Muon spin relaxation in $DyVO_4$ and $TbVO_4$

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Muon spin relaxation experiments have been performed on $DyVO_4$ and $TbVO_4$, both of which exhibit a cooperative Jahn-Teller transition. The data demonstrate that the nature of the magnetic ion, whether Kramers or non-Kramers, has a decisive effect on the nature of the observed spin relaxation. We interpret this result in terms of the difference in the relaxation induced by the spin-phonon interaction in the two systems.

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There has been much recent interest in phenomena connected with orbital degrees of freedom in various complex oxides, particularly manganites.[1] These include orbital ordering,[2] orbital waves,[3] and the competition between (and coexistence of) Jahn-Teller order and orbital order.[4] The complexity of phenomena that are observed reflects the strong coupling between lattice, orbital and electronic degrees of freedom. The technique of muon spin relaxation (μSR) has previously been applied to various complex oxides that exhibit some of these phenomena (see, e.g., Refs. 5–8), but in order to understand the individual contribution of these effects, it is of value to study carefully chosen model systems that are free of some of this complexity and for which much characterization has already been done. In this context, the rare-earth zircons[9] are particularly attractive as they exhibit a rather well-defined cooperative Jahn-Teller effect (CJTE). In this paper we describe μSR measurements on two rare-earth zircons, $DyVO_4$ and $TbVO_4$, and demonstrate that the nature of the observed spin relaxation depends on whether the rare-earth ion is Kramers or non-Kramers.

We begin our discussion by reviewing the main features of the CJTE. Jahn and Teller showed that the energy of an ion with degeneracy in a nonlinear complex will be reduced by some asymmetric nuclear displacement that removes the degeneracy in first order[10] (except in the case of simple Kramers degeneracy). If the coupling between the electrons and the nuclear environment is sufficiently strong, the complex will undergo a static distortion to a new configuration of minimum energy (for reviews see Refs. 11–14). The elastic energy of the system increases quadratically with the amplitude of the distortion, so that eventually an equilibrium value for the distortion is reached. If the coupling is less strong, so that zero-point vibrational energy is comparable to the energy barrier separating equivalent configurations, the complex exhibits a coupled motion of the electrons and vibrational modes and a stable distortion does not occur. This is known as the dynamical Jahn-Teller effect. An ion in a solid may exhibit a change from a dynamic to a static Jahn-Teller effect with reduction of temperature, for example, the case of Cu^{2+} in a zinc fluorosilicate crystal.[15] In some solids one constituent species of ions may have an interaction between its electronic states and lattice phonons, giving rise to a structural phase transition; this is the CJTE. The phase transition may be first or second order with a symmetry-lowering distortion of the crystal lattice and a splitting of the ions' electronic energy levels. Some spinels containing transition-metal ions with unfilled $3d$ shells exhibit the CJTE.[14] Both the Raman[16] and Brillouin[17] spectra of the rare-earth zircons $DyVO_4$ and $TbVO_4$ have received detailed attention. The crystals undergo a second-order structural phase transition due to the CJTE at $T_D = 14$ K and 34 K, respectively. The crystal space group above T_D is tetragonal ($I4_1/amd = D_{4h}$ for both $DyVO_4$ and $TbVO_4$); there are two equivalent rare-earth ions in the unit cell, each with symmetry $\bar{4}m2 = D_{2d}$. The crystal space group below T_D is orthorhombic [$Imma = D_{2h}^{28}$ for $DyVO_4$ and $Fddd = D_{2h}^{24}$ for $TbVO_4$ (Ref. 18)]. This change to orthorhombic symmetry is a consequence of coupling of the lowest-lying rare-earth electronic states to a zone center B_{1g} vibrational mode in the case of $DyVO_4$ and to a zone center B_{2g} vibrational mode in the case of $TbVO_4$.

