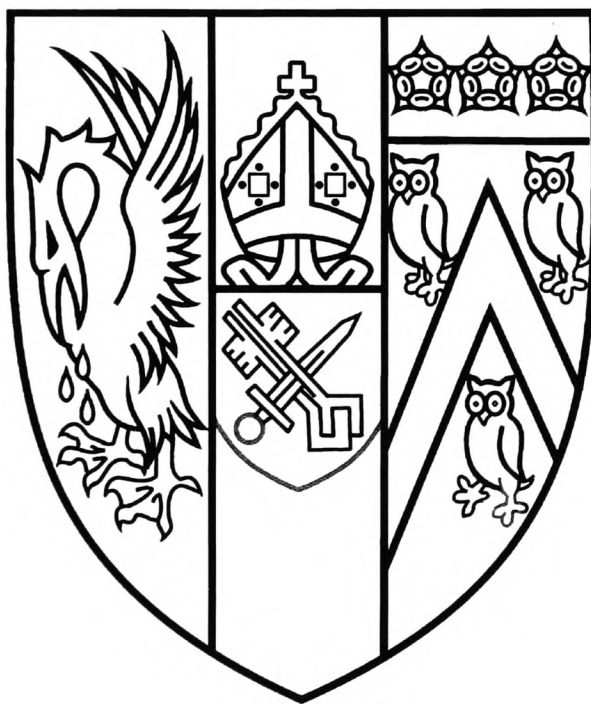


GHz Magnetoconductivity and Spin Resonance Studies of Strongly Correlated Systems



Alessandro Narduzzo
Corpus Christi College

A thesis submitted for the degree of
Doctor of Philosophy
at the
University of Oxford
Michaelmas 2004



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Abstract of Thesis Submitted for the Degree of Doctor of Philosophy

This thesis describes a series of experiments probing the millimetre-wave response of the low-dimensional organic superconductors β'' -(BEDT-TTF)₄[(H₃O)-M(C₂O₄)₃]S, κ -(BEDT-TTF)₂Cu(NCS)₂ and (TMTSF)₂PF₆ in applied magnetic fields.

Chapter 1 introduces the physics of charge carriers in the presence of a magnetic field and field-induced resonant phenomena in the conductivity of metals. The basic concept of Fermi liquid theory, that of the existence of quasiparticles with effective mass, is presented, as well as the principles of electron spin resonance.

Chapter 2 outlines the experimental technique of millimetre-wave spectroscopy, the principle of guided radiation and the use of metallic resonators and for perturbative measurements. Some results on novel dielectric whispering-gallery resonators and hybrid “tunnel-gap” resonators for potential use in pulsed and destructive field experiments are also presented.

Chapter 3 is a detailed angle-, temperature- and frequency- dependent investigation of electron spin resonance in the family of quasi-two-dimensional charge transfer salts β'' -(BEDT-TTF)₄[(H₃O)M(C₂O₄)₃]S, where $M = \text{Cr}^{3+}$ and Fe^{3+} . The effective spin Hamiltonians for the Cr^{3+} and Fe^{3+} ions are identified, and the presence of weak antiferromagnetic correlations established; insight is gained into the relaxation mechanism and the effect of the superconducting state on the localised spins.

Chapter 4 reports the angle-dependent magneto-optical response of isotopically substituted κ -(BEDT-TTF)₂Cu(NCS)₂. Both normal and superconducting states are investigated, and Josephson plasma resonances and Fermi-surface traversal resonances are identified.

Chapter 5 presents some preliminary results from the investigation of the quasi-one-dimensional Bechgaard salt (TMTSF)₂PF₆ under hydrostatic pressure and in applied magnetic field. The millimetre-wave response is investigated as a function of frequency as the field-induced spin-density-wave cascade is crossed. Possible evidence for resonant absorptions due to collective spin excitations is reported.

To Mei Poh, the joy of my life.

So if you do something, you should be very observant, and careful, and alert. Our way is to put the dough in the oven and watch it carefully. Once you know how the dough becomes bread, you will understand enlightenment [...]. We are not so concerned about what flour is, or what dough is.

Shunryu Suzuki

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Chapter 1

Introduction

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1.1 Charge carriers in a magnetic field

The experiments in this thesis investigate the electric and magnetic properties of solid state systems under the influence of an applied magnetic field by means of millimetre-wave spectroscopy. As opposed to the effect of an electric field, a quasistatic magnetic field influences the motion of charge carriers without changing their energy; it is therefore a powerful tool in condensed matter physics. The first part of this Chapter (Sections 1.1.1 to 1.4) provides a summary of the basic principles governing the behavior of charged carriers in crystals under the action of a quasistatic external field, physics underlying the experiments presented in Chapters 4 and 5 (GHz magneto-optical measurements in the organic compounds κ -(BEDT-TTF)₂Cu(SCN)₂ and (TMTSF)₂PF₆). Section 1.5 will describe the concept of a quasiparticle and that of effective mass. The effect of an applied magnetic field on the spin of the electron is introduced in Section 1.6 and developed in more detail in Chapter 3, where electron paramagnetic resonance measurements in the β'' -(BEDT-TTF)₄[(H₃O)*M*(C₂O₄)₃]*S* compounds are presented.

1.1.1 Classical Description

In the presence of a magnetic field, a free charged particle experiences the Lorentz force [1, 2]

$$\mathbf{F} = e\mathbf{v} \times \mathbf{B}, \quad (1.1)$$

e being the charge of the particle, $\mathbf{v}$ its velocity and $\mathbf{B}$ the external magnetic field. The acceleration of the particle is perpendicular to its velocity and to the magnetic field; the particle, therefore, executes a circular orbit in the plane perpendicular to $\mathbf{B}$ with radius

$$r_c = \frac{mv}{eB}, \quad (1.2)$$

m being the mass of the particle and angular frequency

$$\omega_c = \frac{eB}{m}. \quad (1.3)$$

If the quasistatic magnetic field $\mathbf{B} = (0, 0, B)$ is along the z axis and an oscillatory electric field $\mathbf{E} = (E \cos \omega t, 0, 0)$ is polarized along the x axis, the particle obeys the following equations of motion:

$$m\ddot{x} = eE \cos \omega t + eyB, \quad (1.4)$$

$$m\ddot{y} = -exB, \quad (1.5)$$

$$m\ddot{z} = 0. \quad (1.6)$$

Equation 1.6 shows that the motion of the particle in the direction of external field is independent of $\mathbf{B}$ and $\mathbf{E}$. The equations can be re-written as

$$\ddot{x} + \omega_c^2 x = \frac{eE}{m} \cos \omega t, \quad (1.7)$$

$$\ddot{y} + \omega_c^2 y = \frac{eE}{m} \cos \omega t, \quad (1.8)$$

$$m\ddot{z} = 0, \quad (1.9)$$

with a general solution in the x and y directions of the form [2]

$$x = \frac{eE}{m(\omega_c^2 - \omega^2)} \cos \omega t + C \cos \omega_c t + D \sin \omega_c t. \quad (1.10)$$

If the frequency of the oscillatory electric field ω is close to the cyclotron frequency ω_c , then the trajectory of a particle initially at rest in the origin is described by

$$x = \frac{eEt}{2m\omega_c} \sin \omega_c t, \quad (1.11)$$

$$y = \frac{eEt}{2m\omega_c} \cos \omega_c t. \quad (1.12)$$

The particle spirals out of the origin at a constant angular frequency ω_c , with the radius of its orbit projected on the x - y plane increasing with time. The resonant absorption of energy from the oscillatory electric field is called cyclotron resonance.

1.1.2 Quantum Mechanical Description

The Hamiltonian for a free particle with mass m is $H = \mathbf{p}^2/2m$, $\mathbf{p} = -i\hbar\nabla$ being the momentum operator. In the presence of a magnetic field the momentum operator is replaced by $(\mathbf{p} - e\mathbf{A})$, $\mathbf{A}$ being the vector potential, $\mathbf{B} = \nabla \times \mathbf{A}$. By choosing the magnetic field in the z -direction (Landau gauge: $\mathbf{B} = (0, 0, B)$, $\mathbf{A} = (0, Bx, 0)$) the Hamiltonian becomes

$$H = \frac{1}{2m}(p_x^2 + (p_y - eBx)^2 + p_z^2), \quad (1.13)$$

p_i being the components of $\mathbf{p}$. Since $[p_y, x] = [p_z, x] = 0$, the components of the momentum commute with the Hamiltonian, $[H, p_y] = [H, p_z] = 0$, and therefore the eigenvalues of the operators p_y and p_z , namely $\hbar k_y$ and $\hbar k_z$, are constants of motion and the Hamiltonian becomes

$$H = \frac{p_x^2}{2m} + \frac{e^2 B^2}{2m} (x_0 - x)^2 + \frac{\hbar^2 k_z^2}{2m}, \quad (1.14)$$

where $x_0 = \hbar k_y / eB$. The first two terms correspond to Hamiltonian for a simple harmonic oscillator (centred at $x_0 = \hbar k_y / eB$ and with force constant $k = e^2 B^2 / 2m$); the energy eigenvalues are therefore given by

$$E(n, k_z) = \left(n + \frac{1}{2}\right) \hbar \omega_c + \frac{\hbar^2 k_z^2}{2m}, \quad (1.15)$$

where $\omega_c = eB/m$ and $n = 0, 1, 2, \dots$. The energy associated with motion parallel to the applied magnetic field is unaffected, whereas the energy associated with motion in the plane perpendicular to the magnetic field is quantized in a ladder of levels, the Landau levels, separated by $\hbar \omega_c$. Transitions between Landau levels can be excited by photons with energy $\hbar \omega_c$ or multiples of it, if their associated electric field is perpendicular to the quasistatic magnetic field [1, 2]. By means of a quantum mechanical description the features of cyclotron resonance obtained via a classical treatment are reproduced.

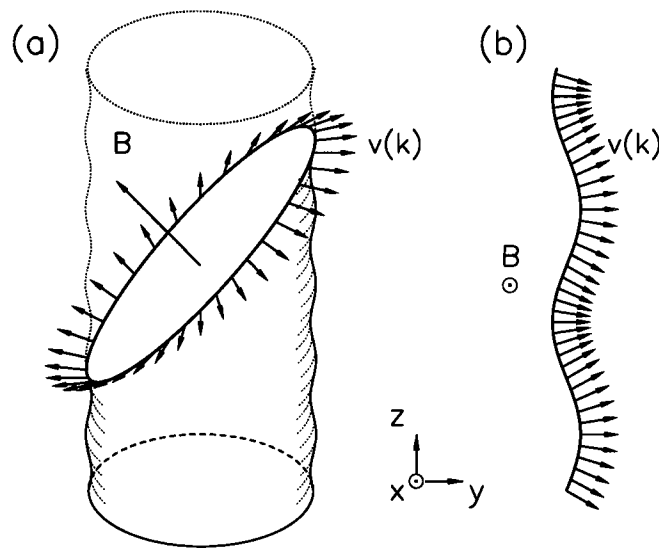


Figure 1.1: Electron orbits in the presence of a quasistatic magnetic field $\mathbf{B}$. a) Around a warped cylindrical Fermi surface. b) Across an open quasi-one-dimensional sheet [3].

1.2 Charge carriers in a crystal

The presence of a periodic potential due to the crystal lattice, and the confinement of the electrons within the finite crystal boundaries have remarkable effects on the dispersion relation of the carriers [1]. The latter is no longer a parabolic function of the electron wavevector $\mathbf{k}$, and the spectrum of allowed energies becomes gapped at certain points in momentum space. The new electron states, called Bloch states [1], have the periodicity of the crystal lattice, and are no longer eigenstates of the momentum operator, so that $\hbar\mathbf{k}$, the crystal momentum, cannot be identified with the real-space momentum of the electron.

The energies of Bloch states are quantized and populated according to Fermi-Dirac distribution [1]

$$f(E) = \frac{1}{e^{((E(\mathbf{k}) - \mu)/k_B T)} + 1}, \quad (1.16)$$

μ being the chemical potential and T the temperature. At zero temperature the Fermi-Dirac distribution is a step function and the filled states define a volume in momentum space enclosed by a surface of constant energy; this surface is called the Fermi surface. If $T \neq 0$, the distribution becomes smeared: electrons with energies within $\sim k_B T$ of the Fermi energy can be thermally excited and can respond to external influences. Even at room temperature this smearing is small and the

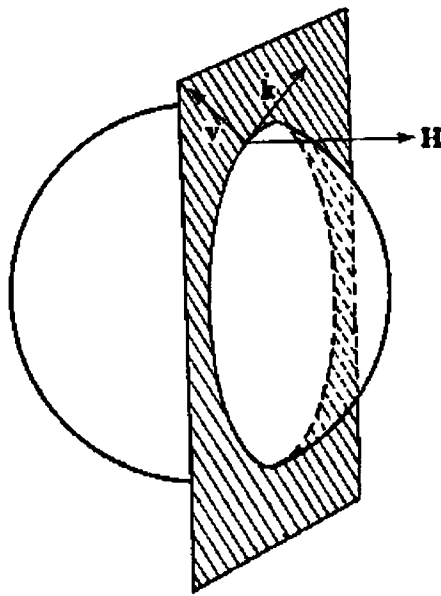


Figure 1.2: Electron orbit on a spherical Fermi surface in an external magnetic field. The intersection of a plane perpendicular to $\mathbf{B}$ with the Fermi surface identifies the orbit in k -space.

Fermi surface maintains its shape (for a typical metal, $E_F/k_B \sim 10^5$ K).

1.2.1 Cyclotron Motion of Electrons in a Metal

Semiclassically, a quasiparticle with charge e in a magnetic field $\mathbf{B}$ experiences the Lorentz force

$$\hbar \dot{\mathbf{k}} = -e(\mathbf{v} \times \mathbf{B}), \quad (1.17)$$

where $\mathbf{k}$ is the crystal momentum. The velocity $\mathbf{v}$ of such a charge carrier (group velocity of its wavepacket) is the gradient of the energy in k -space

$$\hbar \mathbf{v}(\mathbf{k}) = \nabla_{\mathbf{k}} E(\mathbf{k}). \quad (1.18)$$

The component of $\mathbf{k}$ parallel to the magnetic field is unaffected by the Lorentz force. The rate of change of crystal momentum $\mathbf{k}$ is orthogonal to the particle velocity, implying that the motion in k -space follows orbits described by the intersection of a constant energy surface (the Fermi surface) and planes perpendicular to $\mathbf{B}$ (see Figures 1.1 and 1.2).

The k -space orbit is related to the real space orbit by

$$\hbar[\mathbf{k}(t) - \mathbf{k}(0)] = -e[\mathbf{r}(t) - \mathbf{r}(0)] \times \mathbf{B}. \quad (1.19)$$

Thus, the real-space orbit projected on a plane normal to $\mathbf{B}$ has the same shape as the reciprocal space orbit scaled by a factor $eB/\hbar$ and rotated by 90° . The periodic motion of carriers in orbits perpendicular to $\mathbf{B}$ is associated with a characteristic cyclotron frequency

$$\omega_c = \frac{eB}{m_c^*}, \quad (1.20)$$

where the cyclotron mass is defined with respect to the cross-sectional area of the relative k -space closed orbit as [4]

$$m_c^* = \frac{\hbar^2}{2\pi} \frac{\partial A}{\partial E}. \quad (1.21)$$

The effective-mass tensor is often approximated by an isotropic constant effective mass. The previous quantum mechanical analysis of the system shows that the presence of a magnetic field induces a quantisation of the allowed energy states for the motion perpendicular to $\mathbf{B}$ into Landau levels, spaced in energy by $\hbar\omega_c$. In the case of $\mathbf{B}$ taken in the z -direction (Landau gauge), the energy eigenvalues for the Hamiltonian of the system are

$$E(n, k_z) = (n + \frac{1}{2})\hbar\omega_c + \frac{\hbar^2 k_z^2}{2m^*}, n = 0, 1, 2, \dots \quad (1.22)$$

The theory of cyclotron resonance represents the fundamental background for the understanding of its quasi-one-dimensional equivalent presented in Chapter 4, Fermi-surface traversal resonance.

1.2.2 Measurements of Cyclotron Resonance in Metals

Under the influence of an external magnetic field $\mathbf{B}$ electrons move around orbits on the Fermi surface with frequency ω_c given by Equation 1.3. When an oscillatory

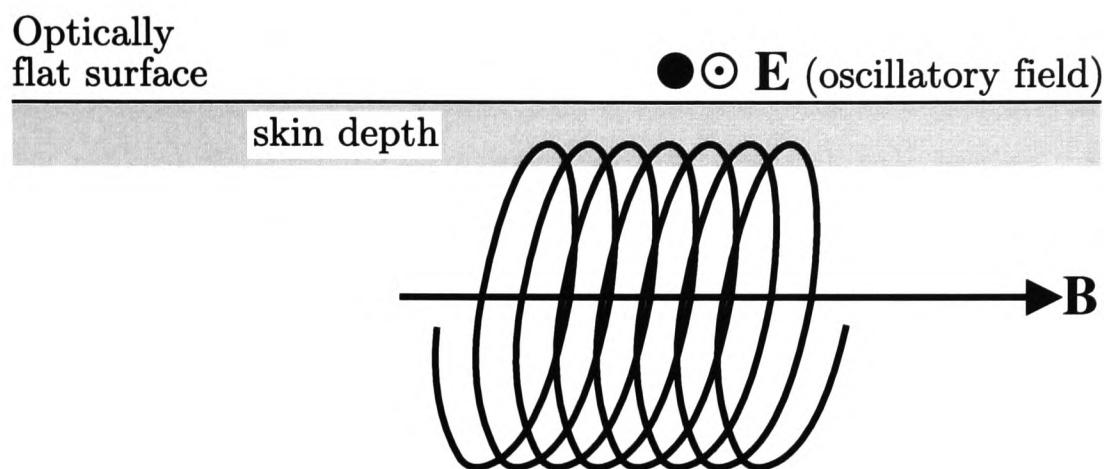


Figure 1.3: The Azbel-Kaner cyclotron resonance geometry [5]. The charge carriers spiral along helical paths in the direction of $\mathbf{B}$ and absorb energy from the oscillatory electric field $\mathbf{E}_{\text{osc}}$, thereby accelerating, only when inside the skin depth of the metal [6].

electric field with angular frequency ω_c is applied perpendicular to $\mathbf{B}$, the electrons can resonantly absorb energy from the electric field, provided that they execute many complete orbits before being scattered;

$$\omega_c \tau \gg 1, \quad (1.23)$$

τ being the scattering time, is the necessary condition for cyclotron resonance to be observed. This resonant behaviour can be observed in the frequency dependent conductivity, $\sigma(\omega)$, of the metal. If the metal has a large conductivity, the penetration of the electromagnetic radiation is confined to the skin depth, screened by the surface currents. The skin depth is defined as the distance in the metal within which the amplitude of the incident wave is attenuated by a factor $1/e$; it is given by:

$$\delta = \frac{1}{\sqrt{\pi \sigma \nu \mu}}, \quad (1.24)$$

where σ is the conductivity of the metal, ν is the frequency of the incident radiation and μ is the relative magnetic permeability [2].

Cyclotron resonance measurements in metals are difficult due to their small skin depth (copper, for example, has a skin depth of about 7×10^{-7} m at a frequency $\nu = 10$ GHz). When both cyclotron radius and mean free path are larger

than the skin depth, the Azbel-Kaner configuration (shown in Figure 1.3) may be implemented [5, 7]. If $\mathbf{B}$ is parallel to the metal surface, the electrons moving along helical paths will periodically penetrate into the skin depth region. Here they will absorb the incident radiation and will be accelerated by its oscillatory electric field. A maximum in absorption will occur when the frequency of the impinging radiation, ω , is a multiple of the cyclotron frequency. Experiments are usually performed by keeping fixed the radiation frequency and sweeping the magnetic field; resonant absorptions will occur at

$$B_c = \frac{\omega m_{\text{cr}}}{ne}, \quad (1.25)$$

where n is an integer.

Magneto-Optical Conductivity Measurements in Anisotropic Metals

Low dimensional metallic systems, such as the organic charge transfer salts, have interlayer conductivities that are much smaller than the in-plane conductivity. Correspondingly, the interlayer skin depth can be as large as the sample dimensions ($\approx 0.1\text{mm}$), thus taking us into the metallic side of the depolarisation regime [8]. This allows the bulk magneto-optical conductivity to be measured in these systems for frequencies as high as 100 GHz.

The Boltzmann transport equation justifies the interpretation of the resonant features presented in Chapter 4. The modulations of the high-frequency conductivity $\sigma(\omega)$ are ascribed to the resonant behaviour of carriers within the quasi-one-dimensional sections of the Fermi surface: the periodic oscillations of their real-space velocities on the corrugated Fermi sheets gives rise to Fermi-surface traversal resonances, FTRs [9, 10].

1.3 The High-Frequency Boltzmann Transport Equation

For a carrier with charge q , velocity $\mathbf{v}$ and wavevector $\mathbf{k}$ in an applied magnetic field $\mathbf{B}$, the Lorentz force is given by $\hbar\dot{\mathbf{k}} = q\mathbf{v} \times \mathbf{B}$ [1]. The velocity of the carrier is defined by the gradient of the energy in k -space [1]:

$$\hbar\mathbf{v}(\mathbf{k}) = \nabla_{\mathbf{k}}E(\mathbf{k}). \quad (1.26)$$

The real-space velocity is therefore always normal to the Fermi surface. The time evolution of its direction and magnitude depend on the shape of the Fermi surface and the direction of the applied field. It is the charge carriers with energies close to the Fermi surface that are responsible for the electrical conductivity in a metal [1]; the way their real space velocities evolve in the presence of an applied magnetic field therefore has an effect on the conductivity of the material.

The way in which the time evolution of the real space velocity of a carrier, $\mathbf{v}(\mathbf{k}, t)$, contributes to the high-frequency conductivity of a metal [1] is expressed by the frequency-dependent Boltzmann transport equation [1, 6]:

$$\sigma_{ij}(\omega) = \frac{e^2}{4\pi^3} \int d^3k \left[-\frac{\partial f_0(\mathbf{k})}{\partial E(\mathbf{k})} \right] v_i(\mathbf{k}, 0) \times \int_{-\infty}^0 v_j(\mathbf{k}, t) \cos(\omega t) e^{\frac{t}{\tau}} dt, \quad (1.27)$$

where τ is the relaxation time, $v_i(\mathbf{k}, t)$ is the i -th component of the velocity of a carrier with wavevector $\mathbf{k}$ at time t , $f_0(\mathbf{k}) = (e^{[E(\mathbf{k})-E_F]/k_B T} + 1)^{-1}$ is the Fermi-Dirac function and $E(\mathbf{k})$ is the energy of the carrier. Boltzmann equation correlates the velocity of a carrier at time zero with its velocity at time t weighted by the scattering probability, and sums the velocity contributions of all the carriers occupying states near the Fermi energy [1, 6]. A velocity $v_i(\mathbf{k}, t)$ can contribute resonantly to the a.c. conductivity; this can be understood with the aid of Figure 1.4: so long as the time variation of the velocity obeys the condition $(\omega - \omega_c) \ll 1/\tau$, its contribution to the time integral in Equation 1.27 will be very large. If on the

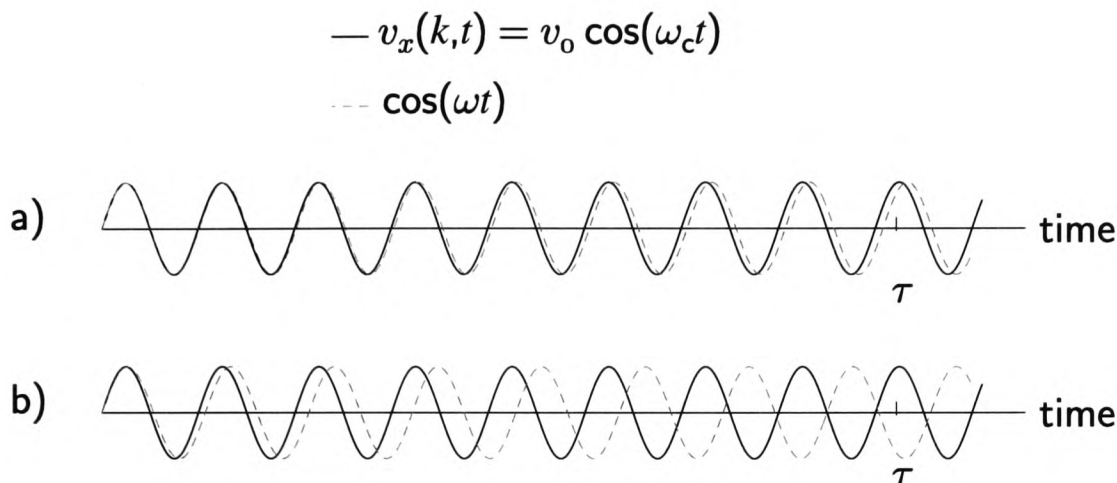


Figure 1.4: Time evolution of $v_x(\mathbf{k}, t)$ and $v_x(\mathbf{k}, 0) \cos(\omega t)$ for (a) a small frequency difference $((\omega - \omega_c)\tau = 0.25)$ and (b) a large frequency difference $((\omega - \omega_c)\tau = 1.7)$. From Reference [6].

other hand the frequency difference is large, then the velocity makes little or no contribution to $\sigma_{ii}(\omega)$.

1.4 Magnetic Quantum Oscillations

The high magnetic field region of the data displayed in Chapter 4 show an oscillatory behavior of the conductivity. This phenomenon, the equivalent of the Shubnikov-de Haas oscillations at high frequencies, can be explained in the following way. The presence of a well defined resonance frequency leads one (via the correspondence principle) to expect the existence of a set of quantum mechanical energy levels (Landau levels) spaced in energy by $\hbar\omega_c$ [1, 11], i.e.

$$E(l + 1, B, k_{\parallel}) - E(l, B, k_{\parallel}) = \frac{\hbar e B}{m_{\text{cr}}^*} = \hbar\omega_c; \quad (1.28)$$

here l is an integer quantum number identifying the Landau level and $k_{\parallel}$ is the component of the electron wave vector parallel to $\mathbf{B}$. Equation 1.28 can be rewritten

ten as

$$(E(l+1, B, k_{\parallel}) - E(l, B, k_{\parallel})) \frac{\partial A(E)}{\partial E} = \frac{2\pi e B}{\hbar}. \quad (1.29)$$

When the energy difference between adjacent levels - $\hbar\omega_c$ - is small compared to the energies of the levels themselves ($\sim \mu$) the following approximation can be made:

$$\frac{\partial A}{\partial E} \approx \frac{A(E(l+1, B, k_{\parallel})) - A(E(l, B, k_{\parallel}))}{E(l+1, B, k_{\parallel}) - E(l, B, k_{\parallel})}. \quad (1.30)$$

Equation 1.29 then becomes

$$A(E(l+1, B, k_{\parallel})) - A(E(l, B, k_{\parallel})) = \Delta A = \frac{2\pi e B}{\hbar}. \quad (1.31)$$

This expression states that the difference in the k -space areas enclosed by two adjacent Landau levels having the same $k_{\parallel}$, is always ΔA , with

$$\Delta A = \frac{2\pi e B}{\hbar}. \quad (1.32)$$

The area enclosed by an allowed orbit is therefore given by [1, 11]

$$A(E(l+1, B, k_{\parallel})) = (l + \zeta)\Delta A = (l + \zeta)\frac{2\pi e B}{\hbar}, \quad (1.33)$$

for $l \gg 1$, where ζ is a constant ($\zeta = \frac{1}{2}$ for a parabolic band [11]).

The allowed k -space orbits are represented by the “Landau tubes”, and consequently the energy dispersion is not continuous; Figure 1.5 [12] shows the occupied states lying on Landau tubes. The k -space area enclosed by each tube increases as the magnetic field increases, the tubes gradually acquiring energies higher than the Fermi energy. A discontinuous change in the occupancy of a tube occurs as it passes through an extremal section of Fermi surface, i.e. each time

$$(l + \zeta)\frac{2\pi e B}{\hbar} = A(E_F), \quad (1.34)$$

where E_F is the Fermi. This leads to oscillations in the free energy and in the

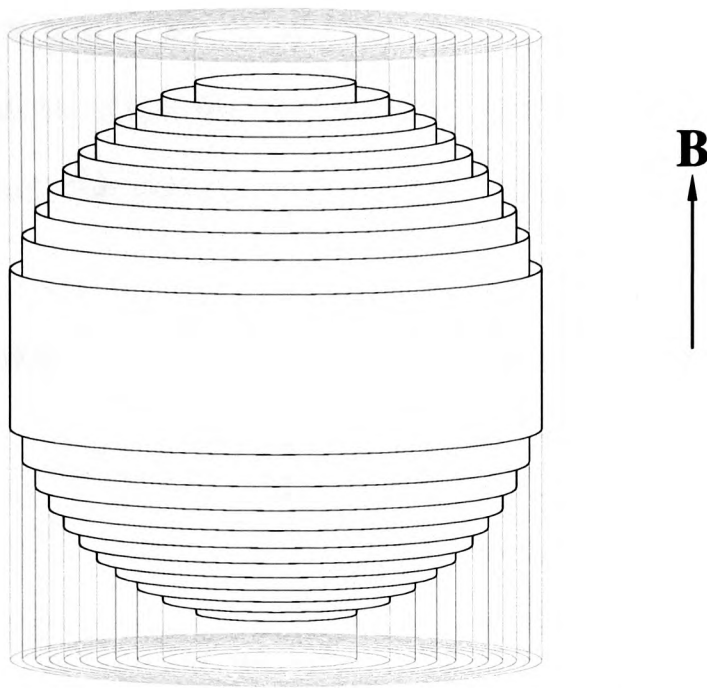


Figure 1.5: In the presence of a magnetic field $\mathbf{B}$, a spherical Fermi surface becomes quantized. The tubes represent the allowed states, the solid lines indicate the filled states [12].

density of states at the Fermi surface [11], inducing the oscillatory behaviour of magnetoresistance (the Shubnikov-de Haas effect) and the magnetization (the de Haas-van Alphen effect) [11]. These oscillations are periodic in $1/B$ with a frequency given by

$$F = \frac{\hbar}{2\pi e} A_{\text{ext}}, \quad (1.35)$$

where A_{ext} is the k -space area of the extremal orbit. The angle dependence of magnetic quantum oscillations can provide detailed information on the number and shape of such extremal orbits.

1.5 Effective Mass Renormalization

The concept of quasiparticle was introduced by Landau to model fermionic systems where many-body interactions play a significant role [1]. These interactions can be accounted for by assuming the charge carriers to possess a mass that differs from their “bare” mass; different experimental techniques are sensitive to different interactions and this gives rise to a number of effective masses. For example, the effective mass obtained from de Haas-Van Alphen/Shubnikov-de Haas exper-

iments differs from the mass that cyclotron resonance in optical measurements provides. Information on the relative strength of the many-body interactions is extracted from the comparison of different masses.

1.5.1 Bare Band Mass and Fermi Liquid Theory

Single-particle band structure calculations provide what is known as the bare band mass m_b of the charge carriers [1]. In the presence of the crystal potential, the free particle dispersion relation is modified and response of an electron to an external force is in general $\mathbf{k}$ dependent and anisotropic, leading to the definition of an effective mass tensor [1]

$$\left(\frac{1}{m_b}\right)_{ij} = \frac{1}{\hbar^2} \frac{d^2 E(\mathbf{k})}{dk_i dk_j}. \quad (1.36)$$

From the dispersion relation, $E(\mathbf{k})$, a scalar, orbitally averaged mass can be extracted. Simple bandstructure calculations ignore the interactions the charge carriers are subject to, both those with the lattice (electron-phonon interactions) and with each other (electron-electron interactions).

Landau Fermi Liquid theory models the electron-electron and electron-phonon interactions by an effective mass enhancement [1]. The new eigenstates of the system are no longer the single-particle states but “quasiparticle” states [1]; near the Fermi energy, the system of interacting fermions behaves like a system of non-interacting fermionic “quasiparticles” with an enhanced mass.

1.5.2 Dynamical Effective Mass

Cyclotron resonance experiments measure the dynamical mass m_λ , which is renormalised by the electron-phonon interactions [13]. In a translationally-invariant system long wavelength perturbations excite only center of mass motion of the electrons [14]. When using long wavelength radiation the oscillating electric field may be treated as varying only with time and all the electrons oscillate in phase with the radiation, i.e. the radiation couples to the center of mass of the system

rather than to individual electrons. This coupling of the radiation to the centre of mass motion is insensitive to interactions between the electrons, since the electrons remain stationary with respect to each other (in a translationally invariant system [14, 6]).

The relationship between the dynamical mass and the bare mass for relatively weak interactions is given by [15]

$$m_\lambda = (1 + \lambda)m_b, \quad (1.37)$$

where λ is the electron-phonon coupling constant. A simple physical argument can provide an intuitive picture of the mass enhancement due to electron-phonon interactions. An electron moving through a solid will induce a local distortion of the crystal lattice thus creating a strain field (virtual phonons) in its vicinity, due to its Coulomb interaction with the positive ions. This in turn affects the motion of the electrons and acts to increase their apparent mass.

1.5.3 Effective Mass

The (thermodynamic) effective mass m_{LK}^* obtained from the measurement of the temperature dependence of Shubnikov-de Haas and de Haas-van Alphen oscillations [11, 16] is renormalised by both electron-phonon and electron-electron interactions [17, 18].

An electron travelling through a metal displaces other electrons because of their mutual Coulomb repulsion; its motion is therefore accompanied by a “cloud” of other electrons. The effect of such interaction is therefore to cause the electrons to have an effective mass heavier than the dynamical mass. The two masses are related by [13, 17]

$$m_{LK}^* = (1 + \frac{F_S^1}{3})m_\lambda, \quad (1.38)$$

where F_S^1 is the $l = 1$ Fermi Liquid parameter.

The relative strength of electron-electron and/or electron-phonon interactions

can be extracted from comparing bare band mass, cyclotron mass, and effective mass.

1.6 The magnetic resonance phenomenon

This section will present the fundamental principles governing resonant phenomena in a magnetic field for systems possessing magnetic dipole moments. This subject is treated in detail in references [2, 19, 20].

A charged particle orbiting around an ion with angular momentum $\mathbf{L}$ will have an associated magnetic dipole moment $\boldsymbol{\mu} = \gamma\mathbf{L}$; in the presence of a quasistatic magnetic field $\mathbf{B}$ such a dipole will precess with frequency $\omega_L = -\gamma B$, the Larmor frequency. Here γ is the so-called gyromagnetic ratio ($\gamma = -\frac{e}{2m}$ for a free electron, $-e$ and m being charge and mass of the electron respectively). The precessing dipole produces an oscillatory magnetic moment in the plane normal to $\mathbf{B}$ which can interact with an oscillatory transverse electromagnetic field of frequency ω_L . The resonant absorption of radiation of frequency ω_L due to the precessing dipole is called electron paramagnetic resonance (EPR). In a simple quantum-mechanical picture, this resonance can be viewed as a transition between the discrete energy levels representing the eigenstates of the total angular momentum operator $\mathbf{J}$. Consider a free atom or ion with a total angular momentum in its electron system due to orbital motion and spin:

$$\mathbf{J} = \mathbf{L} + \mathbf{S}. \quad (1.39)$$

This vector sum of $\mathbf{L}$ and $\mathbf{S}$, each of them being in turn the sum of the orbital and spin angular momenta of all the electrons in the ion, is an appropriate expression in the L-S or Russell-Saunders regime, where the spin-orbit coupling is a weak perturbation with respect to the other relevant energy terms in the Hamiltonian [19, 3]. The magnetic moment of the ion can be written as $\boldsymbol{\mu}_J = -g_J\mu_B\mathbf{J}$, $\mu_B = \frac{e\hbar}{2m}$ being the Bohr magneton and g_J the spectroscopic splitting or Landé

g-factor. The g-factor contains information on the relative contributions of orbit and spin to the total angular momentum. The Zeeman interaction between the magnetic dipole and an external field $\mathbf{B}$ is represented by the Hamiltonian term

$$H_{Zee} = -(\boldsymbol{\mu}_J \cdot \mathbf{B}) = g_J \mu_B (\mathbf{B} \cdot \mathbf{J}). \quad (1.40)$$

This is valid in the case of a group of $(2J + 1)$ levels, degenerate in the absence of an applied field and well separated from other levels [19]. Within such a Zeeman multiplet, a state with magnetic quantum number M , corresponding to a component $M\hbar$ of angular momentum in the direction of the applied field $\mathbf{B}$, has energy $E_M = g_J \mu_B M B$. The frequency of an absorbed or emitted photon in a transition between two states of the multiplet is given by

$$E_i - E_k = \Delta E_{ik} = \hbar \omega_{ik} = g_J \mu_B \Delta M_{ik} B, \quad (1.41)$$

where ΔM_{ik} is the difference of the magnetic quantum numbers of states i and k in the multiplet. The selection rule for magnetic dipole transitions defines the allowed transitions as those with $\Delta M_{ik} = \pm 1$. An oscillatory transverse field will therefore induce a resonant transition between two levels if its frequency ω_{res} is such that [19]:

$$\hbar \omega_{\text{res}} = g_J \mu_B B. \quad (1.42)$$

The experiments described in this thesis are performed by sweeping magnetic field B at a fixed frequency ω ; a resonance (EPR) occurs when $B_{\text{res}} = \hbar \omega / g_J \mu_B$.

In solid state systems, ions are embedded in spatially periodic arrays. If the ions have closed electron shells, no resultant angular momentum and therefore no permanent magnetic dipole moment is present. The type of compounds presented in Chapter 3 of this thesis contain ionic complexes with elements of the $3d$ group; these have partly filled shells: the ions that form the crystalline structure possess a magnetic moment because of their unpaired electrons. The starting assumption

(here and in Section 3.3.1 of Chapter 3) in the search for a suitable Hamiltonian to model the system will be that each localized magnetic dipole is substantially unaffected by the presence of the neighbouring permanent dipoles (diluted paramagnetic substance). The inadequacy of this simplification will then require the inclusion of possible additional interactions in the picture (Section 3.4). The paramagnetic ions are nonetheless affected by the presence of the surrounding “cage” of diamagnetic ions which produce a strong electrostatic field (the ligand field). The crystal-field method in the modelling of such a complex system considers the ligand ions as isolated charges giving rise to an electrostatic potential in which the localised magnetic electrons move [19]. The effect of this ligand field for ions of the $3d$ group is very strong, inducing a total or partial quenching of the orbital angular momentum [19, 3], thereby reducing the role played by the spin-orbit coupling term in the Hamiltonian of the system to that of a small perturbation. The crystal field potential is therefore responsible for the splitting in zero applied magnetic field of the energy levels of the paramagnetic complex, and its symmetry determines the final configuration and degeneracy of states. For example, a local cubic symmetry will induce groups of 1, 2, 3 or 4 degenerate levels; in cases of lower symmetry levels could then be singlets or doublets [19]. An important general theorem due to Kramer applies here. The theorem states that in a system with an odd number of electrons, at least twofold degeneracy will remain if no magnetic field is applied. Such pairs of states, called Kramers doublets, have one state as the time conjugate of the other and can be split by an applied magnetic field (a time-odd operator) but not by perturbations that are even under time reversal, such as an electrostatic field [19]. The ground state multiplet under investigation can then often be conveniently modelled by introducing the concept of an effective spin [19], a fictitious angular momentum whose value and multiplicity yields an adequate description of the experimental spectra. This concept will be successfully applied throughout Chapter 3, where the spin vector $\mathbf{S}$ will always represent an effective spin. There, the concept of an effective spin Hamiltonian

will be particularly useful because of the possibility of its theoretical justification: the knowledge of the local symmetry of the complex will impose restrictions on the form of the Hamiltonian, so that it reflects the same symmetry, thus making its identification a viable task [19].

A general Hamiltonian describing the energy of a paramagnetic crystal in a quasistatic magnetic field $\mathbf{B}$ is the following [21]:

$$H = H_{\text{el}} + H_{\text{cf}} + H_{\text{so}} + H_{\text{zfs}} + H_{\text{Zee}} + H_{\text{hfs}} + H_{\text{Q}} + H_{\text{N}}. \quad (1.43)$$

The first two terms, H_{el} and H_{cf} , electronic energy of the paramagnetic ion in the free state, and the crystal field energy, the interaction energy of the free ion's electronic structure with the crystal's electric field, are in the optical and infrared region of the spectrum ($\approx 10^2 \text{ cm}^{-1} - 10^4 \text{ cm}^{-1}$), and will not be relevant to the experiments presented here. Similarly, the terms of much lower energy involving nuclear spins, namely the hyperfine structure term, H_{hfs} , coupling unpaired electrons to nuclear spins (with energies $\approx 10 \text{ cm}^{-1}$), the nuclear quadrupole and nuclear Zeeman energies, H_{Q} and H_{N} ($\approx 10^{-2} \text{ cm}^{-1}$), will effectively play no role in the description and interpretation of the results presented here. The Zeeman energy previously described, once extended to its more general tensor form which accounts for the presence of the crystalline structure surrounding the ion, and the fine structure zero-field splitting energy, are the relevant leading order terms for the description of the response of the $\beta''\text{-(BEDT-TTF)}_4[(\text{H}_3\text{O})\text{M}(\text{C}_2\text{O}_4)_3]\text{S}$ systems to the energy range of our probing millimetre-wave radiation.

The main aim of Section 3.3 of Chapter 3 will therefore be the identification of the terms in the following effective spin Hamiltonian:

$$H = H_{\text{Zee}} + H_{\text{zfs}}, \quad (1.44)$$

the Zeeman term, which, due to the quenching of orbital angular momentum ($\mathbf{L} = 0$, $\mathbf{J} = \mathbf{S}$), will be expressed as $H_{\text{Zee}} = \mu\mathbf{B} \cdot \mathbf{g} \cdot \mathbf{S}$, and the zero-field splitting

or “fine structure” term, H_{zfs} , which will depend essentially on site symmetry (electrostatic ligand-field contribution) and on the separation of electrons with equal spin orientation within the same ion (magnetic dipolar contribution) [19, 20]. The possible presence of additional spin-spin interactions of dipolar, exchange or superexchange type will be discussed in Section 3.4 of Chapter 3.

Chapter 2

The Experimental Technique

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2.1 Introduction

This Chapter outlines the experimental techniques used in the investigation of the millimetre-wave magneto-optical properties of low-dimensional charge-transfer salts. The broad frequency tunability of sources and detectors combined with a set of cylindrical and rectangular resonators have made it possible to measure electron spin resonance (Chapter 3) and bulk conductivity (Chapters 4 and 5) in anisotropic metallic systems over the range of frequencies from 50 to 313 GHz. Apart from a small set of measurements performed using a Gunn diode as source and a He-cooled silicon bolometer as detector, all magneto-optical studies described in the following Chapters use the millimetre-wave vector network analyser (MVNA) [22] as the source and heterodyne detector of GHz radiation. Section 2.2 outlines the basic principles of operation of the MVNA and Section 2.3 describes the propagation of electromagnetic radiation in rectangular waveguides. Resonators were used to study the millimetre-wave properties of samples as a function of magnetic field, temperature, frequency and orientation; Section 2.4 describes measurements performed on small samples using the cavity perturbation technique. Instruments enabling the rotation of the sample with respect to the quasistatic magnetic field were used to investigate the angle dependence of the various resonant phenomena: electron spin resonance in the β'' -(BEDT-TTF)₄[Fe(C₂O₄)₃]S compounds (Chapter 3), Fermi-surface traversal resonance and Josephson plasma resonance in κ -(BEDT-TTF)₂Cu(NCS)₂ (Chapter 4). Section 2.5 describes the insert used to measure the highly anisotropic properties of the samples investigated as a function of angle between the applied magnetic field and the principal axes of the relevant tensors. Finally, developments of novel dielectric and hybrid metal-dielectric resonators for implementation at high frequencies (above 100 GHz) and in pulsed magnetic fields are presented in the Section 2.6.

