[15] This was based on Table IV of Ref. 5, the value of μ_D obtained in Ref. 7, and the broadening parameter obtained from CH_3D in I. Ozier, W. Ho, and G. Birnbaum, J. Chem. Phys. 51, 4872 (1969).

[16] To our knowledge the smallest line strength previously reported for an identified molecular transition observed with conventional Stark spectroscopy is 4×10^{-10} cm^{-1} [W. D. Gwinn, A. C. Luntz, C. H. Sederholm, and R. Millikan, J. Comput. Phys. 2, 439 (1968)].

[17] S. M. Kirschner and J. K. G. Watson, J. Mol. Spectrosc. 47, 347 (1973).

[18] The values given in Ref. 9 were based in part on frequencies read from Fig. 1 of Ref. 7. The values used here were based rather on the more accurate data of Ozier (unpublished). The changes are slight and do not affect the agreement shown in Table I.

[19] Absorption in the microwave region can also be produced in CH_4 by transitions between excited vibrational levels (see Ref. 6). However, these can be eliminated on the basis of the agreement of the observed frequencies, relative intensities, and relative Stark coefficients with the corresponding values calculated on the assumption that the absorption mechanism is the distortion dipole moment in the ground vibronic state.

Spin-Lattice Relaxation Anisotropy for a Dynamic Jahn-Teller System

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We report a large angular variation in the Orbach relaxation rate for Ti^{3+} in methylammonium alum. This anisotropy is due to the dynamic Jahn-Teller effect, which modifies the spin-phonon interaction by the Ham vibronic reduction factor.

Electron spin-lattice relaxation of paramagnetic crystals by the Orbach process is known to display little or no anisotropy.[1] Relaxation by the Orbach process involves a resonant phonon with energy large compared with the Zeeman splitting whose EPR recovery is being monitored. Since the orbit-lattice interaction operates between one of the ground doublets and an excited state, nonzero matrix elements of this interaction are obtained without including second-order corrections to these states by the magnetic field. Consequently, the Orbach relaxation rate, unlike the direct relaxation rate between a Kramers conjugate pair, is independent of the magnetic field orientation. In this paper, we wish to report a very large anisotropy in the Orbach relaxation rate for Ti^{3+} in methylammonium alum. The Γ_{5g} vibronic ground state of this Jahn-Teller system is split into three doublets by the spin-orbit coupling and a small trigonal crystalline electric field[2,3]; however, the energy splitting is drastically reduced by the Ham vibronic reduction factor.[4] For Jahn-Teller coupling only to Γ_{3g} modes of vibration, the vibronic reduction factor affects matrix elements of electronic operators which transform like the Γ_{5g} or Γ_{4g} representation, but matrix elements of Γ_{3g} operators are unaffected. This preferential coupling of the spin system to the lattice vibrations is shown below to be responsible for the large relaxation anisotropy.

The spin-lattice relaxation measurements of Ti^{3+} in methylammonium alum were performed using a conventional X-band superheterodyne EPR spectrometer and the pulse saturation technique. The (111) face of the sample crystal was mounted on the narrow sidewall of the rectangular cavity operating in the TE_{102} mode. This mounting configuration was employed to preserve EPR sensitivity when the magnetic field was rotated in a horizontal plane and to allow a [111] axis to be contained in the rotation plane. The temperature of the cavity was monitored using a calibrated carbon resistance thermometer. The temperature stability was maintained to within 1%.

Figure 1 shows the angular variation of the spin-lattice relaxation time τ of Ti^{3+} in methylammonium alum measured at 2.07°K. In the temperature range 2.2–1.45°K, the spin-lattice relaxation of this paramagnetic system is dominated by an Orbach process which involves only the first excited doublet located at 9.4 ± 0.5 cm^{-1}.[2,3] This ensures that the measured anisotropy of τ shown in Fig. 1 is only due to one definite Orbach relaxation process.