The lowest-lying electronic levels for both systems are shown in Fig. 1 at temperatures well below and well above T_D. Dy^{3+} ($4f^9$, $^6H_{15/2}$) is a Kramers ion and, above T_D, the tetragonal crystal field splits the $^6H_{15/2}$ manifold into eight Kramers doublets. The lowest two of these doublets each has a large $g_\perp$ and a small $g_\parallel$ and the pair is almost degenerate (Fig. 1). Below T_D the distortion increases the separation of the doublets. Because of the orthorhombic symmetry, the lower doublet then has a large $g_x = 18.9$ and very small values of g_y and g_z, so that $DyVO_4$ is almost an ideal Ising system. Tb^{3+} ($4f^8$, $^7F_6$) is a non-Kramers ion and the $^7F_6$ manifold is split by the crystal field into three doublets and seven singlets;[19] the lowest levels are shown in Fig. 1(b). In this system, there is an actual degeneracy above T_D that helps to drive the cooperative distortion and the g factors behave similarly to $DyVO_4$. A detailed investigation of the dynamics of the electron-lattice interaction[16] shows that the "soft mode" associated with the structural phase transition in $DyVO_4$ is a zone center acoustic mode driven flat by coupling to the electronic mode[20] [Fig. 1(a)]. However, in $TbVO_4$ the soft mode is the transition within the split E doublet [Fig. 1(b)]. The lattice distortions in the $k = 0$ modes of B_{1g} symmetry for $DyVO_4$ and B_{2g} symmetry for $TbVO_4$ give rise to anomalies in the elastic constants $(c_{11} - c_{12})$ for $DyVO_4$ and c_{66} for $TbVO_4$.[17] In the orthorhombic phase