2.2 The Millimetre-wave Vector Network Analyser (MVNA)

The millimetre-wave vector network analyser (MVNA) [22] is a continuously tunable source and heterodyne detector of electromagnetic radiation in the frequency range 8-350 GHz. Gunn diode oscillators [23] can be used together with the MVNA as external sources of GHz radiation to allow measurements at multiples of the fundamental Gunn frequency of approximately 95 GHz. These external sources can be used in the range from 190 to 350 GHz and over a series of narrow frequency bands up to 800 GHz. The frequency range 8-800 GHz corresponds to energies from 0.03 meV to 3 meV, or temperatures from 0.4 K to 40 K (see Figure 2.13 at the end of this Chapter for a convenient energy conversion chart). The possibility of investigating several phenomena of fundamental interest in condensed-matter physics such as cyclotron resonance, electron spin resonance, (anti)ferromagnetic resonance, interband absorption in systems with narrow band gaps, as well as the optical response in the above-mentioned frequency range across phase transitions in, for example, strongly correlated systems, is therefore readily provided by the MVNA, making it a powerful and flexible scientific tool.

2.2.1 The basic principle of operation

Figure 2.1 shows a schematic diagram of the MVNA. It features two yttrium-iron-garnet (YIG) oscillators which are continuously tunable from 8 to 18 GHz (centimetre sources) [24]. In this figure, S_1 and S_2 represent the master and the slave YIG oscillators respectively. The two YIG oscillators are phase locked so that the slave YIG oscillates according to the frequency of the master YIG: the master is set at a frequency (F_{GHz}) chosen by the user and the slave oscillates at an offset frequency ($F_{\text{GHz}} - F_{\text{MHz}}$) where the difference frequency F_{MHz} is computer controlled through a programmable synthesizer. The master YIG sends an oscillating current of chosen frequency (F_{GHz}) along a coaxial cable to a Schottky

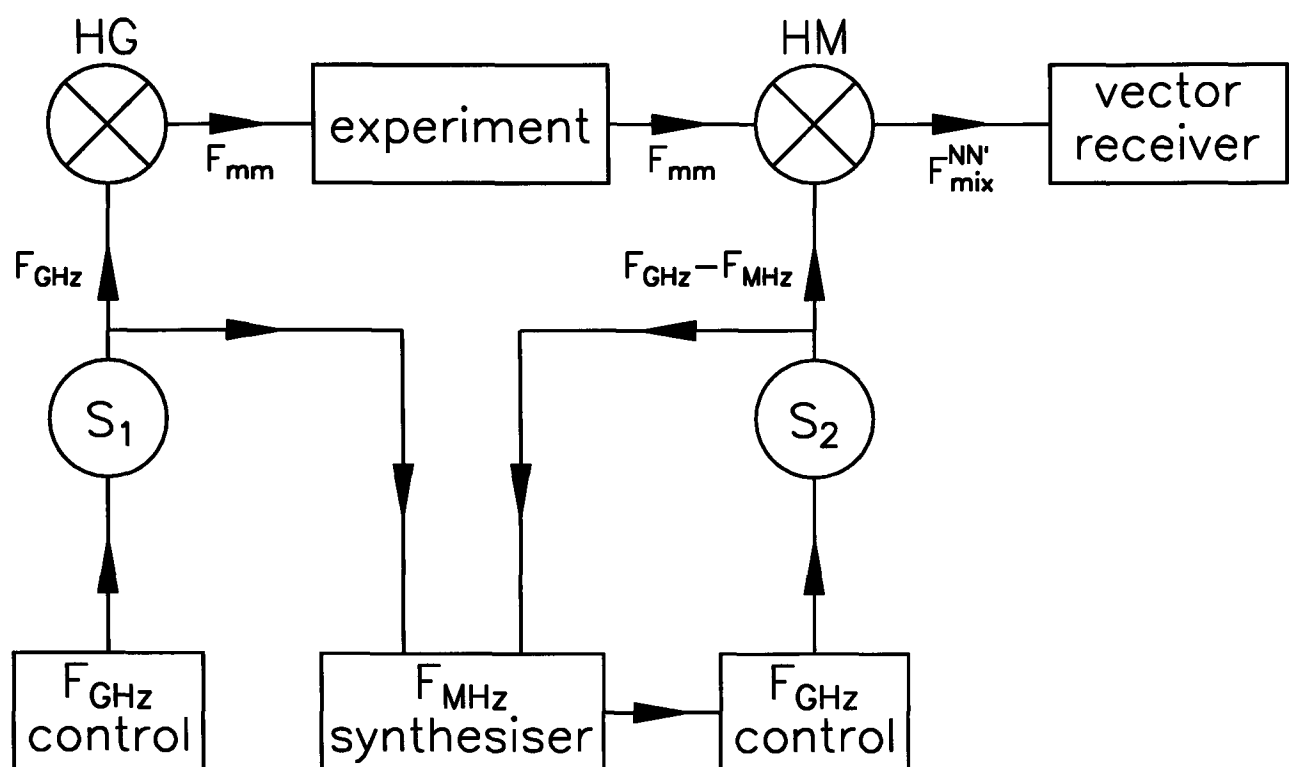


Figure 2.1: A diagram illustrating the principle of operation of the MVNA [22].

diode [23], called the Harmonic Generator (HG). The HG in turn emits the electromagnetic radiation that is guided to interact with the sample. The HG is a non-linear current-voltage device: it is driven by a voltage oscillating sinusoidally at the frequency F_{GHz} and the current through it is made up of a range of Fourier components. It therefore radiates electromagnetic waves at all frequencies that are multiples of F_{GHz} ; a comb of millimetre-wave frequencies (the harmonics) is generated:

$$F_{\text{mm}} = NF_{\text{GHz}}, \quad (2.1)$$

where $N = 1, 2, 3, \dots$

The slave YIG in turn sends an oscillating current at the offset frequency of $F_{\text{GHz}} - F_{\text{MHz}}$ to a second Schottky diode called the Harmonic Mixer (HM). The harmonics $N' \times (F_{\text{GHz}} - F_{\text{MHz}})$, $N = 1, 2, 3, \dots$ are generated by the voltage from the slave YIG and at the mixer they are mixed with the millimetre-wave signal (F_{mm}) received from the experiment to give a comb of difference frequencies

$$F_{\text{mix}}^{NN'} = NF_{\text{GHz}} - N'(F_{\text{GHz}} - F_{\text{MHz}}) = (N - N')F_{\text{GHz}} + N'F_{\text{MHz}}. \quad (2.2)$$

The amplitude of the signal at the frequency $F_{\text{mix}}^{NN'}$ is proportional to the amplitude of the millimetre-wave signal F_{mm} arriving at the mixer; its phase is given by

$$\phi_{\text{mix}}^{NN'} = N\phi_1 + \delta\phi_N - N'\phi_2, \quad (2.3)$$

where ϕ_1 and ϕ_2 are the phases of the master and slave YIGs respectively, and $\delta\phi_N$ is the phase shift due to the experiment. The subset of difference frequencies for which $N = N'$ is in the MHz range: $F_{\text{mix}}^{NN'} = N'F_{\text{MHz}} = NF_{\text{MHz}}$, the rest being GHz frequencies. As the two sources, S_1 and S_2 , are phase locked, the phase of the detected signal is $\phi_{\text{mix}}^{NN'} = N(\phi_1 - \phi_2) + \delta\phi_N = \delta\phi_N$. In the Vector Receiver (“radio”) of the MVNA, F_{mix} is stepped down by mixing with signals from programmable synthesizers that are synchronized with the F_{MHz} synthesizer. The receiver is optimized to work at either of two frequencies: $NF_{\text{MHz}} = 9.010488$ MHz, used for $N \leq 3$ or 34.010488 MHz, for $N > 3$; the choice of harmonic used therefore determines the difference frequency F_{MHz} : $F_{\text{MHz}} = 9.010488/N$ MHz for $N \leq 3$ or 34.010488/ N MHz for $N > 3$. Control software automatically calculates the appropriate difference frequency and programs the synthesizers. By modifying the difference frequency F_{MHz} for each chosen harmonic, the synthesizer allows the changes in amplitude and phase at the experiment (occurring at the frequency F_{mm}) to be preserved and detected either at 9.010488 MHz or at 34.010488 MHz. The presence of sidebands at the vector receiver due to the comb of harmonics results in noise and jitter in the detected signal. This is eliminated by using a narrow bandpass filter and its associated amplifier. The filter lowers the noise floor by 9 dB, but increases the sensitivity of the device to temperature drifts and reduces slightly its otherwise extreme amplitude linearity (MVNA reference

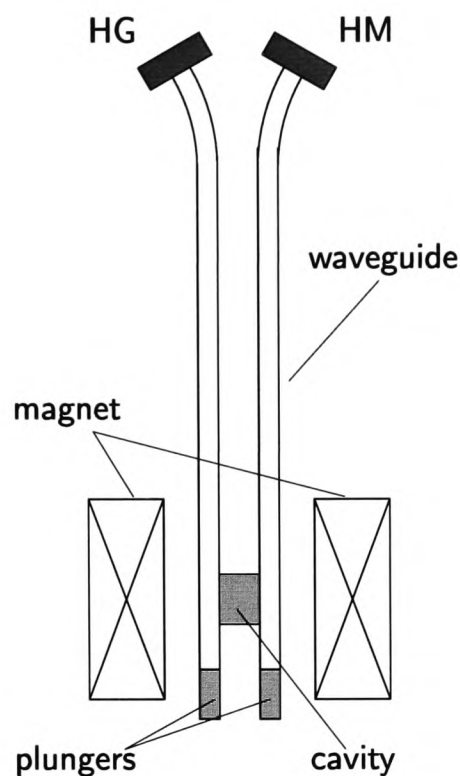


Figure 2.2: A schematic of the cavity transmission insert showing Schottky diodes, waveguides, plungers, and the resonator positioned inside a magnet bore, in the field centre [25].

manual [22]). The signal is finally downconverted to 488 Hz and digitally analyzed by the computer; at this stage the amplitude and phase can be measured by means of a lock-in amplifier or an oscilloscope.

2.2.2 MVNA measurements in high magnetic fields

The experiments described in this thesis all involved the measurement of the response of samples to GHz radiation as a function of temperature and magnetic field. Experiments up to 15 T were performed at the Clarendon Laboratory in Oxford using two superconducting magnets provided by Oxford Instruments and Cryogenic Ltd. Experiments involving stronger magnetic fields were carried out at the National High Magnetic Field Laboratory in Tallahassee, Florida, where resistive (Bitter) magnets are used to supply magnetic fields up to 33 T.

In a typical setup, co-axial cables of length 3-5m are used to connect the MVNA to the HG and HM Schottky diodes so that the Vector Analyzer and computer can be placed far enough from the magnet to prevent the stray magnetic field to inter-

ferre with the software and electronics. The Schottky diodes are connected directly onto two flanges at the top end of the insert which carries the millimetre-wave signal to the sample placed in the field centre of a magnet (see diagram of Figure 2.2). Alternatively, the diodes can be replaced by similar non-linear devices, the ESA Gunn extensions, capable of generating and detecting sets of harmonics at much higher frequencies, allowing access to frequencies up to 800 GHz (ESR resonances recorded at 313 GHz are shown in Chapter 3). Several millimetre-wave inserts are available in Oxford to perform experiments in reflection, simple waveguide transmission and the more sensitive technique of transmission through a resonator. The inserts are built using two pieces of rectangular waveguide about 1.5 m long: one to guide the radiation from the HG down to the field centre of the magnet where the sample sits, the other to take the radiation back to the mixer HM after it has interacted with the sample. Figure 2.2 shows a schematic of an insert with a cavity resonator positioned inside a magnet bore. The waveguides are V-band WG25 thin walled stainless steel (inner dimensions $1.88 \times 3.76 \text{ mm}^2$) with a cut-off frequency at 40 GHz.

Copper and silver waveguides present a much lower attenuation of the guided millimetre-wave radiation than stainless steel does, being much more conducting (and therefore more reflecting). Nonetheless, the desire to carry out experiments at very low temperatures makes steel the preferred material, despite introducing a large signal loss (attenuation of 14 dB per metre). Stainless steel in fact has a low thermal conductivity ($\kappa \approx 30 \text{ Wm}^{-1}\text{K}^{-1}$ [26] at room temperature) compared to that of copper or silver ($\kappa \approx 710 \text{ Wm}^{-1}\text{K}^{-1}$ at room temperature [26]); the consumption of liquid helium during an experiment is greatly reduced and the slower evaporation of helium makes the experiment much more efficient. Additionally, the phenomenon of standing waves within the waveguide which is cause of disturbing complicated backgrounds in the transmitted signal is strongly suppressed by the use of stainless steel, and the reduced space occupied by the thin walled structures is a further advantage due to the small diameter of high field

magnet bores. One disadvantage in the use of stainless steel is the presence of an ESR resonant signal of large intensity ($\sim 15\%$ of the transmitted radiation) at the free electron g -value ($g \approx 2$); this is usually not a problem for high field experiments, but it is for low field experiments, and has been solved by replacing the bottom section of the insert, the part that enters the magnet bore, with an equivalent section made of copper. The stainless steel structure is equipped with a low temperature thermometer (RuO_2) placed as close to the sample as possible and in good thermal contact with it, and a heater usually made of constantan wire. The insert fits into a metal sheath or “jacket” which can possess an evacuated chamber in its lowermost part if ^3He is used to achieve temperatures as low as 400 mK.

2.3 Wave propagation in metallic guides

Consider a monochromatic plane wave travelling in the z direction; its electric and magnetic fields are given by

$$\mathbf{E} = \mathbf{E}_0(z)e^{i(k_z z - \omega t)} \quad \mathbf{B} = \mathbf{B}_0(z)e^{i(k_z z - \omega t)}, \quad (2.4)$$

$\mathbf{E}_0(z)$ and $\mathbf{B}_0(z)$ being constant, mutually perpendicular vectors with zero z -component. By using Maxwell's equations in vacuum [2]

$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t} \quad \nabla \cdot \mathbf{E} = 0 \quad (2.5)$$

$$\nabla \times \mathbf{B} = \frac{1}{c^2} \frac{\partial \mathbf{E}}{\partial t} \quad \nabla \cdot \mathbf{B} = 0, \quad (2.6)$$

and the following boundary conditions appropriate in the assumption of perfectly conducting waveguide walls:

$$E_{\parallel} = 0, \quad (2.7)$$

$$B_{\perp} = 0, \quad (2.8)$$

the field distribution inside the waveguide can be derived. Only specific modes are allowed to propagate in the z direction; in the case of a rectangular waveguide [2, 21]:

- Transverse Electric (TE) waves with $E_z = 0$ and $B_z \neq 0$,
- Transverse Magnetic (TM) waves with $E_z \neq 0$ and $B_z = 0$.

The solutions are standing waves having an integer number of half wavelengths in the x - and y -directions between the waveguide walls. For a waveguide with transverse dimensions a and b in the x - and y -directions respectively, the allowed wavevectors can take the quantized values $k_x = m\pi/a$, $k_y = n\pi/b$ where m, n are integer numbers. The modes are therefore labelled TE_{mn} and TM_{mn} , according to the number of half-wavelengths they possess in the two orthogonal transverse directions [21]. The total wavevector of the radiation travelling in the z -direction with wave number $k_z = \kappa$ is

$$\mathbf{k} = \left(\frac{\pi m}{a}, \frac{\pi n}{b}, \kappa \right), \quad (2.9)$$

and its frequency if propagating in vacuum is [2]

$$\omega = c|\mathbf{k}| = c\sqrt{\kappa^2 + \pi^2(m/a)^2 + \pi^2(n/b)^2}. \quad (2.10)$$

The z -component of the wavevector is related to the radiation frequency by

$$\kappa = \frac{1}{c}\sqrt{\omega^2 - \omega_{mn}^2}, \quad (2.11)$$

$\omega_{mn} = c\pi\sqrt{(m/a)^2 + (n/b)^2}$ being the cutoff frequency [2]. For electromagnetic radiation whose frequency is lower than the cutoff frequency, $\omega < \omega_{mn}$, the wavenumber in the direction of propagation is imaginary and the amplitude of the wave is therefore exponentially attenuated along z , resulting in the forbidden propagation. For a waveguide with cross-sectional area $a \times b$, $a \geq b$, the cutoff frequency

is

$$\omega_{01} = c\pi/a. \quad (2.12)$$

WG25, the waveguide used for the construction of our inserts, has dimensions $a = 3.76$ mm and $b = 1.88$ mm, leading to a cutoff frequency of $f_{01} = c/2a = 39.9$ GHz.

2.4 Metallic resonators

Millimetre-wave measurements can be performed without resonators; simple waveguide transmission has been used for some experiments described in Chapter 3, where a high sensitivity is obtained by using a field modulation coil, and in Chapter 5. In this case the sample is positioned inside the waveguide in the centre of the applied quasistatic magnetic field. Part of the radiation interacts with the sample and, attenuated and phase shifted, travels in a U-bend into the second waveguide towards the mixer or a different detector. Most of the experiments described in this thesis are however carried out by mounting the sample in a resonator. A qualitative comparison of these two different experimental methods is presented at the end of Section 2.4.

A resonator is essentially a terminated piece of waveguide. The highly conducting walls reflect the radiation and a standing wave mode forms within the cavity. Coupling holes allow energy in the form of electromagnetic radiation to enter and leak out of the resonator; when this radiation has the appropriate frequency it will selectively be stored inside the cavity. When a sample is placed inside a cavity, it becomes part of the resonator, usually partially disrupting the well shaped resonant mode by modifying the boundary conditions determined by the walls of the resonator. Resonant phenomena such as cyclotron resonance or electron spin resonance can occur in the sample at the frequency of the millimetre-wave electric or magnetic fields, and the absorption of radiation they cause can be detected as soon as it exceeds the instrument sensitivity threshold.

The equations modelling a millimetre-wave resonator are identical to those for an LRC circuit or a damped simple harmonic oscillator [21]. For an oscillator with a damping term the generalized equation of motion is [27]

$$\ddot{x} + \gamma\dot{x} + \omega_0^2 x = E_0 e^{-i\omega t}. \quad (2.13)$$

In the specific case of a millimetre-wave resonator, x represents the amplitude of the electromagnetic wave within the cavity walls, γ is a damping constant, ω_0 is the resonant frequency and $E_0 e^{-i\omega t}$ is the amplitude of the radiation exciting the resonator through a coupling hole. The steady state solution is [27]

$$x = E_0 \frac{(\omega_0^2 - \omega^2) + i\omega\gamma}{(\omega_0^2 - \omega^2)^2 + \omega^2\gamma^2} e^{-i\omega t}, \quad (2.14)$$

its amplitude is

$$|x| = \frac{E_0}{\sqrt{(\omega_0^2 - \omega^2)^2 + \omega^2\gamma^2}}, \quad (2.15)$$

and the phase is given by

$$\tan \phi = \frac{\omega\gamma}{\omega_0^2 - \omega^2}. \quad (2.16)$$

The amplitude and phase of the radiation transmitted through a real resonator are shown in Figure 2.3[6].

Each resonant mode of a cavity is characterized by its frequency and a quality factor, Q [21]:

$$Q = 2\pi \frac{(\text{Energy stored})}{(\text{Energy lost per cycle})}; \quad (2.17)$$

an alternative way to express the Q -factor is

$$Q = \frac{\omega_0}{\Gamma}, \quad (2.18)$$

where ω_0 is the resonant frequency of the cavity and Γ is the full width at half maximum (FWHM) of the Lorentzian representing the amplitude of the signal transmitted through the resonator centred at the resonant frequency. The recip-

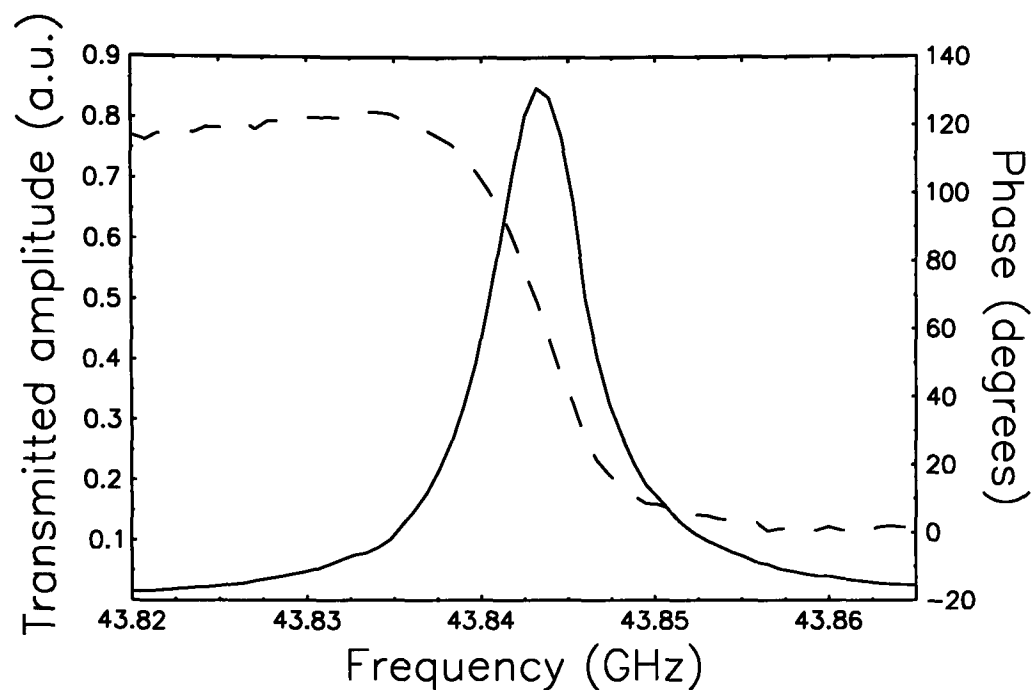


Figure 2.3: Amplitude (solid line) and phase (dashed line) of the signal transmitted through a metallic resonator as the resonant frequency is swept [6].

rocal of the Q -factor provides a measurement of the energy losses; as used in an experiment the resonant cavity differs from an ideal resonator in four main sources of losses: Ohmic losses due to dissipation in the cavity walls, radiation losses through the coupling holes, additional dissipation due to the presence of the sample and of the dielectric medium filling the resonator, gaseous or liquid Helium in most cases:

$$1/Q = 1/Q_{\text{walls}} + 1/Q_{\text{coupling}} + 1/Q_{\text{sample}} + 1/Q_{\text{diel}}. \quad (2.19)$$

Rectangular resonators

A rectangular resonator consists of a portion of rectangular waveguide terminated by the addition of two further metallic walls perpendicularly to the axis of the waveguide. The electromagnetic field distribution inside the resonator is obtained in the same way as for the waveguide by solving Maxwell's equations (Equations 2.5 and 2.6) with the appropriate boundary conditions provided by Equations 2.7 and 2.8 [21, 23]. The field distribution is exactly the same as that found in the corresponding waveguide mode, consisting of standing waves with an integer number of half wavelengths between the cavity walls. If the resonator

has dimensions $a \times b \times c$ in the x -, y -, z -directions, then the wave vectors take the quantized values $k_x = m\pi/a$, $k_y = n\pi/b$ and $k_z = p\pi/c$, m , n and p being the number of half wavelengths contained along the respective direction. These cavity modes are labelled as TE_{mnp} and TM_{mnp} [21].

The electric and magnetic field patterns of the TE_{102} mode are shown in Figure 2.4 and the currents induced in the cavity walls are shown in Figure 2.5 [21, 25].

A scale drawing of a rectangular cavity is shown in Figure 2.6 [6]. The body of the resonator is obtained from a section of silver WG26 waveguide with inner dimensions $1.55 \times 3.10 \times 6.00$ mm³. The top and bottom open ends of the body are closed by stainless steel endplates screwed on to brass lugs soldered to the body. To enhance the reflectivity at the body terminations, silver foil (thickness ~ 100 μ m) is placed between the endplates and the resonator body.

A simple algebraic expression relates the resonant frequencies of the TE_{mnp} and TM_{mnp} modes of a rectangular resonator to its dimensions [21]:

$$f_0 = \frac{1}{2} \sqrt{\frac{(m/a)^2 + (n/b)^2 + (p/c)^2}{\mu\epsilon}}, \quad (2.20)$$

ϵ and μ being the permittivity and permeability of the medium filling the cavity. For our resonators with inner dimensions $3.10 \times 1.55 \times 6.00$ mm³ the resonant frequency of the main TE_{102} mode is 69.5 GHz.

A crucial parameter in the optimization of the coupling of radiation in and out of a cavity is the size of the coupling holes located at the centre of the two walls with larger dimensions, as shown in Figure 2.6: they are in fact responsible for the radiation losses as well as allowing radiation to enter the resonator. The condition $\lambda_g \gg d \gg t$ where λ_g is the wavelength of the coupling radiation, d is the diameter of the coupling hole and t the cavity wall thickness [21, 6] has to be satisfied as much as practical constraints permit; a diameter of 0.8 mm has been chosen as the best compromise for our resonators [25].

The diagram in Figure 2.7 shows the rectangular cavity when clamped in

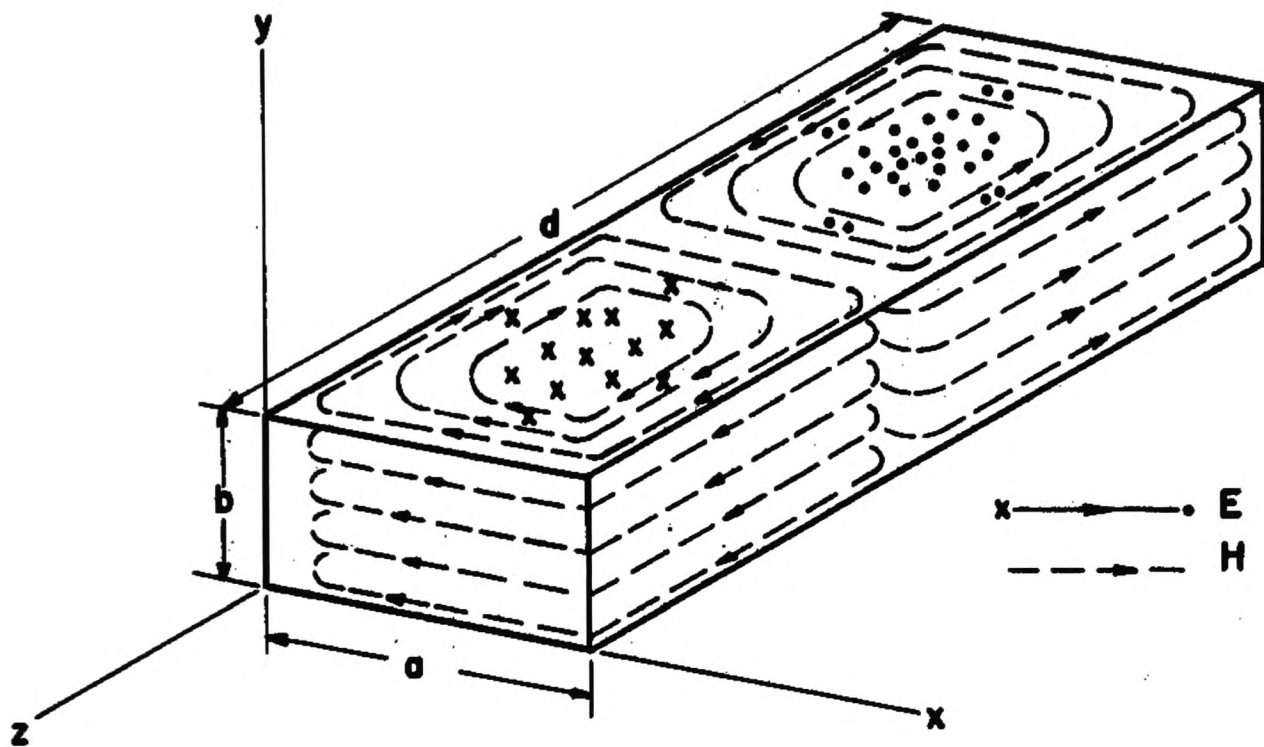


Figure 2.4: The field distribution in the rectangular TE_{102} mode [21, 6].

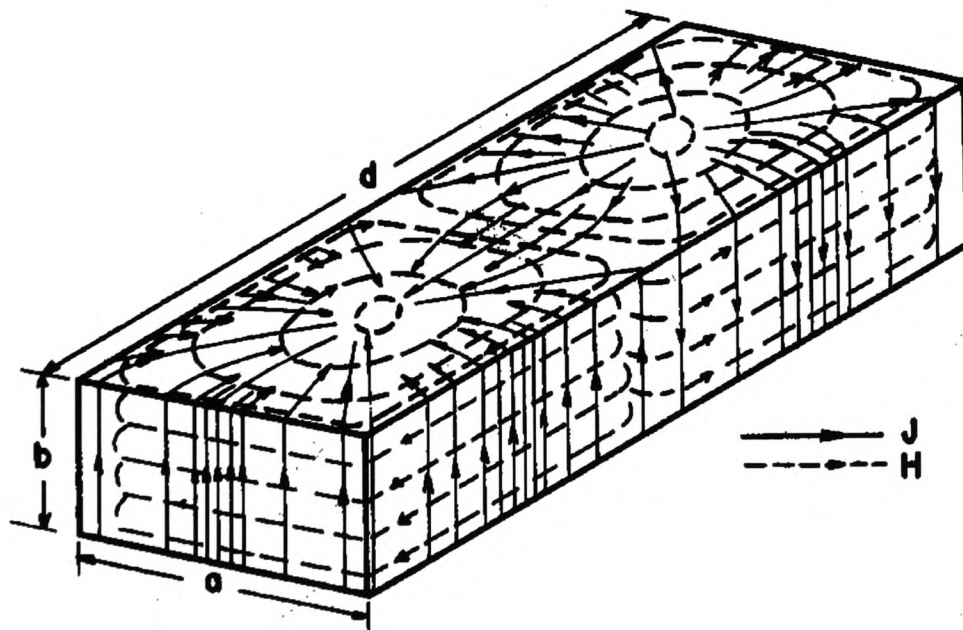


Figure 2.5: Current distribution induced in the resonator walls by the rectangular millimeter-wave mode TE_{102} [21].

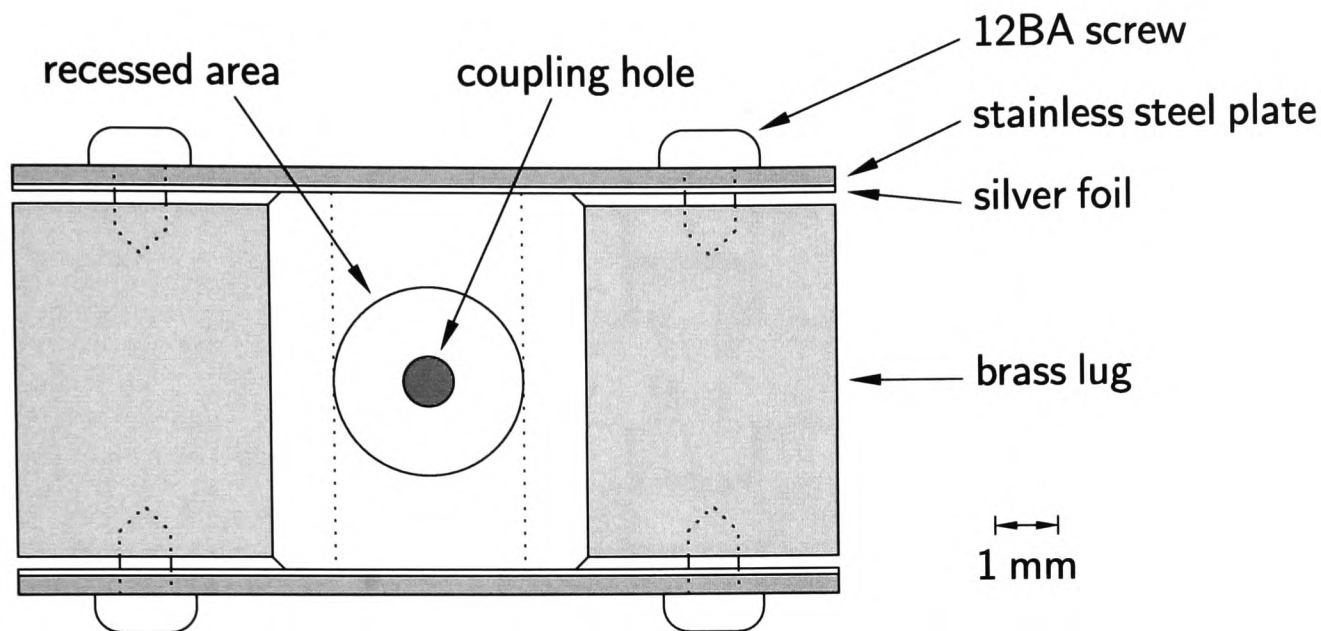


Figure 2.6: A scale drawing of the rectangular resonator, from Reference [6].

position between the waveguides; the latter can be loosened and the cavity can be removed. Two small cylinders ($d = 3$ mm) made of Rexolite, a dielectric material transparent to millimetre-waves, are placed inside the waveguides and protrude out of these to fit the recessed area around the cavity coupling holes; they are responsible for keeping the resonator in place and favoring the coupling of the millimetre-waves. The copper plungers then allow the optimization of the waveguide/resonator radiation coupling by ensuring control on the standing wave field distribution in the waveguide; for maximum signal coupling in fact the field pattern in the waveguide should match along the length of the guides that of the resonant mode to be excited in the cavity [21].

Cylindrical resonators

The angle-dependent measurements described in this thesis were all made using rectangular resonators and the “FTR” insert described in Section 2.5. The frequency dependent ESR studies reported in Chapter 3 on the other hand were obtained using a tunable cylindrical resonator operating at frequencies between 40 GHz (Q band) and 71 GHz (V band), and in overmoded configuration up to 313 GHz. Figure 2.8 shows the electromagnetic field distribution of a cylindrical

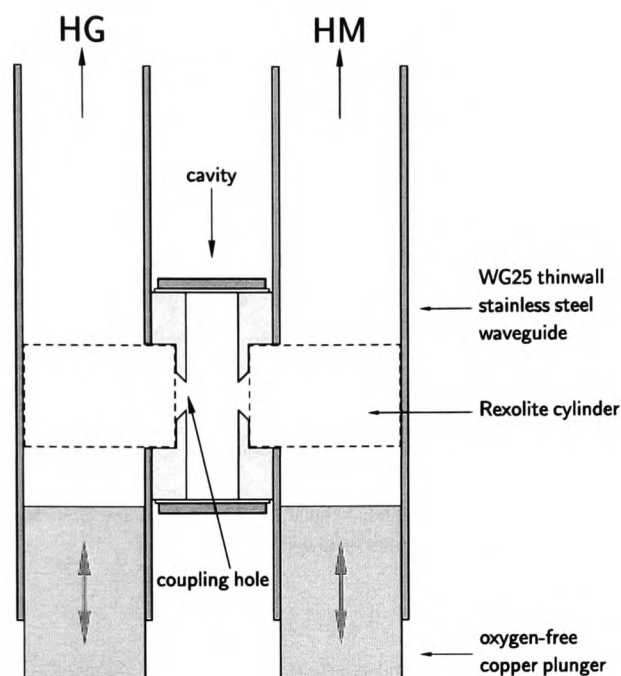


Figure 2.7: A cross-section diagram of the bottom end of the “FTR” insert, showing a rectangular cavity positioned between the waveguides [6].

TE_{011} mode, after Reference [21]. Cylindrical resonators possess both TE_{mnp} and TM_{mnp} modes, where in this case the integers m , n , p refer to the number of half wavelengths in the angular (ϕ), radial (r), and longitudinal (z) directions, respectively [21].

Made out of machined brass and gold coated, these resonators have Q -factors that are in general about one order of magnitude larger than those of rectangular resonators ($\sim 10^4$ as compared to $\sim 10^3$): this is a consequence of the fact that cylindrical cavities have a larger volume to surface ratio and can therefore store more energy [21] (see Equations 2.17 and 2.19). Figure 2.9 shows a schematic of a tunable cylindrical cavity; here one end plate of the resonator is replaced with a close-fitting plunger, controlled via a gear mechanism by a rod the length of the insert. The variation of the height z_0 of the inner space allows the continuous tunability of the resonant frequency of a given mode [21, 6]. For the experiments carried out in Chapter 3, the samples were placed at the bottom of the cavity in the antinode of the oscillatory magnetic field located at $(r, z) = (0.48r_0, 0)$, r_0 being the resonator radius, $r_0 = 4.5$ mm in our case.

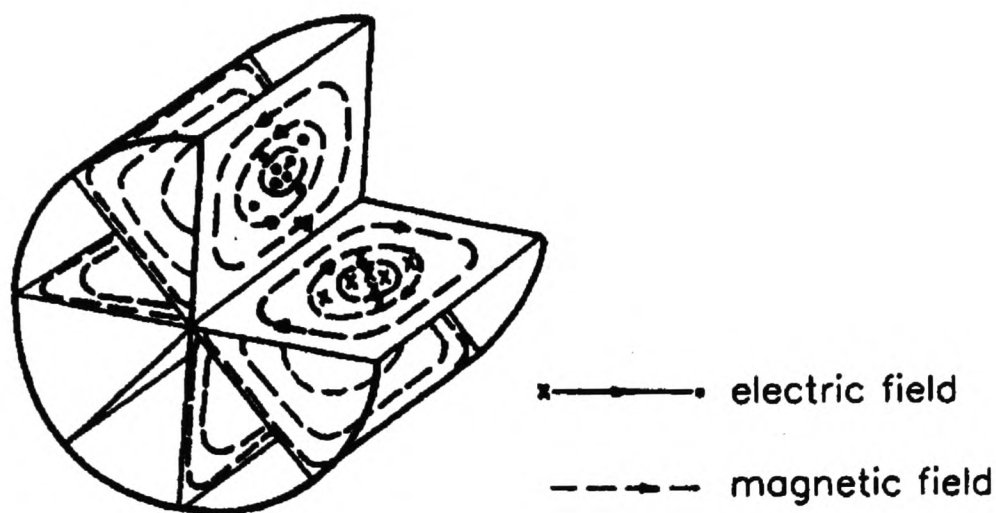


Figure 2.8: The electromagnetic field distribution pattern in the TE_{011} mode of a cylindrical resonator [21].

2.4.1 The measurement of sample properties

The well defined electromagnetic field distribution inside a resonator, with regions experiencing an oscillatory electric field and other regions an oscillatory magnetic field, makes the choice of the sample position of some importance. In fact, magnetic resonance phenomena require the presence of an oscillatory magnetic field perpendicular to the external quasistatic field $\mathbf{B}$ [2], whereas cyclotron resonance can be observed if an oscillatory electric field is present and perpendicular to $\mathbf{B}$ [2].

The resonant technique measures changes in the properties of the resonant system as a whole, the sample being part of the system. A certain change in the properties of the sample caused by the applied magnetic field will affect both the resonant frequency and the quality factor of the resonator: $\omega_0 \rightarrow \omega_0 - \Delta\omega_0$, $Q \rightarrow Q - \Delta Q$. Assuming to be in a regime of linear response, or equivalently that the changes in sample properties are small and represent only a perturbation to the properties of the resonator, the two following conditions are valid: $\Delta\omega_0 \propto \Delta\epsilon'$ and $\Delta Q \propto \Delta\epsilon''$, for a sample with a complex permittivity $\epsilon = \epsilon' + i\epsilon''$ in an electric field antinode [8, 28]; $\Delta\omega_0 \propto \Delta\chi'$ and $\Delta Q \propto \Delta\chi''$, for a sample with complex susceptibility $\chi = \chi' + i\chi''$ in a magnetic field antinode [21].

By means of a feedback loop through a frequency counter/stabilizer (EIP 578,

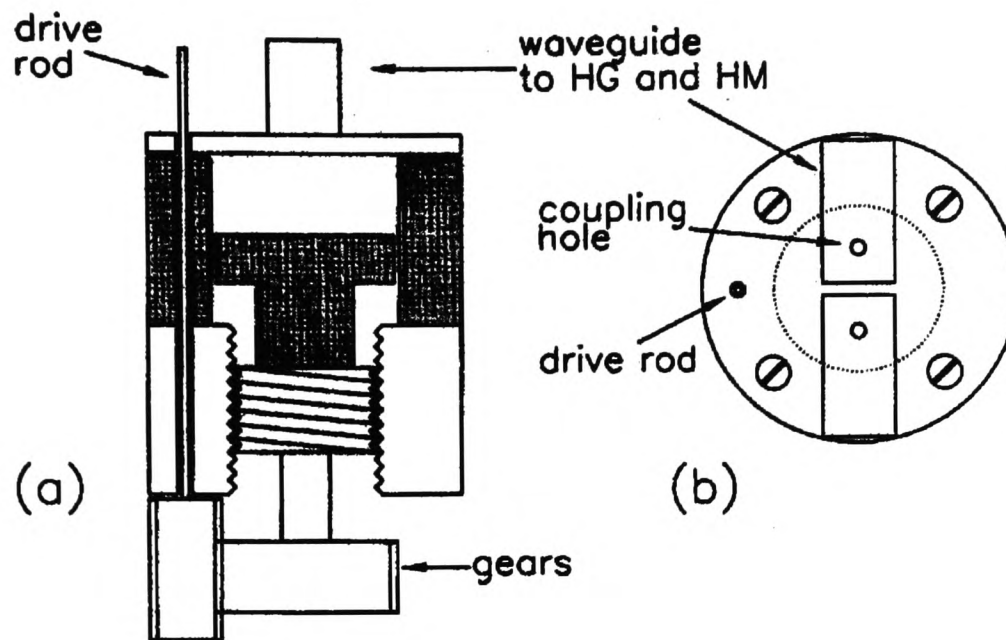


Figure 2.9: A drawing of the tunable cylindrical cavity mechanism (a) vertical cross section, (b) top view [6].

manufactured by EIP Microwave Inc.) the frequency of the MVNA signal is locked at the resonant frequency of the loaded resonator. The condition that the presence of the sample and the changes in its properties only represent a small perturbation to the resonator electromagnetic field distribution, and therefore the changes in Q -factor are small throughout the measurement, is fundamental for the validity of the resonant technique ($\Delta Q/Q \ll 1$ or $\Delta\omega_0/\Gamma \ll 1$). With the frequency locked at resonance, a small change in the signal amplitude is proportional to a change in the Q -factor and therefore inversely proportional to the power being dissipated in the resonator, and a small change in the resonant frequency of the cavity is proportional to a change in the phase of the signal. Mixing of amplitude and phase signal are induced if the frequency shift is no longer small compared with the frequency width of the resonance Γ , making the quantitative information obtained from the experiment of difficult interpretation [8].

