ^c	23.486 ^c
^d NaCl	20	Inter	2.436	2.0025 ±0.0015	1362.2 ±1.5	A _S = 44.6 ± 1.0	
^e KCl	20	Inter	2.72	2.0033 ±0.0001	1378.4 ±0.2	37.16	17.03
^d KBr	20	Inter	2.898	2.0080 ±0.0020	1347.4 ±3.0	A _S = 133.5 ±1.5	A _D = 44.5 ±7
^f CaSO ₄				2.0048 ±0.0001	1391.4 ±0.3		

a Hall and Schumacher (1962).

b Welber (1964).

c Hodby (1965).

d Kerkhoff, Martienssen and Sander (1963).

e Spaeth (1965).

f Kon (1964).

Other entries are from the present work.

Baird (1960)) for the fluoride crystals and smaller for the other halides. In the inert gas matrices both increases and decreases occur. However, for all the ionic lattices the g shift relative to the free hydrogen atom is positive. In the inert gas matrices it is without exception negative.

The e.p.r. results indicate that a good starting point for describing any of the trapped hydrogen systems is the free hydrogen $1s$ function. However, in accordance with the Pauli exclusion principle this must be orthogonalised to the occupied ligand orbitals of like spin. The hydrogen electron is then described by

$$\psi = \left[1 - \sum_i |\langle 1s | \phi_i \rangle|^2 \right]^{-\frac{1}{2}} \left[|1s\rangle - \sum_i \langle 1s | \phi_i \rangle |\phi_i\rangle \right] \quad (23)$$

where the ϕ_i are ligand orbitals. Where the ligands are halide ions the outer electrons are in a p shell. The p_π orbitals are orthogonal to the hydrogen $1s$ function so the ϕ_i include only the p_σ and s orbitals.

An immediate effect of orthogonalisation is to change the proton hyperfine interaction which is proportional to $|\psi(0)|^2$. The normalisation constant introduced into (23) is always greater than one, leading to a proton hyperfine interaction (neglecting the amplitude of the ϕ_i at the proton) (25)

$$A = \left[1 - \sum_i |\langle 1s | \phi_i \rangle|^2 \right]^{-1} A_0 \quad (24)$$

That this does not adequately explain the present results is shown by a calculation for the CaF_2 spectra. We derive the $2s$ and $2p_\sigma$ admixture parameters from the measured nearest neighbour hyperfine parameters. Treating these admixtures as equal to the overlap integrals leads to a calculated increase in proton hyperfine interaction for the interstitial site of 25% and for the substitutional site of 19% (omitting any consideration of overlap with the Ca^{2+} ions. The measured increases are 2.8% and 1.4%. A similar discrepancy was found by Hall and Schumacher who calculated the overlap integrals for the interstitial site using the free ion wave functions. Their calculated increase was 17%.

These results and the positive g shifts suggest that there is appreciable admixture of the configuration in which an electron of opposite spin is transferred from the ligand to the hydrogen. This increases the ligand hyperfine interaction and reduces that of the proton. We replace the overlap integrals $\langle 1s | \phi_i \rangle$ by parameters a_i leading to an impurity wavefunction

$$\psi = \left[1 - 2 \sum_i a_i \langle 1s | \phi_i \rangle + \sum_i a_i^2 \right]^{-\frac{1}{2}} \times \left[|1s\rangle - \sum_i a_i |\phi_i\rangle \right] \quad (25)$$

where $a_i \sim \langle 1s | \phi_i \rangle + \tau_i$ and τ_i represents the charge transfer

admixture. The ligand hyperfine parameters now give the values of the a_1^2 . Making the simplifying assumption that charge transfer occurs only from the $2p_\sigma$ orbital because the $1s$ and $2s$ orbitals are low lying, and again omitting any consideration of the Ca^{2+} ions, the observed proton hyperfine interaction can be used to solve for the charge transfer parameters and the overlap integrals. The results are given in Table 6.6. For the CaF_2 interstitial site the $2p_\sigma$ overlap of 0.08 so obtained may be compared with Hall and Schumacher's value of 0.135 calculated from the free ion wavefunctions. The above rather crude process undoubtedly overestimates the charge transfer contribution. Marshall and Stuart (1961) have pointed out the likelihood of radial expansion of the central ion wavefunction due to overlap with the ligand charge clouds. This would lead to a reduction of spin density at the proton and hence accounts for some of the reduction in the hyperfine interaction from that predicted by simple orthogonalisation. Secondly crystal field admixture of excited states will also reduce the interaction. Blum (1965) has calculated a reduction from this cause of 6% for the interstitial site in CaF_2 . Reasonable agreement with experiment is then obtained with $\tau_{p\sigma} = 0.03$.

The importance of charge transfer is illustrated by Sammel's (1965) calculation for interstitial hydrogen in alkali halides. He determined the hydrogen crystal field

Table 6.6. First Order Calculated Values of P_σ Overlap Integrals and Charge Transfer Parameters for Hydrogen in Alkaline Earth Fluorides

Site	λ_s^2	$\lambda_{P\sigma}^2$	$\langle 1s P_\sigma \rangle$	Charge Transfer
CaF ₂ Inter	0.0022	0.023	0.08	0.07
SrF ₂ Inter	0.0016	0.019	0.07	0.07
BaF ₂ Inter	0.0008	0.014	0.06	0.06
CaF ₂ Subs	0.0019	0.025	0.08	0.08
SrF ₂ Subs	0.0010	0.017	0.07	0.06

Table 6.7. Calculated and observed values of A_s and the fluorine-fluorine spacing R in undistorted CaF₂, SrF₂ and BaF₂

Hydrogen Site	R Å	A_s calc. Mc/s	A_s obs. Mc/s
CaF ₂ interstitial	2.359	62	104
SrF ₂ "	2.54	31	75
BaF ₂ "	2.678	18.5	41
CaF ₂ substitutional	2.725	15.5	91
SrF ₂ "	2.93	7	49

wavefunction as a linear combination of $1s$, $4f$ and $5g$ functions with adjustable radial parameters, using the point ion lattice variational method. The best value obtainable for the proton hyperfine interaction in NaCl after orthogonalising this function to Hartree-Fock ligand orbitals was 2000 Mc/s as compared with the experimental value of 1362 Mc/s. On the other hand the calculated isotropic interaction with the ligand halide nuclei was in good agreement with experiment. Similar results were obtained for KCl and KBr. Correcting for inadequacies of the point ion model would go some way to reducing the calculated proton interaction but there would still remain a large discrepancy which would be reduced by introducing charge transfer. Maintaining the assumption that this would concern only the P_G orbitals the isotropic ligand interaction should not be greatly altered.

In the inert gas matrices charge transfer effects would be expected to be much reduced because of the very high ionisation energies of 14-20 eV of the inert gas atoms.

Foner, et. al. observed proton interactions within 15 Mc/s of the free hydrogen value. These small changes were satisfactorily explained by Adrian (1960) on the basis of orthogonalisation and van der Waal's interaction alone. The small negative g shifts are also explained on this basis.

Smith has considered in detail the effects of the ligands on the g value of hydrogen trapped in inert gas

matrices (1963; 1964) and on the alkali halide F centre (1965). Essentially, when the hydrogen electron is in the vicinity of a ligand nucleus it experiences a spin-orbit interaction which couples in excited ligand π states. The magnetic field couples these excited states back to the hydrogen $|1s\rangle$ part of the ground state (the ligand part is radially orthogonal) to produce a second order energy shift for $\underline{H}$ perpendicular to the bond axis which is linear in H and S . Although the σ ligand ground state and excited π states individually have quenched orbital momentum their linear combination does not and corresponds to a localised current loop in the part of the impurity wavefunction near the ligand nucleus. The magnetic moment of the induced current opposes the spin magnetic moment. As seen by e.p.r. the crystal therefore appears to contain centres with a g -value reduced from that of the free hydrogen. Adrian gives a rather more convenient approximate expression for the shift in $g_{\underline{1}}$ for each ligand

$$\Delta g_{\underline{1}} = -\frac{4}{3} \frac{a_{p\sigma}^2 \lambda_{p\sigma}}{\overline{\Delta E}} \quad (26)$$

where $\lambda_{p\sigma}$ is the spin-orbit coupling parameter for the p_{σ} orbital and $\overline{\Delta E}$ is an average excitation energy arising from the second order perturbation calculation. Smith (1964) details the reasons for taking $\overline{\Delta E}$ as somewhere near the

excitation energy of the host crystal. For cubic, octahedral and tetrahedral co-ordination the observed g shifts will be isotropic and equal to $16/3 \Delta g_1$, $4 \Delta g_1$ and $8/3 \Delta g_1$ respectively. For hydrogen in CaF_2 the calculated g shift from this cause is about -0.0001 .

The observed positive g shifts are a consequence of comparison with experiment for other host lattices but it is the charge transfer and the reason for the sign being opposite to that arising from single orthogonalisation may be indicated as follows. The wave function of the hydrogen atom in the crystal may be written as a linear combination of eigenstates of the halide ion since they form a complete set. For an orthogonalised hydrogen function such an expansion will not contain any of the occupied states of the halide. The g shift would be given by second order spin-orbit-magnetic field coupling with the excited states. When charge transfer is included the expansion of the impurity wave function will contain an additional term, $-\tau_{2p\sigma}|2p_{\sigma}\rangle$, which will contribute to the g shift through coupling to the $2p_{\pi}$ levels. Since these are closer in energy to the hydrogen ground state than the excited halide states the new contribution will be large. Furthermore the $2p_{\pi}$ levels have lower energy than the hydrogen ground state so the g shift will have the opposite sign to that produced by the excited states. Blum has considered this effect and states the perpendicular g shift per ligand arising from charge transfer

$$\Delta g_{\perp} = \frac{4}{3} \frac{\lambda_{p\sigma} \tau_{p\sigma}}{E - E_{\pi}} \quad (27)$$

For $\tau_{p\sigma} = 0.03$, $E - E_{\pi}$ equal to 1.28 eV gives the measured positive g shift for interstitial hydrogen in CaF_2 .

There are too many uncertainties to permit accurate comparison with experiment for other host lattices but it is significant that the largest positive g shift occurs in KBr where the halide has the largest spin-orbit parameter. In this host also the proton hyperfine interaction has its largest reduction from that of free hydrogen. Allowing for there being only four halide ligands the g shifts are large in KCl and NaCl where again the proton hyperfine interactions are smaller than for free hydrogen.

A point of comparison may be made between the hydrogen e.p.r. spectra and those of the F centre. Formally the two systems are similar if the envelope function picture (Gourary and Adrian (1960)) is used for the F centre rather than the LCAO picture. However, the F centres in alkali halides and CaF_2 and BaF_2 (Arends) have negative g shifts as predicted by the usual theory. If our explanation of the positive hydrogen g shifts is correct this indicates that charge transfer is not predominant for the F centre. This is as expected since the F centre electron neutralises the negative ion vacancy while a hydrogen atom does not. In

support the F' centre is unstable at room temperature in many crystals whereas the H^- ion is the normal valence state on an anion site in a crystal.

On the other hand many F centres in divalent ionic crystals have positive g shifts (Wertz, et. al. (1961)). Charge transfer would be expected for such centres since the vacancy, having trapped one electron, remains positively charged. Recently Bartram and Swenberg (1966) have calculated the g shift produced by admixture of the charge transfer configuration and find this can account for the experimental results.

Gourary and Adrian have given an approximate method of calculating the isotropic hyperfine interaction with ligand nuclei due solely to overlap. They find

$$A_{s\alpha} = \frac{16\pi g_e g_n \mu_B \mu_N}{3 \cdot 10^6 h} A_\alpha |\psi(\alpha)|^2 \quad (28)$$

where $A_{s\alpha}$ is in Mc/s, $\psi(\alpha)$ is the amplitude of the unperturbed central ion wavefunction at nucleus α and A_α is the "amplification factor". A_α is a dimensionless quantity which depends only on the electronic structure of the ion α . For F^- Gourary and Adrian estimate A_{F^-} to be 350. For the method to be valid the central ion wavefunction must change slowly over the region of the ligand wavefunction. This should be satisfied for hydrogen in the ionic crystals since

the Bohr radius is only $0.53\text{\AA}$. Table 6.7 compares the A_s calculated by this method for the alkaline earth fluorides with the observed values, taking the hydrogen $1s$ function as

$$|1s\rangle = (\pi a_0^3)^{-1/2} e^{-r/a_0} \quad (29)$$

and assuming undistorted lattices. The agreement for the interstitial sites is quite good, all calculated values being close to half the measured values. However, the calculated values for substitutional sites are only about $\frac{1}{6}$ of those observed. If the hydrogen wavefunction is not very different for the two sites then $\text{CaF}_2\text{:H}$ substitutional should have much the same interaction as $\text{BaF}_2\text{:H}$ interstitial. We have suggested earlier that charge transfer from the s orbitals is not important. Incorrectness of this assumption for the substitutional site may be one reason for the large experimental values. An alternative is to allow the relaxation of the six fluorine ligands towards the hydrogen. The hydrogen radius is only about $1\text{\AA}$ as compared with the $1.3\text{\AA}$ of the F^- ion it replaces so repulsive interaction has been lost. Also the hydrogen atom is uncharged so electrostatic repulsion is lost. In the interstitial sites the hydrogen would only distort the lattice if it were too big. In fact it fits very well into the smallest lattice, CaF_2 . In view of the interstitial results we use the Gourary and Adrian method to

calculate the positions of the ligands for the substitutional sites which will give half the observed A_g values. For CaF_2 a relaxation towards the hydrogen is required of $0.29\text{\AA}$ and for SrF_2 $0.33\text{\AA}$. Franklin has calculated the relaxation of the six nearest fluoride ions surrounding an anion vacancy in CaF_2 and finds it to be $0.06\text{\AA}$ inwards. Bonding with the hydrogen would probably increase the relaxation in the present case. Although our simple estimate is probably too large there is evidence for some relaxation of the ligands towards the substitutional hydrogen atom.

- Belikov, G.A. and Yakovlev, I.P., 1962. *Phys. Rev.*, **125**, 109.
- Evans, R.J., Gaskell, J.H., Rogers, J.J. and Lee, C.L., 1960. *J. Chem. Phys.*, **32**, 963.
- Franklin, R.D., 1964. *J. Phys. Chem. Solids*, **25**, 933.
- Fritz, 1962. *J. Phys. Chem. Solids*, **23**, 375.
- Seurey, B.S. and Adrian, P.J., 1960. *Solid State Physics*, **10**, 127. Academic Press. Ed. Seitz and Turnbull.
- Hall, J.L. and Schumacher, R.T., 1962. *Phys. Rev.*, **127**, 1892.
- Hayes, W. and Twidell, J.W., 1962. *Proc. Phys. Soc.*, **120**, 1295.
- Hayes, W., Jones, G.D., MacDonald, R.T., Bennett, G., and Elliott, E.J., 1965. *Proc. Roy. Soc.* To be published.
- Hilsch, R. and Pohl, R.W., 1938. *Trans. Faraday Soc.*, **34**, 683.
- Hoddy, J.S., 1963. Thesis, Oxford.
- Jones, G.D., 1964. Thesis, Oxford.