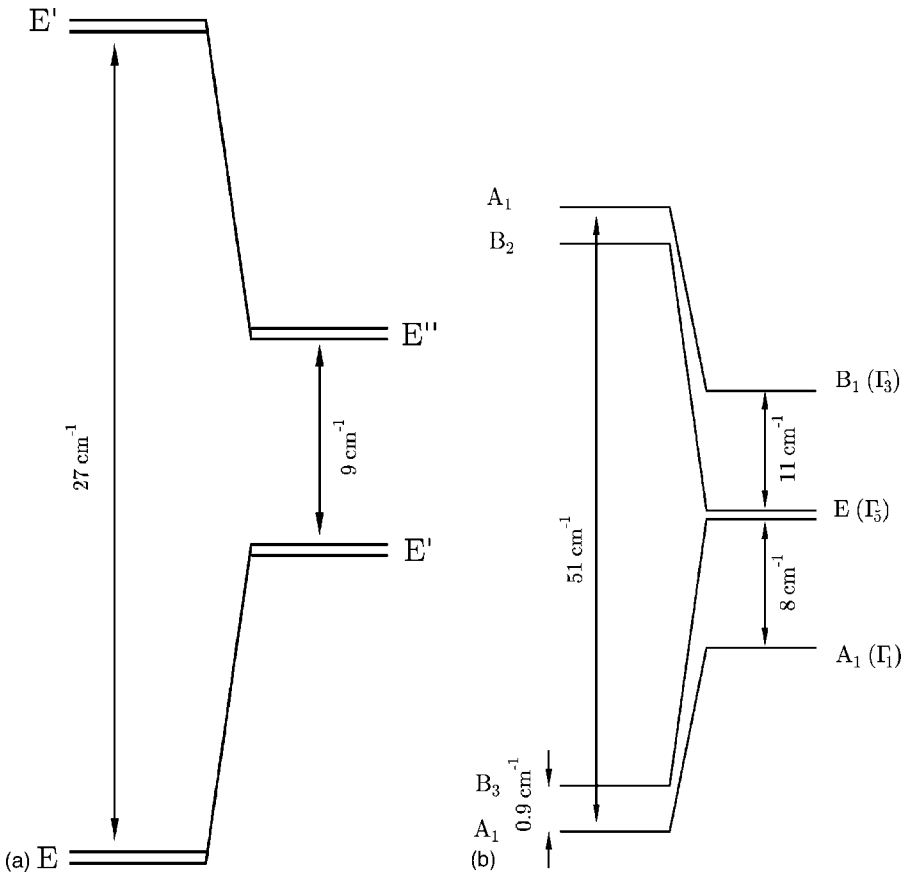

FIG. 1. Schematic of the energy levels in (a) $DyVO_4$ and (b) $TbVO_4$ significantly below (left) and above (right) the Jahn-Teller distortion temperature. Energies are approximate and not drawn to scale (after Refs. 9, 19, and 20).

$DyVO_4$ orders antiferromagnetically with $T_N=3.0$ K (Ref. 21) with moment alignment in the basal plane.[22] For $TbVO_4$, the magnetic interactions are weaker and antiferromagnetic order sets in only below $T_N=0.61$ K.[23]

Small crystals of $DyVO_4$ and $TbVO_4$ were prepared using a flux method and our samples consisted of a randomly oriented collection of such crystals. The μSR experiments were performed on the MuSR spectrometer at the Rutherford Appleton Laboratory, U.K. (using "fly-past mode") and the GPS spectrometer at the Paul Scherrer Institute, Switzerland. In our μSR (Ref. 24) experiments, a beam of almost completely spin-polarized muons was implanted with a momentum of 28 MeV/c into the sample under investigation. These stop quickly (in $<10^{-9}$ s), without significant loss of polarization. The observed quantity is then the time evolution of the muon spin polarization, which can be detected by counting emitted decay positrons forward (f) and backward (b) of the initial muon spin direction; this is possible due to the asymmetric nature of the muon decay, which takes place in a mean time of 2.2 μs. Positrons are detected by using scintillation counters placed in front of and behind the sample. We record the number of positrons detected by forward (N_f) and backward (N_b) counters as a function of time and calculate the asymmetry function, $A(t)$:

$$A(t) = \frac{N_f(t) - \alpha N_b(t)}{N_f(t) + \alpha N_b(t)}, \tag{1}$$

where α is an experimental calibration constant and differs from unity due to nonuniform detector efficiency. The quantity $A(t)$ is then proportional to the average muon spin polarization, $P_z(t)$. The former quantity has a maximum value less than one since the positron decay is only preferentially, not wholly, in the direction of the muon spin. $P_z(t)$ has a maximum value of one. In the case of magnetic fluctuations the muon polarization can be written $P_z(t)=P_z(0)e^{-\lambda t}$. In an applied longitudinal field (LF) B_L, the relaxation rate λ is related to the field-field correlation function by

$$\lambda = \int_0^\infty \gamma_\mu^2 \langle B_\perp(t) B_\perp(0)\rangle \cos \omega_L t dt, \tag{2}$$

where $\omega_L=\gamma_\mu B_L$ is the angular frequency corresponding to B_L, γ_μ is the muon gyromagnetic ratio, and $B_\perp(t)$ is the time-dependent magnetic field perpendicular to the initial muon spin polarization[25] (and hence to B_L). If $\langle B_\perp(t)B_\perp(0)\rangle=\langle B_\perp^2\rangle e^{-\nu t}$, where ν is the field-field correlation rate and $\langle B_\perp^2\rangle=2(\Delta/\gamma_\mu)^2$ is the mean-square field at a given muon site, then evaluating the integral in Eq. (2) yields

$$\lambda = \frac{2\Delta^2 \nu}{\nu^2 + \omega_L^2}. \tag{3}$$

The effect of the LF is hence to decouple the dynamical relaxation, so that $\lambda \to 0$ when $\omega_L/\nu \to \infty$. With no applied LF, $\omega_L=0$, so that $\lambda=2\Delta^2/\nu$.