Chapter 4 deals with measurements of the high frequency conductivity σ of highly anisotropic metals: these are probed by inducing currents in the samples at the millimetre-wave frequencies; such currents are dissipative and whenever σ changes a change in the Q -factor of the resonator is induced, which can be

measured in the amplitude of the transmitted signal. Measurements in an electric field antinode tend to probe the surface properties of an anisotropic metal; if placed in an magnetic field antinode, on the other hand, the bulk conductivity is measured, and it has been shown [6] that the component mainly responsible for the dissipation is the interlayer conductivity. An oscillatory magnetic field parallel to the conducting planes induces a concatenated electric field, which gives rise to oscillatory currents with a component in the direction of low conductivity. The skin depth δ , defined as the distance inside a metal over which the amplitude of the radiation decays by e^{-1} [2], is

$$\delta = \sqrt{\frac{2}{\sigma\mu\omega}}, \quad (2.21)$$

ω being the radiation frequency and μ being the relative magnetic permittivity of the material; for materials as anisotropic as κ -(BEDT-TTF)₂Cu(NCS)₂, subject of the study presented in Chapter 4, at the measurement frequency of about 70 GHz the skin depth in the interlayer direction is of order 0.5 mm, larger than the typical sample thickness, of order 0.1 mm [29, 30].

2.5 Angle-dependent measurements: the “FTR” insert

The “FTR” insert derives its name from Fermi-surface traversal resonance (FTR) [10], a magnetic-field induced resonant phenomenon observed in organic metals with quasi-one-dimensional sections of Fermi Surface; it enables the study of the properties of anisotropic systems as a function of sample orientation with respect to the external quasistatic magnetic field $\mathbf{B}$ to be carried out very conveniently and effectively. In fact, it is possible to rotate the resonator with the instrument inside the cryostat, while keeping all other conditions around the sample (temperature, magnetic field) essentially unmodified. This insert, designed

and built at the Clarendon Laboratory, fits both in the 17 T superconducting magnet in Oxford and in the 33 T Bitter magnets at the NHMFL in Tallahassee, Florida; a diagram of its bottom section is shown in Figure 2.7. It has been used to study the angle dependence of the electron spin resonance spectra in the magnetic charge transfer salts β'' -(BEDT-TTF)₄[(H₃O)M(C₂O₄)₃]S (Chapter 3) and the angle dependence of the superconducting and normal state absorption features (the FTRs) in isotopically substituted κ -(BEDT-TTF)₂Cu(NCS)₂ (Chapter 4). The whole cavity is rotated with respect to the external field **B**; this ensures that the millimetre-wave mode remains unaltered as the angle dependence of the features under investigation is carried out. The rotation is achieved by means of a worm gear mechanism connected via a rod to a dial at the top of the insert. The useful range of angles is $-70^\circ \leq \theta \leq 70^\circ$: beyond such angles the transmitted signal becomes very weak. This is due to the fact that the coupling between waveguides and resonator is itself angle dependent, varying as $\cos \theta$. The transmitted amplitude therefore decreases by $\cos^2 \theta$; when $\theta = 70^\circ$ the signal is reduced by a factor $\cos^2(70^\circ) = 0.12$ [10].

A modification of the final section of the insert, replaced for its terminal 20 cm by an equivalent pair of waveguides made of copper rather than stainless steel, has allowed the removal of a significant background signal (about 10% of the transmitted intensity) at roughly the free electron g -value, allowing for the experiments carried out with this instrument and described in Chapters 3 and 4 to be more effectively performed and analyzed.

2.6 Dielectric resonators

An alternative to metallic structures for the guiding of radiation and the construction of resonators are dielectric materials. In these structures the electromagnetic energy is constrained by total internal reflections from dielectric interfaces [31]. The condition for total internal reflection to take place is that the medium in

which the radiation propagates has refractive index, n_1 , higher than that of the surrounding medium, n_2 . Consider a plane wave impinging at a normal angle of incidence θ_i on the boundary between the two media; Fresnel equations give the amplitudes of the transmitted and reflected waves; in the case of radiation with the oscillatory electric field normal to the plane of incidence:

$$\left(\frac{E_{0r}}{E_{0i}}\right)_N = \frac{n_1 \cos \theta_i - n_2 \cos \theta_t}{n_2 \cos \theta_t - n_1 \cos \theta_i}, \quad (2.22)$$

$$\left(\frac{E_{0t}}{E_{0i}}\right)_N = \frac{2n_1 \cos \theta_i}{n_1 \cos \theta_i - n_2 \cos \theta_t}, \quad (2.23)$$

θ_t being the angle between the transmitted wave and the normal to the boundary.

For angles of incidence greater than a critical angle

$$\theta_c = \sin^{-1}(n_2/n_1) \quad (2.24)$$

the wave is reflected with undiminished amplitude [31]. The amplitude of the wave propagating in the surrounding medium with refractive index n_2 decays exponentially; it is called the evanescent wave.

By solving the wave equation with appropriate boundary conditions the field distribution inside a dielectric medium of given geometry can be obtained. In the case of structures with cylindrical symmetry, the electric field components for a linearly polarized wave can be expressed in terms of Bessel functions as [31]

$$E_y = A_E \frac{J_n(k_{1T}R)}{J_n(k_{1T}a)} \cos(n\phi) = -\left(\frac{Z_0}{n_1}\right) H_x, \quad (2.25)$$

$$E_y = A_E \frac{K_n(\gamma R)}{K_n(\gamma a)} \cos(n\phi) = -\left(\frac{Z_0}{n_2}\right) H_x. \quad (2.26)$$

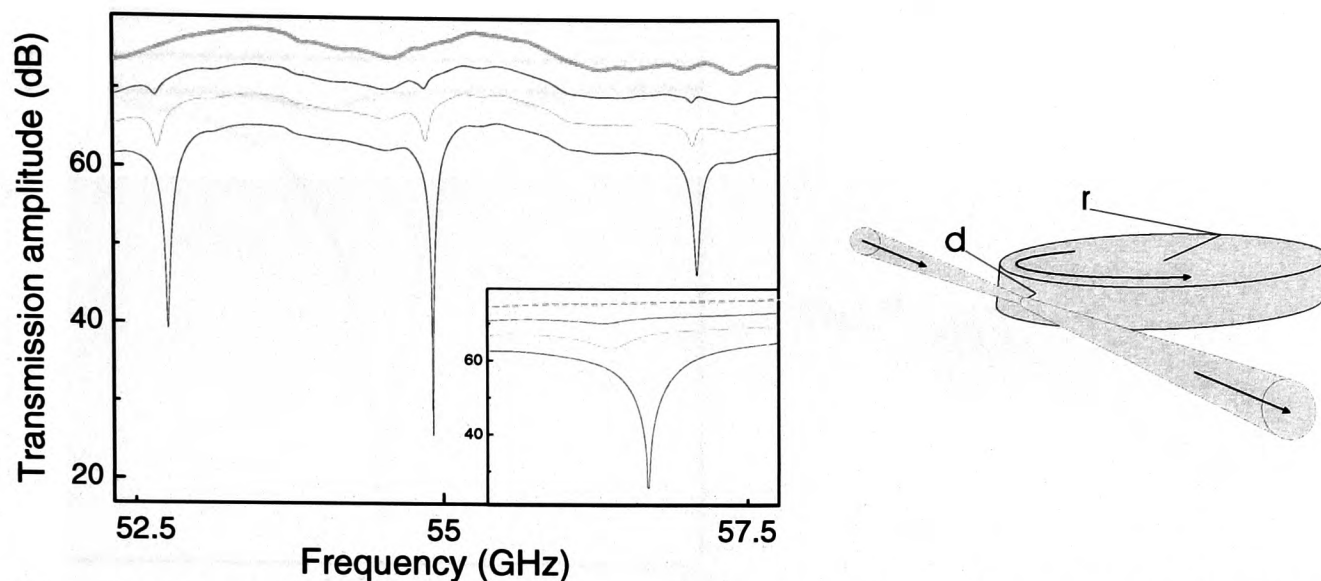


Figure 2.10: Left: a branch of resonances from a whispering gallery dielectric resonator as the distance d between tapered waveguide and resonator is varied: $d=30\text{mm}$, 1mm , 0.5mm , 0.1mm from top to bottom trace. Right: a diagram showing the tapered waveguides and the dielectric resonator; the arrows indicate the direction of the electromagnetic radiation.

2.6.1 Whispering gallery Resonators (WGR)

Whispering gallery resonators are cylindrical disks capable of storing radiation at particular frequencies by means of total internal reflection; they can work up to frequencies of 1 THz with Q -factors as high as 10^5 for sapphire resonators [32]. Inside a WGR, radiation of wavelength λ propagates in a spiral, between the outer radius of the disk, r , and an inner caustic radius: $\rho_c = r - \lambda$. A travelling resonance is obtained when the rephasing condition is fulfilled: $2\pi\rho_c \approx n\lambda$, n being the azimuthal mode index. In such instance, an integer number of wavelengths match the resonator diameter; for a whispering gallery electric mode, WGE, $E_z \approx \cos(n\phi)$, z being the axis of cylindrical symmetry. Figures 2.10 and 2.11, right-hand-side, show a schematic diagram of the setup consisting of a pair of tapered waveguides and the dielectric cylindrical structure; the left-hand-side of the same Figures display the resonant behaviour as a function of frequency and of distance from the coupling waveguides for two different WGR resonators made of polyethylene, one in the frequency region of 55 GHz and the other near 195 GHz. The results shown in all the Figures of this Section were obtained in collaboration with Mario Cassettari and Giuseppe Annino at their Laboratory at

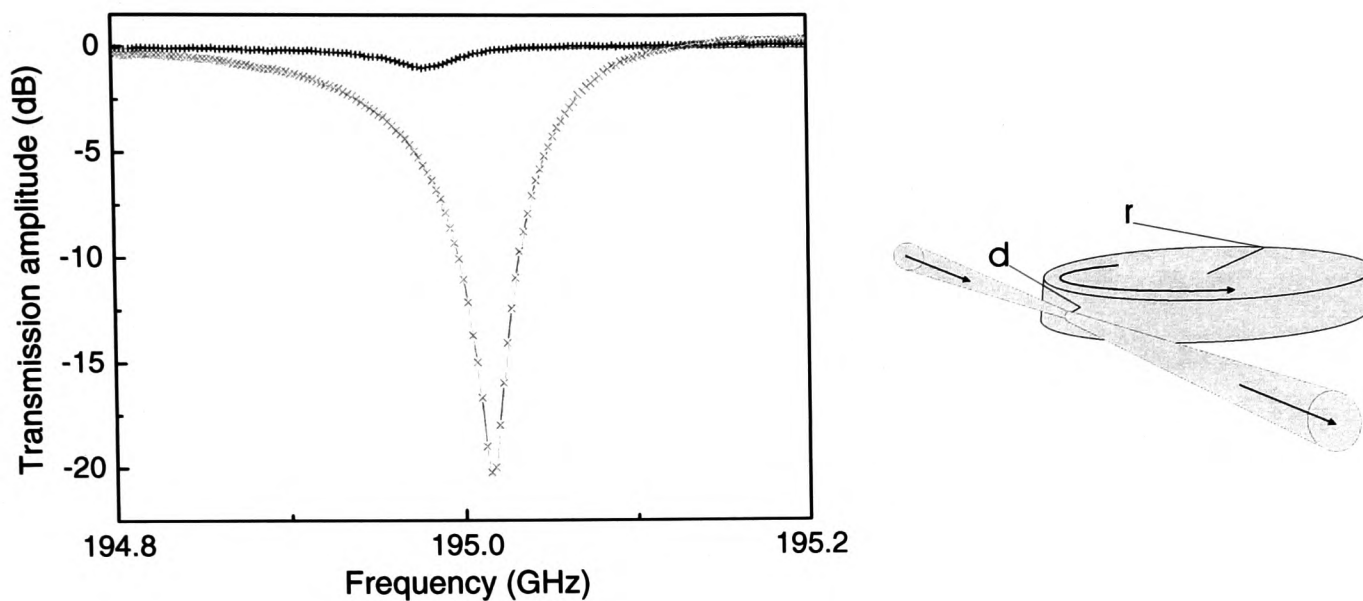


Figure 2.11: Left: the response of a polyethylene WGR excited near 200 GHz with the use of the ESA Gunn extensions [22]. The two traces correspond to a condition of optimal coupling (top trace) and one of “overcoupling” (bottom trace). Right: A schematic of the tapered waveguides and the resonator.

CNR in Pisa, Italy.

2.6.2 Hybrid Resonators

Figure 2.12, shows the reflected signal from a “non-radiative tunnel-gap resonator” together with a diagram of the resonator. The latter consists of a hybrid structure: a cylindrical dielectric disk enclosed between two metallic slabs. The separation between the metallic surfaces, h is such that the radiation impinging on the structure cannot propagate through it, being below cutoff [33]. It therefore acts as a millimetre-wave mirror. The working principle of this type of single-mode resonator can be explained in terms of propagation below and above the cutoff wavelength. Let the cylindrical disk have height h and dielectric constant $\epsilon = \epsilon' + i\epsilon''$; then, if $h < \lambda/2 < h\sqrt{\epsilon}$, λ being the wavelength of the electromagnetic radiation, propagation will be allowed in the dielectric region but forbidden in the outer region between the metallic plates. Radiation can therefore “tunnel” through the forbidden gap [33].

Dielectric resonators already find applications in spin resonance spectrometers, and could find applications in pulsed and destructive magnetic field experiments,

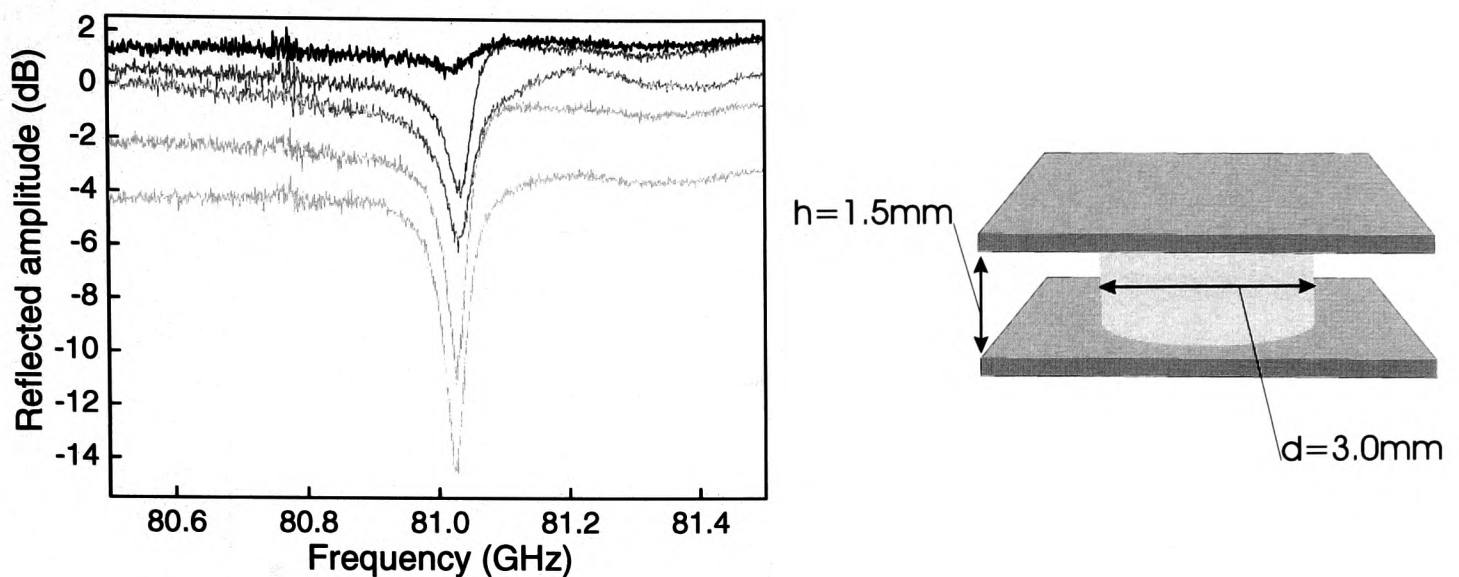


Figure 2.12: Left: the signal reflected by the non-radiative tunnel-gap resonator; the intensity of the resonance increases as the radiation is coupled more strongly to the dielectric enclosed between the metal plates. Right: a schematic of the resonant structure consisting of a dielectric disk sandwiched between two copper plates (h and d are the distance between plates and the diameter of the resonator respectively).

where the presence of metallic structures is the cause of often intolerable vibrational and thermal noise.

2.7 Summary

In this Chapter the fundamentals of guided radiation and millimetre-wave spectroscopy have been outlined. In particular:

- The MVNA, source and heterodyne detector of electromagnetic radiation with continuous tunability in the frequency range 8-350 GHz, has been described.
- Inserts and metallic resonators of rectangular and cylindrical shape used in the investigation of the properties of low dimensional organic metals have been presented.
- The features of new dielectric and hybrid resonators for potential use in pulsed and destructive magnetic field experiments have been outlined and preliminary tests reported.

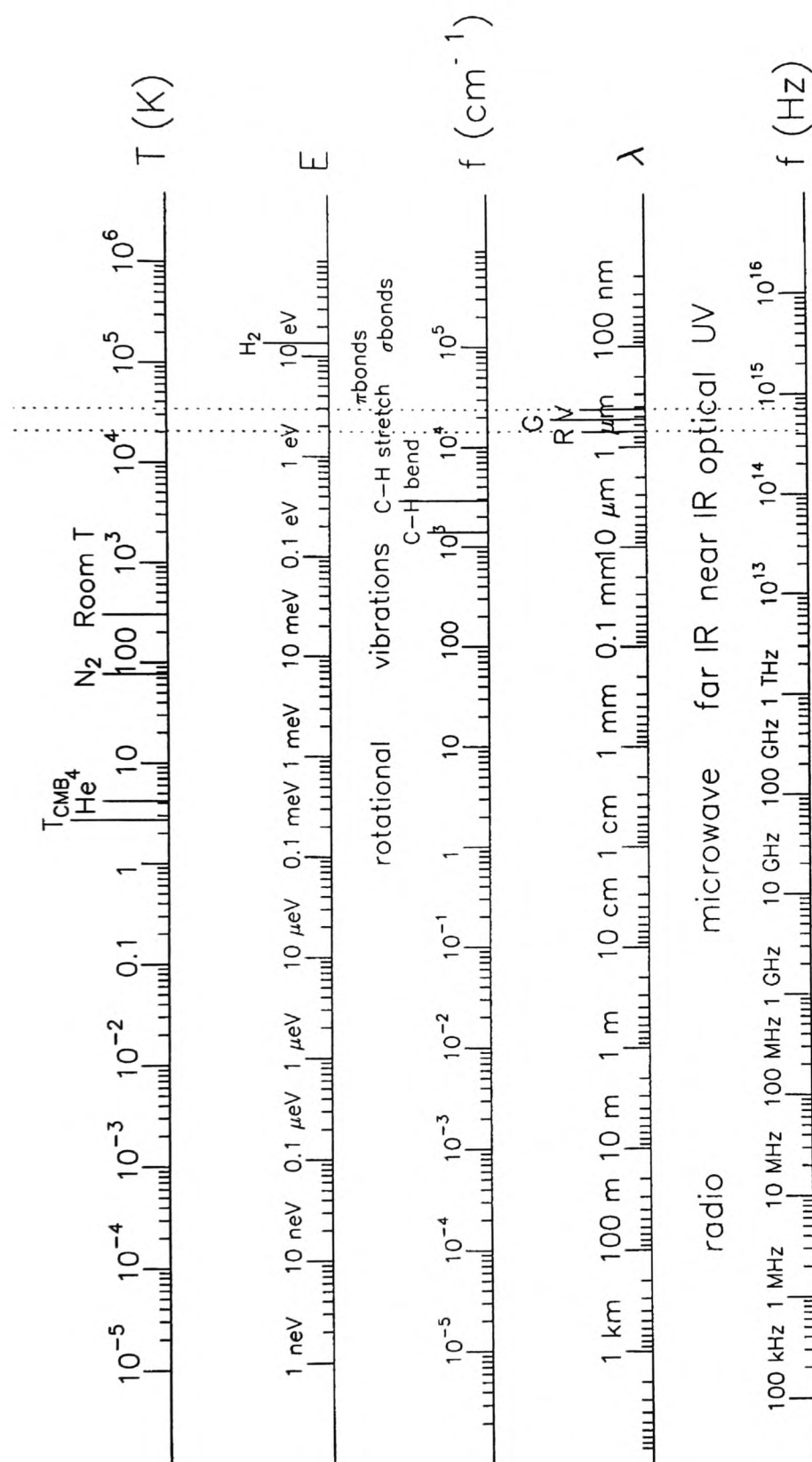


Figure 2.13: The electromagnetic spectrum: a chart for easy conversion between the most commonly used “energy” units [3].

Chapter 3

Electron spin resonance studies of the organic charge transfer salts



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3.1 Introduction

Since its first report by Zavoisky in 1945 [34], electron paramagnetic resonance (EPR) has proved to be a most powerful tool for the understanding of structural and magnetic properties of a wide range of paramagnetic organic and inorganic systems [21, 35, 36, 37]. Comprehensive accounts of the principles, including a wealth of classical results on rare earths and transition metal ions, and of spin resonance studies in the liquid and gas phases, are presented in [19] and [20] respectively.

Recent implementations of the technique in the high frequency-high field region (HFHF, typically $\nu \geq 95$ GHz, $B \geq 5$ T) has proved to be of great advantage for the detailed mapping of the spin Hamiltonians describing single molecule magnets, systems containing a large number of interacting magnetic centres [38, 39, 40, 41, 42]. By doping or coating different materials with EPR-active species, the method has been successfully applied to the study of fullerene-based diamagnetic crystals [43], heavy fermions [44], high temperature and other novel superconductors [45, 46, 47, 48, 49]. HFHF EPR has allowed the observation of spectra from non-Kramers systems, otherwise EPR-silent with conventional fields and frequencies [50]. Multifrequency EPR ($100 \text{ GHz} \leq \nu \leq 1 \text{ THz}$) in pulsed fields up to 50 Tesla allowed the investigation of the magnetic properties of materials across field-induced phase transitions [51, 52].

In the context of organic charge transfer salts, EPR has effectively been used to investigate phase transitions and ordering transformations [53, 54, 55, 56, 57], antiferromagnetism [58, 59, 60] and microwave conductivity [61, 62] in the quasi-two-dimensional BEDT-TTF-based and quasi-one-dimensional TMTCF-based compounds. BEDT-TTF is the organic molecule bis-ethylenedithia-tetrathiafulvalene described in Figure 3.1, and TMTCF is the organic molecule tetramethyl-tetrathiafulvalene if $C=\text{S}$, tetramethyl-tetraselenafulvalene if $C=\text{Se}$. In particular, the low temperature electronic properties of deuterated and protonated superconductors $\kappa-(\text{BEDT-TTF})_2\text{Cu}[\text{N}(\text{CN})_2]\text{X}$, ($\text{X}=\text{Br}, \text{Cl}$) have been investigated

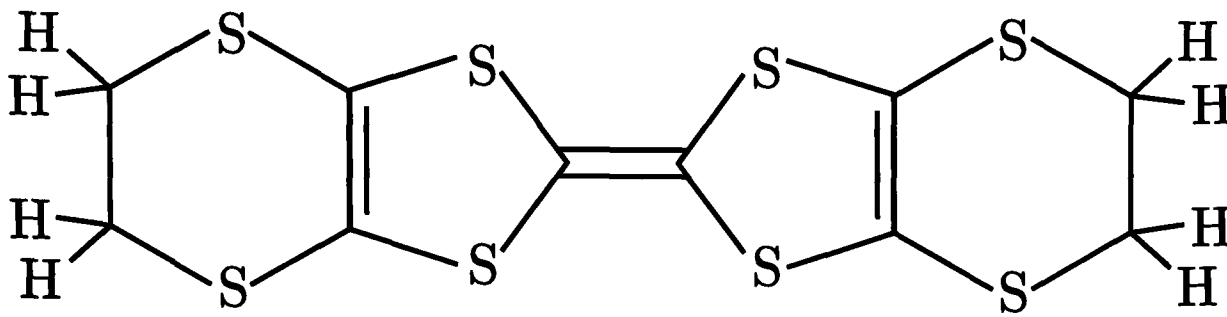


Figure 3.1: The BEDT-TTF (bis-ethylenedithia-tetrathiafulvalene) molecule [63].

by means of EPR; by comparing spin susceptibilities and linewidths, a crossover was established at a temperature of 40 K [56] from a metallic into an insulating phase. The same ordering transition was investigated by Tanatar *et al* [54] as a function of thermal treatment, clarifying how the ordering of the terminal ethylene groups occurs in these compounds through a sequence of phase transitions in the temperature range 60-90 K, and is extremely sensitive to cooling rate. This study shows the coexistence at low temperature of two phases for the deuterated compound containing bromine, namely magnetically ordered insulator and metal. In the very same material, Ito *et al* attributed an EPR signal emerging below 8 K upon rapid cooling to antiferromagnetic resonance, confirming the magnetically ordered phase. [59]. By analysis of the EPR Dysonian line shape for the all organic β'' -(BEDT-TTF) $_2$ SF $_5$ CH $_2$ CF $_2$ SO $_3$ superconductor the anisotropy of the in-plane microwave conductivity was extracted for the first time [62], confirming the electronic band structure and strongly metallic nature of the compound.

A major effort has recently been made in the design of continuous lattices in which two cooperative properties, such as long-range magnetic order and metallic conductivity are simultaneously present [64], [65]. Such coexistence, namely long range antiferromagnetic order and superconductivity, has been verified in several classes of inorganic compounds, among which are the high- T_c superconductors (see [66] and references therein). Within the κ - and λ -(BETS) $_2$ FeX $_4$ family of compounds (X=Br or Cl), metallic conductivity together with the presence of magnetic anions has been reported [67]. T. Mori *et al* provided a theoretical esti-

mate for the π -d interactions in such systems [68]. The synthesis of organic charge transfer salts containing tri(oxalato)metallate anions and BEDT-TTF counterions has provided interesting systems such as a molecular metal ferromagnet [64] and organic superconductors containing the paramagnetic 3d metal ions Fe^{3+} and Cr^{3+} [69, 70, 71, 72].

The interplay between the magnetic and the (super)conducting properties of organic charge transfer salts has recently been the subject of intense experimental and theoretical research, leading to the discovery of reentrant superconductivity and its explanation through the Jaccarino-Peter compensation effect [73] in the λ -BETS salts [74, 75]. Among the organic charge transfer salts of BEDT-TTF containing (oxalato)metallate(III) [64] anions are the molecular superconductors that simultaneously contain paramagnetic metal ions [72]. These materials are of great interest since they display the simultaneous presence of localised magnetic moments and a superconducting condensate [68, 64, 66].

This chapter will report on the low temperature magnetic properties of the family of charge transfer salts $\beta''-(\text{BEDT-TTF})_4[(\text{H}_3\text{O})M(\text{C}_2\text{O}_4)_3]S$, where M is a 3d transition metal and S is a solvent molecule. The experiments performed represent a detailed investigation of the millimetre-wave magneto-optical response of the compounds. With the aim of extracting information on the possible interactions between the localised 3d magnetic moments of the oxalate complex, and between the local moments and the delocalised free carriers, a model spin Hamiltonian for the systems needs to be identified. The fact that the (super)conducting properties in this family of compounds are determined by the nature and size of the host solvent molecules [76] (which sits within the insulating anion layer) raises the question of whether other properties of the magnetic layer affect the superconductivity, or, conversely, if the superconducting transition induces changes in the magnetic response of the unpaired spins to millimetre-waves in an applied external magnetic field.

The possibility of weak antiferromagnetism in the superconducting compounds

β'' -(BEDT-TTF)₄[Fe(C₂O₄)₃]S has previously been reported [69, 72]. Our investigation has the aim of extracting information on the magnetic system (mapping of the spin Hamiltonian and possible onset of long-range order) and indirectly also on the superconducting groundstate. The issues to be addressed are: how do the superconducting condensate and the localised magnetic moments coexist? Do the latter favour or hinder superconductivity, or are they totally indifferent to it? Can any information on the microscopic mechanisms of superconductivity be gained from the investigation of the EPR features across the superconducting transition? Ultimately, what role does the “insulating” anion layer have on the conduction properties of the system, both in the normal and in the superconducting state? Additionally, the magnetic moments of the 3d ions represent a local probe of the superconducting vortex structure [49] and can therefore provide information on field penetration and distribution in the mixed state. This chapter will attempt to answer these questions by looking at samples containing different solvent molecules and different transition metal ions. β'' -(BEDT-TTF)₄[Fe(C₂O₄)₃]C₆H₅CN has been investigated in particular detail by using rectangular and cylindrical cavities over the range 50-312 GHz, and the field modulation technique in simple overmoded waveguide transmission at high fields and frequencies (95-180 GHz). After determining the spin Hamiltonian for the different magnetic complexes, some insight into the reciprocal effects of the coexisting systems will be provided by the analysis of the positions, intensities and widths of the EPR resonant lines. By comparing all the extracted information on the EPR features from a non superconducting compound, namely β'' -(BEDT-TTF)₄[Cr(C₂O₄)₃]C₅H₅N, and two superconducting compounds with different superconducting transition temperatures, the members of the β'' -(BEDT-TTF)₄[Fe(C₂O₄)₃]S subfamily, this study aims at contributing to the understanding of the role played by the metal ion and the solvent molecule in the supermolecular crystalline properties of the β'' -(BEDT-TTF)₄[(H₃O)M(C₂O₄)₃]S system. The temperature, angle and frequency dependencies of the magneto-optical spectra will be used to identify the nature of

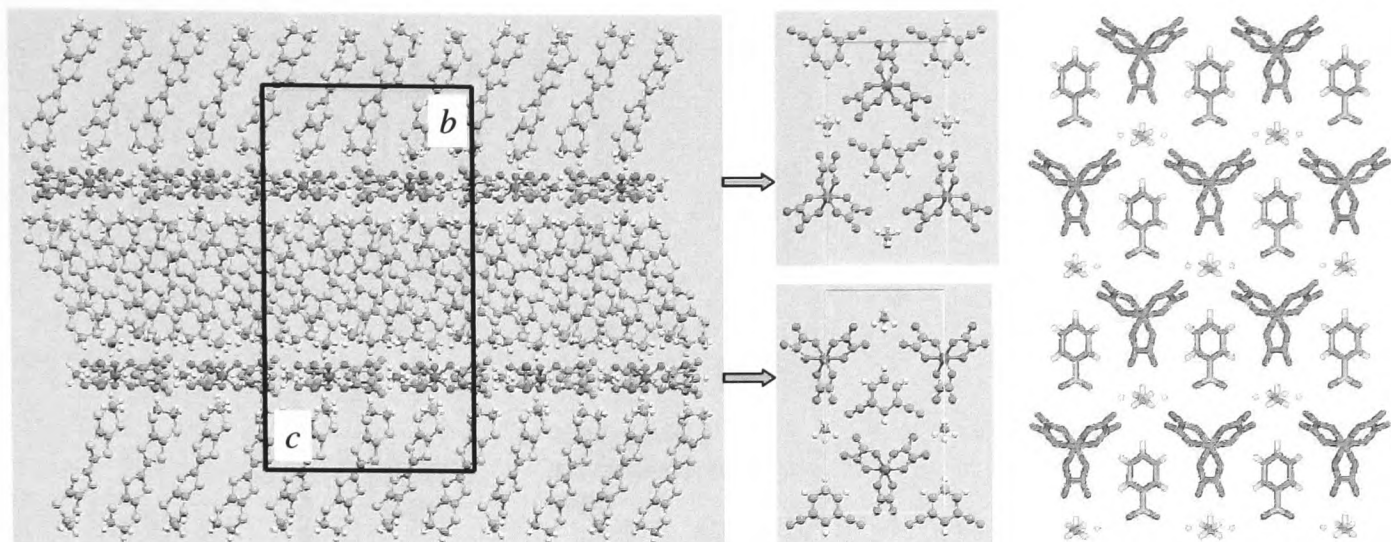


Figure 3.2: Left: the layered structure of the charge transfer salts $\beta''-(\text{BEDT-TTF})_4[(\text{H}_3\text{O})M(\text{C}_2\text{O}_4)_3]S$. Middle: two subsequent anion layers, showing the oxalate complex rotated by 180° from one layer to the next. Right: the anion layer of $\beta''-(\text{BEDT-TTF})_4[\text{Fe}(\text{C}_2\text{O}_4)_3]\text{C}_6\text{H}_5\text{NO}_2$.

the interaction between localised Fe spins and between the local moments (core electrons) and the delocalised carriers (band electrons).

This chapter is organised as follows: Section 3.2 will describe some relevant chemical, structural and electronic properties of the compounds; Section 3.3.1 will outline the fundamental concepts implemented in the analysis of the millimetre-wave spin resonance spectra obtained from various samples of the family $\beta''-(\text{BEDT-TTF})_4[(\text{H}_3\text{O})M(\text{C}_2\text{O}_4)_3]S$. The EPR measurements are presented and compared with simulated spectra in Section 3.3.2. Suitable spin Hamiltonians for the systems under investigation will be identified. Finally, all results concerning the intensity of the spectra, line widths and shifts are analyzed and discussed in Section 3.4.

3.2 Organic charge transfer salts containing tri(oxalato)metallate anions

This paragraph will outline the structural, chemical and electronic properties of the salts belonging to the family $\beta''-(\text{BEDT-TTF})_4[(\text{H}_3\text{O})M(\text{C}_2\text{O}_4)_3]S$, where M is a 3d transition metal and S is a solvent molecule.

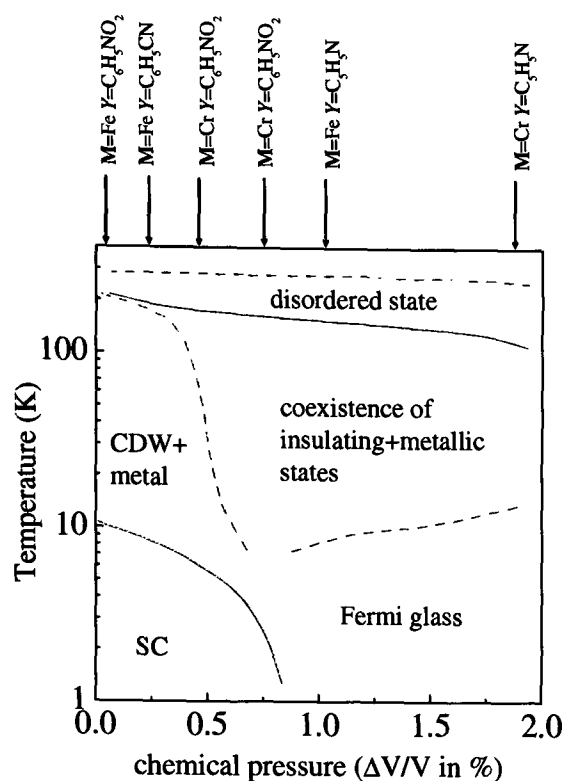


Figure 3.3: The phase diagram proposed in [76], showing the low temperature properties of a number of compounds in the family β'' -(BEDT-TTF)₄[(H₃O)M(C₂O₄)₃]S; CDW and SC stand for charge density wave and superconductivity respectively.

M/S	$a(\text{\AA})$	$b(\text{\AA})$	$c(\text{\AA})$	β	$V(\text{\AA}^3)$	$T(\text{K})$	Ref.
Cr/C ₆ H ₅ NO ₂	10.283	19.917	34.939	93.299	7144.4	150	[72]
Fe/C ₆ H ₅ NO ₂	10.273	19.949	35.030	92.969	7169.6	120	[72]
Cr/C ₆ H ₅ CN	10.240	19.965	34.905	93.69	7121.6	120	[71]
Fe/C ₆ H ₅ CN	10.232	20.043	34.972	93.25	7157	120	[69]
Fe/C ₅ H ₅ N	10.267	19.845	34.907	93.223	7101.0	150	[70]

Table 3.1: Lattice parameters of the magnetic β'' -(BEDT-TTF)₄[(H₃O)M(C₂O₄)₃]S salts ($C2/c$ symmetry group) measured above 100 K.

M/S	$T_c(\text{K})$	$B_{c2\parallel}(\text{T})$	$B_{c2\perp}(\text{T})$
Cr/C ₆ H ₅ NO ₂	5(1)	18(1)	2(0.3)
Fe/C ₆ H ₅ NO ₂ (*)	5(1)	N/A	N/A
Fe/C ₆ H ₅ CN(*)	6(1)	17(1)	3.3(0.3)
Ga/C ₆ H ₅ NO ₂	8(1)	32(1)	6.2(0.3)

Table 3.2: Physical properties of the available superconducting β'' -(BEDT-TTF)₄[(H₃O)M(C₂O₄)₃]S salts [77]. T_c is the superconducting transition temperature, and $B_{c2\parallel}$ and $B_{c2\perp}$ are the in-plane and out-of-plane upper critical fields respectively. The asterisk denotes the salts studied in this Chapter.

The organic molecule bis-ethylenedithia-tetrathiafulvalene (BEDT-TTF) shown in Figure 3.1 is the building block for many quasi-two-dimensional organic compounds [18, 63]. The molecule is approximately flat, so a number of stacking arrangements can be found. The dominant overlapping molecular orbitals are those of the sulphur atoms and they are responsible for the transfer of electrons from molecule to molecule. Two BEDT-TTF molecules donate one electron to the anion; this charge transfer binds the crystal, leaving behind a partially filled band responsible for the high temperature metallic behaviour [18, 63]. Figure 3.2 shows a projection of the crystal structure along the a axis of the $\beta''\text{-(BEDT-TTF)}_4[(\text{H}_3\text{O})\text{M}(\text{C}_2\text{O}_4)_3]\text{S}$ salts, and Table 3.2 gives all available lattice parameters (at a temperature of about 120 K) for the compounds containing paramagnetic anions [76]. The structure consists of alternating layers of BEDT-TTF molecules and inorganic anions, the latter containing the metal tris(oxalate) $[\text{M}(\text{C}_2\text{O}_4)_3]^{3-}$, the ion H_3O^+ and the “guest” solvent molecule, S . The molecules in the anion layer lie in a “honeycomb” arrangement with alternate H_3O^+ and metal oxalates giving an approximately hexagonal network of cavities in which the solvent molecule S lies (see Figure 3.2). The solvent molecule helps to stabilize the structure; the plane of the phenyl ring makes an angle of $\approx 32 - 36^\circ$ to the plane of the oxalate layer [71, 70, 72]. The metal ion M is octahedrally co-ordinated to the oxalate ligands (see Figures 3.4 and 3.6), and the oxygen atoms on the oxalates are weakly bound to the hydrogen atoms on the terminal ethylene groups of the BEDT-TTF molecules, acting to pull these together. The BEDT-TTF molecules adopt the β'' packing arrangement in the ab planes, in which they form roughly orthogonal stacks. The crystallographic structure of our compounds is monoclinic (see Table 3.2) with the (ab) conducting planes at a distance of $d = c/2$ from each other, as shown in Figure 3.2 [70]. By far the shortest S–S distances are within the cation planes, leading to a predominantly two-dimensional bandstructure [69]. Each BEDT-TTF molecule is expected to donate half an electron, leaving two holes per unit cell. Band structure calculations based on the room

temperature crystallographic data suggest that these salts should be compensated semimetals, with a Fermi surface consisting of quasi-two-dimensional electron and hole pockets of approximately equal area. This has been confirmed by recent magnetotransport experiments [76, 78]. The samples investigated were grown using electrocrystallisation techniques as described in references [69, 70, 79]. The phase diagram in Figure 3.3 (from Reference [76]) shows the low temperature properties of those salts within the β'' -(BEDT-TTF)₄[(H₃O)M(C₂O₄)₃]S family containing magnetic anions; the compounds containing iron are found at the far left of the temperature-chemical pressure diagram, whereas the studied chromium compound is located at the far right of the diagram. Substitution of the host solvent molecules induces dramatic changes in the physical properties of the system, going from a superconducting state to insulating behaviour with increasing “chemical pressure” ($= -\Delta V/V$, *i.e.* the fractional difference in unit-cell volume of a particular salt from that of the $M = \text{Fe}$, $S = \text{C}_6\text{H}_5\text{NO}_2$ compound, which has the largest unit cell [70, 76]). The superconductivity in the β'' -(BEDT-TTF)₄[(H₃O)M(C₂O₄)₃]S salts is therefore suppressed by the reduction in volume of the unit cell. The β'' -(BEDT-TTF)₄[Cr(C₂O₄)₃]C₅H₅N compound has a low temperature semiconducting phase, whereas the compounds containing Fe³⁺ ions and the host solvents benzonitrile (C₆H₅CN) and nitrobenzene (C₆H₅NO₂) are both quasi-two-dimensional (Q2D) type-II superconductors, with T_c ranging between 5 and 8 K. T_c has been found to be sample dependent [76, 78], and for the samples investigated here the compound containing benzonitrile displayed a T_c higher ($T_c \approx 6.5\text{K}$) than the ones containing nitrobenzene ($T_c \approx 5.5\text{K}$). The superconducting properties of a number of β'' -(BEDT-TTF)₄[(H₃O)M(C₂O₄)₃]S salts are reported in Table 3.2.

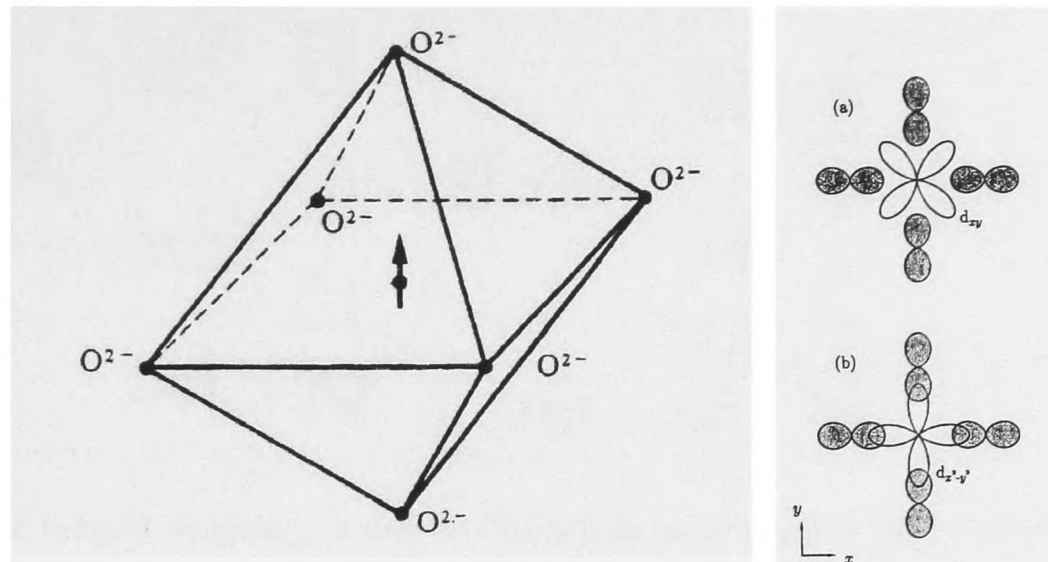


Figure 3.4: Left: an ion within an octahedral cage of oxygen atoms (from [2]). Right: the degeneracies of the d orbitals are lifted by electrostatic interactions with neighboring atoms. The octahedral environment lowers the energy of the d_{xy} orbital (a) with respect to the $d_{x^2-y^2}$ orbital (b) (from [3]).