The orbit-lattice interaction H_{OL}, which is responsible for spin-phonon interaction through the spin-orbit coupling, can be expressed in terms of the normal modes of vibration of the Ti^{3+} nearest-neighbor octahedron:

$$H_{OL} = \sum_{i,l,m} V(\Gamma_{ig} l) C(\Gamma_{ig} l, m) Q(\Gamma_{ig}, m), \qquad (1)$$

where i refers to the irreducible representation of the octahedral group, $V(\Gamma_{ig} l)$ is a coupling coefficient, $C(\Gamma_{ig}l,m)$ is a linear combination of electronic tensor operators of rank l transforming like the mth component of the Γ_{ig} irreducible representation, and $Q(\Gamma_{ig},m)$ is a normal mode having the same transformation property. The explicit expressions for V, C, and Q are given by Orbach and Stapleton.[5]

The Jahn-Teller cluster model which couples a Γ_{5g} electronic state to Γ_{3g} normal modes of vibration has been employed successfully to interpret the EPR spectra of Ti^{3+} in methylammonium alum.[2,3] Since we are only interested in even modes, the spin-phonon interaction includes only operators which transform like either the Γ_{3g} or the Γ_{5g} representation. Γ_{5g} operators are reduced by the vibronic reduction factor, while Γ_{3g} operators are unaffected. The first-order vibronic reduction factor γ for Ti^{3+} in methylammonium alum has been determined to be ~0.1 using EPR spectra and relaxation.[2,3] Incorporating this reduction effect into the orbit-lattice interaction responsible for relaxation, we recognize that the contributions to the spin-phonon transition probability due to Γ_{5g} terms in H_{OL} are severely reduced by a factor of ~100. This large reduction factor ensures that terms transforming like Γ_{5g} in the spin-phonon interaction are negligible in the presence of the dynamic Jahn-Teller coupling for a Γ_{5g} electronic state coupled to Γ_{3g} modes of vibration.

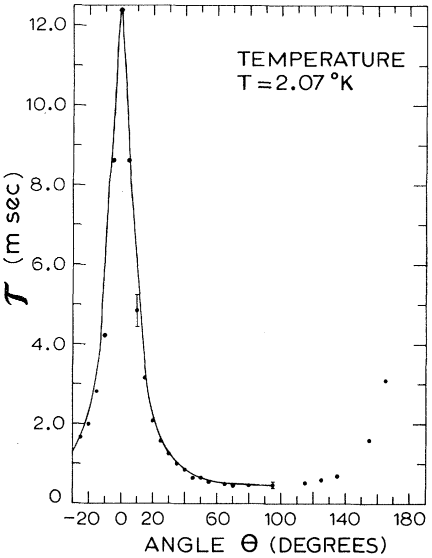

FIG. 1. Angular variation of the spin-lattice relaxation time τ of Ti^{3+} in methylammonium alum as a function of the angle θ between the magnetic field and the projection of a [111] axis. (The projection angle, as a result of experimental misorientation, is 6°; dots, experimental data; solid line, theoretically fitted curve.)

The ground and the first excited state for Ti^{3+} in methylammonium alum have been identified as ${}_2E_{1/2}$ and $E_{3/2}$, respectively.[2] In the presence of a dc magnetic field, the eigenstates for the ${}_2E_{1/2}$ and $E_{3/2}$ doublets are, respectively,[6]

$$\begin{aligned}
|-p\rangle &= \tfrac{1}{2}\sqrt{2}\{-[1-(g_{\parallel}/g)\cos\theta]^{1/2}(-\cos\varphi\,|+X_0\rangle+\sin\varphi\,|-X_+\rangle) \\
&\qquad +[1+(g_{\parallel}/g)\cos\theta]^{1/2}(\cos\varphi\,|-X_0\rangle+\sin\varphi\,|+X_-\rangle)\}, \\
|+p\rangle &= \tfrac{1}{2}\sqrt{2}\{[1+(g_{\parallel}/g)\cos\theta]^{1/2}(-\cos\varphi\,|+X_0\rangle+\sin\varphi\,|-X_+\rangle) \\
&\qquad +[1-(g_{\parallel}/g)\cos\theta]^{1/2}(\cos\varphi\,|-X_0\rangle+\sin\varphi\,|+X_-\rangle)\}, \\
|-q\rangle &= \tfrac{1}{2}\sqrt{2}\{-[1-(g_{\parallel}'/g')\cos\theta]^{1/2}|+X_+\rangle+[1+(g_{\parallel}'/g')\cos\theta]^{1/2}|-X_-\rangle\}, \\
|+q\rangle &= \tfrac{1}{2}\sqrt{2}\{[1+(g_{\parallel}'/g')\cos\theta]^{1/2}|+X_+\rangle+[1-(g_{\parallel}'/g')\cos\theta]^{1/2}|-X_-\rangle\},
\end{aligned}$$