Raw data for both compounds taken in zero applied magnetic field are plotted in Fig. 2. In each case, it is clear that the relaxation speeds up as the sample is cooled. However, the two materials show strikingly different behaviour, with

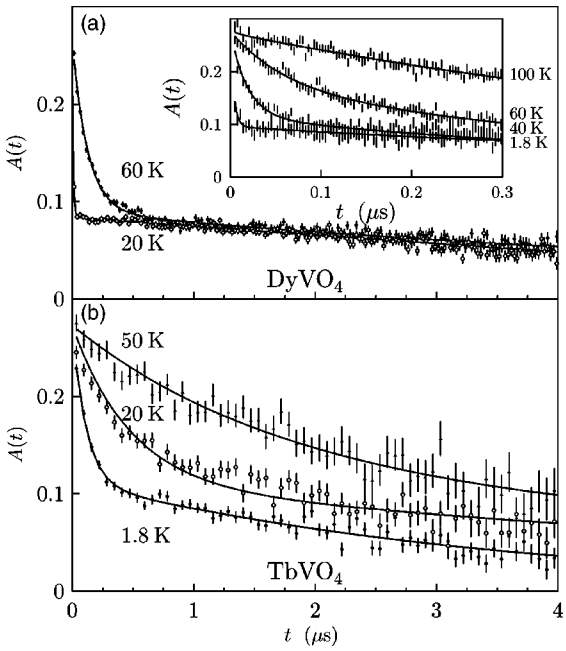

FIG. 2. Raw zero-field μSR data (measured at PSI) for (a) $DyVO_4$ and (b) $TbVO_4$. The inset in (a) shows several traces at short times. The lines are fits to Eq. (4).

the much faster relaxation observed in $DyVO_4$. The data for $DyVO_4$ can be fitted to a form

$$A(t) = A_{bg} + A_f e^{-\lambda t} + A_s e^{-\lambda_s t}, \tag{4}$$

where A_{bg} accounts for muons stopped in the sample holder, and the second and third terms are the fast and slow relaxations, respectively. We find $A_f > A_s$ and $\lambda_s \lesssim 0.03$ MHz. The data for $TbVO_4$ could also be fitted to the form of Eq. (4) also with $A_f > A_s$ and λ_s small ($\lesssim$0.3 MHz) The best fitted values of λ for $DyVO_4$ and $TbVO_4$ are plotted in Fig. 3 (λ_s for both compounds is only very weakly temperature dependent, and A_f, A_s, and A_{bg} were held fixed in the fitting process.[26])

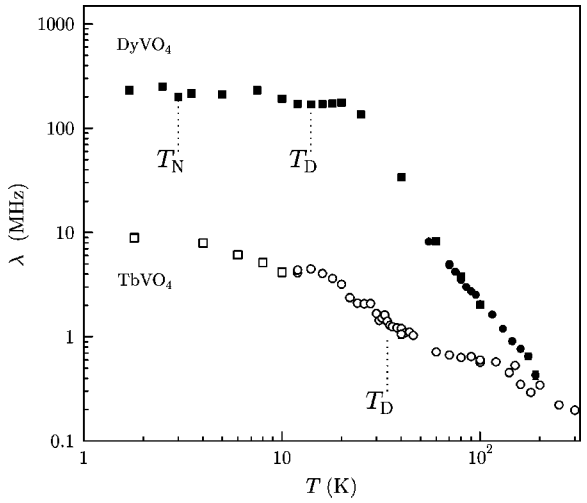

FIG. 3. The fitted values of the zero-field muon relaxation rate for $DyVO_4$ (closed symbols) and $TbVO_4$ (open symbols). The data are from ISIS (circles) and PSI (squares).