3.3 The spin Hamiltonian

3.3.1 Theoretical background

This Section will identify the effective spin Hamiltonian of Cr^{3+} ($S=3/2$) and Fe^{3+} ($S=5/2$), $3d$ transition metal ions embedded in the anion layers of the $\beta''\text{-(BEDT-TTF)}_4[(\text{H}_3\text{O})\text{M}(\text{C}_2\text{O}_4)_3]\text{S}$ compounds. Figure 3.5 shows the lifting of the degeneracy of the electronic orbitals due to the simultaneous presence of crystal field potentials of intermediate strength with octahedral and trigonal symmetry [19]. This paragraph will describe the effects of the crystal potentials on degenerate spin multiplets.

Based on references [19, 20, 3] and Section 1.6, it is reasonable to assume that our systems are in the Russell-Saunders regime and the spin-orbit coupling contribution is further suppressed due to the quenching of orbital angular momentum induced by the strong crystal field surrounding the ions. The two main energy contributions to the spin Hamiltonian are therefore expected to be the zero-field splitting and Zeeman energy terms. Depending on the relative magnitude of the two terms, the regime is named the weak, intermediate or strong ligand field regime [19]. The physical origin of the zero-field splitting term in the spin Hamil-

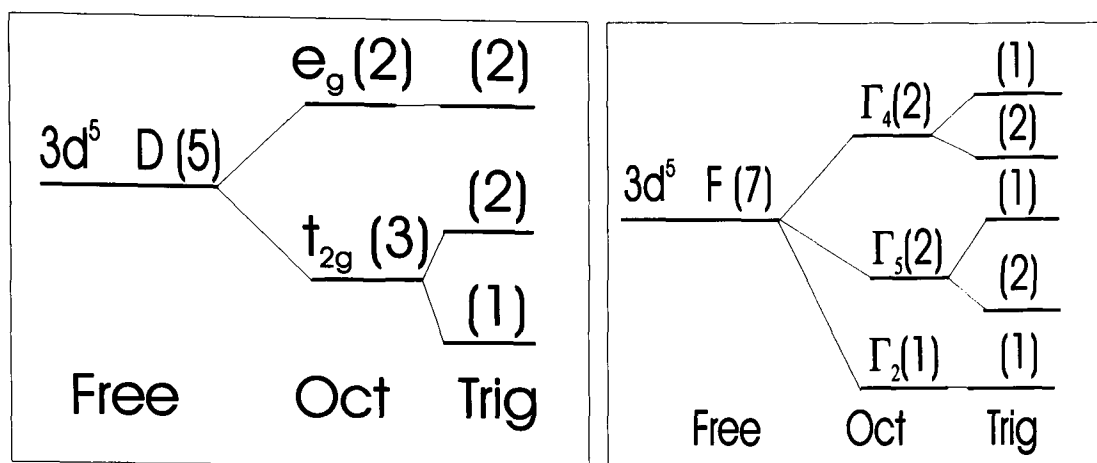


Figure 3.5: Lifting of orbital degeneracy due to the presence of crystal field potentials with octahedral and trigonal symmetry for a $3d$ metal ion [19]; apart from the $L = 0$ case, the D and F states presented here are the only possible configurations for the free ions. The F state corresponds to the studied Cr^{3+} ion. The numbers between brackets indicate the multiplicity of a given level.

tonian is twofold: one contribution is due to the magnetic dipolar interaction between unpaired electrons belonging to the same ion, and the second one is the result of the anisotropic part of the spin-orbit coupling contribution. The effect of the latter is modelled in the effective spin formalism by an anisotropic g -factor, and a further second order correction term to be added to the zero-field splitting.

At small distances, two unpaired electrons will experience a strong dipole-dipole interaction. This electron spin-electron spin interaction is given by the following Hamiltonian which is the classical expression for the dipolar interaction energy:

$$H_{\text{ss}} = \frac{\mu_0}{4\pi} \left[\frac{\mu_1 \cdot \mu_2}{r_{12}^3} - \frac{3(\mu_1 \cdot \mathbf{r}_{12})(\mu_2 \cdot \mathbf{r}_{12})}{r_{12}^5} \right]. \quad (3.1)$$

The magnetic moment operators can be replaced by the corresponding spin operators:

$$H_{\text{ss}} = \frac{\mu_0}{4\pi} g^2 \mu_B^2 \left[\frac{\mathbf{S}_1 \cdot \mathbf{S}_2}{r^3} - \frac{3(\mathbf{S}_1 \cdot \mathbf{r})(\mathbf{S}_2 \cdot \mathbf{r})}{r^5} \right]. \quad (3.2)$$

By expressing H_{ss} in terms of the total spin operator $\mathbf{S} = \mathbf{S}_1 + \mathbf{S}_2$ and carrying out some substitutions and expansions, H_{ss} can be conveniently written in matrix form as [20]:

$$H_{\text{ss}} = \frac{1}{2} \frac{\mu_0}{4\pi} g^2 \mu_{\text{B}}^2 \begin{bmatrix} S_x & S_y & S_z \end{bmatrix} \begin{bmatrix} \frac{(r^2-3x^2)}{r^5} & \frac{-3xy}{r^5} & \frac{-3xz}{r^5} \\ \frac{-3xy}{r^5} & \frac{(r^2-3y^2)}{r^5} & \frac{-3yz}{r^5} \\ \frac{-3xz}{r^5} & \frac{-3yz}{r^5} & \frac{(r^2-3z^2)}{r^5} \end{bmatrix} \begin{bmatrix} S_x \\ S_y \\ S_z \end{bmatrix}$$

or

$$H_{\text{ss}} = \mathbf{S} \cdot \mathbf{D} \cdot \mathbf{S}. \quad (3.3)$$

$\mathbf{D}$ is a second rank traceless tensor and can be diagonalised. In the diagonalised basis, equation 3.3 becomes

$$H_{\text{ss}} = D_{xx} S_x^2 + D_{yy} S_y^2 + D_{zz} S_z^2. \quad (3.4)$$

As the $\mathbf{D}$ tensor is traceless, only two independent parameters are needed to characterise it and equation 3.3 is conveniently written as

$$H_{\text{ss}} = D[S_z^2 - \frac{1}{3}S(S+1)] + E(S_x^2 - S_y^2). \quad (3.5)$$

Even “pure spin” ground state multiplets contain some admixed amount of orbital angular momentum due to interactions with certain excited states [20]. The spin-orbit interaction term

$$H_{\text{so}} = \lambda_{\text{so}} \mathbf{L} \cdot \mathbf{S}, \quad (3.6)$$

is responsible for the departure of the g -factor from its free electron value 2.00232 by an amount $2\lambda_{\text{so}}\Lambda$ and for an additional term $\mathbf{S} \cdot \mathbf{D} \cdot \mathbf{S}$, with $\mathbf{D} = \lambda_{\text{so}}^2 \Lambda$ and Λ being a second rank tensor involving only contributions of orbital angular momentum from excited states. The contribution to the zero-field splitting due to Equation 3.6 is effective only in systems with $S \geq 1$ and needs to be added to Equation 3.3. In fact it cannot be experimentally distinguished from it [20].

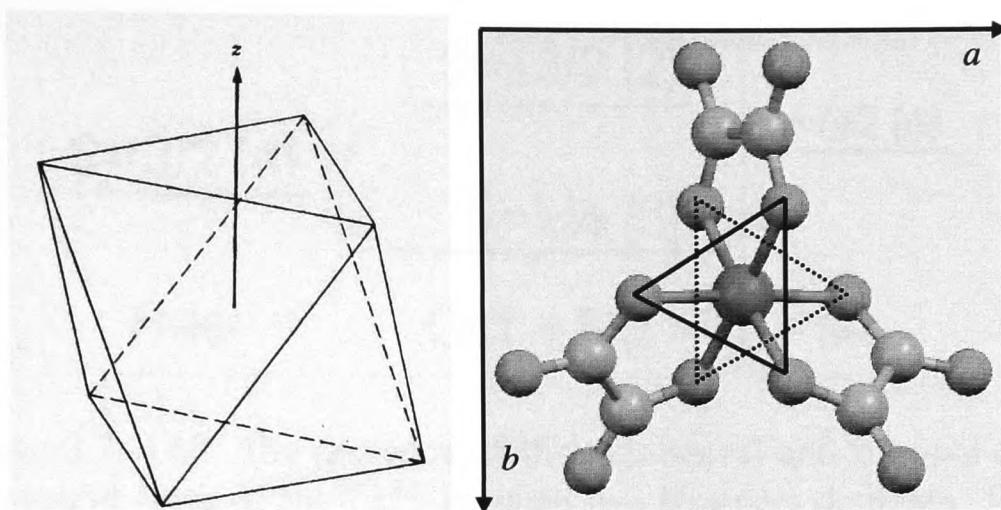


Figure 3.6: Left: a trigonally distorted octahedron, preserving 3-fold symmetry around the z-axis (from [19]). Right: the oxalate group surrounding the 3d metal ion in β'' -(BEDT-TTF)₄[(H₃O)M(C₂O₄)₃]S viewed along the interlayer direction (z-axis).

By putting together the results from Section 1.6 and those outlined above, it seems appropriate to attempt the modelling of the experimental data with the following Hamiltonian:

$$H = \mu \mathbf{B} \cdot \mathbf{g} \cdot \mathbf{S} + D[S_z^2 - \frac{1}{3}S(S+1)] + E(S_x^2 - S_y^2). \quad (3.7)$$

This particular form of Hamiltonian is most suitable given the symmetry of the oxalate complex $(\text{C}_2\text{O}_4)^{6-}_3$ surrounding the ions. The isolated complex is octahedral and therefore has cubic symmetry (see Figure 3.4, left hand side). A trigonal distortion of the complex is expected in the interlayer direction of the monoclinic crystal structure [69]; this is the magnetic z-axis, at a small angle from the crystallographic *c*-axis (see Figures 3.2 and 3.4, left hand side). The trigonal distortion gives rise to the axial term in equation 3.6: $D[S_z^2 - \frac{1}{3}S(S+1)]$. Figure 3.6, right hand side, helps in visualizing the origin of the additional rhombic distortion that makes the point symmetry of the ionic complex D_3 [69, 70, 71]: the six oxygens coordinated to the central ion can be grouped into two subsets of three (dotted and bold triangles). The chirality of the oxalate complex originates from a rigid rotation of one of the triads of oxygens with respect to the other. With reference to Figure 3.6, the complex has the enantiomeric form Λ or Δ depending on whether the lowermost in space along the interlayer direction of the triads is

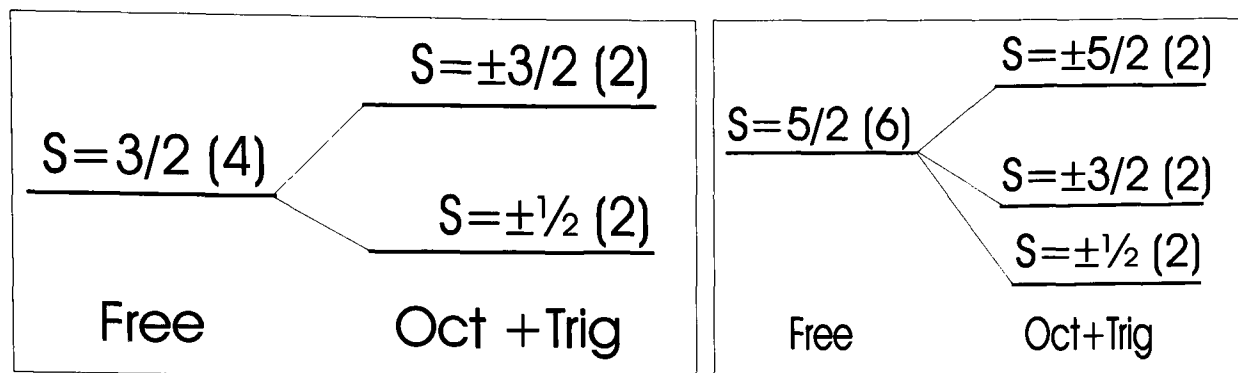


Figure 3.7: Left: the presence of the octahedral and trigonal crystal potentials splits the ground state of the Cr^{3+} ion into two Kramers doublets. Right: the same crystal field splits the six-fold degenerate ground state of the Fe^{3+} ion into three Kramers doublets [20].

rotated clockwise or anticlockwise with respect to the triad lying above it. This rotation is responsible for lowering the symmetry from D_3 to D_{3d} and introducing the rhombic term in equation 3.7: $E(S_x^2 - S_y^2)$. The Cr^{3+} ion ($S = 3/2$) has spin multiplicity $2S + 1 = 4$; as described in Figure 3.7, the effect of the crystal field is to split the fourfold degenerate ground state into two Kramers doublets. Similarly, the six-fold degenerate ground state of the Fe^{3+} ion is split into three Kramers doublets. Each doublet will subsequently be Zeeman split by an applied magnetic field $\mathbf{B}$. The next Section will extract the zero-field splitting parameters D and E from the positions of the spin resonances in the presence of an external field.

3.3.2 Experimental results and simulated spectra

The magneto-optical spectra presented in this chapter have been obtained with a number of different techniques. For all the experiments employing resonators, the MVNA [22] described in Section 2.1 was the source and detector of the millimetre-wave radiation in the frequency range 50-313 GHz. The angle dependence of the spectra for all the compounds $\beta''\text{-(BEDT-TTF)}_4[(\text{H}_3\text{O})\text{M}(\text{C}_2\text{O}_4)_3]\text{S}$ was obtained using the rectangular resonator in the TE_{102} mode with polar angle rotation capability. The samples (typical sizes $1 \times 0.2 \times 0.05 \text{ mm}^3$) come in shapes of hexagonal platelets or needles. It is possible to deduce the upper and lower faces that are par-

allel to the highly-conducting quasi-two-dimensional planes by visual inspection. One sample of β'' -(BEDT-TTF)₄[Cr(C₂O₄)₃]C₅H₅N, one of β'' -(BEDT-TTF)₄-[Fe(C₂O₄)₃]C₆H₅NO₂ and 5 different samples of β'' -(BEDT-TTF)₄[Fe(C₂O₄)₃]C₆H₅CN were investigated.

The samples were placed in the magnetic field antinode of the cavity so as to optimize the condition for EPR, namely maximizing the magnetic component of the oscillatory millimetre wave radiation $\mathbf{B}_{AC}$ perpendicular to the external quasi-static field $\mathbf{B}_{DC}$ [19]. The Variable Temperature Insert (VTI) fitted inside the Oxford Instruments 17 Tesla superconducting magnet allowed access to pumped ⁴He temperature (1.4 K). All temperature dependence studies focussed on the response of the samples below 120 K, with detailed 1 K steps in the region between 10 K and 1.4 K. The angle dependence was limited by the coupling of the radiation from the waveguides to the resonator, the intensity of the detected signal decreasing as $\cos^4 \theta$ [21]. In order to study the frequency and field dependence of the EPR lines, several samples of the superconducting β'' -(BEDT-TTF)₄[Fe(C₂O₄)₃]C₆H₅CN compound were investigated in the tuneable cylindrical cavity over the frequency range 50 to 73 GHz, and, in the same resonator used in an overmoded configuration at frequencies of 209 and 313 GHz. In this latter case, the ESA1 Gunn extensions [22] were used to generate and detect the higher harmonics then downconverted to the optimised lower frequency 32 MHz signal at the MVNA.

For the measurements using both rectangular and cylindrical resonators, care was taken that the presence of the samples could be considered a perturbation of the electromagnetic environment within the cavity (see Section 2.4 of Chapter 2). The sample in a cavity is part of the resonant system and the changes in its physical properties are reflected in changes of the frequency $\Delta\nu$ and the quality factor ΔQ of the resonator [21, 8]. Typical Q-factor changes at room temperature between unloaded and loaded cavity were $\Delta Q \sim 100 - 300$ for $Q \approx 1300$ in the case of the rectangular resonator, $\Delta Q \sim 200 - 400$ for $Q \approx 3000$ in the case of the tuneable cylindrical resonator. Similarly, the shifts in resonant frequency were

$\Delta\nu \sim 200 - 400$ MHz for the rectangular resonator and $\Delta\nu \sim 100 - 200$ MHz for the cylindrical resonator. The Q-factors improve by about 15 per cent upon cooling from room temperature to 4 K, and frequencies shift up by 300-400 MHz as the conductivity of the whole system improves and the metallic walls of the resonator contract.

For the same compound additional EPR spectra at frequencies of 95 and 180 GHz were obtained by overmoded waveguide transmission with field modulation (modulation amplitude 240 mA, modulation frequency 10 kHz) and lock-in detection. The radiation was in this case generated by a Gunn oscillator with frequency doubler and the detector was a ^4He -cooled Silicon bolometer. These last measurements were performed at the High Field-High Frequency (HFHF) Laboratory run by Luca Pardi at the "Istituto per i Processi Chimico-Fisici" (IPCF), Pisa.

The relevant Hamiltonian parameters were extracted by matching simulated spectra to the experimental data. All the simulations were performed using the programme EasySpin [80, 81] for Matlab. The package contains simulation functions that yield absorption or differential cw EPR and ENDOR spectra of single crystals and powder samples once a spin system structure has been specified [80]. The system can contain an arbitrary number of spins, the interaction parameters, matrices and tensors representing the anisotropic g-tensor, the coefficients for the Stevens operators [19], the axial and rhombic zero-field splitting, the hyperfine structure, nuclear quadrupole and nuclear Zeeman terms. The temperature, the orientation with respect to a fixed frame of reference and details for line widths can also be included. Simulations of the temperature and angle dependencies of the cw EPR spectra were obtained for the three compounds $\beta''\text{-(BEDT-TTF)}_4[\text{Cr}(\text{C}_2\text{O}_4)_3]\text{C}_5\text{H}_5\text{N}$, $\beta''\text{-(BEDT-TTF)}_4[\text{Fe}(\text{C}_2\text{O}_4)_3]\text{C}_6\text{H}_5\text{CN}$ and $\beta''\text{-(BEDT-TTF)}_4[\text{Fe}(\text{C}_2\text{O}_4)_3]\text{C}_6\text{H}_5\text{NO}_2$, allowing the determination of the spin Hamiltonians that describe the systems. The energy level diagrams portraying the behavior of the eigenvalues of the spin Hamiltonian as a function of applied magnetic field for the two different 3d ions studied, Cr^{3+} and Fe^{3+} , are displayed in Figures 3.9 and 3.13.

The chromium compound

As outlined in Section 3.3.1, a suitable Hamiltonian for an ion sitting in an environment with trigonally distorted cubic symmetry and an additional rhombic distortion has the form of equation 3.7.

The chromium ion (Cr^{3+}) is in the 3+ oxidation state, with three unpaired electrons, and has spin and angular momentum quantum numbers $S = 3/2$ and $L = 3$ respectively. Due to the quenching of orbital angular momentum, the ion will effectively behave as if $L = 0$ and $J = S = 3/2$. The ground state spin multiplet is then fourfold degenerate ($2S + 1$). If no crystal field were present, the zero field states would be degenerate and only one line could be seen in the EPR spectrum, with the additional hyperfine quartet due to the $I = \frac{3}{2}$ nuclear magnetic moment [20]. In the high field limit, M_S is a good quantum number for the $\hat{S}_z$ operator and the corresponding eigenstates are $|\frac{3}{2}\rangle$, $|\frac{1}{2}\rangle$, $|\frac{1}{2}\rangle$ and $|\frac{3}{2}\rangle$. There is also an axial term in the Hamiltonian due to the trigonal distortion along the crystallographic interlayer direction, and this partially lifts the degeneracy, giving two Kramers' doublets separated in energy by $2D$. Kramers' theorem guarantees at least two-fold degeneracy for systems with an odd number of electrons in the absence of an applied field. The magnetic field then makes three transitions possible, now occurring at different fields, between adjacent levels ($\Delta M_S = \pm 1$), provided $2D$ is not large compared with $h\nu$ [20]. The additional rhombic term modifies the zero-field separation of the two doublets to $2(D^2 + 3E^2)^{1/2}$ [20]. Furthermore, by introducing the operators S_x^2 and S_y^2 that admix the high field spin eigenstates separated by values of $\Delta M_S = \pm 2$ or higher, it weakens the condition on forbidden transitions between such levels.

The temperature dependence of the EPR spectrum obtained from the non superconducting compound $\beta''\text{-(BEDT-TTF)}_4[\text{Cr}(\text{C}_2\text{O}_4)_3]\text{C}_5\text{H}_5\text{N}$ is displayed in Figure 3.8. The external magnetic field is along the interlayer direction of the crystal; this direction corresponds to the axis of trigonal distortion of the octahedral oxalate complex (see Figure 3.6). At the temperature of 40 K three

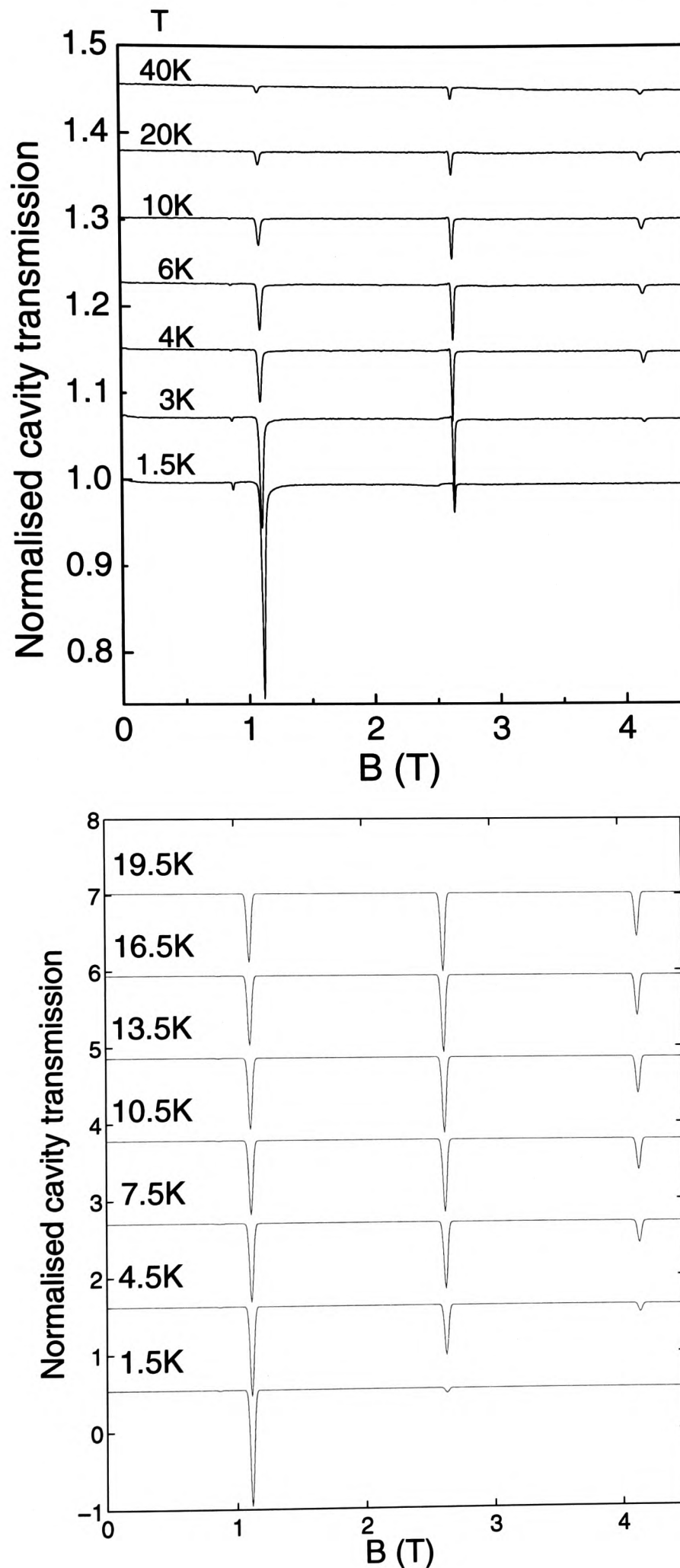


Figure 3.8: Top: temperature dependence of the magneto-optical response of β'' -(BEDT-TTF)₄[Cr(C₂O₄)₃]C₅H₅N at the frequency $\nu \approx 71.2$ GHz, with the external field along the direction of axial symmetry for the system ($\theta = 0^\circ$). Bottom: the simulated spectra using the parameters listed in Table 3.3.2. All traces are vertically offset for clarity.

absorption lines are clearly visible. For a transition between levels with quantum numbers M_S and $M_S + 1$, the intensity of the absorption line is proportional to the square of the matrix element involving the two states and the raising operator ($\hat{S}_+ = \hat{S}_x + i\hat{S}_y$) [20]:

$$| \langle \mathbf{S} | \hat{S}_+ | \mathbf{S} + 1 \rangle |^2 = S(S + 1) - M_S(M_S + 1). \quad (3.8)$$

The relative intensities of the experimental lines quantitatively obey this relationship, assuming the $|M_S\rangle$ states to be the eigenstates of the system [20]. So for Cr^{3+} ions the ESR transitions have the following relative probabilities:

$$\begin{aligned} | \langle -\frac{1}{2} | \hat{S}_+ | -\frac{3}{2} \rangle |^2 &= S(S + 1) - M_S(M_S + 1) = 3 \\ | \langle +\frac{1}{2} | \hat{S}_+ | -\frac{1}{2} \rangle |^2 &= 4 \\ | \langle +\frac{3}{2} | \hat{S}_+ | +\frac{1}{2} \rangle |^2 &= 3 \end{aligned} \quad (3.9)$$

Below 20 K the Boltzmann factor $\exp(-\Delta E/k_B T)$, where $\Delta E = E_{M_S+1} - E_{M_S}$ is the energy difference between the two levels involved in the resonance, is responsible for the growing relative intensity of the low field lines with respect to the high field transitions. Labelling n_a and n_b the populations of the lower and upper levels, for a system of isolated spins in thermodynamic equilibrium with the lattice, the resonance intensity I is proportional to the population difference between the levels [20]:

$$I \propto n_a - n_b = e^{-\frac{E_a}{k_B T}} - e^{-\frac{E_b}{k_B T}} = 1 - e^{-\frac{\Delta E}{k_B T}} \quad (3.10)$$

Upon entering the temperature region where $k_B T$ is comparable with the overall splitting of the energy levels, the comparison of the relative intensities of the absorption lines allows the determination of the absolute sign of the axial field splitting parameter D . In such a temperature region, the population of the lower levels will be increased with respect to that of the higher levels, and transitions

between lowest levels will progressively gain in intensity over transitions between the highest levels; thus the order of the levels can be found, and from this the sign of D [19]. The lower field lines become more intense in the case of the chromium ion, and therefore correspond to transitions between lowest levels; this occurs for negative values of D [19]. The diagram describing the energy levels of this system (Figure 3.9) gives a pictorial view of this effect. The case of the β'' -(BEDT-TTF)₄[Fe(C₂O₄)₃]S compounds (described in the following section) will provide an example of positive axial zero-field splitting parameter D .

Below 6 K a fourth line appears at about 0.85 T. This line can be attributed to a higher order “forbidden” transition between levels that are, in this field region, an admixture of $|\pm \frac{3}{2}\rangle$ and $|\mp \frac{1}{2}\rangle$ (see Figure 3.9). No hyperfine structure is resolved. Being the Cr isotope with nuclear moment $I = 3/2$ with 9.5% abundance, we can then expect the hyperfine quartet to be a contributing factor to the experimental line widths. The limited sensitivity of the experimental configuration is the probable cause preventing the detection of the hyperfine splittings. The temperature dependence is very accurately reproduced by the simulation (see bottom panel of Figure 3.8), which displays all the features visible in the experimental data. The parameters of the fitting Hamiltonian are: $g_{\parallel} = 1.900(2)$, $g_{\perp} = 1.951(2)$, $D = -20700(5)$ MHz, $E = 800(5)$ MHz (the zero field splitting parameters are summarized with the results for all the other compounds in units of inverse wavenumbers in the Table 3.3.2 at the end of this Section). The “forbidden” transition at 0.85 T is present in the simulation, even with the external field along the direction of axial symmetry for the spin Hamiltonian, the z-direction. With reference to Figure 3.9, it can be noticed that in the field region around approximately 0.8 T the eigenvalues for $M_S = +\frac{3}{2}$ and $M_S = -\frac{1}{2}$ approach one another. Due to the presence of the rhombic distortion, the additional spin operators S_x^2 and S_y^2 induce mixing of the eigenstates $|+\frac{3}{2}\rangle$ and $|-\frac{1}{2}\rangle$, creating the anticrossing that allows for the weak absorption line to be visible even with the field strictly in the z-direction.

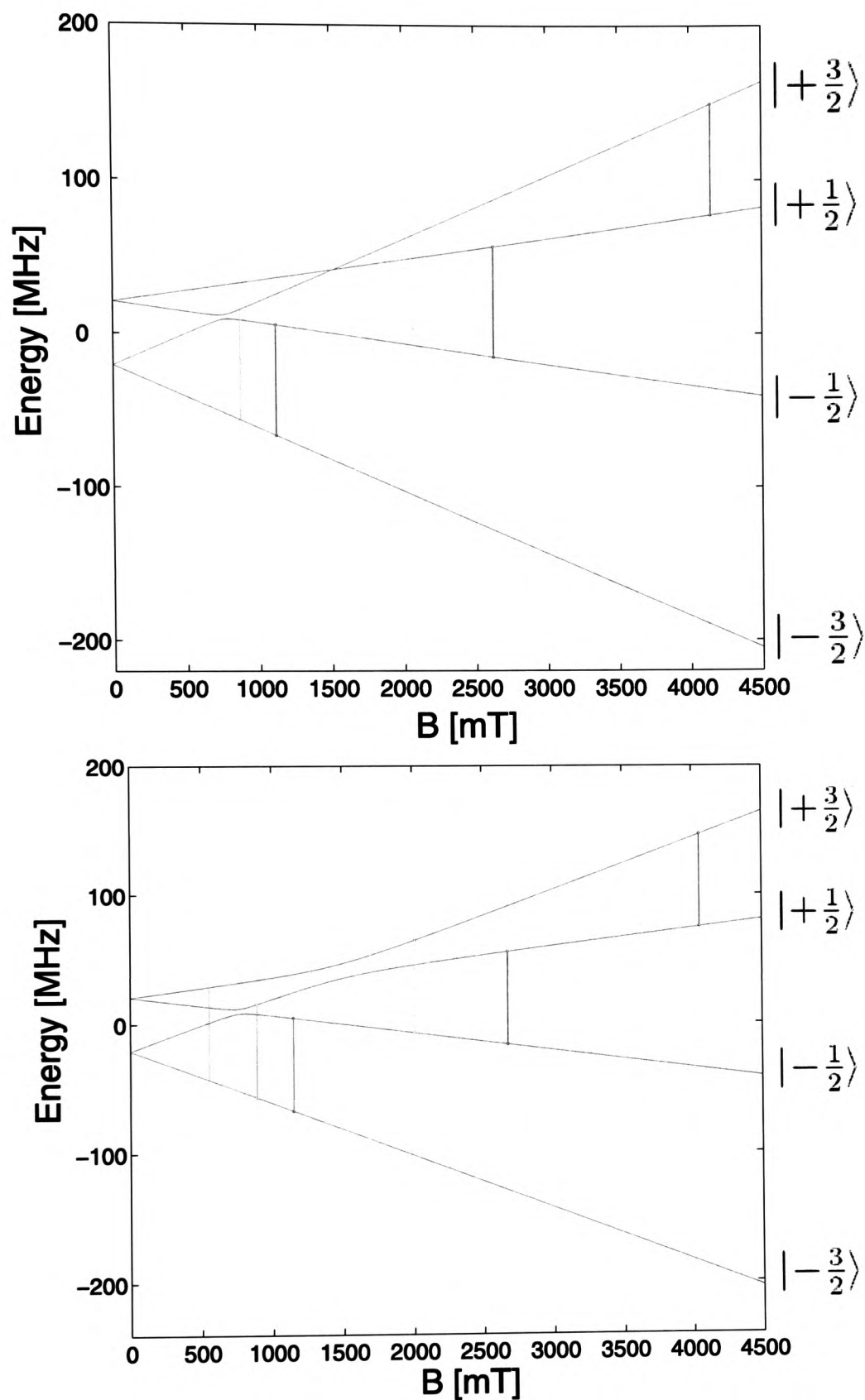


Figure 3.9: Top: energy levels as a function of magnetic field for the β'' -(BEDT-TTF)₄[Cr(C₂O₄)₃]C₅H₅N compound ($S = 3/2$), showing allowed and forbidden transitions at the experimental frequency of 71.25 GHz. Bottom: energy levels for the same system with the external magnetic field tilted by 10° with respect to the spin Hamiltonian axis of symmetry. Notice the appearance of anticrossing due to strong mixing of levels $M_S = +1/2$ and $M_S = +3/2$ (field expressed in milliTesla).

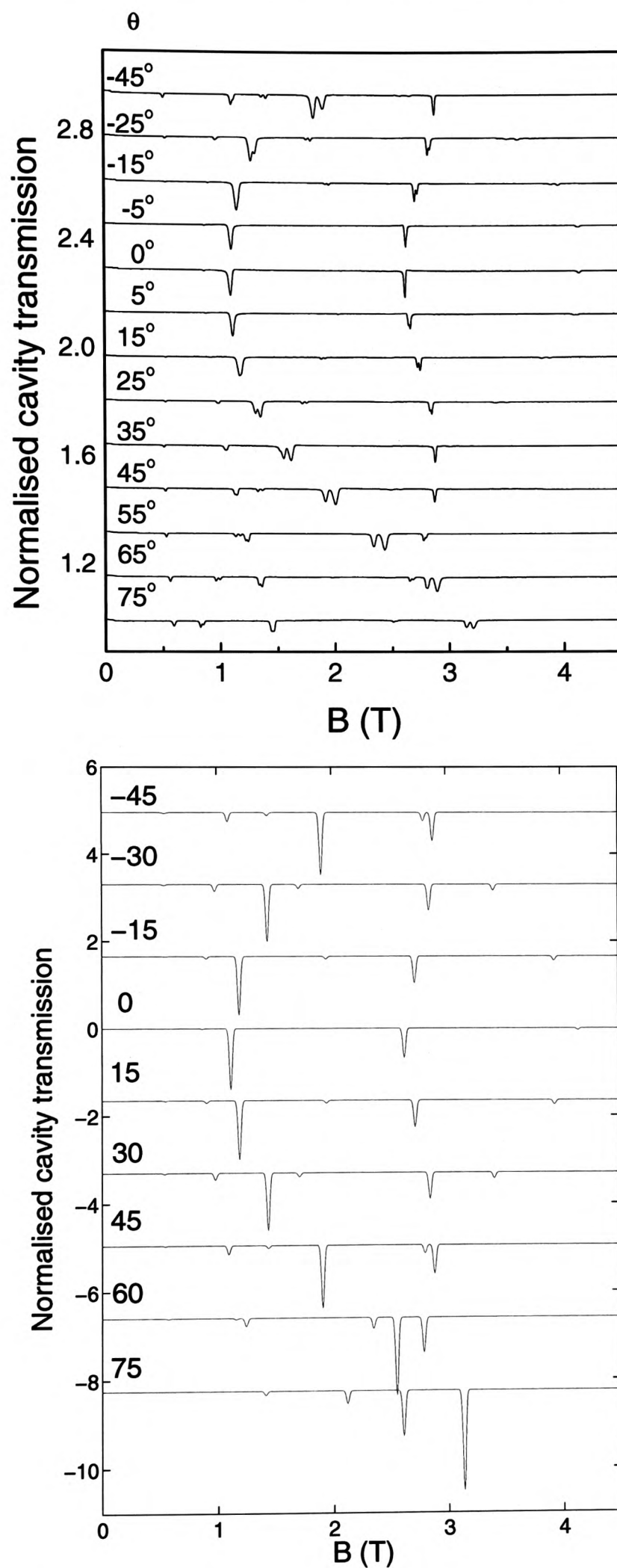


Figure 3.10: Top: angle dependence of the magneto-optical response of β'' -(BEDT-TTF)₄[Cr(C₂O₄)₃]C₅H₅N at the frequency $\nu \approx 71.2$ GHz. Bottom: the simulated spectra using the parameters listed in Table 3.3.2. All traces are vertically offset for clarity.

The energy levels presented in Figure 3.9 illustrate the origin of all the observed transitions and their temperature dependence. The levels represent a plot of the eigenvalues obtained by solving the secular determinant derived from the 4×4 matrix Hamiltonian for a system with effective spin $S = 3/2$ and D and E values as given in Table 3.3.2. The energy levels for the different states are [19]:

$$\begin{aligned} W_{\pm\frac{3}{2}} &= \pm\frac{1}{2}g\mu B_z \pm [(g\mu B_z \pm D)^2 + 3E^2]^{\frac{1}{2}}, \\ W_{\pm\frac{1}{2}} &= \mp\frac{1}{2}g\mu B_z \pm [(g\mu B_z \mp D)^2 + 3E^2]^{\frac{1}{2}}. \end{aligned} \quad (3.11)$$

The absorption spectra as a function of the angle θ between the external field and the symmetry axis of the magnetic complex are displayed in figure 3.10, top panel, with the simulated traces in the panel immediately below for easy comparison. Two more resonant lines appear at about 0.5 T and 2.1 T. These are exactly reproduced in the simulation, and can be loosely attributed to “forbidden” transitions between levels with $\Delta M = \pm 2$. In fact, three are in this instance the reasons for such forbidden transitions to be visible. The first is the already mentioned mixing due to the presence of the spin operators S_x^2 and S_y^2 . Even if the rhombic distortion were not present, the fact that at low field the wave functions are linear combinations of the high-field eigenfunctions implies that the M_S values cannot be assigned as quantum number to the states; the “ $\Delta M = \pm 2$ ” transition is then allowed for the component of the oscillatory field B_{AC} along the direction of the quasistatic field B_{DC} [19, 20]. This component differs from zero as soon as the rectangular resonator is rotated away from $\theta = 0$. Thirdly, when the external field B_{DC} is at an angle with respect to the direction of the principal axes of the magnetic system, the states are mixed by the dipolar spin-spin interaction (see Equation 3.3), and “ $\Delta M = \pm 2$ ” transitions can be observed even with the microwave field strictly orthogonal to the quasistatic field [20]. One feature of the experimental data is not reproduced by the simulated spectra: the splitting of each line into two as the angle is tilted. There are two possible ex-

planations for this phenomenon, one of crystallographic origin and the second related to the in-plane distortion of the magnetic complexes. Subsequent anion layers are rotated by π with respect to one another; this causes the unit cell to enclose along the interlayer direction elements of two neighbouring anion layers, which are crystallographically inequivalent (see Figure 3.2). This crystallographic feature renders alternating layers also magnetically non-equivalent in the ab plane of the crystal, which contains the xy plane of the magnetic frame of reference of the oxalate complex. This causes the presence of two magnetic sublattices sharing the same axis of symmetry and therefore visible only when the applied field is tilted away from this axis. The second possible cause of the observed splittings is that in the ab plane subsequent anion layers also differ in the chirality of the $[\text{M}(\text{C}_2\text{O}_4)_3]^{3-}$ complex. This in itself makes the alternating anion layers magnetically non-equivalent, differing only in the rhombic component of their crystal field Hamiltonian. Such a difference too can be detected only by applying the external quasistatic field away from the magnetic axis of symmetry. The hyperfine origin for the observed splittings is ruled out since this would induce a quartet of equally spaced lines, with the principal ESR resonance lying in the middle point between them. The spectra for the $\beta''\text{-(BEDT-TTF)}_4[\text{Fe}(\text{C}_2\text{O}_4)_3]\text{S}$ compounds presented in the next Section will bring up a similar issue, and an attempt to identify the origin of these splittings will be outlined in that context.

The iron compounds

With the aim of understanding the effect of different solvents on the crystal field symmetry of the Fe^{3+} ion within the trioxalate octahedron, temperature and angle-dependent spectra were recorded for the superconducting compounds $\beta''\text{-(BEDT-TTF)}_4[\text{Fe}(\text{C}_2\text{O}_4)_3]\text{C}_6\text{H}_5\text{CN}$ ($T_c \approx 6.5$ K) and $\beta''\text{-(BEDT-TTF)}_4[\text{Fe}(\text{C}_2\text{O}_4)_3]\text{C}_6\text{H}_5\text{NO}_2$ ($T_c \approx 5.5$ K). As already mentioned, the different templating effect of the solvents has a major role in determining the interlayer transport properties of the materials, whether superconductivity arises or not and what the superconducting transition temperature is [76]. The size of the solvent molecule has been related to the amount of intrinsic disorder present within the different crystalline structures, with smaller solvents essentially allowing for a greater amount of static disorder [70, 76, 82, 79]. The main aim of the following paragraph is to establish what differences exist in the spin Hamiltonians of the Fe^{3+} ions due to the presence of different host solvent molecules.