Kerkhoff, F., References to Chapter 6

- Adrian, F.J., 1960. J. Chem. Phys., 32, 972.
- Anderson, L.W., Pipkin, F.M. and Baird, J.C., 1960. Phys. Rev., 120, 1279.
- Arends, J., 1964. Phys. stat. sol., 7, 805.
- Atkins, P.W., Keen, N., Symons, M.C.R. and Wardale, H.W., 1963. J. Chem. Soc., 1963, 5594.
- Bartram, R.H. and Swenberg, C.E., 1966. Bull. Am. Phys. Soc., 12, 203.
- Blum, H., 1965. U.S.A.E.C. Report BNL 9111.
- Delbecq, C.J., Smaller, B. and Yuster, P.H., 1956. Phys. Rev., 104, 599.
- Delbecq, C.J. and Yuster, P.H., 1956. Phys. Rev., 104, 605.
- Foner, S.N., Cochran, E.L., Bowers, V.A. and Jen, C.K., 1960. J. Chem. Phys., 32, 963.
- Franklin, A.D., 1964. J. Phys. Chem. Solids, 26, 933.
- Fritz, 1962. J. Phys. Chem. Solids, 23, 375.
- Gourany, B.S. and Adrian, F.J., 1960. Solid State Physics, 10, 127. Academic Press. Ed. Seitz and Turnbull.
- Hall, J.L. and Schumacher, R.T., 1962. Phys. Rev., 127, 1892.
- Hayes, W. and Twidell, J.W., 1962. Proc. Phys. Soc., 79, 1295.
- Hayes, W., Jones, G.D., Macdonald, H.F., Sennett, C.T. and Elliott, R.J., 1965. Proc. Roy. Soc. To be published.
- Hilsch, R. and Pohl, R.W., 1938. Trans. Faraday Soc. 34, 883.
- Hodby, J.W., 1965. Thesis, Oxford.
- Jones, G.D., 1964. Thesis, Oxford.

Kerkhoff, F., Martienssen, W. and Sander, W., 1963.
Z.f. Phys., 173, 184.

Kon, H., J. Chem. Phys., 41, 573.

Marshall, W. and Stuart, R., 1961. Phys. Rev., 123, 2048.

Sammel, B., 1965. Phys. stat. sol., 12, K11.

Seitz, F., 1954. Revs. Mod. Phys., 26, 7.

Sierro, J., 1965. Phys. Rev., 138, A648.

Smith, D.Y., 1963. Phys. Rev., 131, 2056.

Smith, D.Y., 1964. Phys. Rev., 133, A1087.

Smith, D.Y., 1965. Phys. Rev., 137, A574.

Spaeth, J.M., 1965. Thesis, Stuttgart.

Twidell, J.W., 1963. Thesis, Oxford.

Ure, P.W., 1957. J. Chem. Phys., 26, 1363.

Welber, B., 1964. Phys. Rev., 136, A1408.

Wertz, J.E., Orton, J.W. and Auzins, P., 1961. Disc.
Faraday Soc., 31, 140.

negatively charged F⁻ ion by the positive charges of the

hydrogen atom.

2) The pseudo dipole-dipole interaction between the

nearest fluorine nuclei should give excellent agreement of

the corresponding NMR lines. The expected splitting can

be calculated from the hyperfine constants derived from the

s.p.v. measurements.

3) The relationship of any intermolecular interaction to the

substitutional hydrogen atom. These are used to explain

for explaining the fact that the splitting of the

splitting of the splitting of the splitting of the

Chapter 7

FLUORINE ENDOR OF SUBSTITUTIONAL HYDROGEN
ATOMS IN CALCIUM FLUORIDE

7.1 Introduction

4) The e.p.r. measurements of substitutional hydrogen atoms in CaF_2 show that the six nearest fluorine ions surround the hydrogen in a regular octahedron. The Ca^{2+} ions have no nuclear moment so the e.p.r. linewidth of 3.2 G between points of maximum slope must be due to interaction with more distant fluorines. Fluorine ENDOR measurements of these unresolved interactions are of interest and serve to confirm the substitutional site assigned to the hydrogen atom.

Information on the following points would also be expected:-

- 1) Any distortion of the lattice caused by replacing a negatively charged F^- ion by the rather smaller neutral hydrogen atom.
- 2) The pseudo dipole-dipole interaction between the nearest fluorine nuclei should give resolved splittings of the corresponding ENDOR lines. The expected splittings can be calculated from the hyperfine parameters derived from the e.p.r. measurements.
- 3) The relationship of any interstitial fluorines to the substitutional hydrogen atoms. These are basic to one model for explaining the fact that on moving from substitutional

sites the hydrogen atoms are observed by e.p.r. only in perfect interstitial sites. An interstitial fluorine in the nearest site would give a large splitting of the e.p.r. lines, which was not observed. ENDOR is needed to detect more distant interstitials.

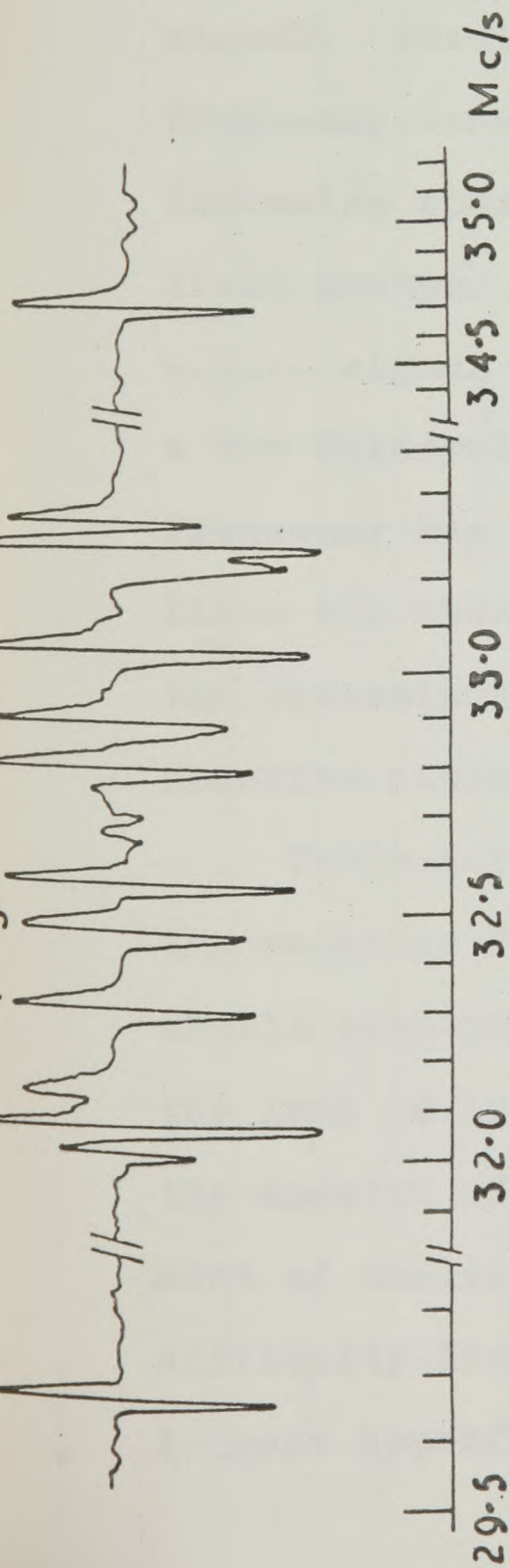
4) Hall and Schumacker (1962) have measured the interaction of the interstitial hydrogen with its second and third fluorine shells. The substitutional site allows the measurement of the interactions with fluorine nuclei rather nearer the hydrogen atom. Up to and including the sixth, the n^{th} fluorine shell is $\sqrt{n}$ from the hydrogen in units of the $[100]$ $F^- - F^-$ spacing. This function increases rather more slowly than that for the interstitial site, allowing closer investigation of the falling off of bonding to the fluorines

7.2 ENDOR of Distant Fluorine Shells

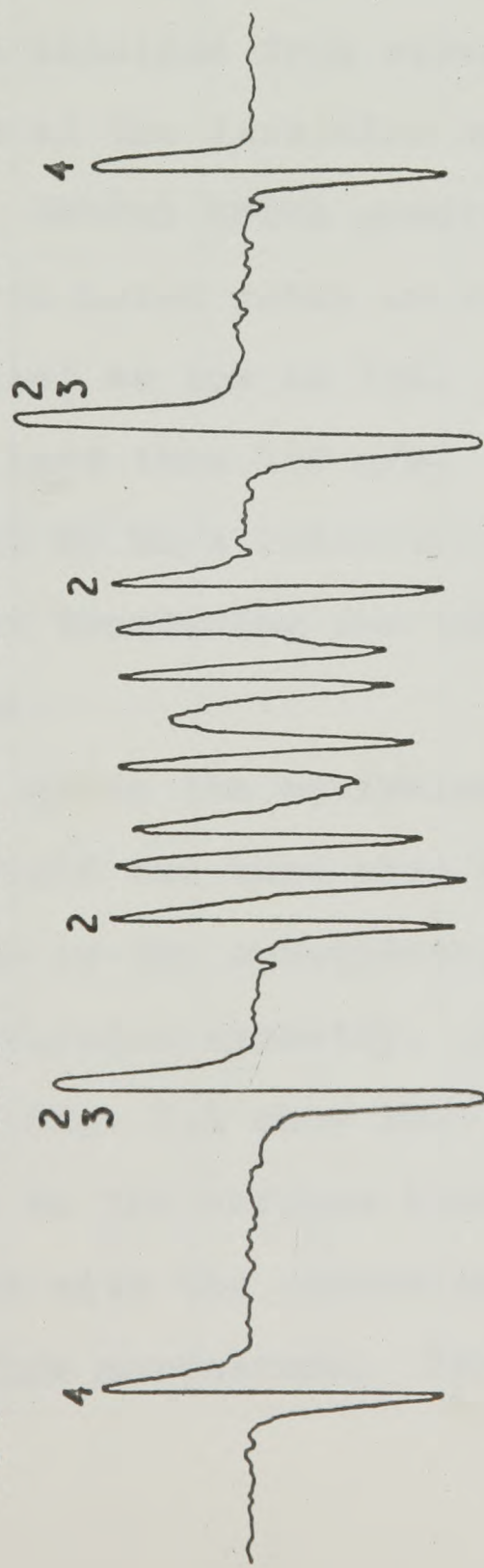
Since the interaction with nearest fluorine nuclei is of the order of 100 Mc/s the ENDOR spectrum centred around the free fluorine n.m.r. frequency will be due to second and more distant shells. This spectrum was obtained at K band using the X-irradiation crystal and its appearance for $H \parallel [001]$, $[110]$ and $[111]$ is shown in Fig. 7.1. Using the I.F.I. and E.M.I. distributed amplifiers driven by the G.R. Bridge Oscillator a good signal to noise ratio was obtained at 77°K using a 10 second time constant. The signal to noise ratio could be improved by a factor of two or three by

(a) [111]

ENDOR Spectra of
Distant Fluorine
Shells



(b) [100]



(c) [110]

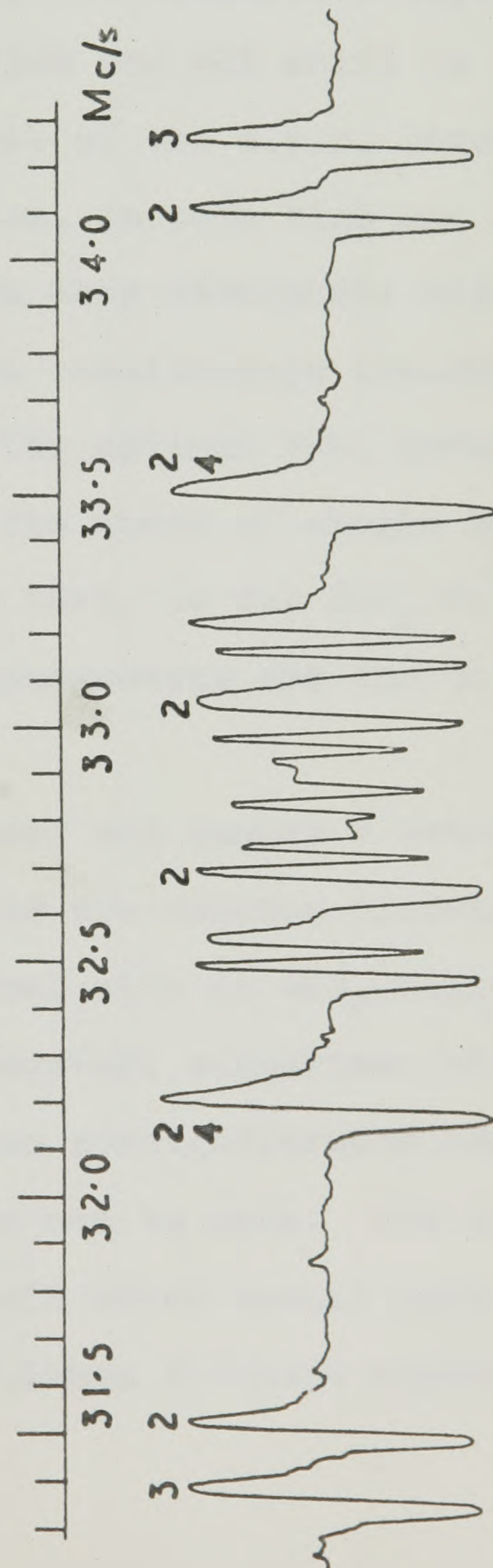
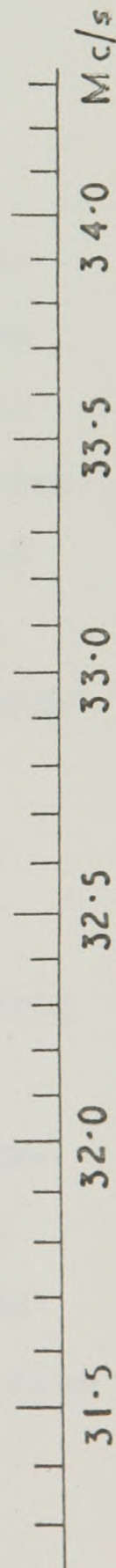


Fig 7.1.



pumping the liquid nitrogen via a manostat to a pressure of 4-6 cms, corresponding to a temperature of 70°K . For most of the measurements this was unnecessary.

The e.p.r. absorption spectrum saturated readily at 77°K at less than 100 μW microwave power with a cavity Q of 5000. Best ENDOR signals were obtained with microwave power just sufficient to begin saturating the dispersive e.p.r. signal. Identical spectra apart from overall shift in frequency were obtained from several of the e.p.r. lines, including some of the forbidden ones, in both high and low field groups. Useful ENDOR spectra were obtainable with an e.p.r. signal to noise ratio on the oscilloscope (bandwidth a few kilocycles) as low as 3:1. The optimum F.M. modulation frequency was less than 100 c/s. The width of single ENDOR lines was about 20 kc/s indicating that, as for $\text{CaF}_2:\text{Tm}^{2+}$, the predominant broadening was inhomogeneous and due to other fluorine nuclei.

Table 7.1 gives the equivalences and angles θ between the magnetic field and bond axes for the various fluorine shells relative to the substitutional site in CaF_2 neglecting the lack of inversion symmetry. However, comparison with the spectra of Fig. 7.1 show that no straightforward assignment of nuclei to the various lines can be made. The main difficulty lies with the second shell which should have the largest hyperfine parameters. The lines furthest removed from

Table 7.1. Fluorine equivalencies for the anion site in Calcium Fluoride

	1st Shell		2nd Shell		3rd Shell		4th Shell	
	$\cos^2\theta$	No. of fluorines	$\cos^2\theta$	No. of fluorines	$\cos^2\theta$	No. of fluorines	$\cos^2\theta$	No. of fluorines
H// [100]	1	2	$\frac{1}{2}$	8	$\frac{1}{3}$	8	1	2
	0	4	0	4			0	4
H// [110]	$\frac{1}{2}$	4	1	2	$\frac{2}{3}$	4	$\frac{1}{2}$	4
	0	2	0	2	0	4	0	2
H// [111]	$\frac{1}{3}$	8	$\frac{2}{3}$	6	1	2	$\frac{1}{3}$	6
			0	6	$\frac{1}{9}$	6		

the free fluorine resonance would then occur for $H \parallel [110]$ when the bond axes of two second shell fluorines are parallel to the magnetic field; in fact the largest splitting occurs for $H \parallel [111]$. This was checked very carefully with the spectrometer parameters adjusted for best signal-to-noise ratio on the observed spectrum. Different samples and temperatures were used and the N.M.R. waveform in the cavity was checked with a high frequency oscilloscope. Under no conditions was any ENDOR line observed at a frequency higher than that of the extreme line in Fig. 7.1(c). On the other hand the extreme lines of the $[111]$ spectrum always bore a constant relationship to the central part of the spectrum whichever hydrogen e.p.r. line was saturated and in all samples, showing that they were not lines associated with some other centre.