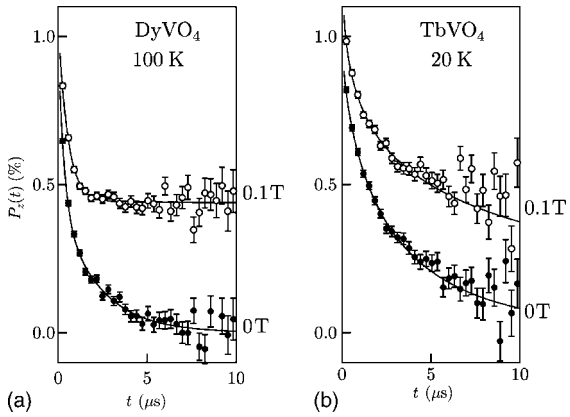

FIG. 4. Longitudinal-field dependence of μSR data for (a) $DyVO_4$ (100 K) and (b) $TbVO_4$ (20 K).

These data demonstrate that λ is nearly two orders of magnitude greater in $DyVO_4$ than in $TbVO_4$. In both cases λ increases with cooling, reflecting the slowing down of thermally induced fluctuations from the ground state. In $DyVO_4$, this increase stops once the sample is cooled below T_D. No very sharp features are found at T_N in $DyVO_4$ or at T_D in $TbVO_4$ (T_N in $TbVO_4$ was lower than the lowest temperature accessible in this experiment), and in fact there are no very sharp features in the magnetic susceptibility at these temperatures.[27] Assuming the fast-fluctuation limit, the fluctuations in $DyVO_4$ are therefore significantly *slower* than in $TbVO_4$. This view is supported by the effect of a LF that has a much greater effect on the relaxation in $DyVO_4$ [Fig. 4(a)] than in $TbVO_4$ [Fig. 4(b)]. The LF more readily quenches the slow relaxation λ_s than the fast relaxation λ in both compounds. The fast relaxation remains in a LF of up to 0.2 T at both low and high temperatures. A quantitative interpretation of the field dependence of λ is complicated by the fact that the magnetic field not only decouples the muon from the fluctuations but also affects the energy levels and thus may alter the local field distribution and the dynamics as well.

The muon site is likely to be the same in both compounds since the lattice parameters in the two compounds differ by less than 0.5%.[28,29] As the magnetic moments of both rare-earth ions are similar, the marked contrast between the magnitude of the spin relxation in each case is evidence for differing relaxation mechanisms. Because both compounds are tetragonal above the distortion temperature, the *g* values are isotropic in the *xy* plane, but below the distortion temperature the *g* factors become very anisotropic and hence the spins become magnetically Ising-like.[21] The dipole-dipole interaction cannot relax an Ising spin and so we might expect a large change in relaxation at the distortion temperature, but this is observed only for $DyVO_4$ and not for $TbVO_4$. Because Dy is a Kramers ion, the spin-phonon interaction contains no off-diagonal terms[16] and therefore this interaction is also ineffective at relaxing the muon spin. Thus the change in symmetry near T_D causes a change in the dipolar relaxation, producing a maximum in λ near T_D where the fluctuations slow down. In contrast, Tb is not a Kramers ion, and in this

case there are off-diagonal terms that mix states and lead to relaxation by the spin-phonon interaction. Relaxation due to spin-phonon interactions is probably a more significant effect than the dipolar relaxation and therefore no anomaly in λ is visible when the dipolar relaxation becomes strongly reduced as the temperature is lowered through T_D. This additional relaxation mechanism leads to faster fluctuations in $TbVO_4$ than in $DyVO_4$, and a smaller λ.

The origin of the second exponential λ_s is more difficult to determine: it may result from a second muon site for which the muon is less strongly coupled to the rare-earth moment (Δ smaller) or may arise from some other relaxation channel. Our analysis has assumed a single ν, but the field-field correlation function may be more complicated leading to a more complex relaxation function that we are crudely fitting with two exponentials. Further work on these and similar systems may be needed to resolve these issues.

In conclusion, these measurements have attempted to study the effect on muon spin relaxation of systems showing a well-defined cooperative Jahn-Teller transition. They have demonstrated that the nature of the magnetic ion, whether Kramers or non-Kramers, has a decisive effect on the nature of the observed spin relaxation.

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