Figure 3.11, top panel, shows the temperature dependence of the millimetre-wave absorption features for the sample containing benzonitrile, $\beta''\text{-(BEDT-TTF)}_4[\text{Fe}(\text{C}_2\text{O}_4)_3]\text{C}_6\text{H}_5\text{CN}$, placed in the magnetic field antinode of the TE_{102} mode of a rectangular cavity resonating at a frequency of approximately 71 GHz. The external magnetic field is applied perpendicular to the highly conducting layers of the platelet sample. Five transitions are clearly visible already at 80 K. This indicates that the Fe^{3+} ion is in the high spin configuration, with each of the 5 outer shell electrons occupying a different d -orbital, their spins being therefore unpaired ($L = 0$, $J = S = 5/2$). The effective spin of the ground multiplet will then be $S = 5/2$, with degeneracy $M = 2S + 1 = 6$ in the absence of crystal field and in zero applied magnetic field. If the main contribution to the zero-field splitting were due to the octahedral potential of cubic symmetry formed by the 6 oxygen atoms in their undistorted position, the ground state sextet would split into a doublet and a quartet [20], with a high field resonance spectrum consisting of a central line (transition between $|+\frac{1}{2}\rangle$ and $|-\frac{1}{2}\rangle$ eigenkets), and two pairs

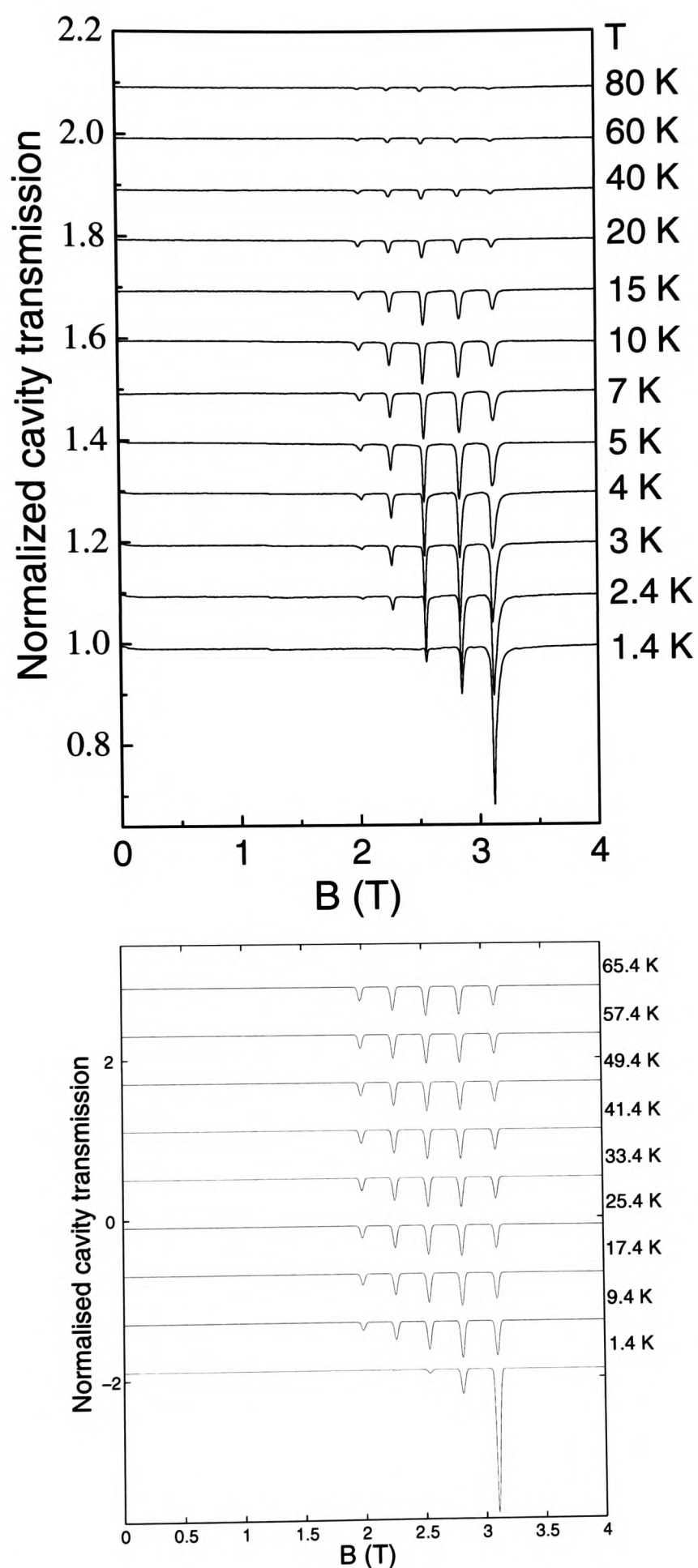


Figure 3.11: Top: temperature dependence of the magneto-optical response of β'' -(BEDT-TTF)₄[Fe(C₂O₄)₃]C₆H₅CN at the microwave frequency $\nu \approx 71.2$ GHz for $\theta = 0^\circ$. Bottom: the simulated spectra using the parameters listed in Table 3.3.2 for different temperatures between $T = 65.4$ K and $T = 1.4$ K. All traces are vertically offset for clarity.

of closely spaced lines appearing as a function of field at equal distance on either side of the central line [20]. The fact that the five experimental lines are to a first approximation all equally spaced in field, and their relative intensities are in the ratio 5 : 8 : 9 : 8 : 5 (and not 8 : 5 : 9 : 5 : 8, as expected for the case of a purely octahedral potential [19, 20]) indicates that a suitable spin Hamiltonian for this system will be of the type of Equation 3.7, with the Zeeman term as the leading one, followed by the zero-field axial and rhombic terms; the spin-orbit contribution will be small, its effect contained in the effective g and D tensors as described earlier in Section 3.3.1. The sextet is split into 3 Kramers doublets ($|\pm \frac{1}{2}\rangle$, $|\pm \frac{3}{2}\rangle$ and $|\pm \frac{5}{2}\rangle$) and the $2S = 5$ transitions correspond to the allowed spin resonance transitions between levels with $\Delta M = \pm 1$ (transitions labelled in red in Figure 3.13). Below 10 K, the relative intensities of the lines depart from the ratio determined by the transition matrix elements, with the transitions at lower field becoming gradually weaker, while the high field ones are becoming more intense. As the temperature becomes comparable with the overall energy spacing of the various eigenstates ($k_B T \approx 5\hbar\omega$ when $T \simeq 10$ K in this case), the transitions occurring between levels having an energy relatively higher than the others gradually disappear due to their progressive depopulation determined by the Boltzmann factor, in the same way as for the temperature dependence of the β'' -(BEDT-TTF)₄[Cr(C₂O₄)₃]C₅H₅N spectra previously described. This low temperature behavior allows the determination of the sign of D (see Table 3.3.2). Similarly to the case of the compound containing chromium, the interlayer direction turns out to be the direction of axial trigonal distortion. In this orientation ($\theta = 0$), no forbidden transitions are visible.

Figure 3.12, top panel, shows the absorption spectra for a second sample of β'' -(BEDT-TTF)₄[Fe(C₂O₄)₃]C₆H₅CN with the magnetic field applied parallel to the highly conducting planes, along the principal x -axis of zero-field splitting. The sample is placed in the magnetic field antinode of the TE_{011} mode of the tuneable cylindrical resonator described in Chapter 2.1; field sweeps are performed at fixed

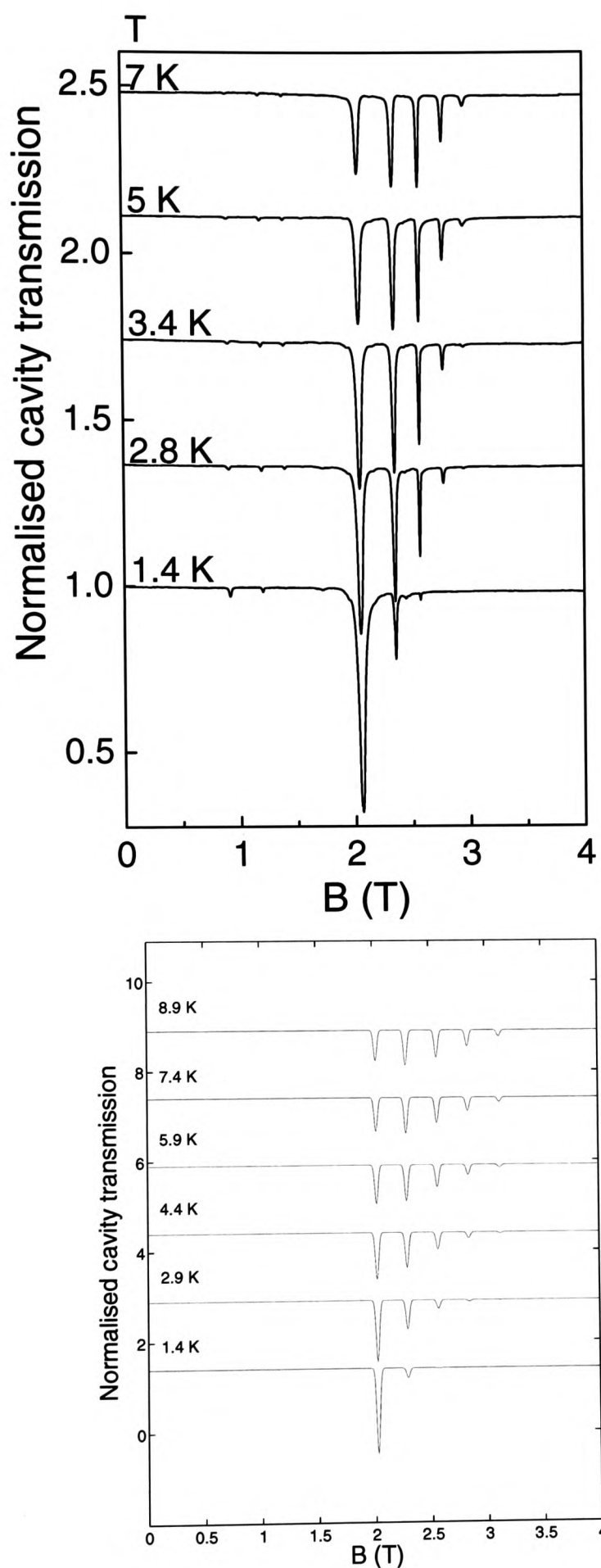


Figure 3.12: Top: temperature dependence of the magneto-optical response of β'' -(BEDT-TTF)₄[Fe(C₂O₄)₃]C₆H₅CN at the microwave frequency $\nu \approx 71.3$ GHz, for $\theta = 90^\circ$; from top to bottom the measured temperatures vary as indicated above each trace from $T = 7$ K to $T = 1.4$ K. Bottom: the simulated spectra using the parameters listed in Table 3.3.2 for different temperatures between $T = 8.9$ K and $T = 1.4$ K. All traces are vertically offset for clarity.

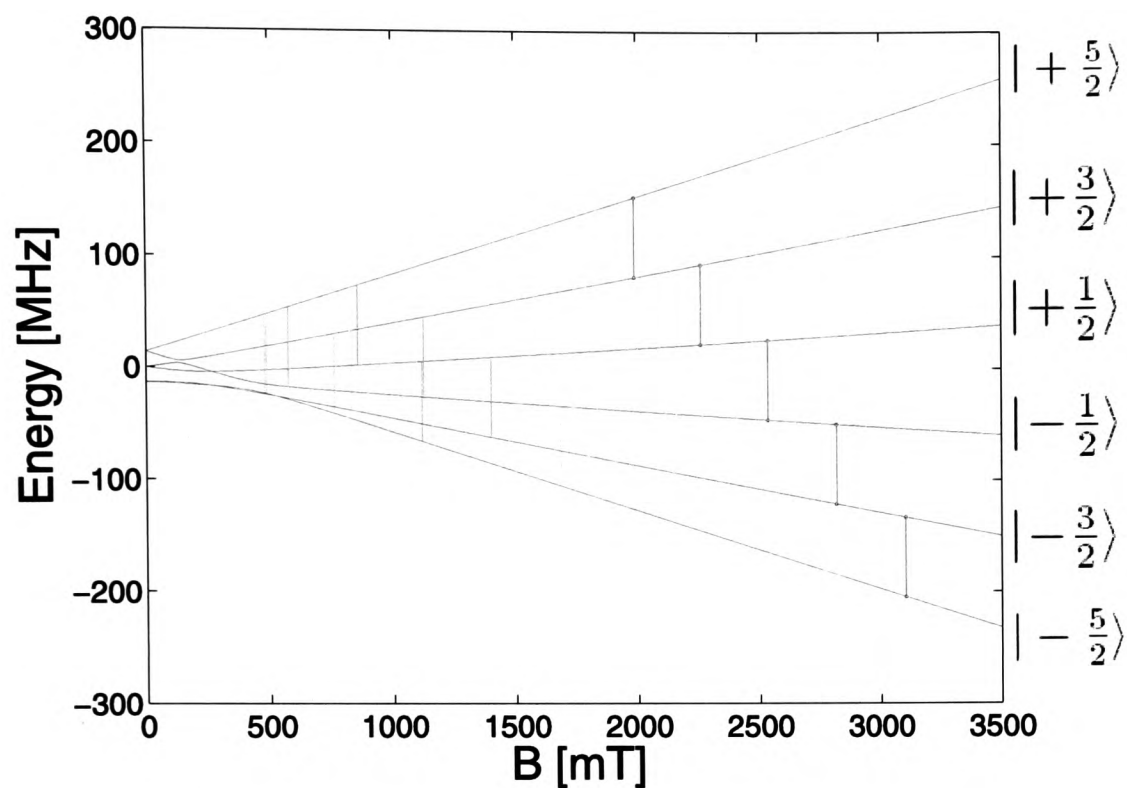


Figure 3.13: Energy levels as a function of magnetic field for the β'' -(BEDT-TTF)₄-[Fe(C₂O₄)₃]C₆H₅CN compound ($S = 5/2$), showing allowed and forbidden transitions at the experimental frequency of 71.31 GHz.

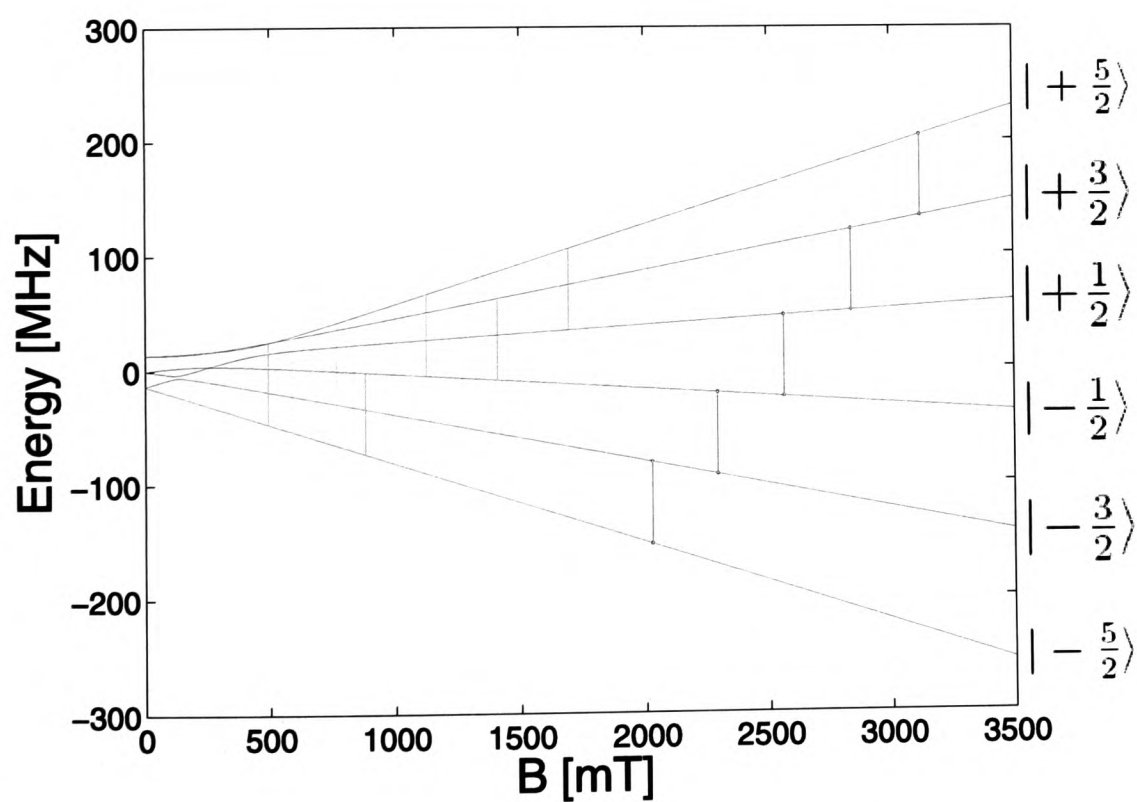


Figure 3.14: Energy levels for the same system as in the previous Figure with the external magnetic field at 90° with respect to the spin Hamiltonian axis of symmetry.

frequency (71 GHz) for the data presented in this picture. It is now the low field transitions that become more intense as the temperature decreases. Such a phenomenon is due to the angle dependence of the dominant contribution to the zero-field splitting, the axial term in the spin Hamiltonian, $D[S_z^2 - \frac{1}{3}S(S+1)]$ [19]. Assuming the system to have axial symmetry with respect to the z -axis ($g_z = g_{\parallel}$, $g_x = g_y = g_{\perp}$, $D_x = D_y = -\frac{1}{2}D_z = -\frac{1}{3}D$) in the strong field regime ($g\mu_B B \gg D$), let the external quasistatic field $\mathbf{B}$ be in the xz -plane, at an angle θ with respect to the z -axis. By transforming to a new system of axis (x' , y' , z') in order to diagonalize the Zeeman Hamiltonian, the energy of the state $S'_z = M_S$ is

$$W = g\mu_B B M_S + D \left[3 \frac{g_{\parallel}^2}{g^2} \cos^2 \theta - 1 \right] \left[M_S^2 - \frac{1}{3}S(S+1) \right], \quad (3.12)$$

where $g = g_{\perp}^2 \sin^2 \theta + g_{\parallel}^2 \cos^2 \theta$ and terms of higher order in D have been neglected. The angular variation of

$$D' = D \left[3 \frac{g_{\parallel}^2}{g^2} \cos^2 \theta - 1 \right] \quad (3.13)$$

corresponds to that of the spherical harmonic

$$3z^2 - (x^2 + y^2 + z^2) = 3z^2 - r^2 = r^2(3 \cos^2 \theta - 1); \quad (3.14)$$

the latter describes the symmetry of the crystal potential that determines the axial distortion represented in the spin Hamiltonian by the operators $3S_z^2 - (S_x^2 + S_y^2 + S_z^2) = 3S_z^2 - S(S+1)$. This gives rise to a quadrupolar distortion in the magnetisation density on the ion. The angle θ between z' and z is the angle made by the spin axis (direction of $\mathbf{B}$ in the strong field limit) and the local axis of symmetry of the magnetic ion. When $\theta = 90^\circ$, the splitting of the energy levels is only half that at $\theta = 0^\circ$, and the absorption lines occur in the reverse order (D' changes sign); all lines overlap for $\theta = 54^\circ 44'$ (see Figure 3.15). Departures from this behavior come from the presence of additional terms in the Hamiltonian when

the symmetry is lower than axial and higher order terms in D when evaluating the energy levels of the system [19]. In the spectra of Figure 3.12, top panel, the four transitions corresponding to $\Delta M = \pm 2$ are clearly visible due to the presence of the operators S_x^2 and S_y^2 , deriving from the additional rhombic distortion; their intensity is higher than the simulation predicts (Figure 3.12, bottom panel), probably due to the presence of a non-zero oscillatory field along the direction of the quasistatic field.

The simulated spectra as a function of temperature and angle (bottom panels of Figures 3.11 and 3.12), together with the simulation of a powder spectrum to match the data obtained from a pellet made of β'' -(BEDT-TTF)₄[Fe(C₂O₄)₃]-C₆H₅CN mixed with wax and KCl at 95 and 190 GHz, allowed a very accurate determination of the parameters defining the spin Hamiltonian for this compound (Table 3.3.2). The energy levels for two different values of the angle θ (Figures 3.13 and 3.14) describe the evolution of the eigenvalues for the three Kramers' doublets split by a magnetic field and show the inversion of position between high and low field resonances as a function of angle. In the low field region, M_S is not a good quantum number and the selection rule for allowed transitions does not strictly hold. Due to the mixing of states, the "higher order" transitions are not forbidden: they are indicated by grey lines in Figures 3.13 and 3.14. Only those loosely labelled as $\Delta M = \pm 2$ are visible in the experimental data. Additionally, the octahedral field operator contains terms in S_z^4 and $S_{\pm}^4$, which couple states with spin quantum number M_S differing by ± 4 so that even the transition at about 0.5 T in Figures 3.13 and 3.14 is an allowed transition and observable in principle. The experimental spectra obtained for the sample containing nitrobenzene, β'' -(BEDT-TTF)₄[Fe(C₂O₄)₃]C₆H₅NO₂, show the same qualitative behavior as those for the sample containing benzonitrile, β'' -(BEDT-TTF)₄[Fe(C₂O₄)₃]C₆H₅CN; a comment on the only relevant qualitative difference between the two Fe³⁺ compounds will be presented below, when the issue of the splittings of the absorption lines will be addressed. The simulations reveal that the

spectra for the two compounds are reproduced by the very same model spin Hamiltonian with axial anisotropy of Equation 3.7, by inputting different values for the g -tensor and the zero field splitting parameters, as summarized in Table 3.3.2. The principal values of the axial g -tensor are for both compounds closer to the free electron value than those of the $\beta''\text{-(BEDT-TTF)}_4[\text{Cr}(\text{C}_2\text{O}_4)_3]\text{C}_5\text{H}_5\text{N}$ compound, and they both have a positive D value. A pronounced difference exists in the values of the rhombic term E , which is much larger for $\beta''\text{-(BEDT-TTF)}_4\text{[Fe(C}_2\text{O}_4)_3\text{]C}_6\text{H}_5\text{CN}$ ($-0.0410(3) \text{ cm}^{-1}$) than it is for $\beta''\text{-(BEDT-TTF)}_4\text{[Fe(C}_2\text{O}_4)_3\text{]C}_6\text{H}_5\text{NO}_2$ ($-0.0217(4) \text{ cm}^{-1}$). This remarkable difference is clearly visible in Figure 3.16, left hand side, where the angle dependent spectra for the two different compounds at a temperature of 1.4 K are directly compared. This figure also clearly shows a second difference in the resonant spectra of the two compounds: each of the three visible resonances at this temperature splits into two lines for the $\beta''\text{-(BEDT-TTF)}_4\text{[Fe(C}_2\text{O}_4)_3\text{]C}_6\text{H}_5\text{NO}_2$ compound but into four lines for the $\beta''\text{-(BEDT-TTF)}_4\text{[Fe(C}_2\text{O}_4)_3\text{]C}_6\text{H}_5\text{CN}$ compound. Figure 3.16, right hand side, shows the temperature dependence of the split lines with the external field at an angle of 45° with respect to the fine structure symmetry axis. The line at 2.55 T represents the transition between levels $|\pm \frac{1}{2}\rangle$. In some measurements this transition line has also been seen to split into four. The two lines at higher field are at this angle broad convolutions containing structure; as the temperature is lowered, they become more intense and better resolved: four lines can clearly be identified in place of the single transition between levels $|+\frac{1}{2}\rangle$ and $|+\frac{3}{2}\rangle$ at about 2.5 T, and two main lines with two additional shoulders instead of the transition line between levels $|+\frac{3}{2}\rangle$ and $|+\frac{5}{2}\rangle$ at about 3 T.

The already mentioned presence of a rotation by an azimuthal angle of π between subsequent anion layers, and the simultaneous presence of the two different enantiomeric species Λ and Δ of the $[\text{M}(\text{C}_2\text{O}_4)_3]^{3-}$ complex, also alternated in every other anion layer, explains the single splitting observed in the $\beta''\text{-(BEDT-TTF)}_4[\text{Cr}(\text{C}_2\text{O}_4)_3]\text{C}_5\text{H}_5\text{N}$ and in the $\beta''\text{-(BEDT-TTF)}_4\text{[Fe(C}_2\text{O}_4)_3\text{]-}$

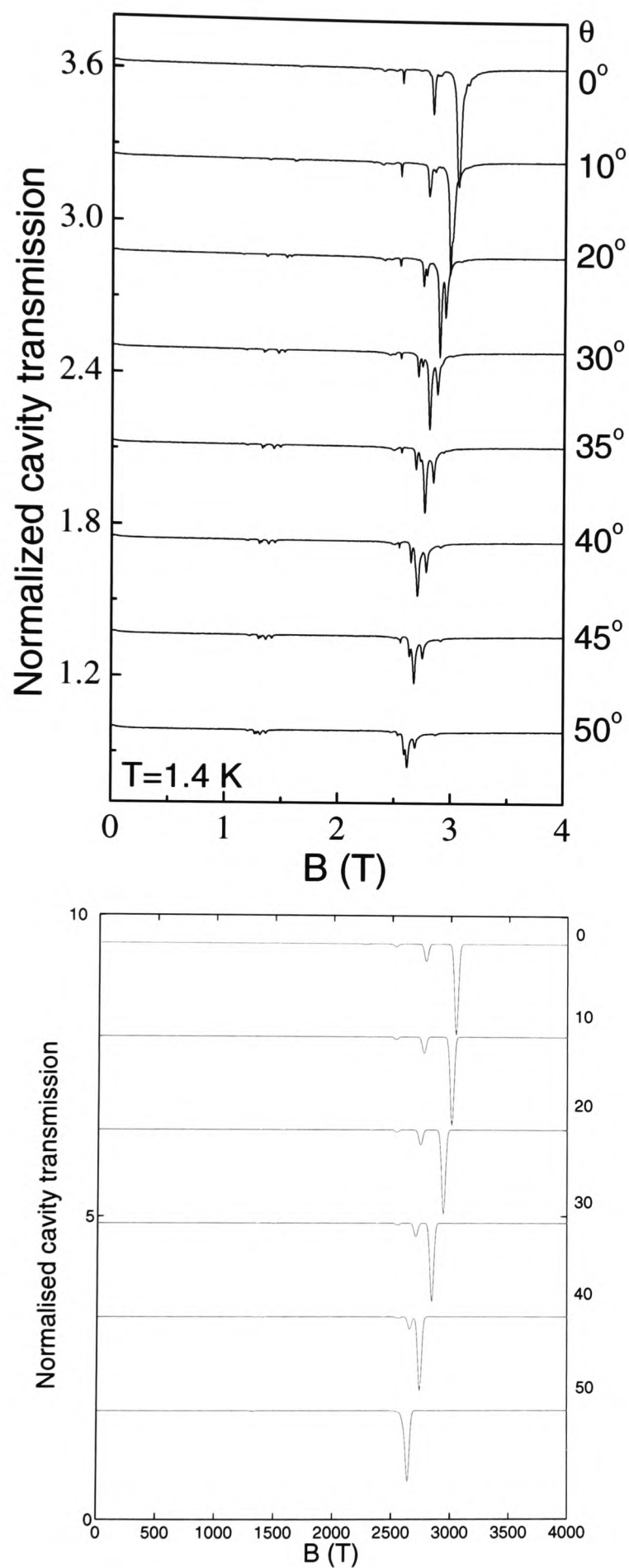


Figure 3.15: Top: polar angle dependence of the magneto-optical response of β'' -(BEDT-TTF)₄[Fe(C₂O₄)₃]C₆H₅NO₂ at the frequency $\nu \approx 71.2$ GHz. Bottom: the simulated spectra for the same range of angles. All traces are vertically offset for clarity.

C₆H₅NO₂ spectra. Two magnetically non-equivalent sites are present due to these two combined effects. The β'' -(BEDT-TTF)₄[Fe(C₂O₄)₃]C₆H₅CN compounds on the other hand reveal the presence of 4 splittings. This additional splitting has been observed in several samples containing benzonitrile, both in rectangular and cylindrical resonators. The most remarkable difference in the spin Hamiltonians for the two Fe compounds is the magnitude of the E value in the zero-field splitting term. The rhombic distortion is therefore much larger for one compound than it is for the other. This would allow any fine in-plane differences to be better resolved in the spectrum for the one compound with larger value of E , essentially due to the larger separation of lines. Still, the further splitting can only be explained by assuming the presence of an additional magnetically non-equivalent spatial configuration of the [M(C₂O₄)₃]³⁻ complex within the crystal structure. The additional features are present at high temperatures and only become sharper and therefore more resolved as the temperature is lowered (Figure 3.16, right-hand side). It cannot be concluded from the presented spectra whether such difference is present within a given anion layer, or if it is due to local domain formation. In either case, the data would imply a higher degree of static disorder to be present in the β'' -(BEDT-TTF)₄[Fe(C₂O₄)₃]C₆H₅CN samples than in the β'' -(BEDT-TTF)₄[Fe(C₂O₄)₃]C₆H₅NO₂ samples. An alternative possible origin of these splittings, only hinted at here, is the following hypothesis: as the polar angle θ , initially zero, is changed, the direction of the quasistatic field $\mathbf{B}_{DC}$ is tilted away from the local symmetry axis, the z -axis; the oscillatory field $\mathbf{B}_{AC}$ on the other hand rotates together with the sample, remaining orthogonal to the z -axis and therefore acquiring a component along the quasistatic field as well as the one perpendicular to it. As already mentioned, the presence of the higher order spin operators S_x^2 and S_y^2 , due to the rhombic crystal field term, and S_z^4 and $S_{\pm}^4$, due to the additional underlying octahedral crystal field, is bound to bring about some mixing of the states, much more so as the assumption of being in the strong field limit (strictly $|B| = \infty$) is relaxed. The appearance of additional splittings of the resonant lines,

Table 3.3: spin Hamiltonian parameters for the three different β'' -(BEDT-TTF)₄-[(H₃O)M(C₂O₄)₃]S compounds investigated.

compound	$g_{\parallel}$	$g_{\perp}$	D (cm ⁻¹)	E (cm ⁻¹)
β'' -(BEDT-TTF) ₄ [Cr(C ₂ O ₄) ₃]C ₅ H ₅ N	1.900(1)	1.951(1)	-0.6905(3)	0.0267(2)
β'' -(BEDT-TTF) ₄ [Fe(C ₂ O ₄) ₃]C ₆ H ₅ CN	1.982(1)	2.0027(3)	0.1306(2)	-0.0410(3)
β'' -(BEDT-TTF) ₄ [Fe(C ₂ O ₄) ₃]C ₆ H ₅ NO ₂	1.988(1)	2.0108(3)	0.1206(2)	-0.0217(4)

excited by the orthogonal and the longitudinal component of the oscillatory field respectively, between levels that are no longer pure eigenkets of type $|\pm S\rangle$, and therefore do not impose any selection rules for allowed or forbidden transitions any longer, could possibly be explained. Spin orbit coupling, present albeit weak, could also come to play a more relevant role as the precession of the magnetic moments occurs under the conflicting influences of the two leading terms of the spin Hamiltonian in Equation 3.7, namely the Zeeman and the axial fine structure terms.

To summarize, this Section has shown that different solvents induce different zero-field splitting parameters for the respective spin Hamiltonians. The solvent does not only affect superconductivity and T_c , but also the local symmetry of the oxalate octahedron surrounding the 3d ions. It is therefore mainly via the induced distortion of the electrostatic crystal field that the 3d ions can be sensitive to changes in the supramolecular crystal properties. In the next section (3.4) the relevant parameters extracted from the absorption lines, namely line position, linewidth and integrated intensity, and their variations with temperature, will shed light on the degree of coupling between the localised magnetic moments of different ions, and between the localised spins and the itinerant charge carriers also present in the β'' -(BEDT-TTF)₄[Fe(C₂O₄)₃]S compounds.

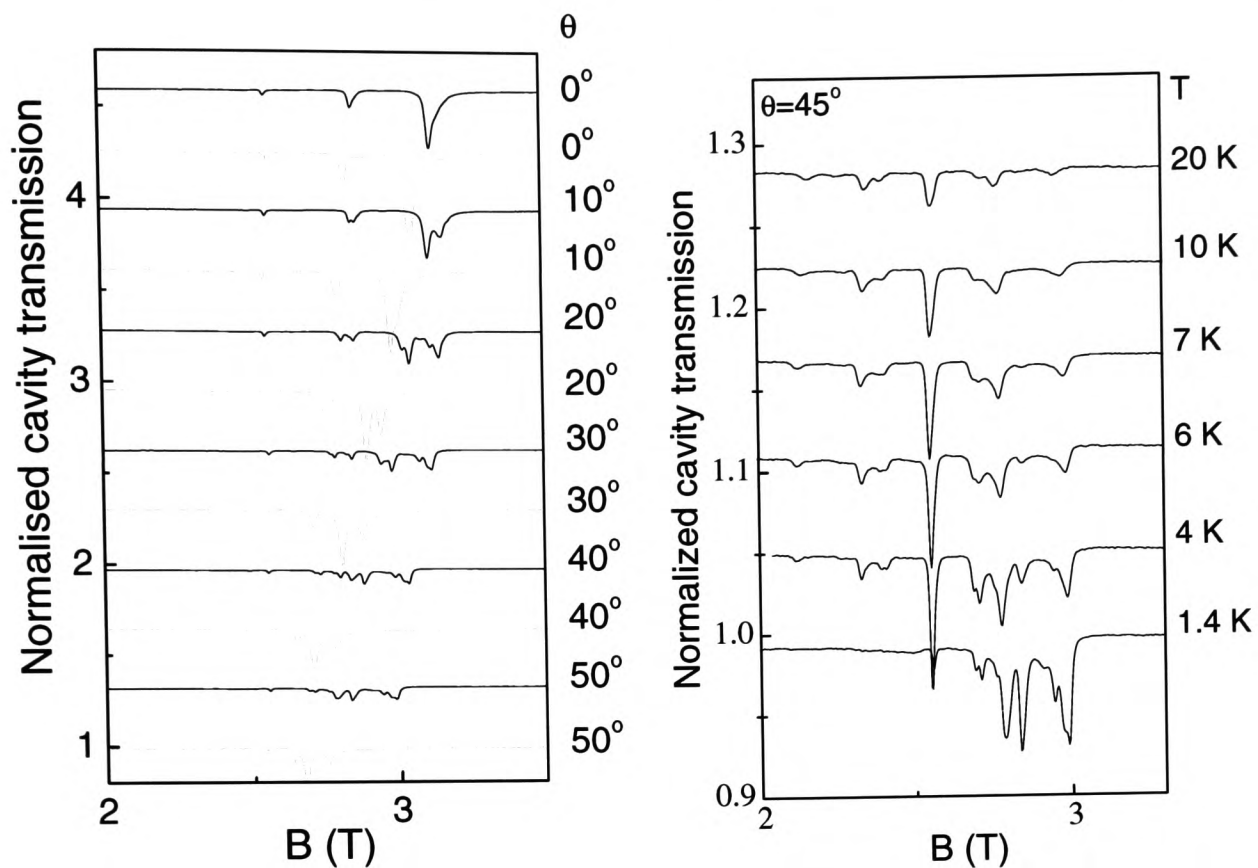


Figure 3.16: Left: the polar angle dependence for the two compounds β'' -(BEDT-TTF)₄[Fe(C₂O₄)₃]C₆H₅CN and β'' -(BEDT-TTF)₄[Fe(C₂O₄)₃]C₆H₅NO₂ plotted together for sake of comparison. Right: temperature dependence of the ESR response of a single crystal of β'' -(BEDT-TTF)₄[Fe(C₂O₄)₃]C₆H₅CN at an angle of 45° with respect to the external magnetic field. The microwave frequency is $\nu \approx 71.2$ GHz, and all traces are vertically offset for clarity.

3.4 Intensities, lineshifts and linewidths

The description and comparative interpretation of the data presented in Figures 3.17, 3.18, 3.19, 3.20, 3.21 is the primary aim of this section. These five figures show the temperature dependence below 50 K of the magnetic susceptibility χ (top panels), the relative shifts in line positions (middle panels) and the widths (bottom panels) of the resonances for a number of different samples belonging to the β'' -(BEDT-TTF)₄[(H₃O)M(C₂O₄)₃]S family. A measurement of the magnetic susceptibility is derived from the total integrated intensity of the resonant lines, obtained by fitting the absorption features with Lorentzian curves and extracting the areas enclosed by the curves and the base background signal.

In order to understand the nature of the magnetic interactions, the top panels show a plot of χT versus T , and the inset a plot of χ^{-1} versus T [2, 19, 3].

In order to illustrate any possible shifts of the resonant lines, the middle panels and their insets show a plot of the changes in effective g -values normalized for each line with respect to their values at the maximum recorded temperature: $\Delta g_{\text{eff}}/g_{\text{eff}} = [g_{\text{eff}}(T) - g_{\text{eff}}(T_{\text{max}})]/g_{\text{eff}}(T_{\text{max}})$. The insets of Figures 3.17, 3.18 and 3.19 show a magnified version of the low temperature region (below 10 K) of the full scale panel, whereas the insets of Figures 3.20 and 3.21 show different lines from those present in the full scale panel, both in order to achieve more clarity (otherwise prevented by the overlapping of the traces) and because of the different purpose the latter two figures serve in the analysis that follows. The resonant lines are labelled as *Line 1* to *Line 5*, numbered in the order they appear as the external magnetic field is swept. They are displayed in Figures 3.8, 3.11, 3.12 described in the previous Section 3.3.2.

The bottom panels show a plot of the linewidths, defined as the separation between the inflexion points of the Lorentzian curves fitting the experimental absorption lines (“peak-to-peak linewidth”). Figure 3.17 refers to the β'' -(BEDT-TTF)₄[Cr(C₂O₄)₃]C₅H₅N compound, which is an insulator at low temperatures [76], whereas the subsequent four figures all refer to samples of the superconducting β'' -(BEDT-TTF)₄[Fe(C₂O₄)₃]C₆H₅CN compound. Figure 3.18 is obtained from the response of a sample placed in a rectangular resonator at the frequency of 71.2 GHz, with the quasistatic field *along* the symmetry axis of the magnetic ion (z -axis), while Figure 3.19 is obtained from a sample of the same compound placed in a cylindrical resonator at approximately the same frequency (71.3 GHz) but with the external magnetic field at 90° with respect to the magnetic axis of symmetry, and parallel to the highly conducting planes. The comparison of Figures 3.17 and 3.18 will provide some insight into the different response of ions embedded in an insulating and a superconducting compound, while the comparison of Figures 3.18 and 3.19, given the large anisotropy of the upper critical field in this material [76], will allow the identification of any effect due to anisotropy in the response of the spin systems and, more crucially, provide information on

the different millimetre-wave response of the superconducting system when in the normal state and when in the mixed state.

The last two panels of similar kind, Figures 3.20 and 3.21, display the response of the very same sample as in Figure 3.19, with the cylindrical cavity tuned at different resonant frequencies, 64.3 GHz and 50.7 GHz respectively. A comparison of these last three figures will provide an understanding of the field dependence of the resonance features and of the possible differences in the response caused by the ESR resonances taking place with a different fraction of the sample in the superconducting state. Confirmation that the β'' -(BEDT-TTF)₄-[Fe(C₂O₄)₃]C₆H₅CN samples undergo a superconducting transition is provided by Figure 3.23 which shows the Q -factor of the loaded cylindrical resonator as a function of temperature. In the temperature range between 200 K and 10 K, the resonance Q -factors at zero and at high field are identical; below the superconducting transition temperature, $T_c = 6.5$ K, the Q -factor in zero magnetic field is by about 10% higher than the one computed beyond the upper critical field B_{c2} of the sample, indicating a transition from a state with low energy dissipation to a state with an increased presence of dissipative currents within the resonator. B_{c2} varies between 2 T and 15 T in the temperature range 6 K to 1.4 K. With reference to Section 2.4 of Chapter 2, the behavior of the Q -factor is a clear signature of the transition from the superconducting into the broad mixed state and eventually to the normal state.

3.4.1 The magnetic susceptibility

Let us first focus on the susceptibility data displayed in the top panels. Some trends can clearly be identified (although it is difficult to extract absolute quantitative values from the graphs, the number of spins detected depending on size, skin depth, position and orientation of the sample within the resonator as well as on the coupling of the radiation from the waveguides to the cavity, all factors that change from one experimental session to another and can vary even

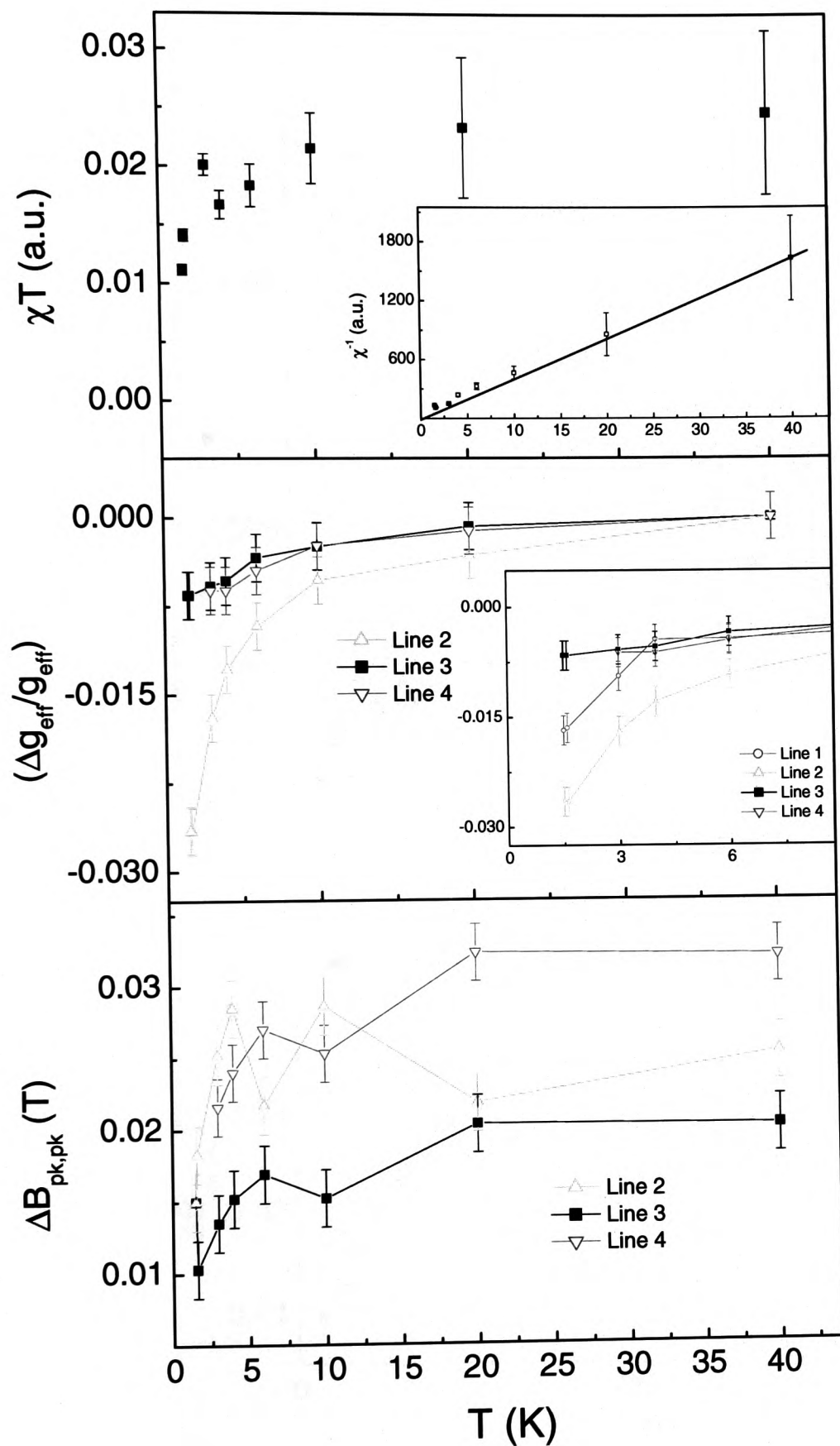


Figure 3.17: The magnetic susceptibility χ proportional to the total integrated line intensity (top panel), the relative shifts in the positions of the different resonance lines (central panel) and the peak-to-peak line widths (bottom panel) extracted from the β'' -(BEDT-TTF)₄[Cr(C₂O₄)₃]C₅H₅N ESR spectra and plotted as a function of temperature. In this and the following three graphs the absorption features are numbered by the order in which they occur with respect to increasing magnetic field.