Some ENDOR lines were indeed observed below the lowest frequency $[110]$ line shown in Fig. 7.1(c). However, they were not matched by corresponding lines above the free fluorine resonance frequency, they had opposite phase and different temperature dependence from the central spectrum and their field dependence was too small. They are assigned to nearest neighbour transitions and discussed in Section 7.12.

Simple consideration of the e.p.r. linewidth indicates that the second neighbour lines must be contained in the

spectra of Fig. 7.1. Since these spectra, in principal directions only, contain insufficient information for an assignment of the various lines it is necessary to make continuous angular plots of the spectrum.

7.3 Angular Characteristics of ENDOR Spectra

We assume that the hyperfine interaction with second and more distant fluorine shells has an isotropic part, A_s , and a dipolar part, A_p . Following the discussion of section 4.1 each nucleus then gives rise to a pair of lines very nearly symmetrically placed about the free fluorine resonance frequency and separated by $A_s + A_p (3 \cos^2 \theta - 1)$ Mc/s. Departures from true axial symmetry are ignored in the following.

As the magnetic field is rotated in the horizontal plane a given pair of lines will reach a maximum separation when the bond axis is in the same vertical plane as the field. The bond axis is not necessarily then parallel to the magnetic field, but at 90° from this field orientation θ for that particular nucleus must be 90° .

If the bond axis makes an angle α with the horizontal the angular variation of the pair separation is given by

$$\Delta V(\phi) = A_s + A_p (3 \cos^2 \phi \cos^2 \alpha - 1) \quad (1)$$

where ϕ is the angle of rotation of the magnetic field from

the maximum separation position. It should be noted that if α is incorrectly assumed to be zero (i.e. ϕ put equal to θ) the angular variation of the pair separation can be fitted by using incorrect values A_s' and A_p' where

$$\begin{aligned} A_s' &= A_s + A_p (\cos^2 \alpha - 1) \\ A_p' &= A_p \cos^2 \alpha \end{aligned} \quad (2)$$

The form of the angular variation (1) shows that the separation of a complementary pair of lines executes one complete sinusoidal cycle as the magnetic field is rotated through 180° . From the symmetry properties of a sine curve the complete cycle can be constructed from measurements over only part of it. This is very useful when a line gets lost in the central, poorly resolved part of the spectrum. Lines which do not vary in frequency over the whole rotation of the magnetic field are due to nuclei on the axis of rotation for which θ is always 90° .

For the size of hyperfine interaction being considered the spectrum is very closely symmetrical about the free fluorine frequency so the angular variation of only half of it need be measured. The plots of lines which disappear through the free fluorine frequency may be completed by reflecting those of their partners in the measured half of the spectrum.

The actual direction of any hyperfine tensor principal

axis may be found by carrying out angular plot in some second plane and finding the new direction of maximum separation. However, in certain cases the symmetry properties

7.4 (110) Plane Angular Plot
of the crystal may be used to obtain this information from a

The sample was ground as accurately as possible to have a single angular plot. Consider a line which reaches a maximum separation with the magnetic field along an n -fold symmetry axis. If the tensor axis is not actually along this direction then the line is due to n equivalent off-axis two of $[111]$ type. The angles at which the substitutional nuclei (or n equivalent pairs of nuclei if the impurity site has inversion symmetry). If n is greater than 2 these nuclei cannot have the same angular variation as the field is moved off the n -fold axis. Thus, if the line does not split off-axis its tensor axis must be along the symmetry axis.

The argument may be put differently: having brought a line to maximum separation with H along an n -fold axis rotate the crystal about the magnetic field by $360/n$ degrees. θ is unchanged by this so the line is in the same position. (see Fig. 7.2). There are no equivalent directions to allow

Now move the magnetic field off axis in this new plane.

Since this is equivalent to the old plane the angular plot must be identical. Provided it is not crossed by another line as H comes parallel to the n fold axis the original line must trace out the same path as before, i.e. one peaking with H along the axis. Thus angular plots in two different planes give maximum separation for H along the same crystal axis which must, therefore, be the tensor axis. The failure of

the argument if n is only 2 is obvious since then the two equivalent plots are, in fact, in the same plane.

7.4 (110) Plane Angular Plot

The sample was ground as accurately as possible to have a plane perpendicular to the $[110]$ cleavage edge and was mounted on this plane on the bottom of the cavity. The (110) plane contains one axis of each of types $[100]$ and $[110]$ and two of $[111]$ type. The angles at which the substitutional e.p.r. spectra gave best alignment for these four directions were found and the r.m.s. error of ten settings along each was 0.1° . Within these limits the angles between the four directions showed that the crystal was accurately on a (110) plane.

A strong ENDOR spectrum was obtained at 77°K and the magnetic field aligned along the $[110]$ direction to within 0.1° using the splitting of the extreme lines as a monitor (see Fig. 7.2). There are no convenient crossings to allow the same precision of alignment along $[111]$ or $[100]$. (For this reason the accurate e.p.r. measurements were made with $H \parallel [110]$ using the ENDOR spectrum for alignment.) The angular plot was carried out in steps of 2.5° round to the $[110]$ direction using the central e.p.r. line of the low field multiplet. The constancy of the magnetic field throughout was checked by measuring the frequency of the reverse phase free fluorine resonance line at each angle. The central

part of the ENDOR spectrum was measured by sweeping the n.m.r. oscillator slowly with respect to the time constant and line width and noting the frequency as the pen passed through the central zero of each line. The positions of the many poorly resolved lines were estimated by interpolation on the chart. Every definite line was measured but crowding led to loss of some lines especially near [100]. The well separated, extreme lines of the spectrum were measured individually at each angle. Since the angular plots are symmetrical about the [110] direction and [100] direction the complete angular cycle of 180° can be constructed from the measured quadrant. All the points measured or deduced in this way are plotted in Fig. 7.2.

Because, for the substitutional site in CaF_2 the successive fluorine shells become more distant rather slowly many nuclei contribute to the spectrum within 0.6 Mc/s of the free fluorine frequency. As Fig. 7.2 shows, this allows considerable freedom to draw almost any desired curves through the measured points. However, the more important lines stand clear of the central confusion for a large part of the cycle and the symmetry properties of the sinusoidal variation allow their paths to be completed with confidence. These are plotted as continuous lines in Fig. 7.2.

7.5 Discussion of (110) Plane Angular Plot

Fig. 7.3 represents a cubic lattice of fluorines only,

containing a substitutional hydrogen atom, with a (110) plane horizontal. The figures refer to the different fluorine shells and the letters to the sets of nuclei in each shell which remain equivalent for rotation of H in this plane. Fig. 7.2 shows that there are ENDOR lines which reach maximum separation for each of the three principal crystal axes. Since the [111] direction is a threefold axis the argument of section 7.3 indicates a nucleus (or pair of nuclei) with bond axis along [111]. The most likely candidates are from the third fluorine shell, 3a. Further support is provided by their being equivalent for $H \parallel [110]$ and $[100]$ with a set of nuclei following an identical angular variation 70.5° out of phase. These would be nuclei 3b. The remaining third shell nuclei, 3c, should be equivalent to 3a and 3b for $H \parallel [100]$ and then move in to $\theta = 90^\circ$ for $H \parallel [110]$. This trajectory is wholly within the poorly resolved part of the spectrum and its identification is not unequivocal. It is shown dashed in Fig. 7.2, being calculated from the hyperfine parameters which describe curves 3a and 3b.

The [100] direction is a four-fold axis for the pure fluorite lattice but a [100] direction through the substitutional hydrogen is only a two-fold axis since translational symmetry has been lost. The two-fold symmetry arises only from the Ca^{2+} ions and the [100] direction is still a fourfold axis of the fluorine sublattice. If we treat the effect of

the Ca^{2+} ions on the hyperfine tensor as unimportant the symmetry arguments and Fig. 7.2, indicate a fluorine nucleus along a $[100]$ direction from the hydrogen. Apart from nearest neighbours, which are out of the question, the nearest suitable lattice site is the fourth shell, 4a. The other four nuclei of shell 4 are always equivalent and have $\theta = 90^\circ$ for $\text{H} \parallel [100]$. Their maximum value of $(3 \cos^2 \theta - 1)$ in this plane is only $\frac{1}{2}$, for $\text{H} \parallel [110]$, so they never emerge from the poorly resolved part of the spectrum. Their trajectory, 4(b), calculated from the parameters describing curve 4a, is shown dashed in Fig. 7.2.

The line 2a, peaking with $\text{H} \parallel [110]$ cannot definitely be assigned to the missing second neighbours since the $[110]$ direction is only a twofold axis. Also the apparent hyperfine parameters are smaller than for the curves assigned to the third neighbours. However, the curves 2b and 2c, peaking about 35° from $[100]$, are consistent with what fluorine sets 2b and 2c would produce for these values of the parameters, becoming equivalent for $\text{H} \parallel [100]$ or $[110]$. Secondly the invariant line at about 32.1 Mc/s is in the correct position for the two fluorines 2d on the axis of rotation of the magnetic field.

7.6 Angular Plot in the (111) Plane

To confirm the axis of the fluorines producing the $[110]$ peaking lines a second angular plot was made in the convenient

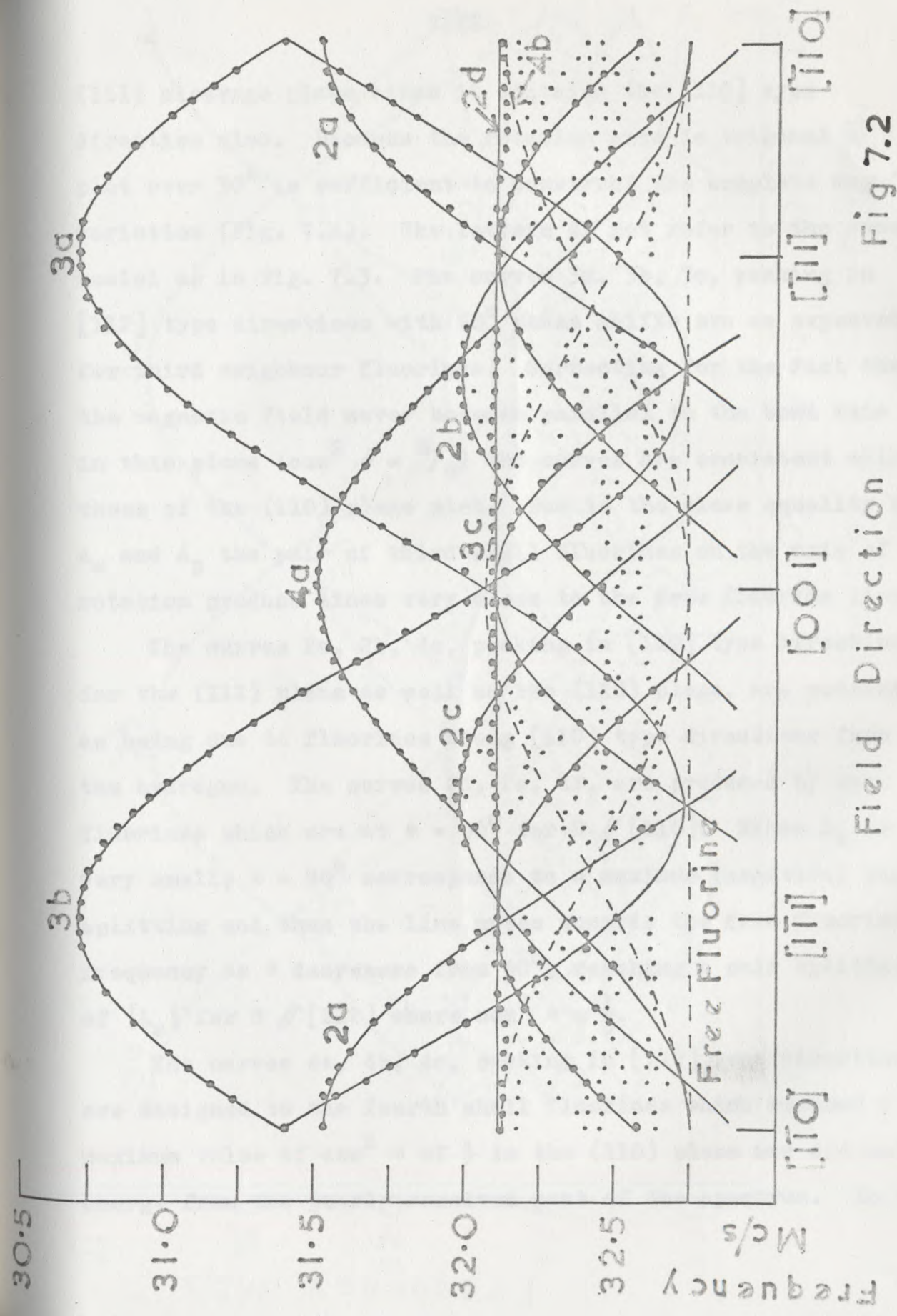
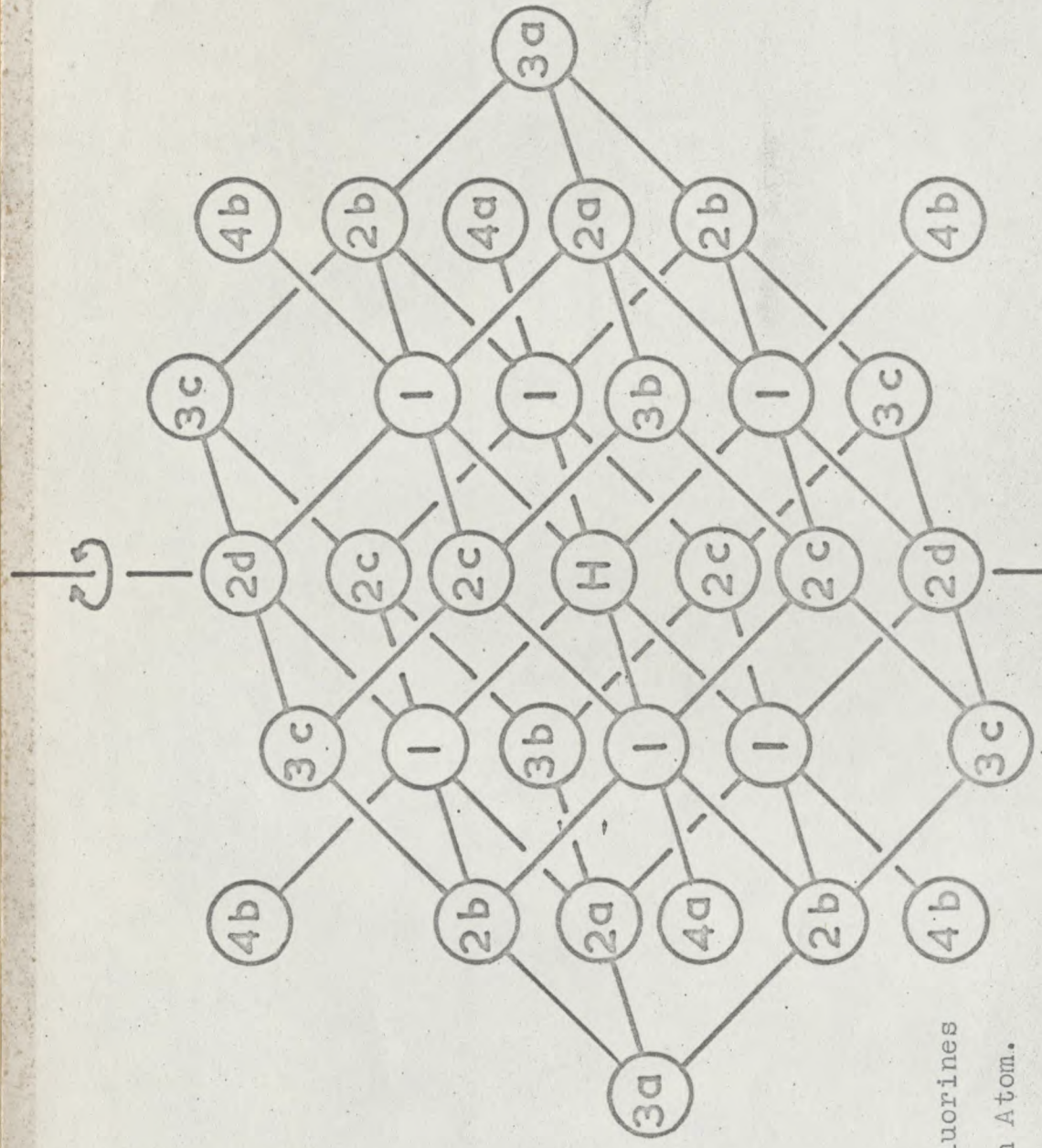