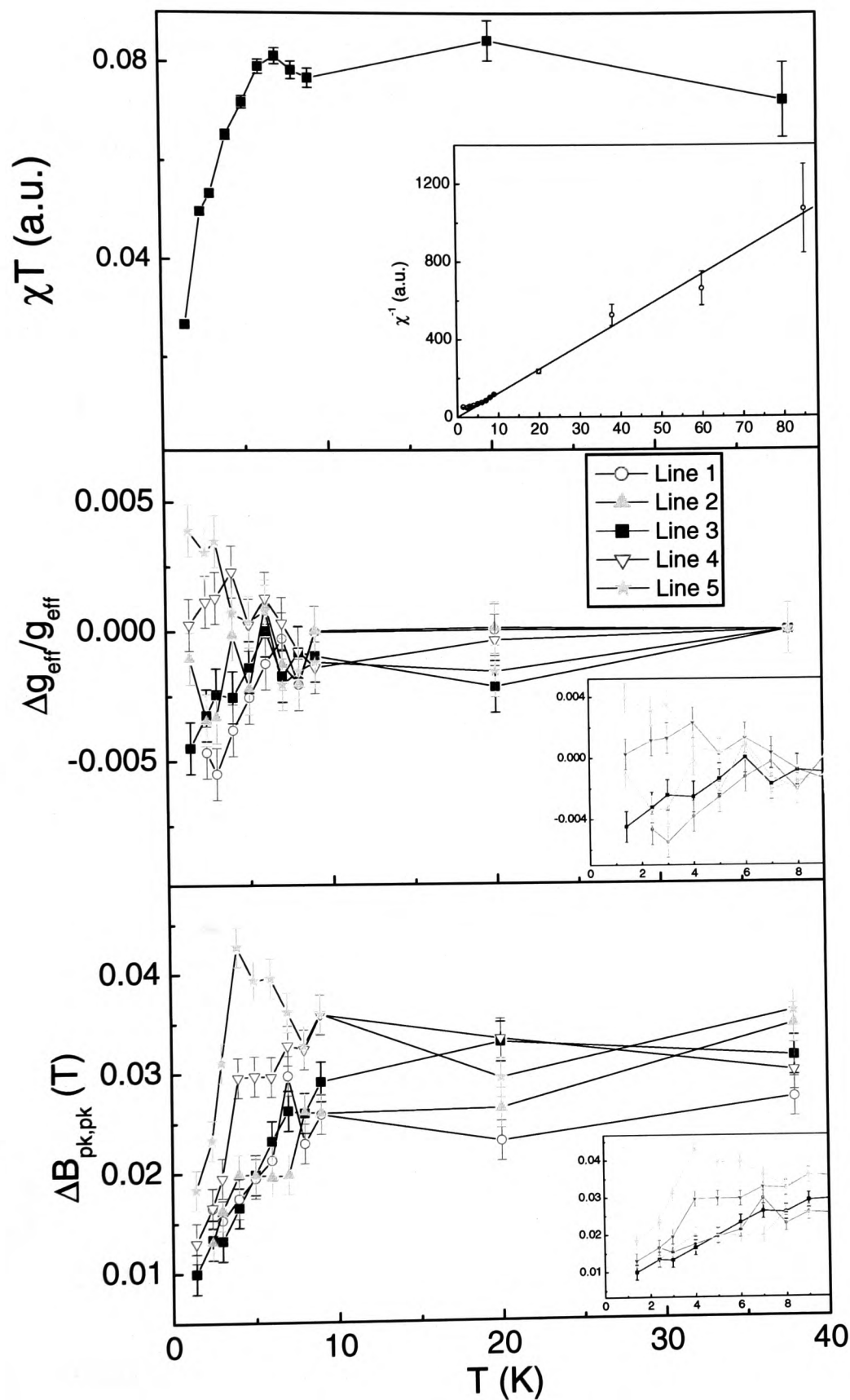


Figure 3.18: Magnetic susceptibility times temperature(top) and inverse susceptibility in the inset, line shifts (middle) and line widths (bottom) for the β'' -(BEDT-TTF)₄-[Fe(C₂O₄)₃]C₆H₅CN compound with the external field B applied perpendicularly to the highly conducting planes, along the axis of trigonal distortion; the microwave frequency is $\nu = 71.25$ GHz, and the resonant lines appear between 2 and 3.5 Tesla.

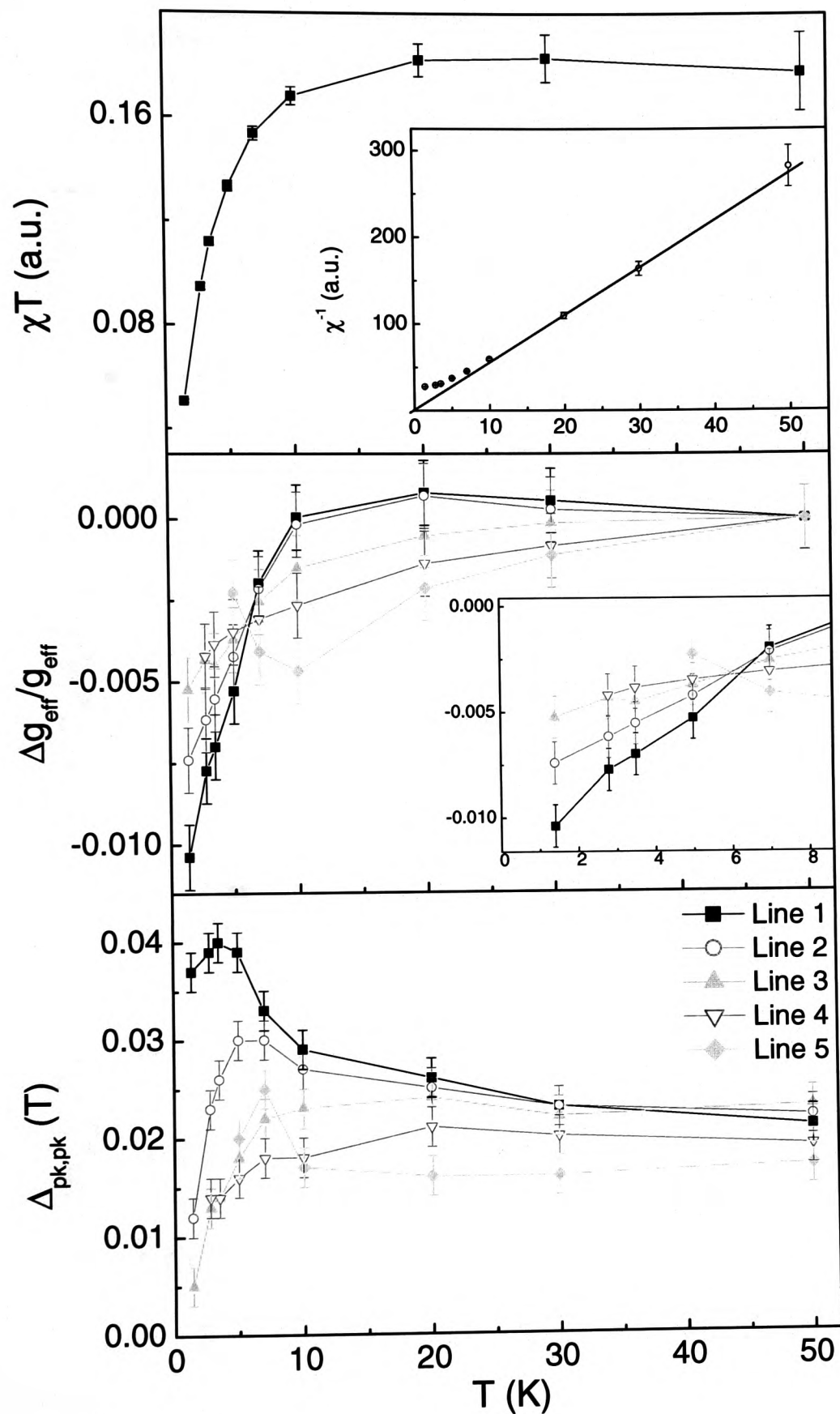


Figure 3.19: Magnetic susceptibility (top), line shifts (middle) and line widths (bottom) for the β'' -(BEDT-TTF)₄[Fe(C₂O₄)₃]C₆H₅CN compound with the external field B applied “in plane”, along the crystallographic b axis; the microwave frequency is $\nu = 71.3$ GHz, and the resonant lines appear between 2 and 3 Tesla.

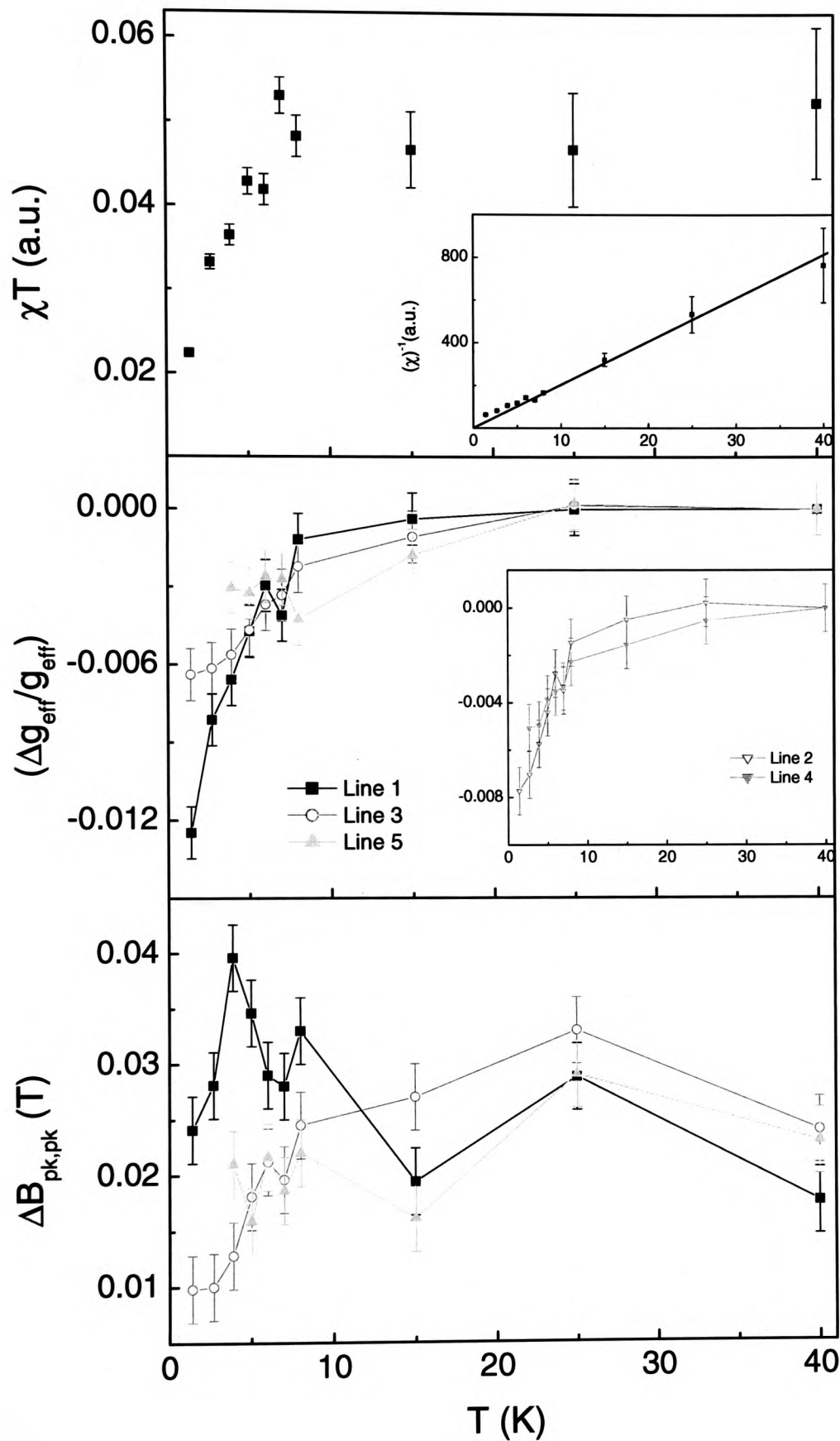


Figure 3.20: Magnetic susceptibility (top), line shifts (middle) and line widths (bottom) for the β'' -(BEDT-TTF)₄[Fe(C₂O₄)₃]C₆H₅CN compound with the external field **B** applied “in plane”, along the crystallographic *b* axis; the microwave frequency is $\nu = 64.3$ GHz.

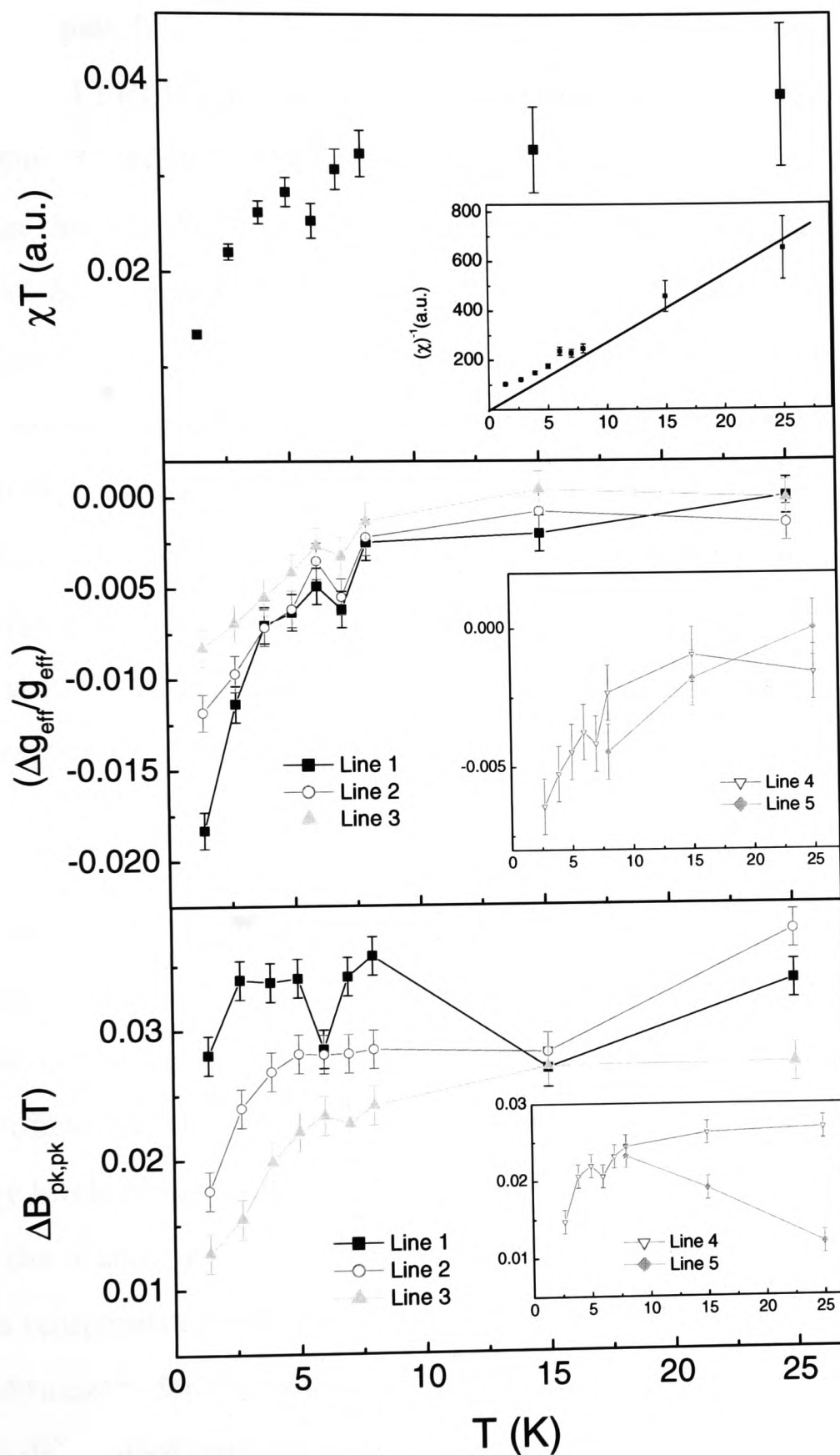


Figure 3.21: Magnetic susceptibility (top), line shifts (middle) and line widths (bottom) for the β'' -(BEDT-TTF)₄[Fe(C₂O₄)₃]C₆H₅CN compound with the external field B applied “in plane”, along the crystallographic b axis; the microwave frequency is $\nu = 50.7$ GHz, and the resonant lines appear between 1 and 2.5 Tesla.

during one single session) . For all compounds, as the temperature falls below 10 K χT departs from the constant value typical of the response of a diluted paramagnet [2, 3], falling to about half the high temperature value for the $\beta''\text{-(BEDT-TTF)}_4[\text{Cr}(\text{C}_2\text{O}_4)_3]\text{C}_5\text{H}_5\text{N}$ compound and to about one third that value for the $\beta''\text{-(BEDT-TTF)}_4[\text{Fe}(\text{C}_2\text{O}_4)_3]S$ compounds. The more pronounced decrease for the Fe^{3+} ions is in agreement with their higher spin configuration, $S = 5/2$ compared to $S = 3/2$ for the Cr^{3+} ions, indicating that the effect is connected to the localised moments. This result is also clearly shown in the χ^{-1} versus T plot, where the data from a linear paramagnetic behavior obeying Curie's law turn at low temperature into a quadratic temperature dependence, tending to a non-zero finite value as the temperature tends to zero. This could be interpreted as the onset of short range antiferromagnetic correlations, confirming, for the $\beta''\text{-(BEDT-TTF)}_4[\text{Fe}(\text{C}_2\text{O}_4)_3]\text{C}_6\text{H}_5\text{CN}$ compound, previous reports from susceptibility measurements on polycrystalline samples [69, 71].

Let us try and identify the most likely origin for the observed behavior of the magnetic susceptibility. The possible causes are [2, 3, 19]: onset of antiferromagnetic long range interactions, of either dipolar or exchange type; effects due to the zero-field splittings, and to the depopulation at low temperatures of the higher energy levels of the multiplets; indirect interactions of superexchange type, mediated by the diamagnetic ionic cage surrounding the transition metal ions; the presence of a temperature independent part of the susceptibility (Van Vleck susceptibility); additionally, for the (super)conducting samples, indirect interactions mediated by the delocalised carriers; a diamagnetic contribution (Landau diamagnetism), and an additional diamagnetic effect due to the superconducting condensate for the samples in the mixed state. All these can additively contribute to the behavior of the susceptibility observed in the graphs. Let us start by identifying the effect due to the zero-field splittings, present in all compounds, and to antiferromagnetic interactions.

Effects due to spin-spin interactions and fine structure

The magnetic susceptibility is defined as [3]:

$$\chi = \lim_{B \rightarrow 0} \frac{\mu_0 M}{B}; \quad (3.15)$$

where M is the total magnetisation of the sample and B the magnitude of the external field. In small applied fields we can therefore write

$$\chi = \frac{\mu_0 M}{B}. \quad (3.16)$$

For a system of quantised energy levels the magnetisation can be obtained from the partition function and the free energy [2, 19, 3] and expressed by the Brillouin function, a function of B/T only. In the limit of small B/T , the Brillouin function leads to the following expression for the susceptibility of a diluted paramagnet, Curie law:

$$\chi = \frac{\mu_0 M}{B} = \frac{\mu_0 N g^2 \mu_B^2 S(S+1)}{3kT} = \frac{C}{T}, \quad (3.17)$$

where C is Curie constant and the total angular momentum has been assumed to be the spin angular momentum ($L = 0$, $J = S$: quenched orbital angular momentum). As we depart from the small B/T limit, Curie's law is no longer valid, and the magnetisation is expected to reach a saturation value. As the temperature is taken below 10 K, a deviation from equation 3.17 is expected and observed in the top panels. By expanding the partition function as a power series, the term in T^{-2} can be evaluated. Assuming the Hamiltonian to include the Zeeman term and the fine structure term of Equation 3.7, the only contribution proportional to T^{-2} is found to be [19]:

$$-\frac{\mu_0 N g_z^2 \mu_B^2}{30(kT)^2} (l^2 g_x^2 D_x + m^2 g_y^2 D_y + n^2 g_z^2 D_z) S(S+1)(2S-1)(2S+3). \quad (3.18)$$

The zero-field splitting anisotropy therefore induces a deviation from Curie law [19]; the observed low temperature behavior of the susceptibility could therefore be accounted for by the presence of the fine structure term. One feature of this contribution is that it should vary as the orientation of the external magnetic field is changed with respect to the principal axes of the local crystal field, and should also change sign according to the sign of D along the direction of the applied field. By comparing the susceptibility for the $\beta''\text{-(BEDT-TTF)}_4[\text{Fe}(\text{C}_2\text{O}_4)_3]S$ samples at the two different orientations of Figures 3.19 and 3.18 and the response of the $\beta''\text{-(BEDT-TTF)}_4[\text{Cr}(\text{C}_2\text{O}_4)_3]\text{C}_5\text{H}_5\text{N}$ sample in Figure 3.17, it is clear that this contribution to the susceptibility is not the dominant one: the quadratic decrease in χ should be reversed when going from the configuration with the field along the z -axis ($D_z = \frac{2D}{3} = 0.13 \text{ cm}^{-1}$) to the one with the field along the x -axis ($D_x = -\frac{D}{3} + E = -0.03 \text{ cm}^{-1}$), and much more so for the compound containing chromium, for which $D_z = -0.69 \text{ cm}^{-1}$; This is not observed, indicating that the zero field splitting does not determine the behavior of the susceptibility at low temperature. If the Hamiltonian includes the following spin-spin interaction term:

$$H = \sum_{i>j} \mathbf{S}_i \cdot J_{ij} \cdot \mathbf{S}_j, \quad (3.19)$$

the susceptibility includes the following term, evaluated along the z -axis, of order T^{-2} [19]:

$$-\frac{\mu_0 N g_z^2 \mu_B^2 S^2 (S+1)^2}{9(kT)^2} \sum_{i>j} (J_{zz})_{ij}. \quad (3.20)$$

This term is additive and altogether similar to the one due to the electrostatic crystal field potential described by equation 3.18. The principal axis of the zero-field splitting and spin-spin interaction tensors are in general independent, and their contributions to the susceptibility could have the same sign for certain orientations of the external field and opposite sign for other orientations. This makes it difficult to distinguish quantitatively the two contributions in the experimental results. Nevertheless, the previous considerations on the discrepancies between

the fine structure coefficients and the susceptibility data support the fact that spin-spin interactions need to be taken into account for a satisfactory justification of the low temperature behavior of the susceptibility. If dipolar interactions between spins of neighbouring ions are considered, the additional energy term is given by Equation 3.1, which only depends on the distance and relative orientation of the magnetic dipoles. If exchange interactions of the type represented by the Hamiltonian term of Equation 3.19 are considered, the information on its contribution is mainly contained in the anisotropy of the exchange coupling tensor. By introducing the concept of an internal or molecular field, $\mathbf{B}_{\text{mf}}$, the modelling of long range spin-spin interactions is successfully simplified: $\mathbf{B}_{\text{mf}}$ is a fictitious magnetic field that allows the interactions between pairs of spins described by equation 3.19 to be replaced by an effective interaction between the moments and such an internal field. $\mathbf{B}_{\text{mf}}$ is proportional to the total magnetisation $\mathbf{M}$ of the sample:

$$\mathbf{B}_{\text{mf}} = \lambda_{\text{mf}}\mathbf{M}, \quad (3.21)$$

and the total field experienced by a given moment is

$$\mathbf{B}_{\text{eff}} = \mathbf{B}_{\text{DC}} + \mathbf{B}_{\text{mf}}. \quad (3.22)$$

In this approximation the magnetisation can be written as

$$\mu_0\mathbf{M} = \frac{C}{T}(\mathbf{B}_{\text{DC}} + \lambda_{\text{mf}}\mathbf{M}) \quad (3.23)$$

and the Curie law is modified into the Curie-Weiss law to take into account the presence of (anti)ferromagnetic interactions [2, 3]:

$$\chi = \frac{C}{T - \lambda_{\text{mf}}C/\mu_0} = \frac{C}{T - \theta} \quad (3.24)$$

If $\lambda_{\text{mf}} > 0$, $\theta > 0$, called the Weiss temperature, is the temperature where the susceptibility diverges due to the onset of ferromagnetic order; if $\lambda_{\text{mf}} < 0$, $\theta < 0$

and $|\theta|$ is known as the Néel temperature and defines the onset of long range antiferromagnetic interactions. In the next section, the concept of an effective internal field will be applied to the interpretation of the observed line shifts.

3.4.2 Effective g -values and linewidths

Depopulation effects, internal field and the superconducting state

Let us turn our attention to the middle panels of the figures under investigation, and focus at first on the results for the $\beta''\text{-(BEDT-TTF)}_4[\text{Cr}(\text{C}_2\text{O}_4)_3]\text{C}_5\text{H}_5\text{N}$ compound displayed in Figure 3.17. As described earlier (see Section 3.3.2 and in particular Figure 3.9), the three main transition lines are *Line 2*, transition between levels $|- \frac{3}{2}\rangle$ and $|- \frac{1}{2}\rangle$, *Line 3*, transition between levels $|\pm \frac{1}{2}\rangle$, and *Line 4*, transition between levels $|+ \frac{1}{2}\rangle$ and $|+ \frac{3}{2}\rangle$; *Line 1* is the forbidden transition between levels $|\pm \frac{3}{2}\rangle$. It is important to bear in mind that the transition between levels $|\pm \frac{1}{2}\rangle$, *Line 3* in this case, is the only one that occurs *within* a Kramers' doublet, the other transitions occurring between levels belonging to different doublets. This implies that *Line 3* is not directly affected by the modifications of the zero field splitting parameters, whereas the energy difference between the levels of the other resonant lines, and therefore the line positions, are directly affected by changes in the D -tensor. As outlined in Section 3.3.1, *Line 3* provides information only on the changes in the anisotropy of the g -tensor, which differs from the free electron value ($g_e = 2.00323$) because of the small effects due to spin-orbit coupling [20]:

$$\mathbf{g} = g_e \mathbf{1} + 2\lambda_{\text{so}} \mathbf{\Lambda}, \quad (3.25)$$

where λ_{so} is the spin-orbit coupling constant introduced in equation 3.6. Spin-orbit coupling favours the (parallel or antiparallel) alignment of spin and orbital angular momentum; a zero-field splitting of axial symmetry tends to align the spins with its own symmetry axis. Nonetheless, the D -tensor contains both a contribution due to dipolar spin-spin interactions and an additional contribution

due to the anisotropic part of the spin-orbit coupling, the latter being [20]:

$$\mathbf{D} = \lambda_{\text{so}}^2 \mathbf{\Lambda}. \quad (3.26)$$

Depending on the actual magnitude of this contribution, the competing effects of spin-orbit coupling and zero-field splitting will be more or less pronounced. In any case, changes in the spin-orbit coupling constant would induce a more pronounced modification to the zero-field splitting tensor than to the g -tensor. On the other hand, changes in the intra-ionic spin-spin interactions would affect D directly but not g ; only the inter-ionic spin-spin interactions could affect the g -tensor, and, by giving rise to an effective internal field, $\mathbf{B}_{\text{mf}}$, they would equally affect the positions of all the observed resonant lines. The more pronounced anisotropy of the g -tensor reported in Table 3.3.2 suggests that the spin-orbit interaction is larger for the β'' -(BEDT-TTF)₄[Cr(C₂O₄)₃]C₅H₅N compound than it is for the β'' -(BEDT-TTF)₄[Fe(C₂O₄)₃]S compounds; we would therefore expect spin-orbit coupling to play a more significant role for the former.

The temperature dependence of the line positions for the chromium compound reveal a small negative shift of *Line 3*, indicating either a modification of λ_{so} as the temperature falls below 10 K or the presence of antiferromagnetic correlations, or the simultaneous occurrence of both phenomena. Also *Line 2* and *Line 4* both have a negative shift, the one of the lower field line (*Line 2*) being at 1.4 K four times the shift of the high field line (*Line 4*); additionally, *Line 4* seems to level off or resist slightly the trend at the lowermost temperatures. By inspecting the energy level diagram for the β'' -(BEDT-TTF)₄[Cr(C₂O₄)₃]C₅H₅N compound shown in Figure 3.9 and their algebraic expression given by equations 3.11, one can see that modifications in the zero field splitting parameter D would induce shifts to *Line 2* and *Line 4* that are of opposite sign when, as in this case, the field is applied along the z -axis. The observed lines all shift to high field as the temperature is lowered, with the contribution to a positive shift for *Line 4* being just noticeable.

Shifts of all lines to higher fields can be explained by assuming the onset of antiferromagnetic interactions, of either dipolar or exchange nature; the different relative shifts of the three lines also point to the presence of an effective internal field: such a field in fact would contribute different relative shifts to resonant lines occurring at different magnetic field values. Let us evaluate the strength of the interionic dipolar interaction for the Cr^{3+} ions within the $\beta''\text{-(BEDT-TTF)}_4\text{[Cr(C}_2\text{O}_4)_3\text{]C}_5\text{H}_5\text{N}$ compound. The distances between ions are relatively large ($r \approx 10\text{\AA}$), and therefore the effect due to magnetic dipolar interaction can be expected to be small. Let us estimate the local field at a given ion site due to the presence of a neighbouring ion: $B_{\text{loc}} = \frac{\mu_0}{4\pi} \frac{\mu_{\text{eff}}}{r^3}$, where $\mu_{\text{B}} = \frac{e\hbar}{2m_e} = 9.27 \times 10^{-24}\text{J/T}$ and $\mu_{\text{eff}} = 2\mu_{\text{B}}\sqrt{S(S+1)}$; using $S = 3/2$ for the Cr^{3+} ion, $B_{\text{loc}} = 0.0062\text{ T}$. The relative shifts in the effective g -values due to the presence of this additional negative field vary between -0.0066 at $B_{\text{res}} \approx 1\text{ T}$, -0.0026 at $B_{\text{res}} \approx 2.5\text{ T}$ and -0.0013 at $B_{\text{res}} \approx 4\text{ T}$ (see Figure 3.17 for the positions of the resonant lines); these correspond to about one fifth of the observed shifts for *Lines 2* and *4*, and one third of the observed shift for the transition within the Kramers' doublet $|\pm \frac{1}{2}\rangle$. The data can be accounted for by considering a modification of the zero-field splitting parameters as the higher energy levels become depopulated, and the simultaneous onset of a negative effective internal field of dipolar origin. This could be associated with a structural modification of the oxalate cage below 10 K; the fact that all these transformations are continuous as a function of temperature suggests the effect is due to the progressive depopulation of energy levels rather than to any structural transition involving the oxalate complex. The primary cause for the observed effects is therefore the gradual reorganisation of the energy eigenvalues due to changes in the intra-ionic spin-spin interactions as the higher energy states become depopulated, accompanied by a change in the spin-orbit coupling constant λ_{so} . The interpretation of the low temperature data for the $\beta''\text{-(BEDT-TTF)}_4\text{[Cr(C}_2\text{O}_4)_3\text{]C}_5\text{H}_5\text{N}$ compound therefore suggests modifications of the fine structure constants and spin-orbit coupling constant, together with

the onset of weak antiferromagnetic interactions of dipolar origin. This scenario is supported by the susceptibility data previously described. The measurements carried out on the compounds containing iron for different orientations of the external field and at different frequencies will present a similar scenario, with the additional ingredient of the transition to a superconducting state below $T_c \approx 6.5$ K.

Consider now the middle panel of figure 3.18, presenting the line shifts for the superconducting β'' -(BEDT-TTF)₄[Fe(C₂O₄)₃]C₆H₅CN compound; here the external field B_{DC} is applied perpendicularly to the highly conducting planes, along the axis of trigonal distortion, and the microwave frequency is $\nu = 71.25$ GHz. The resonant lines appear between 2 and 3.5 Tesla and are labelled *Line 1* to *Line 5* indicating the order in which they appear as the magnetic field is swept. In this configuration the upper critical field $B_{c2} \approx 1$ T at $T = 1.4$ K [78]; the transitions therefore all occur with the sample in the normal state. With reference to Figures 3.11 to 3.14 described in Section 3.3.2, *Line 3* is the intra-Kramers doublet line, being the transition between levels $|\pm \frac{1}{2}\rangle$, and the other four lines are transitions between levels belonging to different Kramers doublets. The shifts reveal a symmetric displacement of the side lines towards *Line 3*, with negative shifts (displacements to higher fields) for the lines occurring at lower magnetic field values and positive shifts for the lines occurring at higher fields with respect to the central intra-Kramers doublet line. This behavior can be accounted for by considering a smooth change in the D -value as T is lowered: in this orientation in fact, the line positions are to first order spaced by $\pm \frac{4D}{g_{\parallel}\mu_{\text{eff}}}$ (*Line 5* and *Line 1*) and by $\pm \frac{2D}{g_{\parallel}\mu_{\text{eff}}}$ (*Line 4* and *Line 2*) with respect to *Line 3*. The positive D -value ($D = 0.13$ cm⁻¹) is therefore reduced as the temperature is lowered below 10 K, i.e. as the higher levels start depopulating, and this reduction is larger than that of $g_{\parallel}$. As for the β'' -(BEDT-TTF)₄[Cr(C₂O₄)₃]C₅H₅N compound, the continuous transformation confirms this modification to be due to the depopulation of the levels rather than to any structural transition involving the oxalate cage. Addi-

tionally, *Line 3* has a relative shift of -0.005 , indicating a reduction of $g_{\parallel}$ due to a modification of λ_{so} . A small relative shift of about -0.1% of all lines is also noticeable. The magnitude of the D -value is in this case much smaller than for the Cr^{3+} ion and therefore the assumption of being in the strong field regime is here even more appropriate; additionally, the spin-orbit coupling is much smaller as the anisotropy of the g -tensor shows (see Table 3.3.2). A modification of the zero-field splitting parameters and of the spin-orbit coupling constant are therefore confirmed, together with possible weak antiferromagnetic correlations.

Any effects due to the presence of superconductivity, and more precisely of the mixed state of this type II superconductor, will be observable in the middle panels of Figures 3.19, 3.20 and 3.21, where the ESR lineshifts are reported for three different experimental frequencies in the range 50-72 GHz. Here in fact the external field is applied parallel to the highly conducting layers, and $B_{c2} \approx 17$ T as estimated in reference [78]; in all three cases the ESR lines occur with the sample crossing from the normal into the mixed state at some temperature between $T_c = 6.5$ K and 1.4 K. The actual presence of the superconducting transition is revealed by the changes in the resonant cavity Q-factor as a function of temperature and magnetic field, as described previously in Section 3.3.2 and Figure 3.23. $\mathbf{B}_{\text{DC}}$ now is no longer along the axis of trigonal distortion, and the zero field splitting term in the field direction has in this orientation a negative value: $D_{xx} = -\frac{D}{3} + E = -0.085$ cm^{-1} . In Figure 3.19, the symmetric displacement of the side lines towards the central transition below $T = 10$ K is superimposed on a shift of all lines to higher fields, resulting in a negative effective shift to all lines. The behavior reveals once again the simultaneous modification of zero-field splitting and spin orbit coupling parameters, and the need to include a possible contribution due to antiferromagnetic interactions. The fact that also in this orientation, with $D_{xx} < 0$, the separation between lines decreases confirms the continuous reduction of $|D|$ as the temperature is lowered. Antiferromagnetic interactions of dipolar origin can be estimated; the local field at a given ion site due to its interaction with

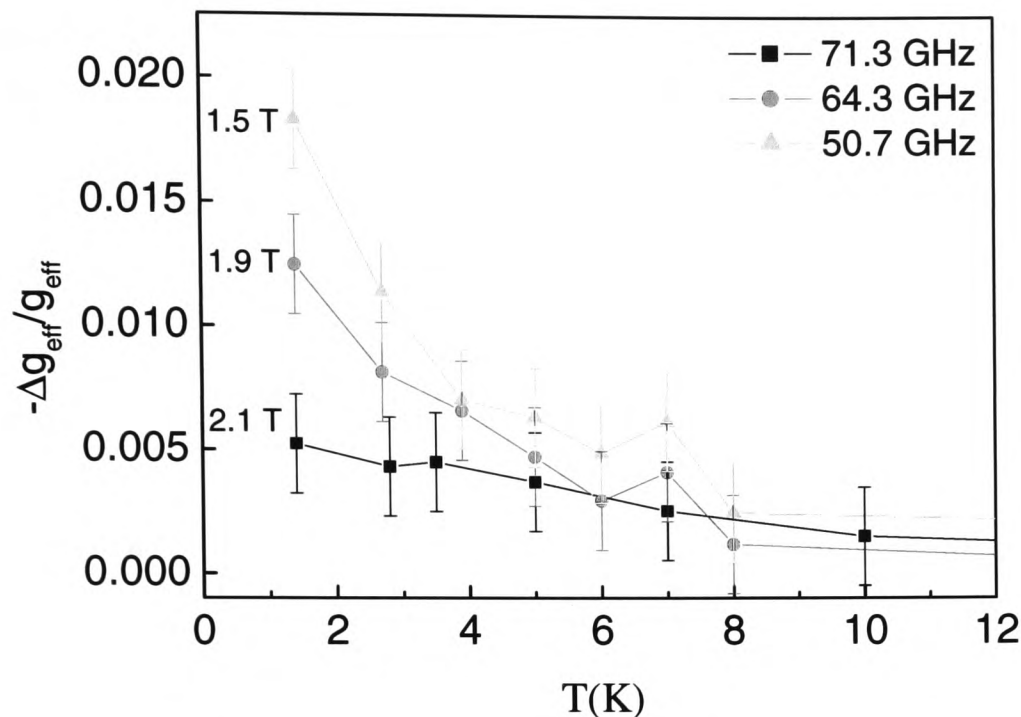


Figure 3.22: Comparison of the relative line shifts for the transition $|- \frac{5}{2}\rangle \longleftrightarrow |-\frac{3}{2}\rangle$ occurring at different frequencies (and therefore at different magnetic field values) as the mixed state of the type II superconductor β'' -(BEDT-TTF)₄[Fe(C₂O₄)₃]C₆H₅CN is entered.

a neighbouring ion is $B_{\text{loc}} = \frac{\mu_0 \mu_{\text{eff}}}{4\pi r^3}$, where $\mu_B = \frac{e\hbar}{2m_e} = 9.27 \times 10^{-24} \text{ J/T}$ and $\mu_{\text{eff}} = 2\mu_B \sqrt{S(S+1)}$. By using $S = 5/2$ and a distance between nearest neighbours $r \approx 10 \text{ \AA}$, $B_{\text{loc}} \approx 0.0095 \text{ T}$. The relative shifts in the effective g -values due to such a field would produce half of the variations observed for the transition within the Kramers' doublet $|\pm \frac{1}{2}\rangle$ shown in Figures 3.19, 3.20 and 3.21, and only a much smaller fraction of the shifts observed for the transitions occurring at lower fields. The actual magnitude of the possible magnetic dipolar contributions is difficult to evaluate; in fact, the planar pattern of oxalate complexes has a triangular or hexagonal shape, inevitably leading to frustration for antiferromagnetic interactions.

The fact that negative lineshifts become more and more pronounced as the experimental frequency is lowered from $\nu=71.3 \text{ GHz}$ (Figure 3.19) to $\nu=64.3 \text{ GHz}$ (Figure 3.20) and $\nu=50.7 \text{ GHz}$ (Figure 3.21) and the magnetic field value at which the lines occur diminishes accordingly, is plausible evidence for the presence of an additional contribution to the magnetisation of the sample, namely that due to

superconductivity. Figure 3.22 directly compares the relative shifts for the transition $|-\frac{5}{2}\rangle \longleftrightarrow |-\frac{3}{2}\rangle$ at different values of the resonant frequency. The same trend is just discernible for the transition $|-\frac{3}{2}\rangle \longleftrightarrow |-\frac{1}{2}\rangle$, and is absent within experimental error from the behavior of the resonant lines occurring at higher magnetic fields. This “lowermost” line shifts from 2.1 T to about 1.5 T as the frequency is changed from 71.3 GHz to 50 GHz. The relative shifts indicate that at $T = 1.4$ K, only below the field value of about 2.1 T can any effects on the ESR resonant lines due to the mixed state be clearly resolved. The appearance and growth of the observed shift in addition to the already described effects due to the crystal field and possible antiferromagnetic interactions confirms the presence of the mixed state of the superconductor. For a type II superconductor, three regimes of mixed state can be identified [83]: one of low flux density with well spaced vortices, one of intermediate flux density, and a regime near B_{c2} , where the vortices are packed so tightly that the cores fill almost all the volume. Using the linearized Ginzburg-Landau equations in the latter case, Abrikosov showed that the local flux density is less than the applied field by an amount proportional to the local value of the order parameter, $|\psi(\mathbf{r})|^2$, leading to a negative magnetisation that goes to zero linearly as B_{c2} is approached: $M \sim -(B_{c2} - B)$ [83]. Figure 3.22 aims to emphasize the *increase* in the diamagnetic response of the superconductor as temperature and magnetic field are lowered. The data suggest that at 1.4 K and beyond 2.1 T the vortices already fill up much of the sample, and full field penetration occurs at least within the “insulating” anion layers. Only below such values of temperature and field can the additional effects on the ESR lines due to the presence of the Shubnikov or mixed phase be observed. The relative lineshifts displayed in the middle panels of Figures 3.19, 3.20, 3.21 can therefore be accounted for by assuming the simultaneous presence of crystal field modifications, weak antiferromagnetic interactions and the diamagnetic response of the superconductor in the mixed state. The importance of further investigating the resonances at lower fields and at temperatures below 1.4 K as a valuable tool

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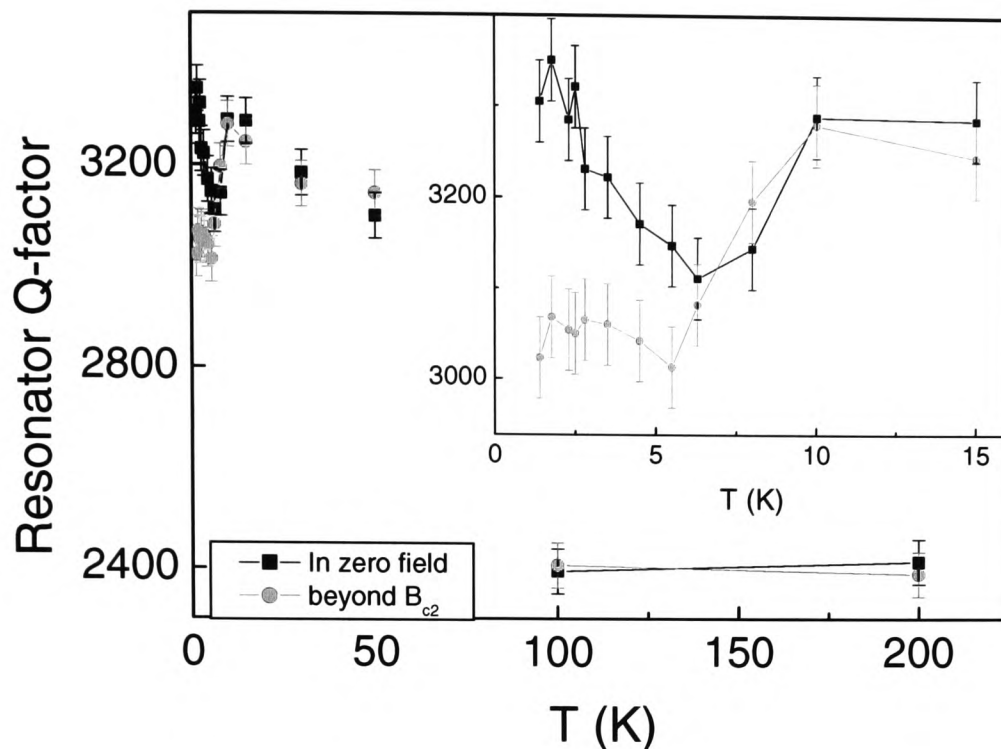


Figure 3.23: Comparison of the Q-factors of the loaded cylindrical resonator with the sample in the superconducting (zero applied field) and normal state ($|\mathbf{B}| > B_{c2}$).

to explore the mixed state of these superconductors naturally emerges from the presented results.