Fig 7.2

(110) Plane Angular Plot



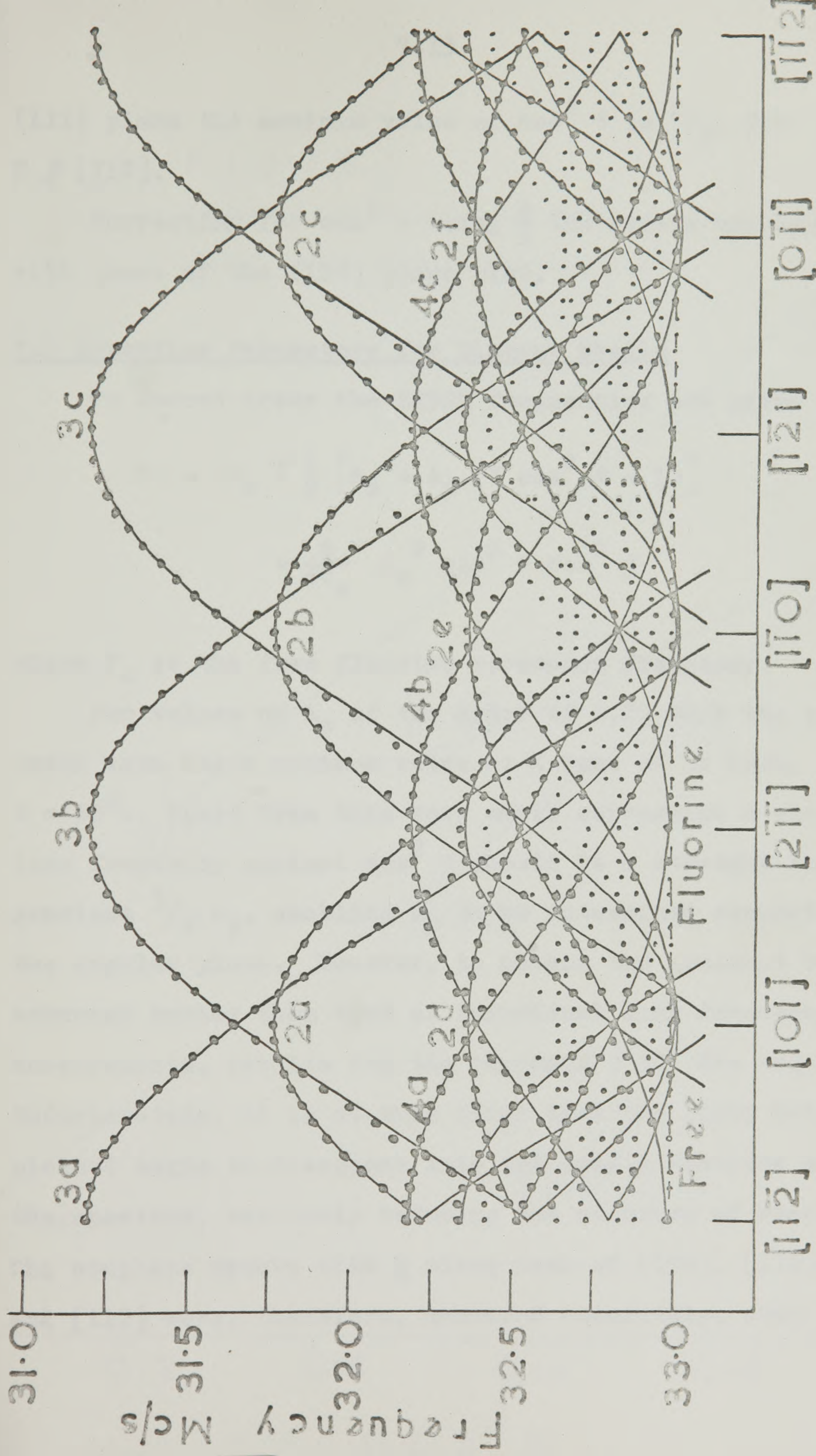
(110) Plane Horizontal

Fig 7.3

(111) cleavage plane since it contains the [110] type direction also. Because the rotation axis is trigonal a plot over 30° is sufficient to construct the complete angular variation (Fig. 7.4). The letters do not refer to the same nuclei as in Fig. 7.3. The curves 3a, 3b, 3c, peaking in [112] type directions with 60° phase shifts are as expected for third neighbour fluorines. Correcting for the fact that the magnetic field never becomes parallel to the bond axis in this plane ($\cos^2 \theta = 8/9$) the curves are consistent with those of the (110) plane plot. Due to the close equality of A_s and A_p the pair of third shell fluorines on the axis of rotation produce lines very close to the free fluorine line.

The curves 2a, 2b, 2c, peaking in [110] type directions for the (111) plane as well as the (110) plane, are confirmed as being due to fluorines along [110] type directions from the hydrogen. The curves 2d, 2e, 2f, are produced by such fluorines which are at $\theta = 90^\circ$ for $H \parallel [110]$. Since A_s is very small, $\theta = 90^\circ$ corresponds to a maximum (negative) pair splitting and thus the line moves towards the free fluorine frequency as θ decreases from 90° , reaching a pair splitting of $|A_s|$ for $H \parallel [112]$ where $\cos^2 \theta = \frac{1}{3}$.

The curves 4a, 4b, 4c, peaking in [112] type directions are assigned to the fourth shell fluorines which reached a maximum value of $\cos^2 \theta$ of $\frac{1}{2}$ in the (110) plane and did not emerge from the poorly resolved part of the spectrum. In the



Field Direction

Fig 7.4.

(111) Plane Angular Plot

(111) plane the maximum value of $\cos^2 \theta$ is $2/3$, for $H \parallel [112]$. Fig 7.5.

Correcting for $\cos^2 \alpha$ being $2/3$ the curves are consistent with those of the (110) plane plot.

7.7 Hyperfine Parameters for Distant Shells

To second order the ENDOR frequencies are given by

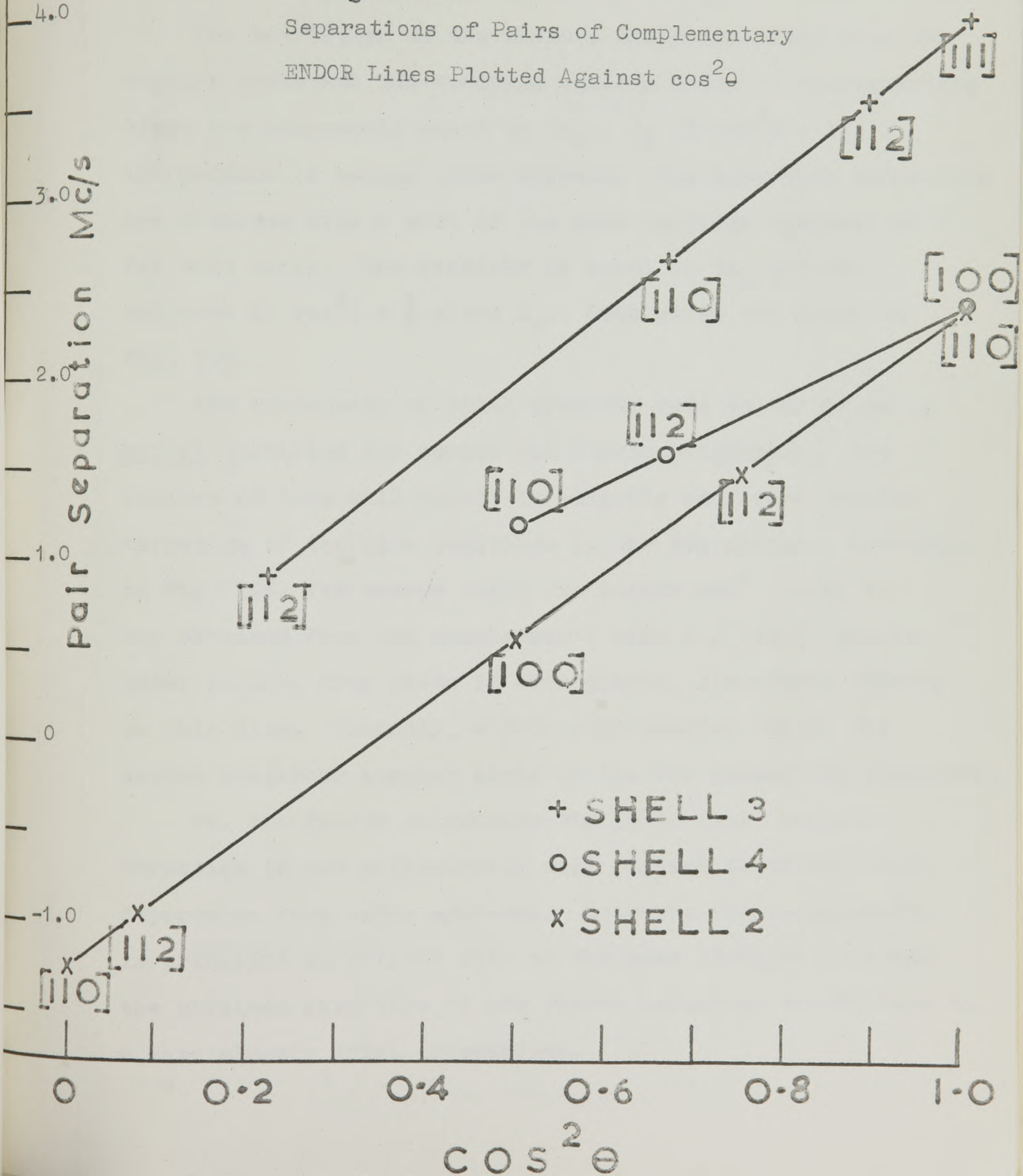
$$\begin{aligned}
 \nu = \nu_0 + \frac{1}{2} [A_s + A_p (3 \cos^2 \theta - 1)] \\
 + \frac{9}{8\nu_0} A_p^2 \sin^2 \theta \cos^2 \theta
 \end{aligned}
 \tag{3}$$

where ν_0 is the free fluorine resonance frequency.

For values of A_p of the order of 1.25 Mc/s the second order term has a maximum value at K band of 14 Kc/s, for $\theta = 45^\circ$. Apart from this very small correction a plot of line frequency against $\cos^2 \theta$ should be a straight line of gradient $3/2 A_p$, enabling A_p to be determined accurately from the angular plots. However, to obtain the gradient to accuracy better than that of individual line frequency measurements, results for the region $\theta > 30^\circ$ are required. Unfortunately, it is at this point that the lines being plotted begin to disappear into the poorly resolved part of the spectrum, seriously reducing the accuracy of measurement. The complete spectra with H along each of [100], [110], [111] and [112] were, therefore, measured accurately, each resolved

Fig 7.5.

Separations of Pairs of Complementary
ENDOR Lines Plotted Against $\cos^2 \theta$



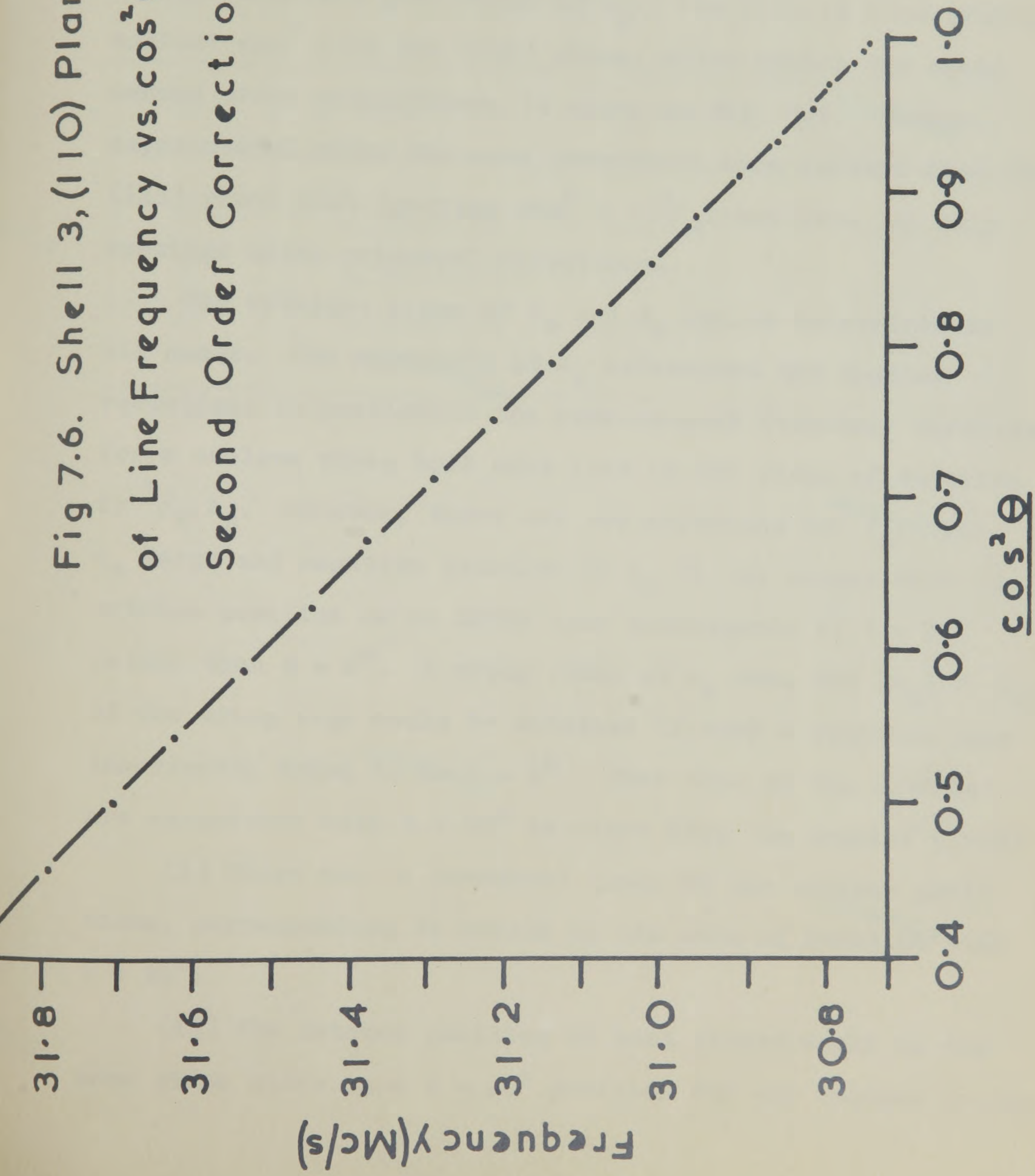
line being measured four times and the frequencies corrected to a common magnetic field as for the $\text{CaF}_2:\text{Tm}^{2+}$ measurements.

The identities of the various lines are known from the angular plots and the spacings between pairs of complementary lines are accurately equal to $\{A_s + A_p (3 \cos^2 \theta - 1)\}$ independent of second order effects. The hyperfine parameters are obtained from a plot of the pair spacings against $\cos^2 \theta$ for each shell. The gradient is equal to $3A_p$ and the ordinate at $\cos^2 \theta = \frac{1}{3}$ gives A_s . Such plots are shown in Fig. 7.5.

The assumption of axial symmetry made so far is not a priori justified for second and fourth neighbours. Any failure of this will result in slightly different angular variation of the line positions in the two planes. However, in Fig. 7.5, for second shell the points $\cos^2 \theta = 0, 1.0$ are obtained from the measurements with $H \parallel [110]$, and the other points, from plots in both planes, lie almost exactly on this line. Secondly, within experimental error, the second neighbour angular plots in the two planes are identical.

For the fourth neighbours the (111) plane angular variation is not sufficiently well defined to detect small departures from axial symmetry. However, the measurements in principal directions fall on the same straight line and the physical situation of the fourth neighbour should lead to a very closely axial interaction.

Fig 7.6. Shell 3,(110) Plane: Plot
of Line Frequency vs. $\cos^2 \theta$ After
Second Order Correction.



The third neighbour hyperfine tensor should be axial since the bond direction is the threefold $[111]$ direction. The angular variation in both planes can be followed far enough to give a good value of A_p . The plot of line position against $\cos^2 \theta$ in the (110) plane, after making the small second order corrections, is shown in Fig. 7.6. Within experimental error the same parameters were derived from the (111) plane plot (putting $\cos^2 \alpha = 8/9$) and from the pair spacings along principal directions.

The relative signs of A_s and A_p can be determined in all cases. The magnitude of A_p determines the angular variation; in particular the peak-to-peak frequency variation for a nucleus whose bond axis lies in the plane of rotation is $3/2 A_p$. However, there are two solutions for A_s . For A_s large and negative relative to A_p it can happen that the extreme position of an ENDOR line corresponds to $\theta = 90^\circ$ rather than $\theta = 0^\circ$. A wrong value of A_s and, for $|A_s| > |A_p|$, of the wrong sign would be obtained if such a position were incorrectly taken to be $\theta = 0^\circ$. That none of the extreme are associated with $\theta = 90^\circ$ is clear from the angular plots:

(i) There are no invariant lines at the extreme positions, corresponding to nuclei on the axis of rotation with $\theta = 90^\circ$.

(ii) The extreme position in both planes would be the same since there is a $\theta = 90^\circ$ position for any nucleus in any

plane of rotation. This is not observed for third or fourth

Table 7.2. Hyperfine parameters for the second, third and fourth fluorine shells for Substitutional Hydrogen in CaF_2

Shell	A_s (Mc/s)	A_p (Mc/s)	$A_{D_{\text{calc.}}}$ (Mc/s)
2	-0.020 ± 0.01	1.223 ± 0.02	1.313
3	1.371 ± 0.01	1.339 ± 0.01	0.713
4	0.806 ± 0.02	0.821 ± 0.02	0.413

the correction is only 0.1% and is neglected here.

7.8 Discussion of Hyperfine Parameters of Distant Shells

The third and fourth shells are remarkable in having anisotropic parameters of about twice the dipolar value and large isotropic parameters. This indicates a significant amount of bonding. On the other hand the second shell has an anisotropic interaction slightly less than the dipolar and the very small isotropic interaction is negative. Both parameters, therefore, contain a net negative contribution from bonding about equivalent, however, to that for the third and fourth shells.

Fig. 7.7(a) shows a (100) plane of CaF_2 containing the hydrogen atom. The nearest neighbor fluorine hyperfine interaction indicates an electron density in the $2p_z$ orbital

plane of rotation. This is not observed for third or fourth neighbours.

The absolute signs of the hyperfine parameters and the relative signs between different shells cannot be determined. A_p has been taken as positive in all cases since it is expected to be due mainly to dipolar interaction. The experimental values of A_s and A_p for shells 2, 3 and 4 are given in Table 7.2 which also includes the calculated point dipole interaction, A_D , assuming an undistorted lattice. The measured parameters should be corrected for interaction of the electron with the proton (see sect. 6.4) but at K band the correction is only 0.1% and is neglected here.

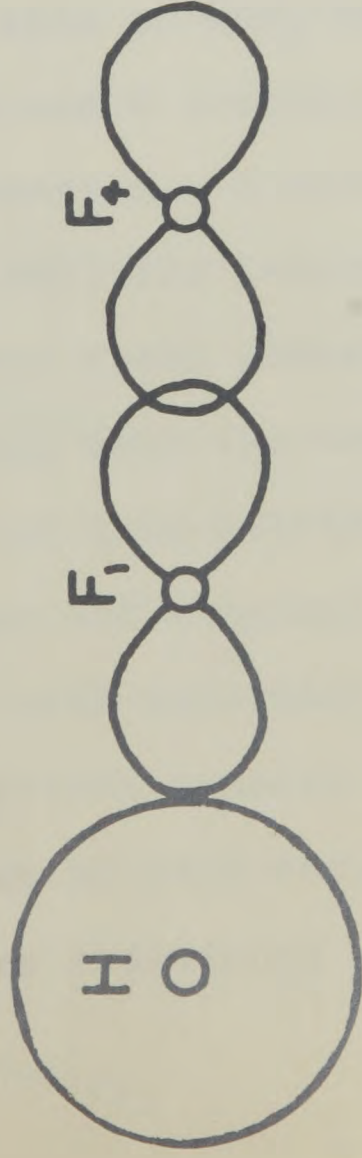
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(100) Plane.

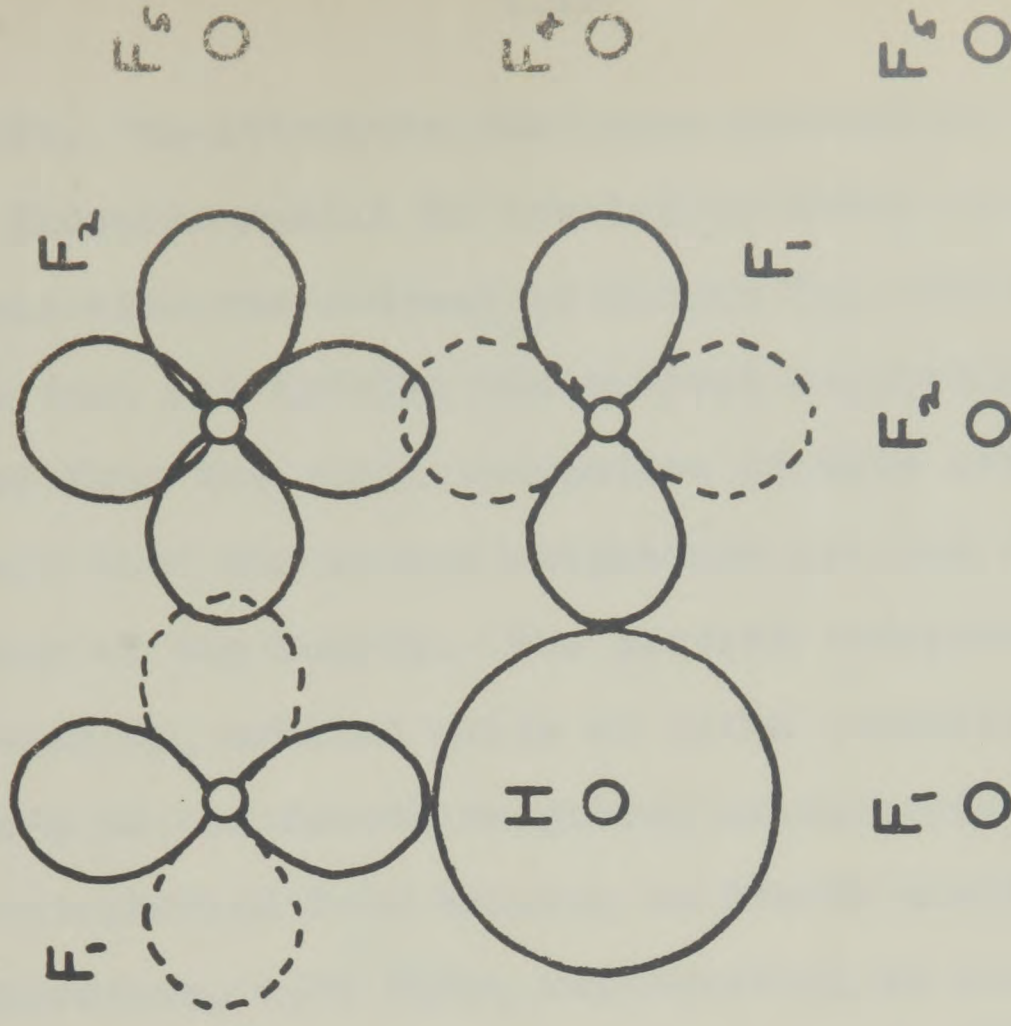
F_1 O F_2 O F_3 O



F_1 O F_2 O F_3 O

(a) With Shell 4.

(100) Plane.



(b) With Shell 2.

Fig 7.7. Bonding Between Hydrogen and Distant Fluorines in CaF_2 .

of 0.025. We attribute the large parameters for the fourth shell fluorine nuclei to overlap of their $2s$ and $2p_{\sigma}$ orbitals with the nearest neighbour $2p_{\sigma}$ orbital. That the effect does not involve the nearest neighbour $2s$ orbital is deduced from the small occupation of this orbital (0.002) and the fact that the second neighbours are not affected in the same way as the fourth. The partial occupation of the nearest neighbour $2p_{\sigma}$ orbital makes an extra contribution of about 0.1 Mc/s to the fourth neighbour anisotropic interaction. The contribution from bonding in fourth shell $2p_{\sigma}$ orbitals is, therefore, 0.26 Mc/s, representing an occupation of 1.7×10^{-4} . The $2s$ occupation is 1.7×10^{-5} . The super-exchange effect occurs in such a pronounced way for the substitutional hydrogen site in CaF_2 because the hydrogen and fluorines of shells 1 and 4 are in a straight line with the smallest $\text{F}^- - \text{F}^-$ separation. A similar effect has been observed by Spaeth (1965) for interstitial hydrogen in KCl. Interaction with second shell potassium nuclei was almost entirely due to overlap with the nearest neighbour chlorine ions. A calculation of this overlap using Hartree-Fock functions for the ions and a hydrogen $1s$ function gave reasonable agreement with experiment.

The unpaired electron density on the two nearest neighbour fluorine ions adjacent to each second shell fluorine (Fig. 7.7(b)) should make an additional dipolar contribution of

about 0.1 Mc/s. We then have to account for a reduction through bonding of 0.19 Mc/s. The calculated second shell isotropic interaction using the Gourary and Adrian method (sect. 6.13) is 0.2 Mc/s which again is reduced, to -0.02 Mc/s by bonding. Fig. 7.7(b) shows a possible mechanism involving spin orbit coupling on the first shell fluorines. This admixes π states, of opposite spin to the ground state, which are, therefore, directed towards the second shell ions giving a non-negligible overlap with their $2p_{\sigma}$ and $2s$ orbitals. The opposite spin will then lead to interaction with the fluorine nucleus in opposition to the direct interaction with the hydrogen electron. 20% of the natural abundance of calcium

The most promising explanation for the very large third shell parameters is again transferred interaction, via the Ca^{2+} ions which are nearest neighbours to the hydrogen.

There would be a tendency for electron transfer from the fluorine $2p_{\sigma}$ orbital to the unoccupied Ca^{2+} orbital and on to the hydrogen. The alternative of a lattice distortion geometrical relationship to the substituted hydrogen as would require the third shell nuclei to be closer to the hydrogen than the undistorted second shell, which is out of the question. The major objection to interaction via the Ca^{2+} ions is that the tetrahedral site symmetry makes this possible for only four of the eight third shell fluorines. Identical angular plots, but described by smaller parameters, would be expected for the other four and these cannot spectrum, relegating any interstitials at least to the third

positively be identified in Figs. 7.2 and 7.4. Taking their interaction as the classical dipole value of 0.713 Mc/s the maximum separation of their endor lines from the free fluorine is 0.713 Mc/s which is in the poorly resolved part of the spectrum. However, for $H \parallel [112]$ the separation would be 0.594 Mc/s and in fact Fig. 7.4 shows lines in this region which are not included in the second, third or fourth shell angular plots. Thus the experimental evidence does not rule out the proposed mechanism. A significant test would be an ENDOR measurement of the hyperfine interaction with the cation nucleus. This is, of course, impossible for CaF_2 but in BaF_2 ~ 20% of the natural abundance of cation nuclei have magnetic moments. A sufficiently strong substitutional spectrum may possibly be produced by rare earth doping of the crystal.

7.9. Interstitial Fluorine Ions

The second nearest interstitial site has the same geometrical relationship to the substitutioned hydrogen as the second shell lattice fluorines do to the interstitial hydrogen. Hall and Schumacher have measured these hyperfine parameters from which the separations of the ENDOR lines from the free fluorine resonance are calculated as 0.842 Mc/s for $H \parallel [100]$, 0.723 Mc/s for $[110]$ and 0.763 Mc/s for $[111]$. No such lines were observed in the substitutional ENDOR spectrum, relegating any interstitials at least to the third

nearest site. The (111) plane angular plot suggests that they may be even further than this.

7.10 Associated F Centres

Low temperature X-irradiation of the hydrogenated crystals also produces F centres. It is important for possible formation mechanisms to know if these are closely associated with the substitutional hydrogen atoms. A splitting of any of the ENDOR lines at the extremes of the spectrum by down to 10 Kc/s could be detected. Treating the F centre as a point spin magnetic moment it would have to be more than seven $F^- - F^-$ spacings away not to produce such a splitting. Since no splitting was observed any close association between hydrogen and F centre is ruled out.

7.11 ENDOR of Interstitial Hydrogen Atoms

A crystal containing substitutional hydrogen atoms was warmed to just above the transition temperature. As soon as the hydrogen had moved to the interstitial sites the crystal was cooled again to 77°K and the ENDOR spectra measured for $H \parallel [100]$ and $[110]$. The crystal was then X-irradiated for 11 hours at room temperature and the interstitial ENDOR measurements repeated at 77°K. The spectra were identical for the two cases and the hyperfine parameters derived are given in Table 7.3 and compared with Hall and Schumacker's results.