Some valuable information can be extracted from the bottom panels of Figures 3.17, 3.18, 3.19, 3.20 and 3.21, describing the temperature dependence of the linewidths of the respective ESR resonances. For spin systems whose Hamiltonians contain the crystal field potential as the dominant term, the main relaxation mechanism is the coupling of the spins to the lattice vibrations, mediated by the modulations of the crystal field itself [19]. A wealth of different processes can simultaneously contribute to the spin-lattice relaxation rate $1/\tau_1$, the most relevant being direct, Raman and Orbach processes, each giving rise to one term in the following expression for the temperature dependence of the relaxation rate:

$$\frac{1}{\tau_1} = a \coth\left(\frac{h\nu}{2k_B T}\right) + bT^n + \frac{c}{\exp\left(\frac{\Delta}{k_B T}\right) - 1}. \quad (3.27)$$

1. Direct processes involve phonons with the same energy as the magnetic resonance quantum of absorbed energy $h\nu$; for these two regimes can be identified:

- (i) the high temperature limit ($\frac{h\nu}{k_B T} \ll 1$) where $\frac{1}{2} \coth\left(\frac{h\nu}{2k_B T}\right) \rightarrow \left(\frac{k_B T}{h\nu}\right)$ and

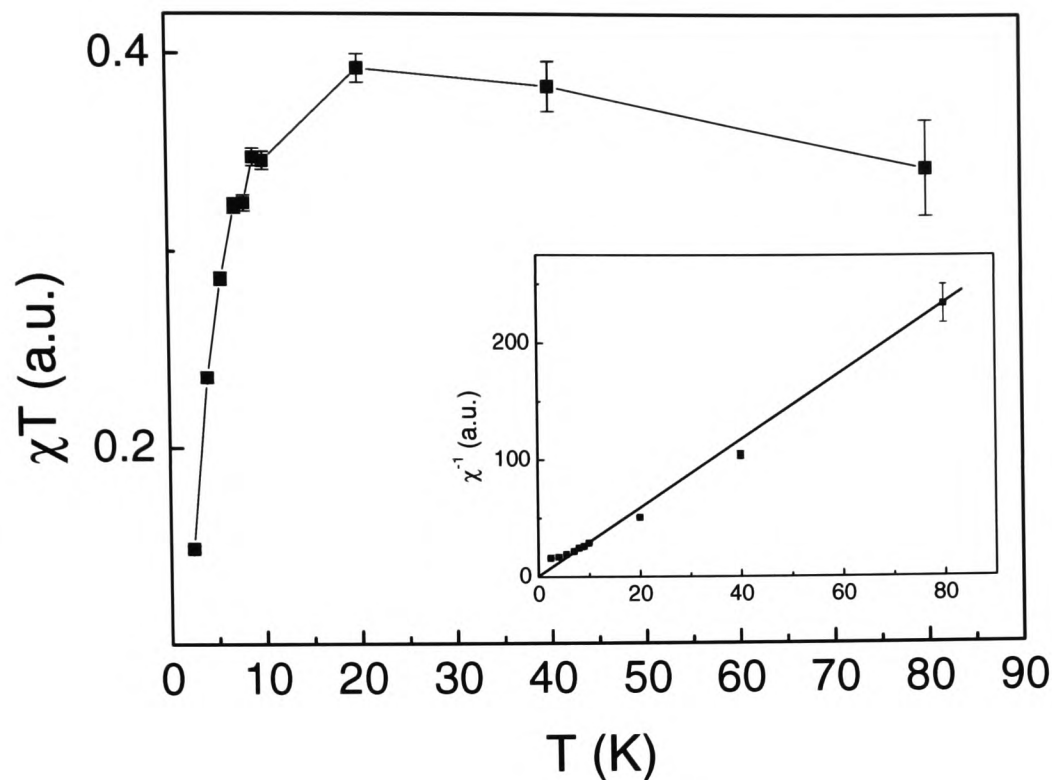


Figure 3.24: Magnetic susceptibility in the usual χT vs T plot, and inverse susceptibility versus temperature for the β'' -(BEDT-TTF)₄[Fe(C₂O₄)₃]C₆H₅NO₂ compound with the external field B applied perpendicularly to the highly conducting planes, along the crystallographic c axis; the microwave frequency is $\nu = 71.2$ GHz.

their contribution to the linewidth grows linearly with temperature;

(ii) the low temperature limit, where phonons of energy $h\nu$ are no longer thermally excited ($\frac{h\nu}{k_B T} \gg 1$) and $\coth(\frac{h\nu}{2k_B T}) \rightarrow 1$, leading to a constant contribution to the linewidth.

2. Raman processes are two-phonon processes in which all available phonons can be involved, giving the strong T dependence of the second term, where $n = 5$ for a multiplet with small splitting, $n = 7$ for a non-Kramers doublet, $n = 9$ for a Kramers doublet.

3. Orbach processes give the third term in equation 3.27; this kind of process involves excitation of the spin system via direct phonon absorption to a much higher level at energy Δ above the ground multiplet, and subsequent emission of a phonon of slightly lower energy so that the magnetic ion is indirectly transferred from one level to another of the ground multiplet; this process strongly depends on the availability of phonons of energy Δ for the excitations to occur, and its contribution to the linewidth is therefore also strongly temperature dependent.

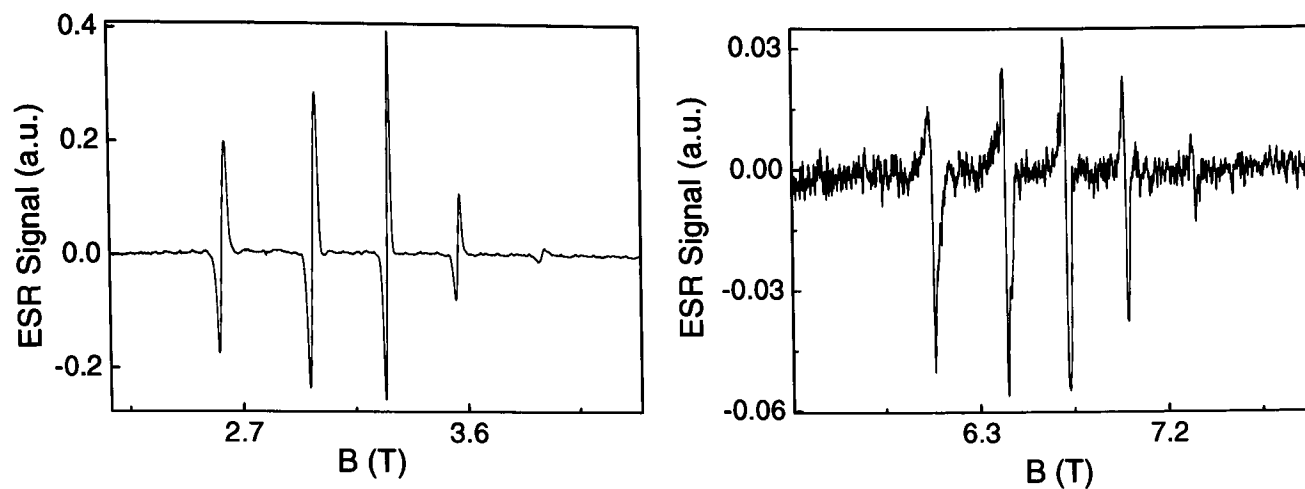


Figure 3.25: ESR with field modulation and no resonator at the frequencies of 95 GHz and 190 GHz.

When $\Delta \gg k_B T$, the last term in Equation 3.27 approximates to $c \cdot \exp(-\frac{\Delta}{k_B T})$.

All five Figures show a common trend in the temperature dependence of the line widths: roughly constant at high temperature, then dropping below 10 K, as $k_B T$ becomes smaller than the overall level separation. This is compatible only with the functional expression describing Orbach processes; these must therefore represent the main contribution to the relaxation rate. For the β'' -(BEDT-TTF)₄-[Fe(C₂O₄)₃]C₆H₅CN compound, the transition between levels $|-\frac{5}{2}\rangle \longleftrightarrow |-\frac{3}{2}\rangle$ shows a clear line broadening in the range between 4 and 10 K, either due to changes in specific phonon modes the spins couple to or due to the additional onset of the weak antiferromagnetic dipolar interaction. The broadening is a specific feature of given transitions, namely the ones that become more populated as the temperature decreases ($|+\frac{3}{2}\rangle \longleftrightarrow |+\frac{5}{2}\rangle$ and to some extent $|-\frac{3}{2}\rangle \longleftrightarrow |-\frac{1}{2}\rangle$), and not of whether they occur at low or at high field. On the other hand, as the transitions take place “deeper” into the mixed state (Figures 3.19, 3.20 and 3.21), the broadening becomes less pronounced: the presence of the superconducting fraction of the sample with its diamagnetic contribution either affects the relevant phonons involved in the relaxation process or reduces the effect of the dipolar interaction.

The compound containing Fe³⁺ described so far in this section is the one with benzonitrile as solvent molecule. Figure 3.24 shows the magnetic susceptibility of

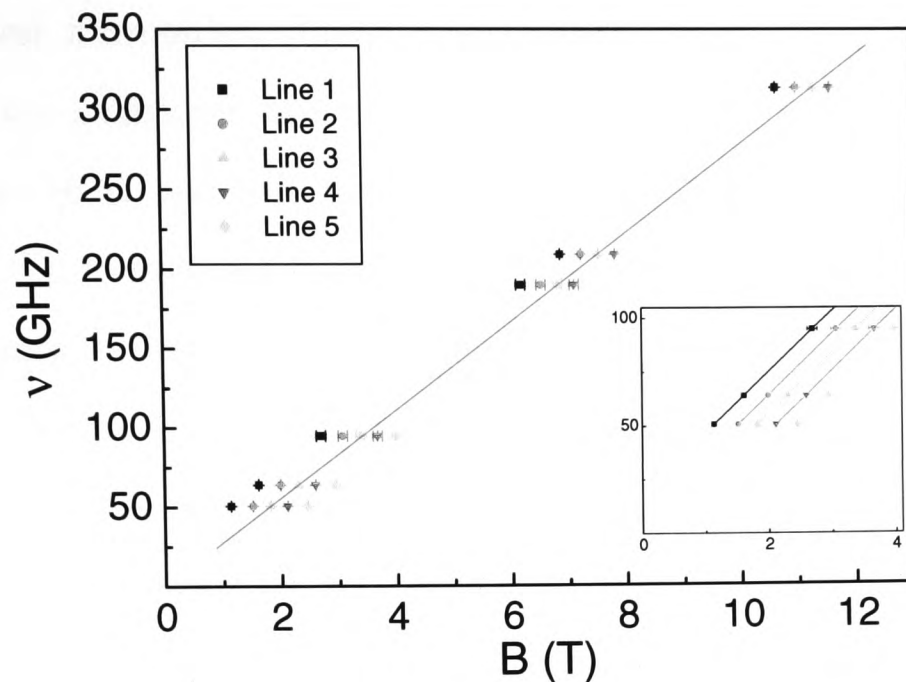


Figure 3.26: Frequency versus magnetic field position for the 5 resonant lines of the β'' -(BEDT-TTF)₄[Fe(C₂O₄)₃]C₆H₅CN compound.

a sample containing nitrobenzene, β'' -(BEDT-TTF)₄[Fe(C₂O₄)₃]C₆H₅NO₂. The external magnetic field is in this case along the axis of symmetry of the magnetic site, the *z* direction. The susceptibility behaves exactly like that obtained for the β'' -(BEDT-TTF)₄[Fe(C₂O₄)₃]C₆H₅CN compound displayed in Figure 3.18; in fact, also lineshifts and linewidths for the latter match the trends obtained for the former. At least with the quasistatic magnetic field along the magnetic symmetry axis (the only configuration investigated for the β'' -(BEDT-TTF)₄[Fe(C₂O₄)₃]C₆H₅NO₂ compound) the presence of either benzonitrile or nitrobenzene appear to induce no difference in the extracted quantities.

Frequency versus field position

One final test for the presence of an effective internal field for the compound β'' -(BEDT-TTF)₄[Fe(C₂O₄)₃]C₆H₅CN is provided by the graph of frequency versus field position for the resonant lines. The data span a frequency range between 50 and 315 GHz. Data at the lower frequencies up to 73 GHz were obtained with the tuneable cylindrical resonator used in the TE₀₁₁ single mode. The same resonator operated in an overmoded configuration was used at the frequencies of 209 and 315 GHz, with the ESA Gunn extensions [22] providing generation and

detection of the highest harmonics. These measurements were performed at 10 K, 5 K and 1.4 K. Two additional sets of data at the frequencies of 95 and 190 GHz were obtained at 10 K and 5 K with the field modulation and waveguide transmission setup; in all these cases the external field was applied parallel to the highly conducting planes of the quasi-two-dimensional crystals.

By extrapolating the data shown in Figure 3.26 for the transition between levels $| -\frac{1}{2} \rangle \longleftrightarrow | +\frac{1}{2} \rangle$, the one transition that is not affected by the zero-field crystal potential and its modifications, an internal effective field can be extracted; while for temperatures above 5 K B_{mf} is zero within experimental error, at 1.4 K, $B_{mf} = -0.028 \pm 0.003$ T. This value is compatible with the relative shifts in line positions described earlier, giving values for $\Delta g_{eff}/g_{eff}$ between 0.001 and 0.016 for the range of frequencies between 71 and 50 GHz.

3.5 Summary

This Chapter has identified the effective spin Hamiltonians for the 3d transition metal ions Cr^{3+} and Fe^{3+} contained in an approximately octahedral oxalate cage embedded in the anion layers of the organic charge transfer salts $\beta''\text{-(BEDT-TTF)}_4[\text{Cr}(\text{C}_2\text{O}_4)_3]\text{C}_5\text{H}_5\text{N}$, $\beta''\text{-(BEDT-TTF)}_4[\text{Fe}(\text{C}_2\text{O}_4)_3]\text{C}_6\text{H}_5\text{CN}$, $\beta''\text{-(BEDT-TTF)}_4[\text{Fe}(\text{C}_2\text{O}_4)_3]\text{C}_6\text{H}_5\text{NO}_2$. The electrostatic crystal field due to the oxalate complex is adequately modelled by a zero-field Hamiltonian containing an axial trigonal term and an additional rhombic distortion. The temperature dependencies of magnetic susceptibility, resonant line positions and widths reveal, for both the $\beta''\text{-(BEDT-TTF)}_4[\text{Cr}(\text{C}_2\text{O}_4)_3]\text{C}_5\text{H}_5\text{N}$ and $\beta''\text{-(BEDT-TTF)}_4[\text{Fe}(\text{C}_2\text{O}_4)_3]S$, the presence of a continuous modification of the zero-field splitting parameters and g -tensor due to the progressive depopulation of the higher energy eigenstates as $k_B T$ becomes of the order of the separation of the levels $\Delta g \mu_B B$, together with the onset of an effective negative internal field due to interionic antiferromagnetic interactions of dipolar nature: the occurrence of both phenomena can suitably account for the observed low temperature trends.

For the superconducting $\beta''\text{-(BEDT-TTF)}_4[\text{Fe}(\text{C}_2\text{O}_4)_3]\text{C}_6\text{H}_5\text{CN}$ compound with applied magnetic field B_{DC} parallel to the highly conducting layers, the frequency dependence of the relative shifts of the resonant lines reveals an additional contribution to the negative internal field (for $B_{\text{DC}} < 2.1$ T and $T < 3$ K), most probably due to the diamagnetic screening currents present within the superconducting portions of the samples; this piece of information can provide an upper limit for B_{c2} , or at least identify the region of the $B - T$ diagram where full field penetration occurs within the “insulating” anion layers. The Josephson vortices of the mixed state fully penetrate the two dimensional layers containing the ion sites already at $B = 2.1$ T and $T = 1.4$ K, despite $B_{c2\parallel} \approx 18$ T [78].

The picture we can deduce from the EPR spectra is that of a three dimensional superconductor consisting of weakly coupled two dimensional superconducting planes separated by insulating layers. In the mixed state, interlayer transport

occurs via normal quasiparticle and Cooper pair tunneling events. The superconducting condensate affects the response of the localized spins to the incoming millimetre-wave radiation indirectly, by means of its diamagnetic screening currents, modifying the penetration of both quasistatic and oscillatory fields inside the samples. The localized moments interact weakly among themselves and are mainly coupled to the phonons; they form an additional internal field that lowers the upper critical field B_{c2} of the compounds with magnetic anions with respect to the non-magnetic members of the oxalate family, β'' -(BEDT-TTF)₄[Ga(C₂O₄)₃]S [78]. It should be mentioned that for several samples of the superconducting β'' -(BEDT-TTF)₄[Fe(C₂O₄)₃]C₆H₅CN compound, a very broad resonant feature with $g \approx 2.4$ has been observed, both in cavity and in non-resonant field modulation experiments; anisotropic and sample size dependent, it has been tentatively attributed to the delocalised carriers, although further investigations are required to clarify this point. Additional valuable information on the mixed state of the superconductor will come from performing similar measurements at lower temperatures and lower magnetic fields, with care to the fact that as the low field region is entered the mixing of the energy levels will become more pronounced and might add to the complexity of the ESR spectra.

Chapter 4

High-frequency magneto-optical response of isotopically substituted κ -(BEDT-TTF)₂Cu(SCN)₂

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4.1 Introduction

$\kappa\text{-(BEDT-TTF)}_2\text{Cu(NCS)}_2$ is a superconducting charge-transfer salt based on the organic molecule BEDT-TTF [18, 84, 63] described at the beginning of Chapter 3. This compound shares many features with other correlated systems, the high-temperature (high- T_c) cuprate superconductors in particular: anisotropy and quasi-two-dimensionality of their bandstructure and possible unconventional superconductivity [18, 63]. The organics, unlike the high- T_c superconductors, are very clean systems and their Fermi surface topology can be accurately measured and modelled using simple tight-binding bandstructure calculations [18].

In this Chapter a millimetre-wave resonant cavity technique is used to investigate the optical response of the organic superconductor $\kappa\text{-(BEDT-TTF)}_2\text{Cu(NCS)}_2$ as a function of applied magnetic field. Two resonant absorptions of millimetre-waves are observed in the superconducting state of $\kappa\text{-(BEDT-TTF)}_2\text{Cu(NCS)}_2$. The angle dependence of these resonances is investigated using the “FTR” insert. Shibauchi *et al.* [85] first interpreted the observation of these features in analogy to results from measurements on high- T_c superconductors. These two absorptions are therefore attributed to Josephson Plasma Resonance (JPR) [85], the fundamental at low fields ($B \approx 0.25$ T) and a broader higher harmonic at higher fields ($B \approx 3$ T). In the normal state at high field, the modulations of the conductivity are attributed to Fermi-surface traversal resonances, absorptions due to the motion of carriers along corrugated quasi-one-dimensional sections of the Fermi surface [6]. The crystal structure and the properties of $\kappa\text{-(BEDT-TTF)}_2\text{Cu(NCS)}_2$ are described in Sections 4.2, 4.3 and 4.4. The measurements are presented in Section 4.6 and discussed in Section 4.7.

4.2 Crystal Structure

Figure 4.1 shows the unit cell ($a = 16.2$ Å, $b = 8.4$ Å, $c = 13.1$ Å) and the arrangement of molecules in $\kappa\text{-(BEDT-TTF)}_2\text{Cu(NCS)}_2$ [4]. Two BEDT-TTF molecules

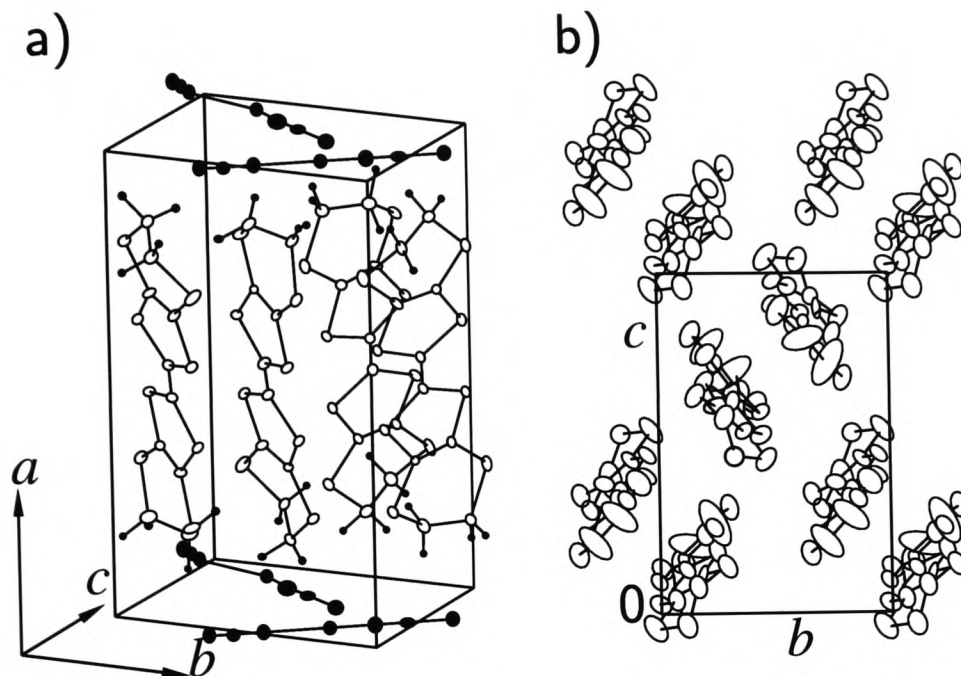


Figure 4.1: The crystal structure of the charge-transfer salt κ -(BEDT-TTF)₂Cu(NCS)₂. Open circles represent the atoms of the BEDT-TTF molecule and the filled circles the anion atoms. a) Unit cell with $a = 16.2$ Å, $b = 8.4$ Å, and $c = 13.1$ Å. b) View along the a -axis onto the BEDT-TTF planes showing the packing arrangement of the molecules [4].

donate one electron to the anion; this charge transfer binds the crystal, leaving behind a partially filled band responsible for the high temperature metallic behaviour [18, 63]. The BEDT-TTF molecules form dimers, each unit cell containing two. The layers of BEDT-TTF molecules are separated by the anions Cu(NCS)₂. There is good orbital overlap within the BEDT-TTF layers, and very little in the interlayer direction. This leads to a quasi-two-dimensional bandstructure [18, 63].

4.3 Normal State Properties of κ -(BEDT-TTF)₂Cu(NCS)₂

κ -(BEDT-TTF)₂Cu(NCS)₂ is a type-II superconductor with $T_c = 10.4$ K at ambient pressure [18]. At low temperatures above T_c , κ -(BEDT-TTF)₂Cu(NCS)₂ is an anisotropic conductor. Shubnikov-de Haas [18], de Haas-van Alphen [18], Fermi-surface traversal resonance [29] and angle-dependent magnetoresistance os-

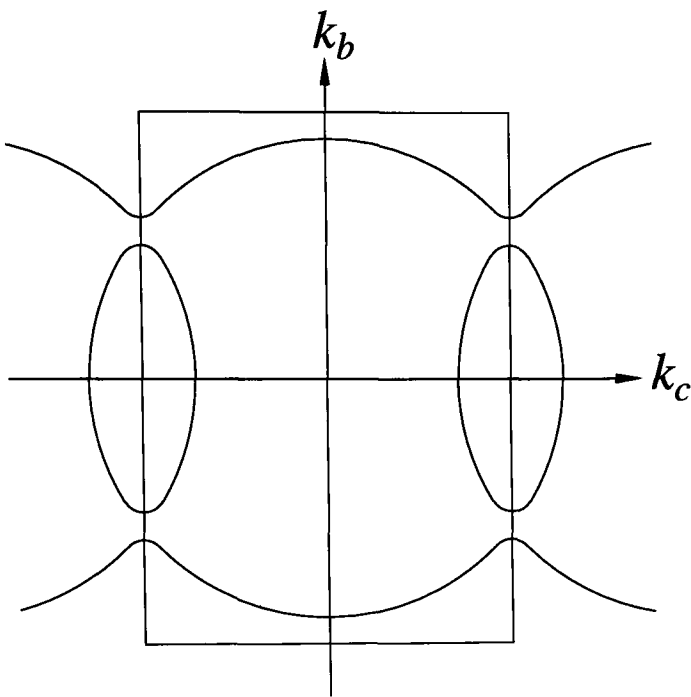


Figure 4.2: Cross section of the Fermi surface of κ -(BEDT-TTF)₂Cu(NCS)₂ consisting of quasi-two-dimensional cylinders and quasi-one-dimensional sheets [86].

cillation [87, 88] experiments all point to a Fermi surface consisting of quasi-two-dimensional pockets and quasi-one-dimensional sheets, as shown in cross section in Figure 4.2. The normal state at low temperatures is therefore well described by Fermi Liquid theory [18]. The conductivity in the highly conducting (b, c) plane is $\sigma_{\parallel} = 3.8 \times 10^5 (\Omega\text{m})^{-1}$ ($T=12$ K) and the anisotropy ratio of the in-plane to interplane conductivity is $\sigma_{\parallel}/\sigma_{\perp} \sim 600$ [89, 90]. The in-plane scattering time derived from measurements of the Drude conductivity is $\tau_{\text{parallel}} = 0.1$ ps [90], about a factor of 30 smaller than the value obtained from Shubnikov-de Haas measurements ($\tau_{\text{parallel}} = 2.6$ ps) [91]. Further investigations of the frequency dependence of the scattering rate are necessary to shed light on this issue [25, 90].

4.3.1 Fermi Surface Traversal Resonance

As outlined in Chapter 1, the motion of the carriers along open orbits across corrugated quasi-one-dimensional Fermi surface sheets gives rise to resonant absorptions, called Fermi-surface traversal resonances or FTR [9, 10]. This model has been applied to interpret the modulations of the high frequency magneto-

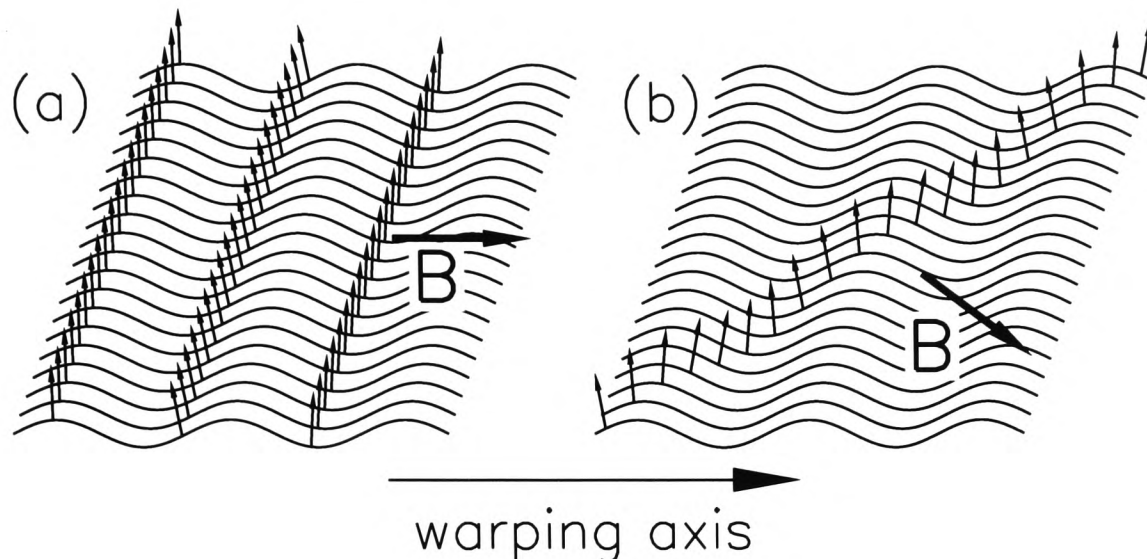


Figure 4.3: The path taken by a carrier across a corrugated quasi-one-dimensional Fermi surface when (a) $B_{\parallel}$ is parallel to the warping axis and (b) $B_{\parallel}$ is at an angle to the warping axis. The small arrows indicate the real space velocity.

conductivity of α -(BEDT-TTF) $_2$ KHg(NCS) $_4$ [6] and hydrogenated and deuterated κ -(BEDT-TTF) $_2$ Cu(NCS) $_2$ [92].

The physical origin of FTR can be explained with reference to Figure 4.3. Assuming the external magnetic field, $B_{\parallel}$, to be contained in the plane of the sheet, two possible trajectories followed by a charge carrier across a section of corrugated quasi-one-dimensional Fermi surface are shown [6]. In (a), $B_{\parallel}$ is parallel to the warping axis and the particle follows a path parallel to the corrugations. When following the path depicted in (b), the component of the carrier velocity parallel to the Fermi sheet, $v_{\parallel}$, oscillates periodically due to the corrugations of the Fermi surface; this leads via the Boltzmann transport equation, described in Chapter 1, to a resonant contribution to the high frequency conductivity at the frequency of oscillation of $v_{\parallel}$ [6]. The identification of the FTRs can be achieved by studying the behaviour of the resonances as a function of angle. In fact, the frequency ω_{1D} of the oscillatory component of the velocity, $v_{\parallel}$, is proportional to $\sin \psi$, ψ being the angle the external field makes with the warping axis, and to $B_{\parallel}$. In the experiments presented here the frequency, ω_0 , of the millimetre-waves is kept constant and the magnetic field is swept. The field at which resonance occurs,

B_{res} , is therefore given by

$$\frac{\omega_0}{B_{res}} = A \sin \psi, \quad (4.1)$$

A being a constant related to the periodicity of the Fermi surface k -space corrugation. The reciprocal of the field position at which the resonance takes place describes a sinusoidal arch as the direction of the magnetic field changes within the plane of the sheet, its maximum occurring when the field is orthogonal to the axis of corrugation.

A quasi-one-dimensional effective mass

In cyclotron resonance experiments the carrier effective mass, m_{CR}^* , is defined by the relation $\omega_c = qB/m_{CR}^*$, providing a measure of the “inertia” of the particle to the motion around closed orbits. In a similar manner, a quasi-one-dimensional effective mass, m_{1D}^* , can be defined, which provides information on how rapidly the quasi-one-dimensional corrugations are crossed. For a carrier travelling in the direction of the warping axis

$$\omega_{1D} = \frac{qB_{\parallel}}{m_{1D}^*}. \quad (4.2)$$

4.4 Superconducting Properties

The response of a superconductor to a quasistatic magnetic field determines its classification as a Type I or a Type II superconductor, depending on the value of the Ginzburg-Landau order parameter:

$$\kappa = \frac{\lambda}{\xi}, \quad (4.3)$$

where λ is the London penetration depth and ξ is the coherence length [83]. The coherence length ξ is a measure of the spatial decay distance of the superconducting wavefunction. The penetration depth λ is the thickness of the surface layer where screening currents circulate so as to achieve perfect diamagnetism in

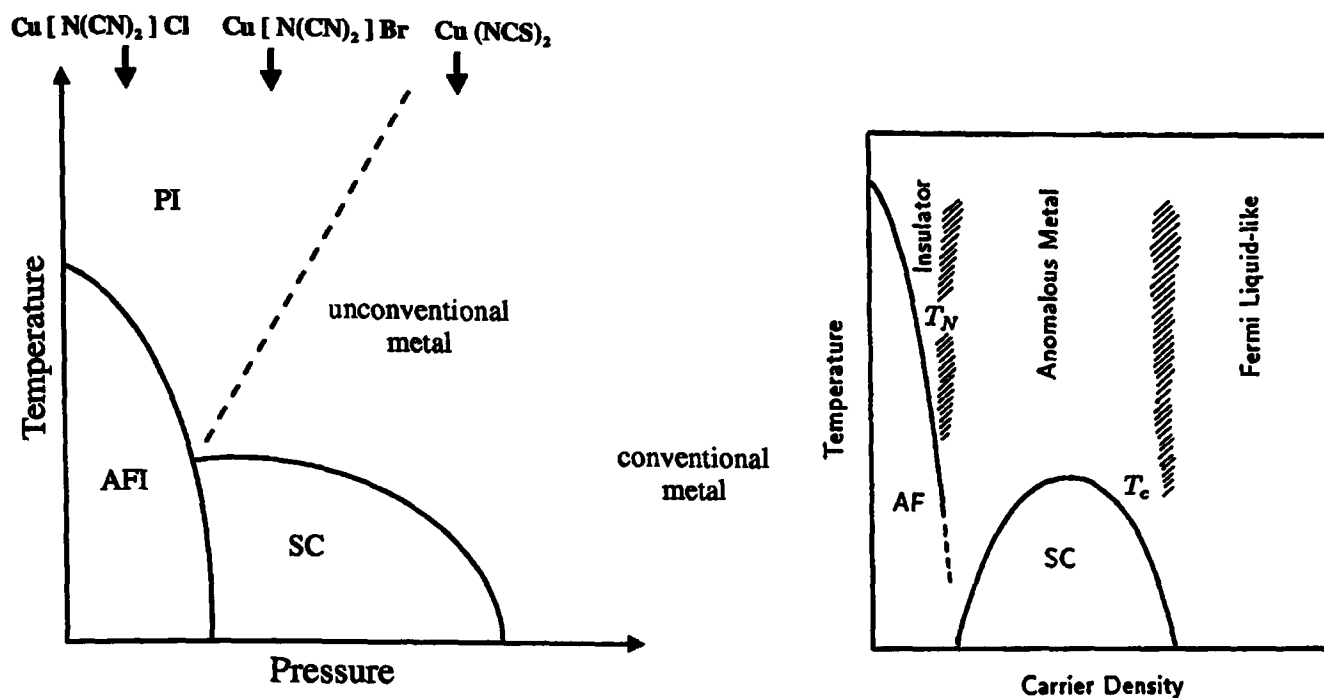


Figure 4.4: A comparison of the phase diagrams of the κ -(BEDT-TTF)₂X salts (left) and of the high- T_c cuprates (right) [25]. The role of pressure in the organics is replaced by hole doping in the cuprates

the bulk of the material when an external field is applied [83]. For both type of superconductors the external field can partially penetrate to within a distance λ from the surface. In type-II superconductors it is energetically favorable for the system to allow flux penetration in the form of quantized units ($\xi \ll \lambda$). This generates a mixed state consisting of superconducting material and vortices of flux having a normal non-superconducting core. As the magnetic field is increased, the flux lines, at first well separated, gradually come to overlap and occupy, beyond the upper critical field B_{c2} , the whole volume of the material. κ -(BEDT-TTF)₂Cu(NCS)₂ is a highly anisotropic type-II superconductor ($T_c = 10.4$ K). In-plane resistivity measurements of the critical field give an estimate of the in-plane coherence length $\xi_{\parallel}(0) \approx 50 - 80$ Å [93]. AC susceptibility measurements provide an upper limit for the interlayer penetration depth of $\lambda_{\perp} \sim 220$ μm [94]. In previous experiments using millimetre-waves $\lambda_{\perp}$ was reported to be ~ 120 μm [85]. The in-plane penetration depth is $\lambda_{\parallel} \sim 0.5 - 0.8$ μm [90, 93], therefore giving an anisotropy parameter of $\gamma \equiv \lambda_{\perp}/\lambda_{\parallel} \sim 150 - 440$.

The origin of superconductivity in the quasi-two-dimensional organics is still controversial [18]. Schlueter *et al.* have reported the presence of an inverse isotope effect ($\Delta T_c = 0.25 - 0.8$ K [95]) upon replacement of the eight hydrogen atoms of the BEDT-TTF molecule with deuterium; this effect is contrary to the predictions of BCS theory. Replacing the carbon and sulphur atoms with heavier isotopes does not, on the other hand, substantially affect the value of T_c . The carbon- and sulphur- substituted compounds are the ones under investigation in this Chapter. The aim is to gain insight into the superconducting pairing mechanism from the millimetre-wave response of the samples.

There are many similarities between the phase diagrams of high- T_c cuprates and the κ phase BEDT-TTF salts [25] (see Figure 4.4). For both, the superconducting region is next to an antiferromagnetic phase. A picture of superconductivity mediated by antiferromagnetic fluctuations is proposed by several theoretical calculations ([96], [97] and [98]); all these models lead to a d -wave order parameter. Reference [18] reviews the recent experimental work concerning unconventional superconductivity in BEDT-TTF salts: evidence seems to support the scenario of d -wave superconductivity mediated by spin fluctuations. The location of the nodes of the order parameter depend on the details of the Fermi surface; hence the importance of measuring its exact topology. The angle-dependent millimetre-wave technique in applied magnetic fields is sensitive to the fine structure of the Fermi surface (which can be accessed at fields higher than B_{c2}), and can provide information on its topology.

4.5 Experimental Details

Millimetre-wave measurements on samples of isotopically substituted κ -(BEDT-TTF)₂Cu(NCS)₂ were made as a function of orientation in an applied magnetic field up to 33 T at $T = 1.4$ K. The single crystal samples of κ -(BEDT-TTF)₂Cu(NCS)₂, obtained from Dr. J. Schlueter at Argonne National Labora-

	δ (μm)	λ (μm)
Currents $\parallel (b, c)$	3	0.5-0.8
Currents $\perp (b, c)$	95	100-200

Table 4.1: Skin depth and penetration depth in the anisotropic conductor κ -(BEDT-TTF)₂Cu(NCS)₂ [25] estimated for $T = 12$ K and $T = 0$ K respectively.

tory, USA, were crystallographically oriented by IR reflectivity for us by Tim Biggs at the Clarendon Laboratory. Cavity resonance experiments allow us to measure the bulk magneto-conductivity of this anisotropic material, as described in Section 2.4.1 of Chapter 2. The sample (of typical size $0.5 \times 0.2 \times 0.05$ mm³) is positioned in the magnetic field antinode of the TE_{102} mode of a rectangular silver resonator (dimensions $6 \times 3 \times 1.5$ mm³, resonant frequency $\nu \approx 71.9$ GHz). The oscillatory magnetic field is polarised along the highly conducting planes, so that both in-plane and interlayer currents are excited, the dominant dissipative contribution being due to the latter [6]. The values of penetration depth and skin depth given in Table 4.1 confirm that the millimetre-wave penetrate the bulk of the sample, both in the superconducting and in the normal state [25]. Typical Q -factors obtained are $Q \approx 1200 - 1500$, with a reduction upon sample insertion of the order of 15-20 % and a frequency shift of 200-400 MHz.

4.6 Measurements and Results

Changes in the cavity transmission were investigated as a function of polar angle θ , the angle between the applied magnetic field $\mathbf{B}$ and the interlayer direction of the crystal (a -axis). The FTR insert described in Chapter 2 allows the rotation of sample and resonator to take place in-situ. A typical set of raw data is presented in Figure 4.5; field sweeps for $25^\circ \leq \theta \leq 85^\circ$ are shown. One very sharp feature at low fields is clearly visible, moving from $B = 0.25$ T at $\theta = 0^\circ$ to $B = 0.89$ T at $\theta = 80^\circ$; a second dip is visible at higher fields, in proximity to the transition from the superconducting to the normal state; this also moves to higher

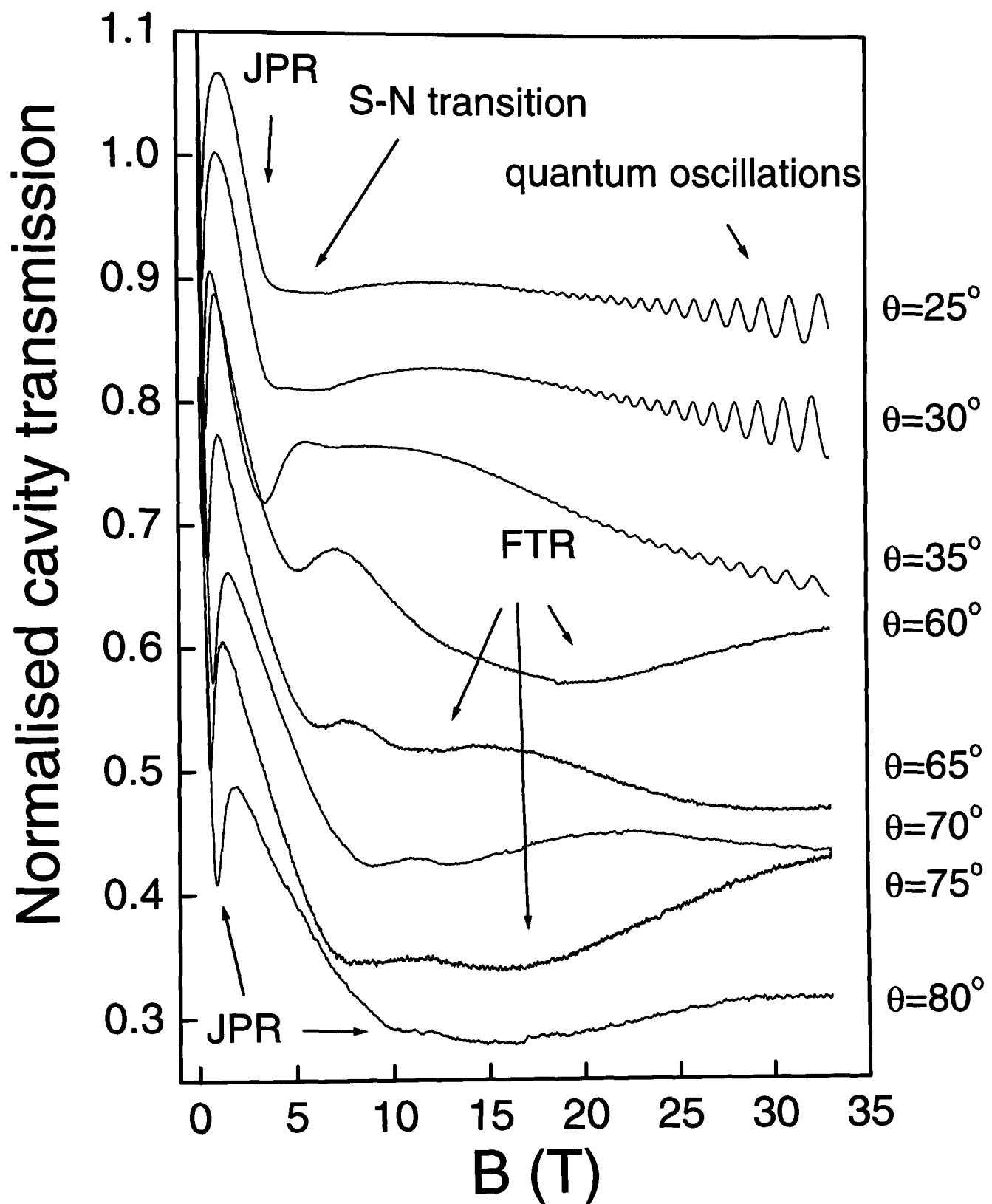


Figure 4.5: Normalized cavity transmission as a function of magnetic field for $25^\circ \leq \theta \leq 80^\circ$. The measurement frequency is $\nu = 71.9$ GHz and the temperature is $T = 1.4$ K. The traces are normalized and offset for clarity.