Table 7.3. Hyperfine Parameters for Shells 2 and 3
for Interstitial Hydrogen in CaF_2

		2nd Shell	3rd Shell
This work	A_s (Mc/s)	0.425 ± 0.020	0.015 ± 0.010
	A_p (Mc/s)	0.876 ± 0.020	0.347 ± 0.020
Hall and Schumacher	A_s (Mc/s)	0.415 ± 0.015	0.020 ± 0.025
	A_p (Mc/s)	0.872 ± 0.015	0.360 ± 0.025
	A_D (Mc/s) Calc.	0.804	0.354

Table 7.4. Calculated nearest neighbour ENDOR frequencies
at K-band for the central fluorine hyperfine line of the
low field hydrogen hyperfine line ($H=8159\text{G}$)

Direction of H	θ°	Number of equivalent fluorines	ENDOR frequencies (Mc/s)
[100]	0	2	51.0 116.3
	90	4	6.3 59.0
[110]	45	4	36.3 92.3
	90	2	6.3 59.0
[111]	54.4	6	28.9 85.0

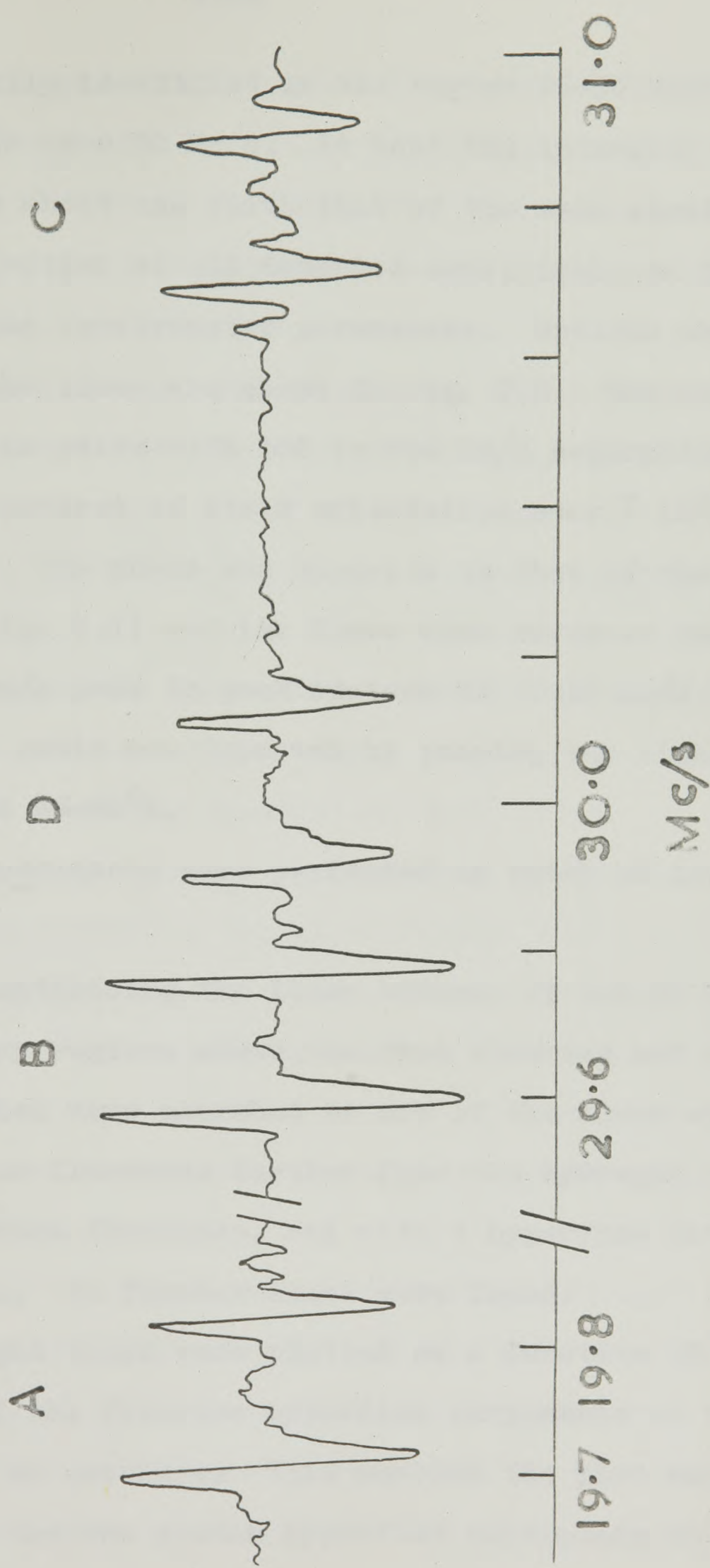
The room temperature irradiation should destroy any close association between hydrogen atoms and fluorine vacancies or interstitials. Since the two ENDOR spectra are identical we conclude that there was also no close association in the case of interstitial atoms produced by low temperature irradiation and controlled warming. More specifically, the transition of the hydrogen atom from the substitutional site does not leave a fluorine vacancy in the second shell of the environment of the resulting interstitial atom and probably not in the third shell either.

7.12 Nearest Neighbour Fluorine ENDOR

As derived in section 6.3 the nearest neighbour ENDOR frequencies (neglecting corrections due to interaction with the proton and fluorine-fluorine coupling) are given by

$$\nu_{sz} = \pm \frac{1}{2} = \left\{ \left(\frac{g_F \beta_n H}{h} \right)^2 \mp \frac{g_F \beta_n H}{h} (A_{//} \cos^2 \theta + A_{\perp} \sin^2 \theta) + \frac{1}{4} (A_{//}^2 \cos^2 \theta + A_{\perp}^2 \sin^2 \theta) \right\}^{\frac{1}{2}} \quad (4)$$

with $A_{//}$, $A_{\perp}$ in frequency units. Table 7.4 gives the approximate ENDOR frequencies expected for the central e.p.r. line of the low field group at K bond, as calculated from the e.p.r. parameters. Because of the equipment available those lines below 50 Mc/s were sought. After careful optimisation of the distant fluorine ENDOR spectrum with $H \parallel [110]$ six new



Nearest Neighbour Fluorine ENDOR Lines for $\underline{H}$ Along $[110]$ Fig 7.8.

lines were finally identified in the region 25-30 Mc/s and another pair near 20 Mc/s. At best the intensity of these lines was about one fifth that of the main spectrum and their observation at all depended sensitively on the adjustment of the spectrometer parameters. Optimum chart recordings of the lines are shown in Fig. 7.8. The eight lines occurred in pairs with 100 to 200 Kc/s separations, which were independent of field orientation over $\pm 10^\circ$ from the [110] axis. The phase was opposite to that of the main spectrum (cf. Fig. 7.1) and the lines were narrower being only about 12 kc/s peak to peak instead of 20-30 kc/s. The signal-to-noise ratio was improved by pumping the liquid [110] nitrogen down to 66-68°K.

Further experiments were performed in order to identify the lines:

(a) After optimising the lines between 25 and 30 Mc/s the complementary regions above the free fluorine and free proton frequencies were searched to see if the lines were due to protons or fluorines further from the hydrogen than the nearest lattice fluorines, and with a hyperfine interaction of about 12 Mc/s. No further lines were found.

(b) All eight lines were plotted as a function of field using as many of the fluorine hyperfine components of the e.p.r. spectrum as possible. This enabled the plot across the gap between the two proton hyperfine multiplets to be

drawn with confidence (Fig. 7.9). The surprising result is that one pair of lines, (D), is field independent over the whole range of 550 G. We can offer no explanation of this but remark that the pair had all the characteristics of real ENDOR lines.

(c) To eliminate the possibility of the line pairings being due to crystal misalignment or twinning other samples were used. The line separations were unchanged and the frequencies were consistent with the earlier measurements.

(d) Over a number of runs there appeared to be some correlation between the line pairs A and B. An angular plot for both pairs was carried out over a few degrees. The [110] direction was a frequency minimum for both pairs.

(e) The crystal alignment was checked by letting it warm up and then observing the interstitial ENDOR spectrum.

(f) The N.M.R. waveform in the cavity was checked at the oscillator amplitude setting which gave the best intensity for the 4 pairs of lines. It was found to have second and third harmonic components strong enough to be detected by eye in the oscilloscope trace.

On the basis of these results we assign the pair of lines A as the third sub-harmonic and the pair B as the second sub-harmonic of a nearest neighbour ENDOR line expected at 59 Mc/s for $\theta = 90^\circ$. This is supported by the N.M.R. waveform, the narrower linewidth and the close agreement

between the appropriate harmonics of the two pairs of lines (see, for example, the composite angular plot, Fig. 7.12). The reversed phase suggests a large hyperfine interaction which is born out by the absence of complementary lines symmetrical about the free fluorine resonance frequency. Further support comes from other properties of the lines described below.

7.13 Magnetic Field Dependence

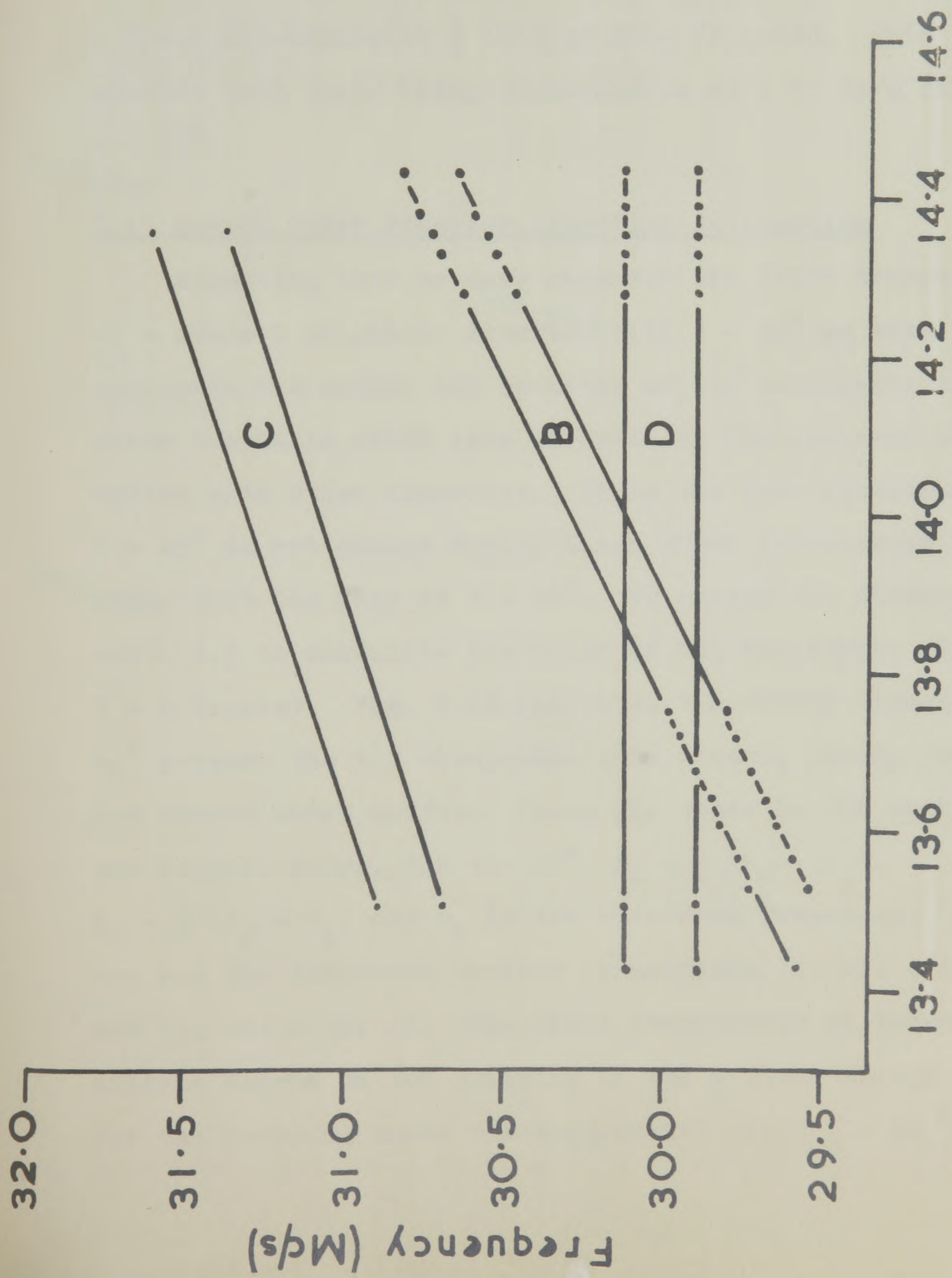
Differentiation of the nearest neighbour ENDOR frequency with respect to field gives

$$\frac{\partial \nu}{\partial H} = \frac{g_F a_n}{h} \cdot \frac{1}{\nu} \left[\nu_0 \mp \frac{1}{2} (A_{\parallel} \cos^2 \theta + A_{\perp} \sin^2 \theta) \right] \quad (5)$$

where ν_0 is the free fluorine resonance frequency and the $\mp$ signs refer to the $|\pm \frac{1}{2}\rangle$ electronic states. Thus the free fluorine field dependence, $g_F a_n/h$ is modified by the factor

$$\frac{1}{\nu} \left[\nu_0 \mp \frac{1}{2} (A_{\parallel} \cos^2 \theta + A_{\perp} \sin^2 \theta) \right].$$

This factor reduces to unity for $\theta = 0^\circ$ or 90° , as required. This reduction factor can clearly have the value zero for some value of θ . However, solving for θ , using the nearest neighbour hyperfine parameters does not lead to a field independent line at the position of the invariant pair D. Further, a line cannot be invariant over a field range as wide



Field (Mc/s for Li^{7})

Fig 7.9. Field Dependence of Nearest Neighbour ENDOR Lines.

as 500 G. ENDOR measurements at X bond may be helpful in deciding the origin of the lines D.

The lines A have a field dependence of $\frac{1}{3}$ and the lines B a field dependence of $\frac{1}{2}$ that of free fluorine. This is consistent with their being subharmonics of a 59 Mc/s line with $\theta = 90^\circ$.

7.14 Second Order Fluorine Hyperfine Interaction

Accepting that we have observed the ENDOR transitions of a nearest neighbour fluorine with $\theta = 90^\circ$ we wish to calculate the number and spacings of the components into which the basic ENDOR line is split by the indirect interaction with other fluorines. Since the four fluorines at $\theta = 45^\circ$ do not change during these ENDOR transitions we consider just the pair at $\theta = 90^\circ$. We extend the discussion of sect. 6.5 to calculate the shift of all the levels of the $I = 1$ triplet. Fig. 7.10 indicates the matrix elements of K_1^T between the two electronic spin states, giving rise to the second order shifts. These are shown in the centre of the diagram where, for $\theta = 90^\circ$, $A_1 = \frac{1}{4} (A_{//} - A_{\perp})$, $B_1 = \frac{1}{4} (A_{//} + A_{\perp})$ and ν_e is the microwave frequency. There are now two different nuclear transitions $|1, +1\rangle - |1, 0\rangle$ and $|1, -1\rangle - |1, 0\rangle$. The exact frequencies of these transitions depend on the ordering of the nuclear energy levels. For the ordering shown the frequencies are $\nu_{\pm 1} = 2A_1^2/\nu_e$.

Fig 7.10. Two Fluorines at $\theta = 90^\circ$. Effect of:

Hyperfine Interaction in Second Order

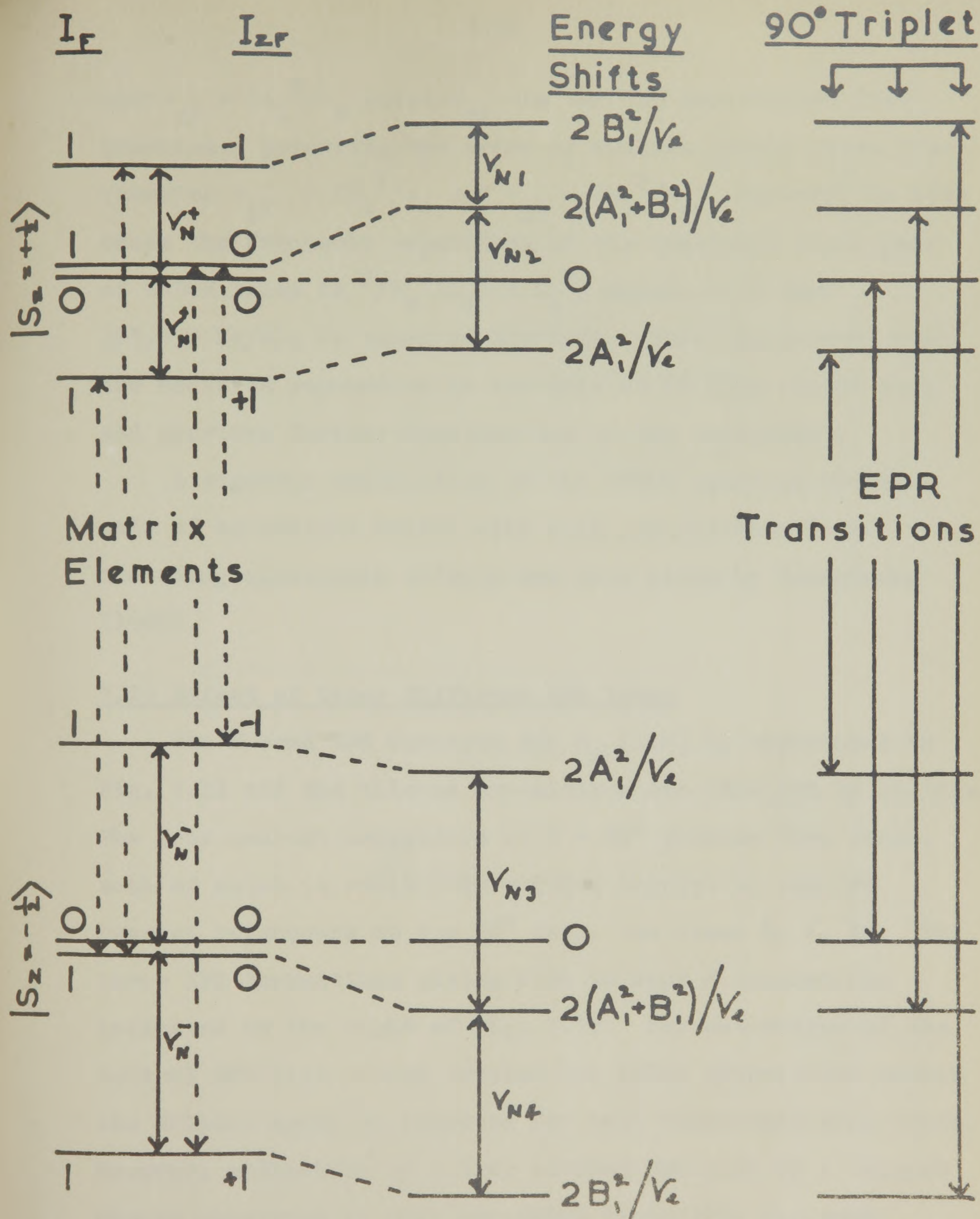


Fig 7.10. Two Fluorines at $\theta = 90^\circ$. Effect of Hyperfine interaction in Second Order.

and $\nu_{\pm\frac{1}{2}} - 2A_1^2/\nu_e$ where $\nu_{\pm\frac{1}{2}}$ are the two unperturbed frequencies. Inverting the order of nuclear levels gives frequencies $\nu_{\pm\frac{1}{2}} + 2A_1^2/\nu_e$ and $\nu_{\pm\frac{1}{2}} - 2B_1^2/\nu_e$. However, in both cases the frequency separation of the resulting close pair of ENDOR lines is $2/\nu_e (A_1^2 + B_1^2)$ which, at K bond (23,650 Mc/s), is equal to 325 kc/s. This agrees well with the measured separation of the pair at 59 Mc/s of 352 kc/s and provides further confirmation of the assignment.

A rigorous calculation of the ENDOR spectrum due to a pair of equivalent nuclei with spin greater than $\frac{1}{2}$ and including quadrupole effects has been given by Feuchtwang (1962).

7.15 Effect of Using Different EPR Lines

The K bond EPR spectrum for $H_{\parallel}[110]$ is reproduced in Fig. 7.11 and the allowed transitions are labelled by letters. The four nearest neighbours at $\theta = 45^\circ$ produce five lines, each of which is split into a 1:2:1 triplet by the two nearest neighbours at $\theta = 90^\circ$ (e.g. the lines E, A, D). The three EPR transitions giving rise to such a triplet are indicated on the right of Fig. 7.10. For saturation of the central EPR line of any triplet two ENDOR transitions within the triplet would be expected for each electronic spin state. However, saturation of either extreme EPR line of a triplet should give rise to only one ENDOR transition for each electronic spin state. This was tested; each of the central

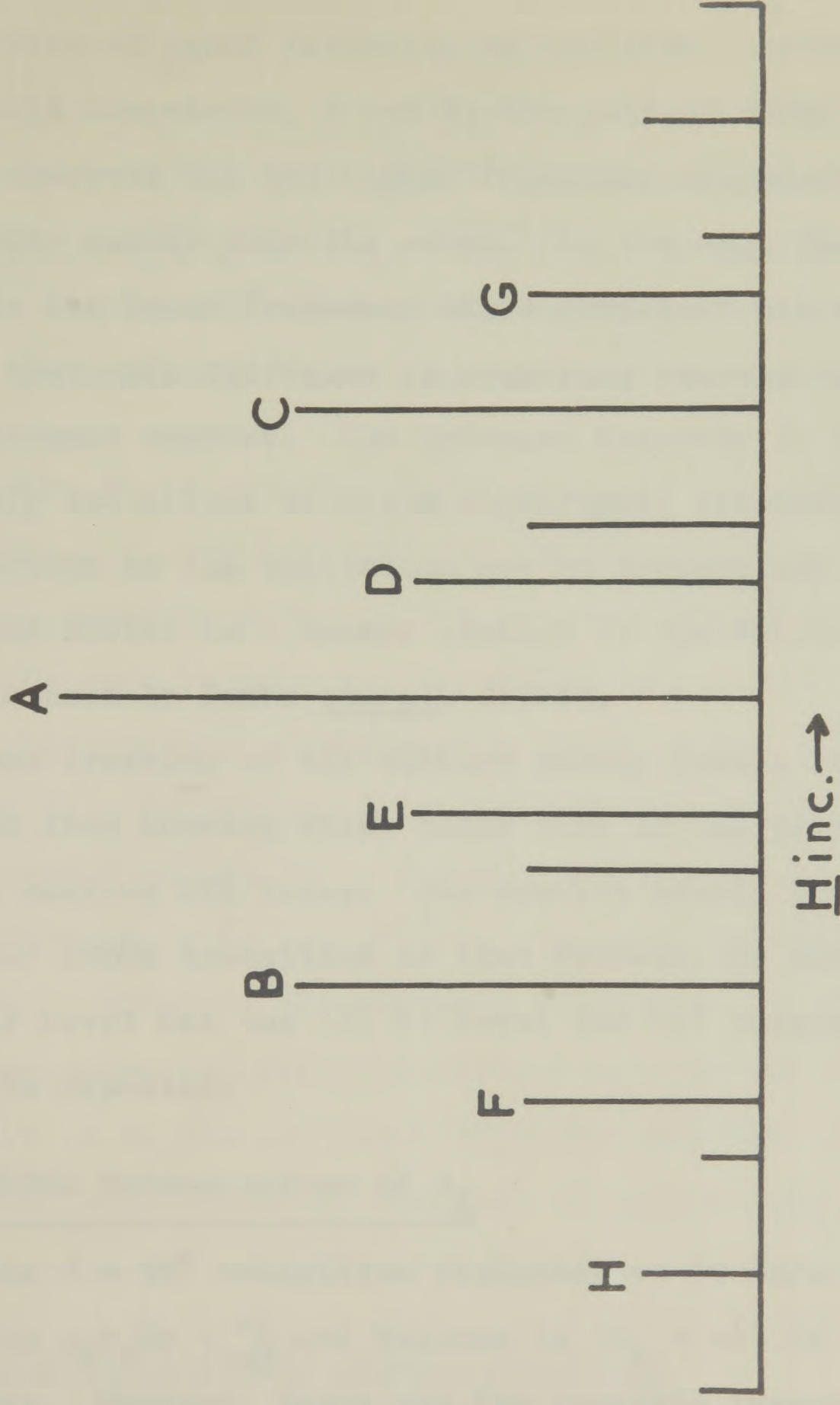


Fig 7.11. $\text{CaF}_2:\text{Subs.H}$, $H//[110]$, Showing EPR Lines Used for Nearest Neighbour ENDOR. (Only Allowed Transitions are Shown).

lines of 90° triplets, A, B, C and H, was used to observe the pair of ENDOR lines at 59 Mc/s. In all cases the two lines were of equal intensity as expected. However, on the low field components, E and F, the pair of ENDOR lines was again observed but the higher frequency component was considerably weaker than the other. On the high field EPR components the lower frequency ENDOR component was weak. This means that spin diffusion is occurring between resonant and non-resonant centres. The hydrogen impurity ($\sim 1:10^4$) is probably too dilute to allow significant electron spin-spin interaction so the excitation may be transmitted via the fluorine nuclei in a manner similar to the "distant ENDOR" effects seen by Lambe et. al. (1961).

The ordering of the nuclear energy levels cannot be deduced from knowing which ENDOR line of the pair is stronger or the various EPR lines. Our results simply show that the stronger ENDOR transition is that between the saturated nuclear level and the $|1, 0\rangle$ level for all possibilities as would be expected.

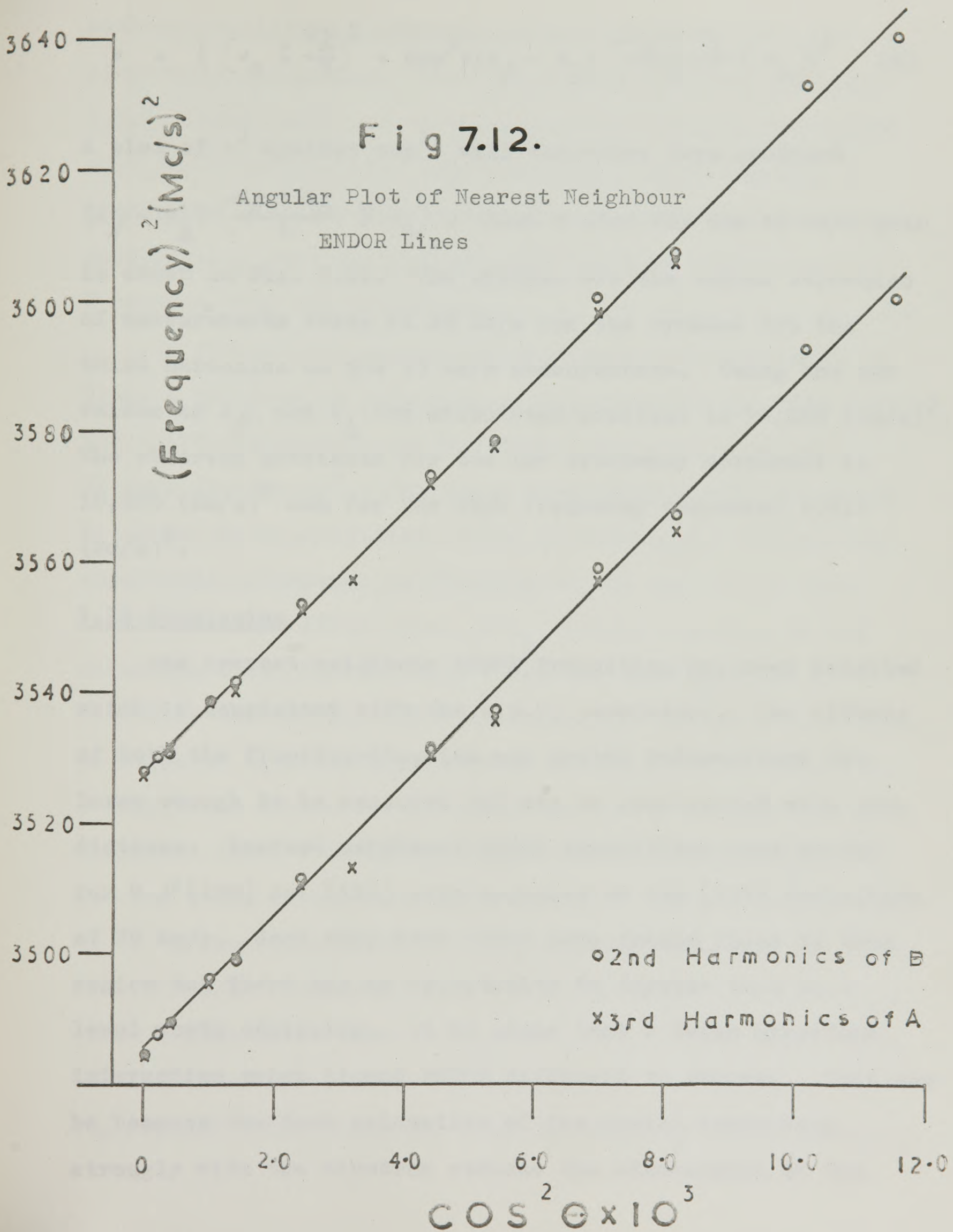
7.16 ENDOR Determination of A_1

The $\theta = 90^\circ$ transition frequency at 59 Mc/s is simply equal to $g_F \beta_n H_0 + \frac{A_1}{2}$ and belongs to $|S_z = -\frac{1}{2}\rangle$ if A_1 is positive. However, there are two possible frequencies, depending on the ordering of the nuclear levels, between the

3640 pair of ENDOR lines which could be taken as the unperturbed
 $\theta = 90^\circ$ frequency. Since the nuclear Zeeman energy is
 greater than A_1 the nuclear energy levels for the spin
 3620 Hamiltonian used will be ordered as in Fig. 7.10. The ENDOR
 frequencies belonging to the two electronic spin states are
 then $\nu_{\pm\frac{1}{2}} - 2A_1^2/\nu_e$ and $\nu_{\pm\frac{1}{2}} + 2B_1^2/\nu_e$. We therefore take the
 3600 unperturbed $\theta = 90^\circ$ ENDOR frequency to be greater than the
 low frequency line of the pair by $\left(\frac{A_1^2}{A_1^2 + B_1^2}\right) \times (\text{pair separation})$.
 3580 This leads to an apparent value of A_1 for the high field
 EPR line of 52.822 Mc/s and for the low field line of 52.776
 Mc/s, as compared with the EPR value of 52.76 ± 0.3 Mc/s.
 3560 The difference between the two ENDOR values is a manifestation
 of the interaction of the proton (sect. 6.4). At K band this
 results in a reduction of the apparent hyperfine parameter
 3540 for hydrogen states $|S_z = \pm\frac{1}{2}, I_{pz} = \mp\frac{1}{2}\rangle$ of 0.1% relative to
 the states $|S_z = \pm\frac{1}{2}, I_{pz} = \pm\frac{1}{2}\rangle$. The expected difference of
 53 kc/s is close to the measured difference of 46 kc/s. The
 3520 ENDOR measurements give, therefore, $A_1 = 52.822 \pm 0.010$ Mc/s.
 Since it is on the low field EPR line that the reduced
 3500 hyperfine interaction is observed we deduce that A_1 has the
 same sign as the hyperfine interaction with the proton.

7.17 Nearest Neighbour Angular Variation

The expression for the nearest neighbour ENDOR frequency
 may be rewritten to show the angular variation more clearly:



$$\nu = \left\{ \left(\nu_0 + \frac{A_{\parallel}}{2} \right)^2 + \cos^2 \theta (A_{\parallel} - A_{\perp}) \left(\frac{A_{\parallel} + A_{\perp}}{4} + \nu_0 \right) \right\}^{\frac{1}{2}} \quad (6)$$

A plot of ν^2 against $\cos^2 \theta$ will therefore have gradient

$(A_{\parallel} - A_{\perp}) \left(\frac{A_{\parallel} + A_{\perp}}{4} + \nu_0 \right)$. Such a plot for the 59 Mc/s pair is shown in Fig. 7.12. The circles are the second harmonics of measurements taken at 29 Mc/s and the crosses are the third harmonics of the 19 Mc/s measurements. Using the EPR values of $A_{\parallel}$ and $A_{\perp}$ the calculated gradient is $10,058 (\text{Mc/s})^2$. The observed gradients for the low frequency component is $10,100 (\text{Mc/s})^2$ and for the high frequency component $9,910 (\text{Mc/s})^2$.

7.18 Conclusion

One nearest neighbour ENDOR transition has been detected which is consistent with the e.p.r. parameters. The effects of both the fluorine-fluorine and proton interactions are large enough to be measured and are in good accord with predictions. Nearest neighbour ENDOR transitions were sought for $H \parallel [100]$ and $[111]$ with emphasis on the $[111]$ transition at 29 Mc/s. Some very weak lines were indeed found in this region but there was no opportunity to improve them to a level worth analysing. It is clear that a large hyperfine interaction makes ligand ENDOR difficult to observe. This may be because the fast relaxation of the nuclei interacting strongly with the electron reduces the enhancement of the

nuclear population difference caused by saturating the electronic transition. This would indicate that greater N.M.R. field would increase sensitivity in these cases and that the "steady-state" ENDOR technique using the EPR absorption signal should work. Seidel (1961) has obtained good signals from the nearest neighbours of alkali halide F centres with the technique.