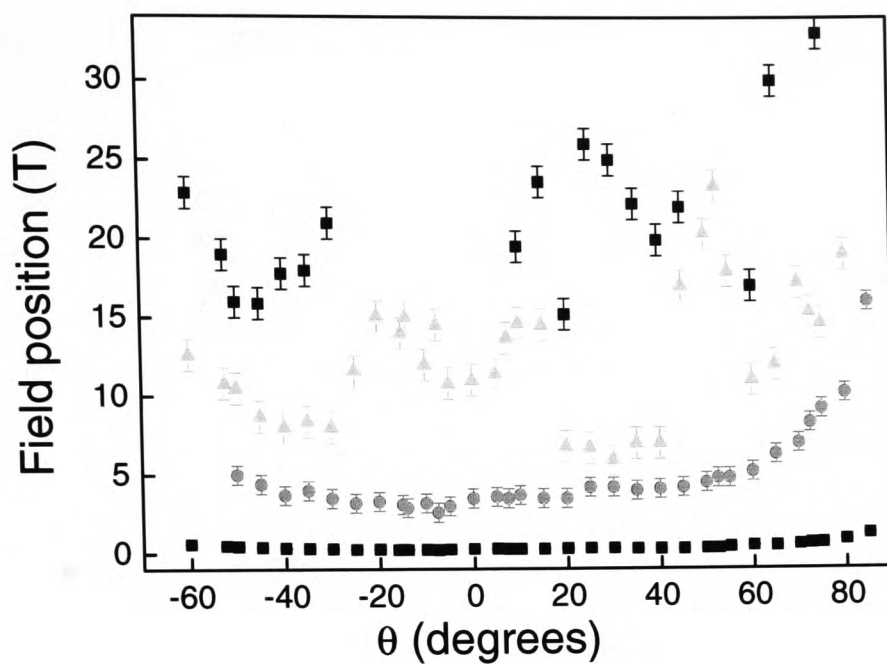


Figure 4.6: The position of all identified resonance minima as a function of the angle θ at 1.4 K and $\nu = 71.9$ GHz.

fields as the angle departs from 0° . Well into the normal state some broader features are present, together with Shubnikov-de Haas oscillations beyond 15 T. The measurements are taken at a temperature of 1.4 K, and all the sweeps in the Figure are offset for clarity. Figure 4.6 shows all the identified minima in the cavity transmission; the following analysis will identify the features in the mixed state of the superconductor as Josephson plasma resonances (JPR) and the normal state absorptions as Fermi-surface traversal resonances.

4.7 Analysis and Discussion

4.7.1 Fermi-surface traversal resonances

The resonant absorptions occurring in the normal state are plotted as $1/B_{\text{res}}$ versus polar angle in Figure 4.7. The resonances appearing in the higher region of the graph (lower magnetic field) are then fitted to the relation

$$\frac{1}{B_{\text{res}}} = A \sin(\theta - \theta_o). \quad (4.4)$$

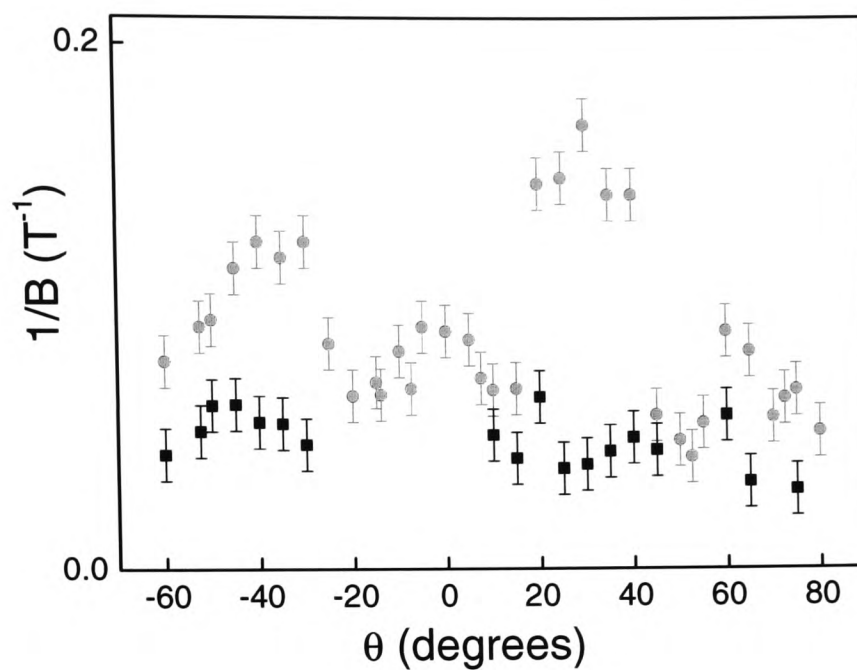


Figure 4.7: The position of the normal state resonant absorption features as a function of the angle θ at 1.4 K and $\nu = 71.9$ GHz.

This relationship is approximate, but can still provide some insight into the properties of the quasi-one-dimensional Fermi surface sections [6]. The fitted data are presented in Figure 4.8. The absence of features in the top part of the “arch” can be attributed to the proximity of the superconducting transition. This fit allows the identification of one of the warping axes of the Fermi sheet; the fit gives $A/\omega_0 = 0.16 \pm 0.005$, and $\theta_0 = (83 \pm 1)^\circ$, θ_0 being the angle between the warping axis and the crystallographic a -axis.

Several other features are present in the lower region of the graph presented in Figure 4.7. These features are most probably due to additional corrugations of the Fermi sheet.

4.7.2 Josephson Plasma Resonance

Let us now consider the millimetre-wave response in the mixed state of the superconductor: two features can be clearly identified (see Figure 4.5). Their polar

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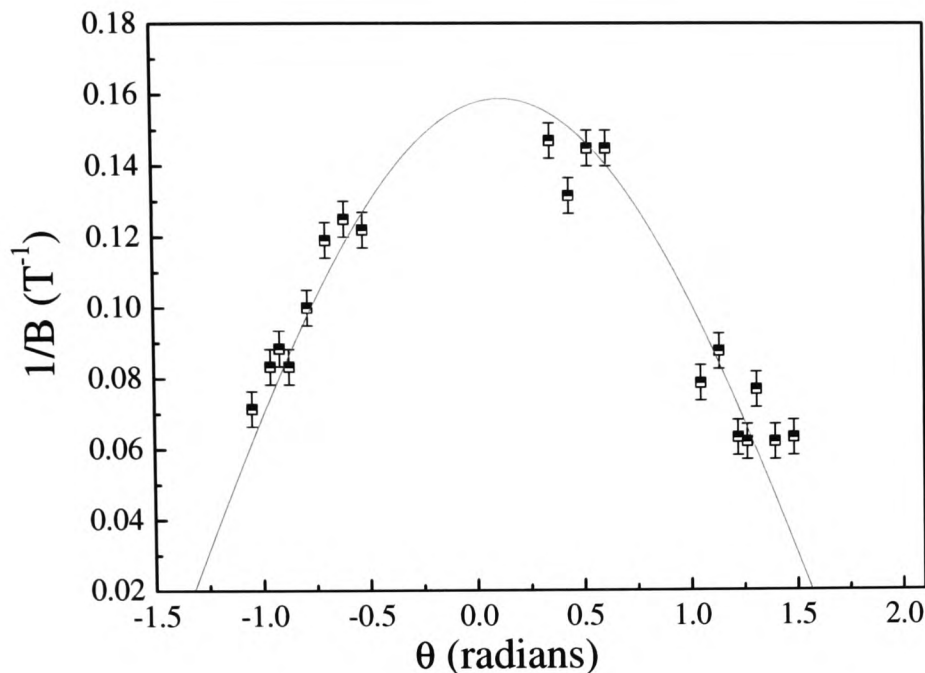


Figure 4.8: A series of normal state resonant features plotted as inverse field versus polar angle θ ; the solid line is a fit to equation 4.4.

angle dependence follows a $\cos \theta$ behaviour:

$$\frac{1}{B} = A \cos \theta. \quad (4.5)$$

Both resonances are well fitted by this expression. This indicates that the absorption depends on the component of magnetic field along the interlayer direction, the dissipation being due to the flow of currents between the highly conducting planes. These absorptions have been observed in κ -(BEDT-TTF)₂Cu(NCS)₂ for the first time by Shibauchi *et al.*, and have been subsequently investigated by Hill *et al.* [99], [100]. Their interpretation in terms of Josephson Plasma Resonance (JPR) is by now established [85], [101], and represents one more common feature between the organics and the high- T_c superconductors.

The c-axis Josephson plasma frequency is related to the maximum Josephson current $J_m(B, T)$ by [85]

$$\omega_p^2(B, T) = \frac{8\pi^2 cs}{\epsilon_0 \Phi_0} J_m(B, T), \quad (4.6)$$

where s is the crystal interlayer spacing, ϵ_0 is the high-frequency dielectric constant and $\Phi_0 = h/2e$ is the flux quantum. The Josephson current is given by

$$J_m = J_0 \langle \langle \cos \phi_{n,n+1}(\mathbf{r}) \rangle \rangle_t \rangle_d, \quad (4.7)$$

where $\phi_{n,n+1}(\mathbf{r})$ is the gauge invariant phase difference between the layers n and $n+1$ at a point $\mathbf{r}$ in the (b, c) plane and the brackets denote thermal and disorder averages; $J_0 = J_0(T)$ is the maximum interlayer Josephson current density in zero magnetic field and corresponds to $J_0(T) = c\Phi_0/8\pi^2 s\lambda_\perp^2(T)$, $\lambda_\perp$ being the interlayer London penetration depth.

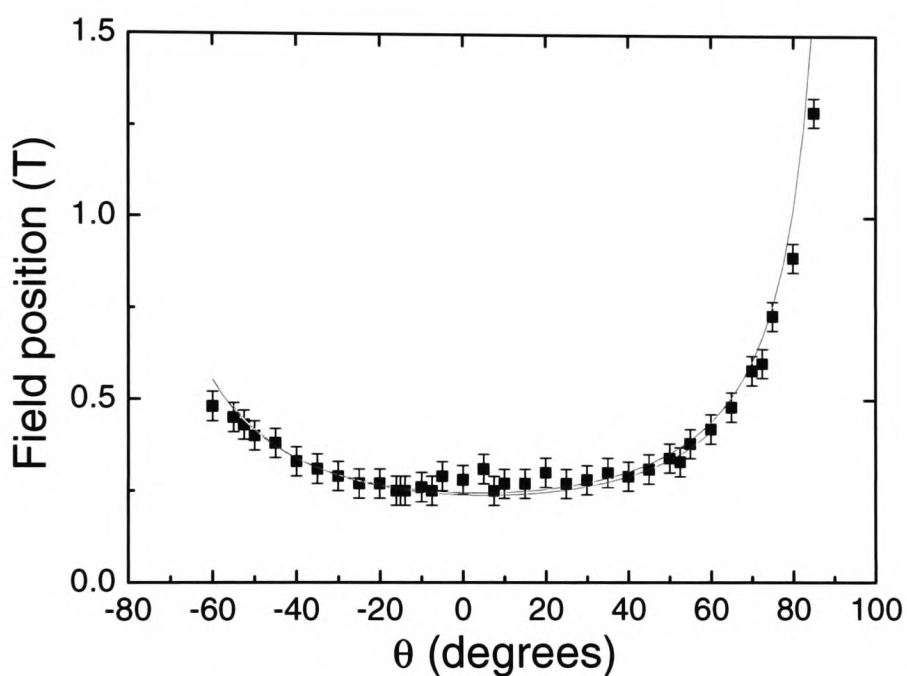


Figure 4.9: The position of the lowest field resonance minimum as a function of the cavity angle θ at 1.4 K and $\nu = 71.9$ GHz. The solid line is a fit to Equation 4.5.

One of the proposed models to describe both high- T_c and organic superconductors (derived from the Lawrence and Doniach model [93]) consists of a series of two-dimensional superconducting planes separated by insulating layers; interlayer transport occurs via Josephson tunneling of Cooper pairs [93], [102]. This model predicts an interlayer Josephson resonance in the microwave region of the spectrum; resonance occurs when the oscillatory frequency of the tunneling superconducting pairs, ω_p , matches the measurement frequency. This phenomenon

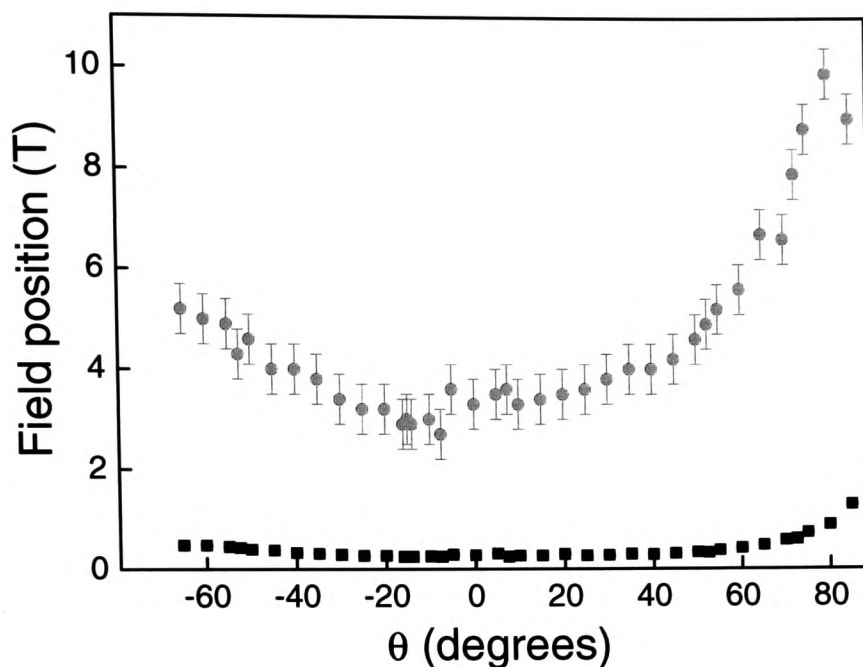


Figure 4.10: The position of both resonant features in the superconducting state as a function of angle θ at 1.4 K and $\nu = 71.9$ GHz.

has been observed in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ [102], $\text{YBa}_2\text{Cu}_3\text{O}_{6-y}$ [103], and $\kappa\text{-(BEDT-TTF)}_2\text{Cu(NCS)}_2$ [29, 85, 99].

A large anisotropy parameter γ causes a suppression of the plasma frequency ω_p , being the latter inversely proportional to the former: $\omega_p = c/\lambda_\perp\sqrt{\epsilon_0} = c/\lambda_\parallel\gamma\sqrt{\epsilon_0}$ [104, 105]. This causes the plasma frequency to be smaller than the superconducting gap, and therefore to be observable below T_c . The application of a magnetic field further reduces the plasma frequency, by introducing the vortex lattice; when this decouples in the interlayer direction (causing the formation of the so-called “pancake” vortices [93], [100]), random phase differences are induced between the adjacent layers, leading to the suppression of the maximum interlayer superconducting current [105].

For both organics and high- T_c materials the Josephson plasma resonance is therefore observable in the microwave/millimetre-wave region of the spectrum [85]. The data reported here confirm the presence of such phenomenon in the isotopically substituted layered superconductor $\kappa\text{-(BEDT-TTF)}_2\text{Cu(NCS)}_2$.

4.8 Summary

The bulk high-frequency magneto-conductivity of the isotopically substituted organic superconductor κ -(BEDT-TTF)₂Cu(NCS)₂ was measured as a function of field orientation at $T = 1.4$ K and $\nu = 71.9$ GHz. The response in both normal and superconducting state was investigated by means of a resonant cavity perturbation technique.

Two absorption features in the superconducting state display a $\cos \theta$ behaviour, indicative of being dependent on the magnetic field component in the interlayer direction. The dissipative mechanism is the presence of interlayer currents, and the features are attributed to Josephson plasma resonances, confirming previous results and interpretations [85].

A number of features in the normal state are fitted to a sinusoidal function, displaying a dependence on the component of the applied field parallel to the quasi-one-dimensional sections of the Fermi surface. This sinusoidal “arch” is identified as a set of Fermi-surface traversal resonances [6], providing information on the warping of the quasi-one-dimensional sections of the Fermi surface.

Chapter 5

High pressure GHz magnetoconductivity of (TMTSF)₂PF₆

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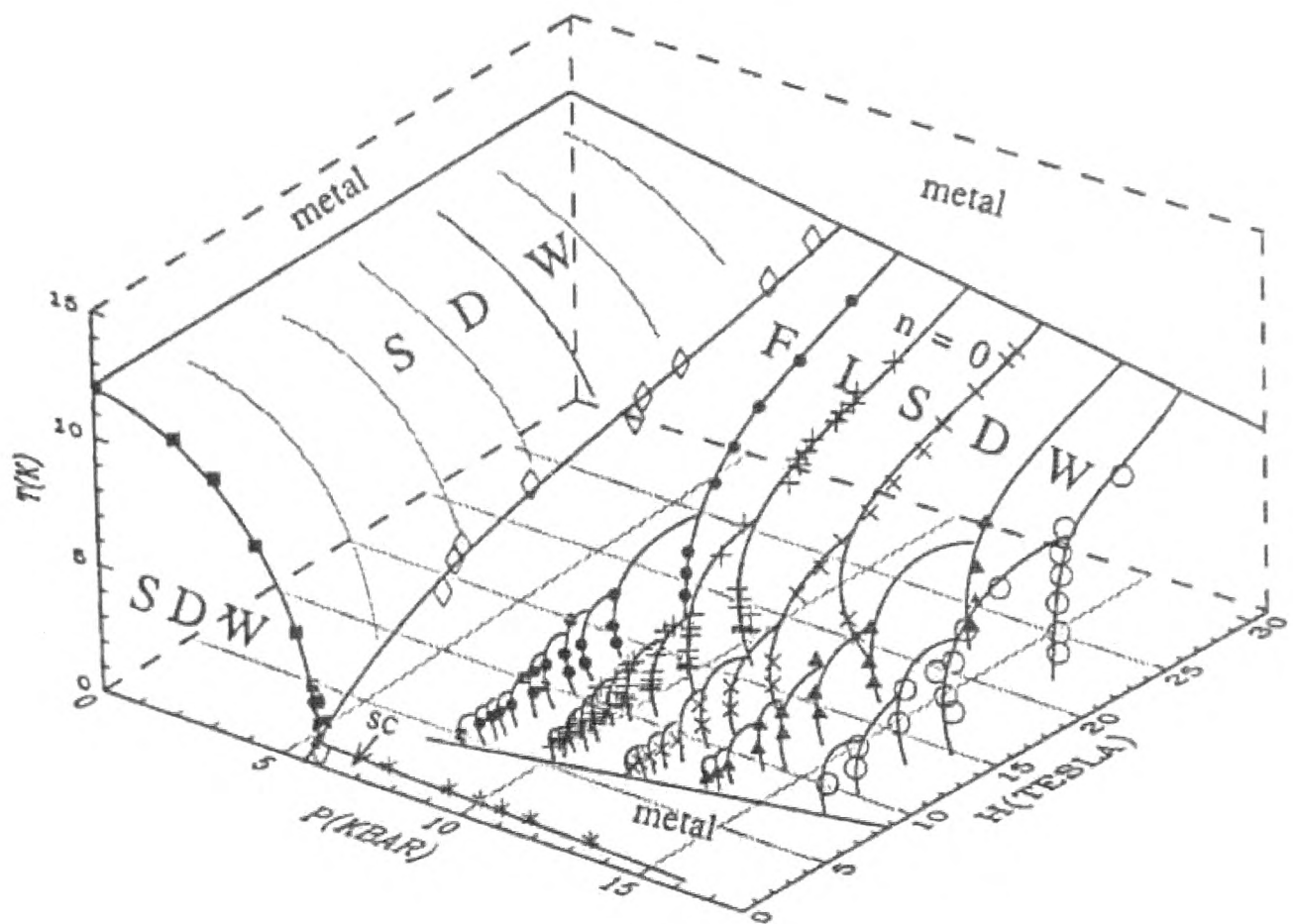


Figure 5.1: The pressure-magnetic field-temperature phase diagram of $(\text{TMTSF})_2\text{PF}_6$ (from Reference [106])

5.1 Introduction

This Chapter presents some preliminary results on the millimetre-wave optical response of the quasi-one-dimensional Bechgaard salt $(\text{TMTSF})_2\text{PF}_6$ (where TMTSF stands for tetramethyltetraselenafulvalene) in the simultaneous presence of a magnetic field and applied hydrostatic pressure. The crystal structure consists of chains of donor TMTSF molecules separated by chains of acceptor anions. $(\text{TMTSF})_2\text{PF}_6$ is an anisotropic quasi-one-dimensional conductor, with bandwidths given by $4t_a : 4t_b : 4t_c = 1 : 0.1 : 0.003$ eV [106]. Its Fermi surface consists of a pair of corrugated sheets; due to thermal scattering, the system is truly one dimensional at room temperature, gradually becoming more two dimensional as the temperature is lowered. Optical experiments report deviations from a simple Drude response as evidence for a Tomonaga-Luttinger liquid [107]. Its phase diagram is extremely rich: as the temperature is lowered below 12 K it

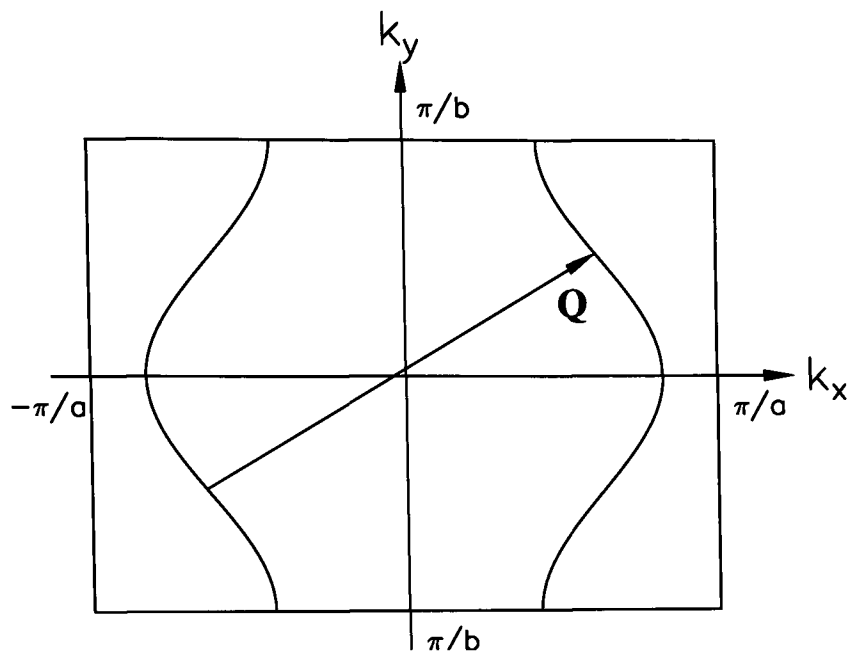


Figure 5.2: The two corrugated sections of Fermi surface of a quasi-one-dimensional metal, showing the nesting vector $\mathbf{Q}$ (from Reference [6]).

undergoes a spin density wave transition (SDW), becoming an insulator. Pressure in excess of 6 GPa suppresses the SDW, and the system becomes superconducting below $T_c \sim 1$ K [106]. Above 6 GPa the application of a magnetic field induces a cascade of field-induced spin density wave (FISDW) transitions (Figure 5.1 shows the pressure-magnetic field-temperature phase diagram for $(\text{TMTSF})_2\text{PF}_6$).

5.2 Density-waves

The band structures of many organic molecular metals contain quasi-one-dimensional bands and their corresponding quasi-one-dimensional Fermi surface sheets. If under translation by a vector $\mathbf{Q}$, two Fermi surface sheets can be superimposed on one another, then the two sheets are said to “nest” well - the electrons on the Fermi sheets couple strongly to perturbations with the wavevector $\mathbf{Q}$ [6]. $\mathbf{Q}$ is then known as the nesting vector (see Figure 5.2).

An example of such a perturbation is the electron-phonon interaction, where electrons couple strongly to phonons of wavevector $\mathbf{Q}$. This interaction gives rise to a modulation of the electron charge density, known as a charge-density-

wave, and a corresponding periodic distortion of the underlying lattice, both with wavevector $\mathbf{Q}$ [108]. The change in the periodicity of the system leads to a modification of the Brillouin zone inducing a gap in the quasi-one-dimensional bands at the Fermi surface. If there are strong interactions between the electron spins, a similar effect on the spin density of the electrons can occur. The resulting modulation of the spin density is known as a spin-density-wave. The corresponding change in the periodicity of the spin-density-wave also modifies the band structure by inducing a gap at the Fermi energy. In both cases, the creation of a gap at the Fermi surface leads to a decrease in the energy of the system, while the ordering of charge or spin leads to an increase in energy. This competition between these two effects determine the stability or instability of the density wave state. If the Fermi surfaces present in the system are all one-dimensional, then the formation of the energy gap as described above will give rise to a metal-insulator transition; this is the case for the one-dimensional TMTSF-based metals.

The FISDW is caused by the competing effects of hydrostatic pressure and magnetic field. A one-dimensional system is unstable against a density wave distortion [106], [109]; pressure increases the dimensionality of the system while a magnetic field reduces it. The competition between the SDW nesting vector and the reciprocal of the magnetic length gives rise to the FISDW [106]. The SDW phases correspond to states with quantized Hall resistance; in fact, the SDW is a necessary condition for the stability of the quantum Hall state, and viceversa [109]. It is important to notice that within each phase the SDW nesting vector changes continuously as the field changes, whereas the change is discontinuous when crossing between one phase into another. The gap resulting from a spin density wave is small and the magnetic fields present can give rise to magnetic breakdown, so that carriers tunnel between Landau levels [109]. Additionally, SDWs have well-defined collective excitations, related to the spatial variation of the phase (phasons) or the amplitude (magnons) [110]. These collective modes as well as possible single-particle excitations will need to be considered in the interpretation

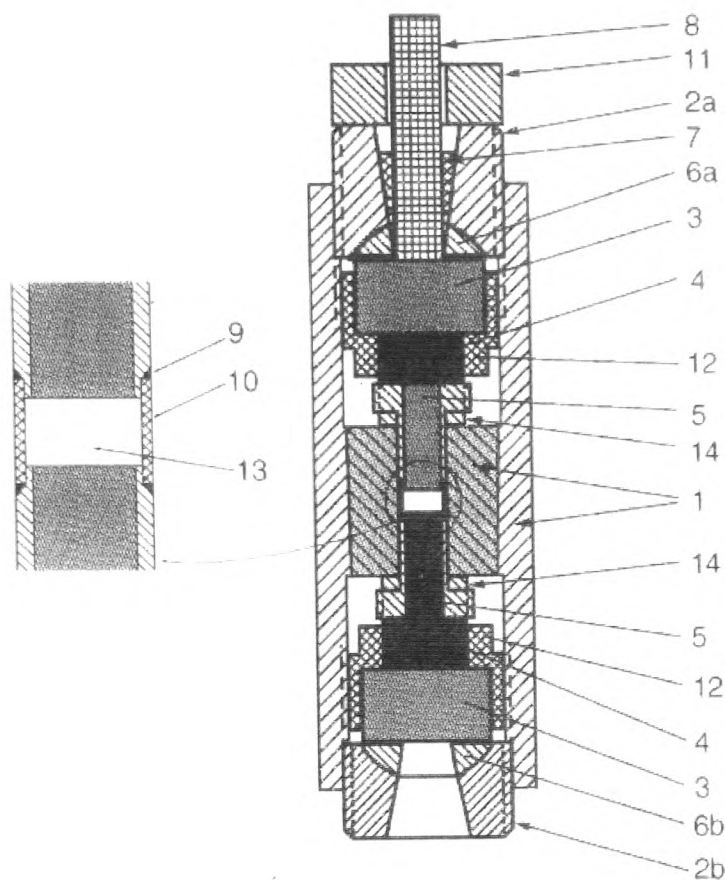


Figure 5.3: A schematic of the pressure cell with optical access used in the experiments (from [111]).

of the millimetre-wave response.

5.3 Magneto-optics under pressure

For this set of experiments, the MVNA was used as source and detector of millimetre-wave radiation together with two sets of harmonic multipliers in order to cover the range 50-130 GHz, the V and W bands. A transmission insert with waveguides was operated in overmoded configuration; the pressure cell at the bottom of the insert provided hydrostatic pressure up to 1.8 GPa. Figure 5.3 shows a schematic of the pressure cell designed and built by Andrei Kornilov. Its main components are the double-walled body, number 1 in the Figure, a cylinder made out of hard non-magnetic Berillium-Copper (BeCu) alloy, a teflon tube for sealing the high pressure volume (number 10) and a sequence of optically polished sapphire pistons (numbers 3, 4 and 5); a pushrod is used for loading the cell (num-

ber 8). The pressure transmitting medium is a Si-based organic liquid which does not solidify up to 35 GPa at room temperature. The insert was lowered inside the magnet bore of a 14 T Cryogenic Magnet.

5.4 Experimental results

The experiment was performed by using a ^3He closed-cycle system, enabling a base temperature of 0.9 K to be achieved. A fine metallic grid was evaporated in order to polarize the electromagnetic radiation along the highly conducting axis of the orientated sample. The in-chain electrodynamics of the anisotropic material was therefore investigated in an orthogonal applied magnetic field. The frequency range 50-130 GHz was covered for three different values of the pressure: at 0 GPa, in order to assess the background response of the instrument, at 0.8 GPa and at 1.2 GPa. Figures 5.4 and 5.5 present the recorded data for a number of frequencies. Consider at first Figure 5.4: a background feature is present between 3 and 4 T; by inspecting the phase diagram of Figure 5.1, the material at $T = 0.9$ K and 0.8 GPa enters the first SDW phase at the magnetic field $B \approx 4.6$ T; at this field the signal at all frequencies falls, and keeps falling in a step-like manner. This is a typical response of a SDW cascade. Several features can be identified as transitions between two neighbouring FISDW states; in particular, the common feature at $B \approx 13.1$ T corresponds to the entrance into the SDW phase characterized by the quantum Hall number $n = 1$ [106]. Additional features appear within one single SDW dome: they either occur at the same field value for different frequencies, or appear to shift to higher fields as the frequency increases. Some of these dips are very sharp and their amplitude and phase behaviour suggests they could be resonant absorptions. The most pronounced resonant features are plotted in Figure 5.6. Transitions due to the excitation of the antiferromagnetic SDW ground state can take place at frequencies appropriate to the respective spin wave spectrum [57]. The resonances occurring away from the transition fields could

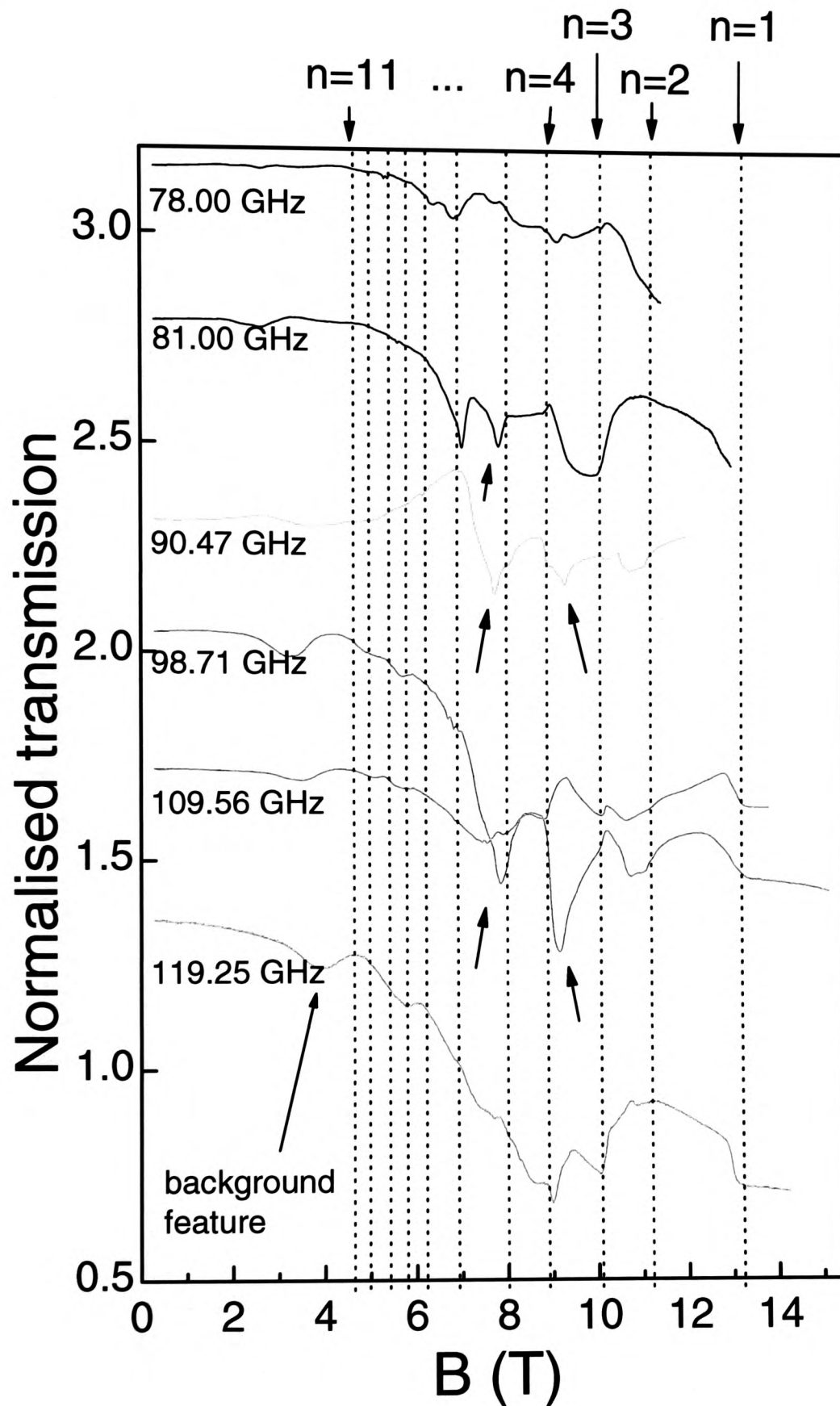


Figure 5.4: Normalized cavity transmission as a function of applied magnetic field for a number of frequencies in the range 70-120 GHz; the applied pressure is 0.8 GPa. The arrows indicate some of the very pronounced features discussed in the text. The dotted lines represent the boundaries between different SDW states [106], labelled by their quantum Hall number n , as customary in the literature. The traces are offset for clarity.

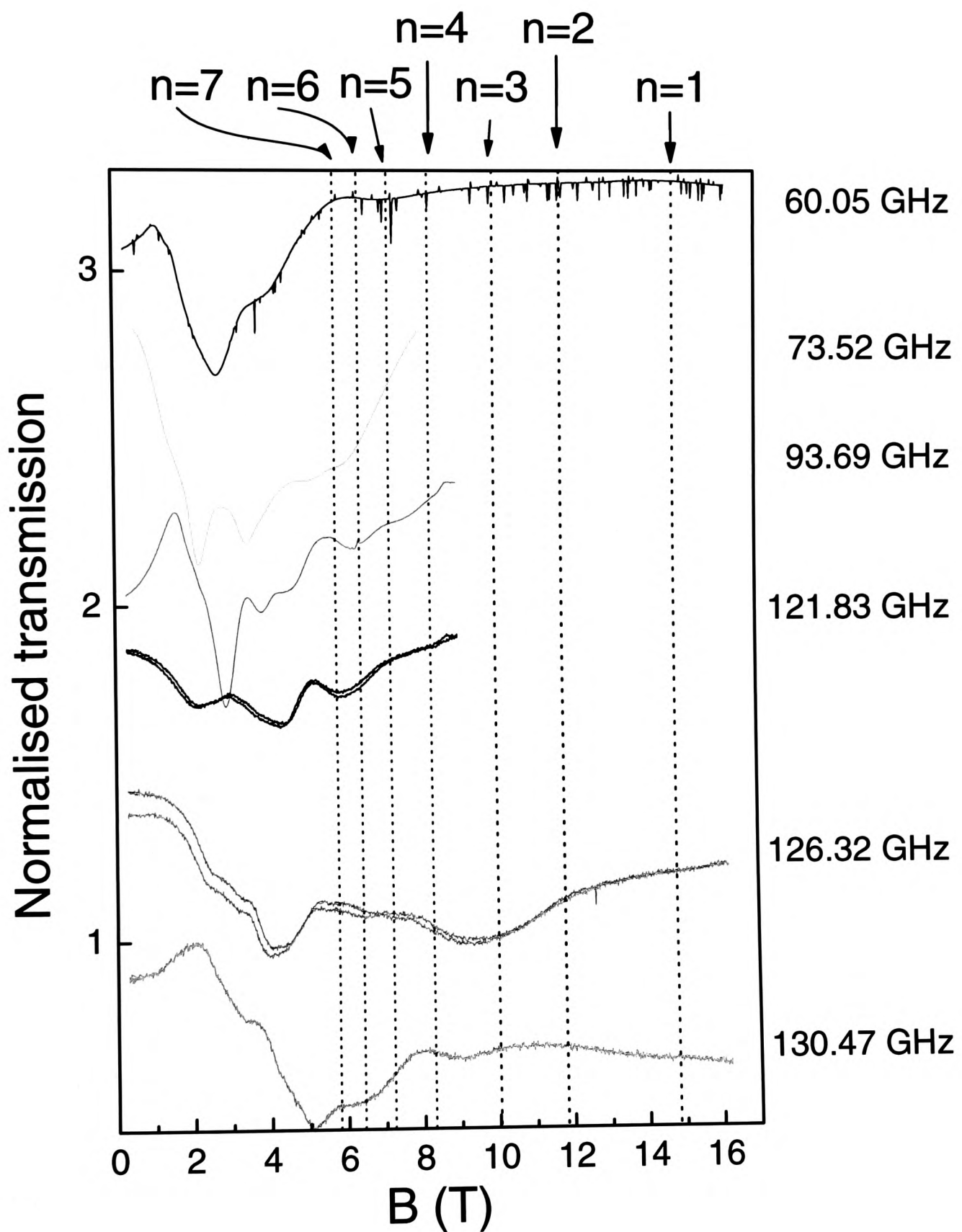


Figure 5.5: Normalized cavity transmission as a function of applied magnetic field for a number of frequencies in the range 60-130 GHz; the applied pressure is here 1.2 GPa. The dotted lines represent the boundaries between different SDW states. The traces are offset for clarity.

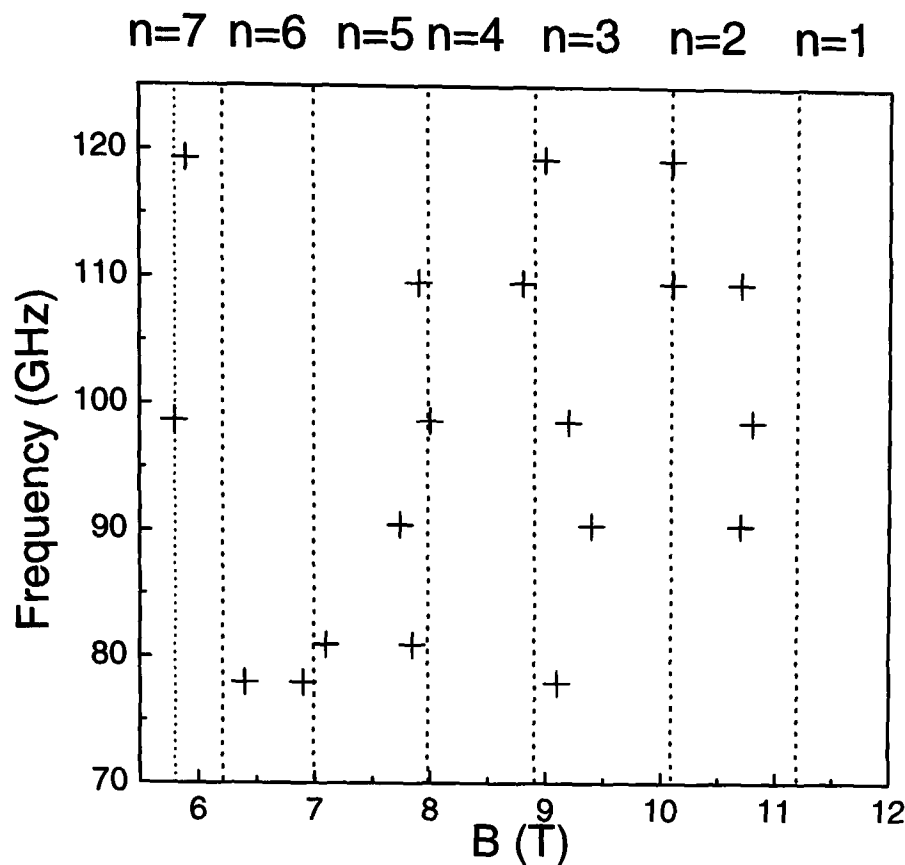


Figure 5.6: The frequency-field dependence of the most pronounced absorption features observed in the field sweeps at 0.8 GPa; some of them occur right at the boundary between adjacent SDW phases, some in the vicinity of the boundary and some well within a single SDW dome.

not be fitted to a single model for antiferromagnetic resonance [58, 112]. This suggests that resonances occurring in different SDW phases are not correlated to one another. They either represent excitations of spinon or phason modes, or, alternatively, quasiparticle excitations across the SDW gap.

The picture that emerges from this brief description is that of a very complex response; as soon as the FISDW cascade is entered, several events can take place: abrupt changes in the response at each phase transition, due to the sudden change in the nesting vector, or smooth changes within each phase as the nesting vector changes continuously. Additionally, the millimetre-wave radiation could be exciting quasiparticles across the very narrow gap of the SDW semiconducting state, or some magnetic collective modes of the system, each SDW phase representing an spin system with its own dispersion spectrum.

The set of data recorded at the pressure of 1.2 GPa presents very striking and unexpected features (Figure 5.5). In fact, large dips and absorptions occur at low

fields and the signal recovers as the magnetic field is increased. It is the metallic state that now seems populated with resonant changes in the a.c. conductivity. At low frequencies (60-90 GHz), the resonances are intense and sharp; as the frequency increases beyond 120 GHz, they gradually become broader and shift to higher fields. If in the data from the previous pressure of 0.8 GPa some patterns were recognizable and could be ascribed to the FISDW cascade, for the present pressure there does not seem to be a relationship between the most pronounced observed features and the phase diagram. The field positions corresponding to transitions between different FISDW states can still be identified by changes in the transmitted millimetre-wave intensity.

5.5 Summary

(TMTSF)₂PF₆ has an extremely rich phase diagram; its millimetre-wave response as a function of magnetic field, appears to be equally complex. The data presented for the pressure of 0.8 GPa are correlated to the features of the phase diagram and the transition from the metallic state into the FISDW cascade can be identified. Within the SDW phases some resonant peaks could represent the excitation of collective spin modes, or excitations across the SDW gap. The data recorded for the pressure of 1.2 GPa, on the other hand, present a very different picture that does not seem to be a continuation of the trends shown at the previous pressure value. More detailed studies are necessary in order to clarify the origin of the observed phenomena.

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