In view of the success in accounting for the pairs of lines A and B it is plausible to suggest that the pair C is the third subharmonic of the ENDOR transition expected at 92 Mc/s for $\theta = 45^\circ$. The field dependence at 92 Mc/s would be close to the calculated value of $0.96 g_F \beta_n$. Taking the unperturbed frequency as the mean of the pair at 92 Mc/s, $\theta = 45^\circ$ and the ENDOR value of $A_\perp$ already obtained we may calculate $A_\parallel$. For the high field EPR line $A_\parallel = 168.06 \pm 0.3$ Mc/s and for the low field line $A_\parallel = 167.55 \pm 0.3$ Mc/s, as compared with the e.p.r. value of 168.11 ± 0.5 Mc/s. The fairly large errors on the ENDOR results cover possible misalignment since $\theta = 45^\circ$ is the position of maximum $\frac{\partial \nu}{\partial \theta}$. The smaller value of the low field result is again a consequence of the proton interaction. In this case the reduction should be 0.17 Mc/s. Correcting the low field value by this amount gives a mean ENDOR value of $A_\parallel$ as 167.89 ± 0.05 Mc/s. where the limits of error cover the uncertainty in selecting the unperturbed ENDOR frequency from the observed pairs of lines.

Weak structure on each line of the pair C (Fig. 7.8) is to be expected from the further splitting caused by the quartet of equivalent $\theta = 45^\circ$ fluorines. The structure was too weak and variable to make an accurate measurement possible. The splittings of ENDOR lines resulting from four equivalent nuclei have been treated by Holton and Blum (1962).

If this assignment of the pair C is correct the obvious problem is the absence of the complementary transition at 36 Mc/s (Table 7.4). However, other workers have discovered enormous differences in the intensities of ENDOR transitions belonging to different electronic states (Seidel; Ranon and Hyde 1966). Also not all the nearest neighbour transitions were observed for $\text{CaF}_2:\text{Tm}^{2+}$ (Chap. 4).

References to Chapter 7

- Feuchtwang, T.E., 1962. Phys. Rev., 126, 1628.
- Hall, J.L. and Schumacher, R.T., 1962. Phys. Rev., 127, 1892.
- Holton, W.C. and Blum, H., 1962. Phys. Rev., 125, 89.
- Lambe, J., Laurance, N., McIrvine, E.C. and Terhune, R.W., 1961. Phys. Rev., 122, 1161.
- Ranon, V. and Hyde, J.S., 1966. Phys. Rev., 141, 259.
- Seidel, H., 1961. Z. f. Phys., 165, 218.
- Spaeth, J., 1965. Thesis, Stuttgart.

used for the g value Chapter 8

in 11 determinations EXPERIMENTAL TECHNIQUES

8.1 More Accurate Determination of g Value

In measurements on hydrogen in CaF_2 a point of interest is the small difference between the g value and that of a free hydrogen atom. To be useful accuracies of order $1:10^4$ are required rather than the more usual $1:10^3$. Basically we require accurate knowledge of the fields for resonance and the klystron frequency. The magnetic field at the sample may differ from that measured by a nuclear resonance magnetometer outside the cryostat because of inhomogeneity of the field and magnetic impurities in the cryostat material. In the present case the correction may readily be made by using the fluorine ENDOR. At the centre of each fluorine ENDOR spectrum is a reverse phase line corresponding to the fluorine N.M.R. frequency in the field at the sample (e.g. Fig. 4.1(b)). This ENDOR frequency could be measured to better than 1kc/s ($5:10^5$ at K band) and compared with the field measured by the magnetometer at some standard position outside the cryostat. Of necessity this calibration is carried out at the field required for the E.P.R. transition. The calibration was performed with the magnetic field in different directions and with the cryostat at the temperature to be

used for the g value determination, 77°K . The R.M.S. error in 11 determinations of the correction factor was $4:10^5$. The field measurement was made with ^7Li nuclei. The ratio of fluorine moment to lithium moment may be obtained to $5:10^6$ from the comparison of each with the proton moment made by Huggins and Sanders (1965). *

Before each calibration run and the g value measurement itself the magnetic field homogeneity was maximised as suggested by the makers: maximum current (24A) for one minute; zero current for two minutes; then up to 50% above the field required and straight down to that field again.

The klystron frequency was determined by a heterodyne method. A 10 Mc/s crystal controlled oscillator followed by a power amplifier drove a frequency multiplier whose output was a mixture of 500 Mc/s and harmonics of 10 Mc/s. This was fed into a microwave crystal detector mounted on one arm of a 10 db cross-coupler off the main waveguide run, thereby producing microwave frequencies at 10 Mc/s intervals. On the opposite arm of the cross coupler a second detector produced the beats with the klystron frequency. Despite using the 47th harmonic of the multiplier output the beats with the K band klystron frequency could readily be detected by a communications receiver. They could be recognized by their characteristic "twittering" against the receiver B.F.O. due to the F.M. noise of the

* Chemical shifts were allowed for, using the data of Gutowsky and Hoffman (1950) and Skripov and Wang I-Ch'iu (1964).

klystron.

The accuracy and stability of the 10 Mc/s standard oscillator was checked against the crystal-locked 10 Mc/s signal from the Rohde and Schwarz WIK frequency synthesiser using Lisajous figures. It remained within 2 c/s of 10 Mc/s over periods of five minutes and was kept to this accuracy throughout measurement by slight adjustment. The Rohde and Schwarz was checked by comparing a 200 kc/s output with the carrier frequency of the B.B.C. Droitwich transmitter which is maintained to 5 parts in 10^9 (B.B.C. 1963). Regular checks over the period of measurement showed the difference to be not more than $1:10^7$.

The actual beat frequency detected by the communications receiver was measured by injecting a signal from the Rohde and Schwarz, taking care not to overload the receiver, and adjusting the frequency for maximum output. This gave the beat frequency to better than 1 kc/s.

The klystron, even when stabilised, drifted by far more than the accuracy of frequency measurement. To combat this the communication receiver was kept tuned to a fixed frequency (with periodic checks on its stability from the Rohde and Schwarz). As each E.P.R. line was measured the klystron reflector voltage was adjusted slightly to bring the beat frequency back into the receiver pass band.

The centre of the E.P.R. lines was detected on the meter of the 115 kc/s phase sensitive detector, there being no 50 c/s field modulation. The proton magnetometer at the standard position in the magnet gap was equipped with small 50 c/s coils to give local modulation of the probe, enabling the signal to be displayed. The R.M.S. error of 10 readings of the positions of line centres was $1:10^5$ in the proton resonance frequency.

As no satisfactorily calibrated K band wavemeter was available the klystron frequency was determined by the field modulation amplitude and audio P.M. frequency and field for resonance of D.P.P.H. There has been some disagreement in the past over its g value (Holden et al. (1950), Townes and Turkevitch (1950)), particularly at very low temperature but there is a fair measure of agreement that at 77°K the value for the powder is 2.0036 ± 0.0002 (Weidner and Whitmer (1953), Singer and Kikuchi (1955)). In fact we have only to identify the klystron frequency within 10 Mc/s so an error of up to 0.0005 could be allowed.

We thus have the klystron frequency to parts in 10^7 and the important error is in determining line positions. Contributions to this come from distortion of the line shape by mistuning, and the field correction factor. If we suggest we can detect an asymmetry of one tenth in an absorption derivative which is 3G. pk-pk, this corresponds to a shift of 0.3G in the zero position or $4:10^5$. Taking

this with the error in the field correction factor we can quote a probable error for the g value of $6:10^5$.

8.2 Measurement of ENDOR Lines

The E.P.R. dispersion signal was used. The microwave bias on the E.P.R. signal was adjusted until noise just appeared on the line peak as seen on the oscilloscope. The magnetic field was set to the central peak of the E.P.R. line and the N.M.R. sweep was started. When an ENDOR line was found the sweep was stopped at one peak and the microwave power, 115 kc/s slightly the ^7Li signal was brought to the centre of the field modulation amplitude and audio F.M. frequency and phase were adjusted for largest signal.

The magnetic field was continuously monitored by a ^7Li magnetometer phase locked to the output of the Rohde and Schwarz frequency synthesiser. The coupling was such that the magnetometer frequency could be varied by 0.1 Mc/s by adjusting the Rohde and Schwarz. The local field modulation of the magnetometer probe allowed display of the ^7Li signal without affecting the main field at the microwave cavity.

When measuring an ENDOR transition frequency the line was drawn out on the chart recorder to check the line symmetry and zero position. The nuclear oscillator was then swept slowly through the line again and the mechanical sweep stopped at the central zero of the line derivative. The apparatus was left for a few seconds to allow relaxation

of the frequency sweep drive mechanism to take place. The output time constant was adjusted to give a noise amplitude of one tenth of the chart width. Final adjustment of the nuclear oscillator frequency was made by varying the D.C. bias on the S.V.C.3 variable capacitance diodes. The nuclear oscillator was assumed to be accurately adjusted to the central frequency when the noise remained symmetrical about the chart zero line for 30 seconds.

At this point, by adjusting the Rohde and Schwarz slightly the ^7Li signal was brought to the centre of the oscilloscope and the frequency measured. The frequency modulation was removed from the N.M.R. oscillator and its frequency measured immediately afterwards. Since the N.M.R. oscillator was very stable ($\sim 1:10^6$) this allowed determination of the ENDOR frequency and the corresponding field in spite of small drifts of the field. Changes to 0.3G are readily made.

8.3 Measurement of E.P.R. Multiplets

When an E.P.R. line has many hyperfine structure components, as for example $\text{CaF}_2:\text{H}$, it is very laborious to measure each line separately by the static field method. Furthermore, during the time consumed tuning can alter, distorting line shapes and causing relative inaccuracies of determination from one line to another. In cases where lines are incompletely resolved such as $\text{CaF}_2:\text{Tm}$ or $\text{SrF}_2:\text{H}$ it is very difficult to decide at what point to measure the line

and almost impossible to keep a record of the point chosen.

The technique evolved for this situation enables each line to be measured in its context in the whole spectrum. The output of the Rohde and Schwarz is sufficient to lock the magnetometer to any frequency. The magnetometer signal is displayed by using its local probe modulation and a very slow sweep through the E.P.R. spectrum is commenced and recorded on the chart.

As the sweep proceeds the magnetometer is locked to successive multiples of 10 kc/s. Each time the magnetometer signal crosses the oscilloscope centre line a voltage pulse is injected into the recorder pen circuit. Thus a chart is produced of the complete spectrum with field markers at 10 kc/s intervals. The field sweep is sufficiently linear to allow accurate interpolation between the markers. Measurements of line positions to 0.3G are readily made.

References to Chapter 8

B.B.C., 1963, Engineering Information Department: Information Sheet No. 1028/2.

Gutowsky, H.S. and Hoffman, C.J., 1950. Phys. Rev. 80, 110.

Holden, A.N., Kittel, C., Merritt, F.R. and Yager, W.A., 1950. Phys. Rev. 77, 147.

Huggins, R.W. and Sanders, J.H., 1965. Proc. Phys. Soc. 86, 53.

Singer, L.S. and Kikuchi, C., 1955. J. Chem. Phys. 23, 1738.

Skripov, F.I. and Wang I-Ch'iu, 1964. Acta Physica Sinica 20, 41.

Townes, C.H. and Turkevitch, J., 1950. Phys. Rev. 77, 148.

Weidner, R.T. and Whitmer, C.A., 1953. Phys. Rev. 91, 1279.

APPENDIX

Angular Characteristics of Ligand
Hyperfine Structure in Cubic Crystals.

(a) Ligand hyperfine interactions in E.P.R. spectra are normally evaluated by mounting the crystal with a known plane horizontal and rotating the magnetic field until the various low index crystal directions ($[100]$, $[110]$, $[111]$, etc.) in this plane are located. The low index directions commonly have higher numbers of ligands equivalent than a general direction in the plane and they are located by looking for the resulting simplification of the ligand hyperfine structure of the E.P.R. spectrum. However, there are dangers in applying this technique indiscriminately and simply looking for a spectrum consistent with the ligand equivalence of the low index direction being sought. A good example of this is the case of a centre with six-fold octahedral ligand interaction and the magnetic field in a (110) - type plane. Four of the ligands are equivalent for all directions in this plane and so the ligand hyperfine structure (assuming nuclear spins of $\frac{1}{2}$) consists of three overlapping quintets for all directions (except $[111]$ in which all six ligands are equivalent). In particular the directions $[100]$ and $[110]$ are not specially distinguished from other directions in this plane by their spectra

and if, for example, the sharpness of the central line is being used as a monitor for alignment in these directions, erroneous results may be obtained from what is only an accidental coincidence of lines from different quintets.

To indicate where special care must be taken we give below for both sixfold and eight-fold co-ordination the ligand equivalences for general directions in the three principal planes, together with the equivalences for the directions of higher equivalence in these planes. The planes are labelled so as to be consistent with the labelling of the low index directions they contain but the results are of course identical for any plane of the same type. The stated numbers of lines which should be observed assume a ligand nuclear spin of $\frac{1}{2}$.

Six-fold Octahedral Co-ordination.

Plane of $\underline{H}$	Direction of $\underline{H}$	Ligand Equivalences	No. of Lines
(001)	General	3 pairs. (1 pair always at $\theta = 90^\circ$).	$3 \times 3 \times 3$
	[100]	1 pair, 1 quartet	3×5
	[110]	1 pair, 1 quartet	3×5
(011)	General	1 pair, 1 quartet	3×5
	[111]	1 sextet	7

N.B. The directions [100], [011], [211] have no higher equivalence than a general direction in this plane.

Plane of $\underline{H}$.	Direction of $\underline{H}$.	Ligand Equivalences	No. of Lines
(T11)	General	3 pairs	3 x 3 x 3
	[110]	1 pair, 1 quartet	3 x 5
	[211]	1 pair, 1 quartet	3 x 5

Eight-fold Cubic Co-ordination.

Plane of $\underline{H}$.	Direction of $\underline{H}$.	Ligand Equivalences	No. of Lines
(001)	General	2 quartets	5 x 5
	[100]	1 octet	9

N.B. The [110] direction has no higher equivalence than a general direction in this plane.

(OT1)	General	2 pairs, 1 quartet	3 x 3 x 5
	[100]	1 octet	9
	[011]	2 quartets	5 x 5
	[111]	1 pair, 1 sextet	3 x 7

N.B. The [211] direction has no higher equivalence than a general direction in this plane.

(T11)	General	4 pairs (1 pair always at $\theta = 90^\circ$).	3 x 3 x 3 x 3
	[100]	2 quartets	5 x 5
	[211]	2 pairs, 1 quartet	3 x 3 x 5

In a practical situation the total number of lines indicated in the last column of the above table is usually not observed due to overlapping of lines from the various

component multiplets. However, the extreme lines of the extreme multiplets are usually unaffected in this way and their intensity ratios can be used to determine the number of equivalent nuclei responsible. The intensity ratio between first and second lines of a multiplet produced by N equivalent nuclei of spin $\frac{1}{2}$ is $1:N$. This fact can be used to check that the extreme line at each end of the spectrum has not been missed. This intensity ratio can be used to start the analysis of a complicated ligand hyperfine structure.

(b) Low index directions in a plane, not otherwise distinguishable, may be found by rotating the magnetic field by the appropriate amount from a direction which is identifiable through having a higher ligand equivalence. Secondly, if exact alignment of a particular spectrum is not possible due to inaccurate crystal mounting it may be possible to obtain better alignment along some other direction at which the identical spectrum re-appears. We give below the magnetic field orientation, relative to an arbitrary zero, at which various types of spectra are observed as the magnetic field is rotated through half a circle in each of the three principal planes. Identical spectra are of course repeated at angles of 180° greater than those given.

Plane of <u>H</u> .	Type of Spectrum	Angle (deg.)
(001)	[100]	0, 90
	[110]	45, 135
(011)	[100]	0
	[011]	90
	[111]	54.75, 125.25
	[211]	35.25, 144.75
(T 11)	[110]	0, 60, 120
	[211]	30, 90, 150