where + and − in the ket indicate, respectively, the parallel and antiparallel orientation of the effective spin; $|X_0\rangle$ and $|X_\pm\rangle$ are vibronic triplet wave functions expressed in a complex trigonal basis; θ is the angle between the magnetic field and the symmetry axis; g and g' are the spectroscopic splitting factors of ${}_2E_{1/2}$ and $E_{3/2}$, respectively, which are related to the parallel and perpendicular components by $g^2=g_{\parallel}^2\cos^2\theta+g_{\perp}^2\sin^2\theta$; and

$$\tan 2\varphi=\frac{\sqrt{2}[-(\frac{1}{2}\lambda^2+\frac{1}{3}\lambda v)f_a+\gamma\hbar\omega\lambda]}{(\frac{1}{3}v^2-\frac{1}{4}\lambda^2+\frac{1}{3}\lambda v)f_a-\gamma\hbar\omega(v-\frac{1}{2}\lambda)}=-\frac{\sqrt{2}\lambda}{v-\frac{1}{2}\lambda}\,.$$

We note that the coefficient $\tan 2\varphi$ can be reduced to an expression involving only the trigonal distortion parameter v and the spin-orbit coupling constant λ. The reduced expression for $\tan 2\varphi$ is independent of the first- and second-order vibronic reduction factors γ and f_a and has the identical form as the corresponding coefficient obtained in static-crystal-field theory. This point appears to have been overlooked previously.[6-8]

The angular dependence of the spin-lattice relaxation rate τ^{-1} for the ground doublet $|\pm p\rangle$ interacting with the excited doublet $|\pm q\rangle$ through the Orbach process is dominated by the square of the matrix element of $\langle -p|H_{OL}|-q\rangle\langle -q|H_{OL}|+p\rangle$.[9] Neglecting the Γ_{5g} terms in H_{OL} and taking $g_\perp{}'=0$,[6,10] the Orbach relaxation rate τ^{-1} is found to be proportional to

$$\left\{\left[1-\left(\frac{g_\parallel}{g}\cos\theta\right)^2\right]+\left(\frac{4XY}{(X+Y)^2}\right)\tan^2 2\varphi+\left(\frac{X-Y}{X+Y}\right)^2\tan^2 2\varphi\left(\frac{g_\parallel}{g}\cos\theta\right)^2 +2\left(\frac{X-Y}{X+Y}\right)\tan 2\varphi\left(\frac{g_\parallel}{g}\cos\theta\right)\left[1-\left(\frac{g_\parallel}{g}\cos\theta\right)^2\right]^{1/2}\right\}, \tag{2}$$

where X and Y are parameters related to $V(\Gamma_{3g}l)$ and $Q(\Gamma_{3g},m)$. We take $\langle r^2\rangle=1.893$ a.u. and $\langle r^4\rangle=7.071$ a.u. for Ti^{3+},[11] and the distance between Ti^{3+} and its nearest neighbors in methylammonium alum to be 1.87 Å.[12] Using a point-charge calculation the parameters X and Y are equal, and the angular dependence of the Orbach relaxation rate given in Eq. (2) then reduces to the simple expression

$$1+\tan^2 2\varphi-\frac{g_\parallel{}^2\cos^2\theta}{g_\parallel{}^2\cos^2\theta+g_\perp{}^2\sin^2\theta}. \tag{3}$$

The theoretical angular dependence of τ is calculated using Eq. (3), with $g_\parallel=1.40$, $g_\perp=1.61$,[2,3] $\tan 2\varphi=0.15$, and taking account of the 6° experimental misorientation of the [111] axis. This calculated angular dependence is plotted as the solid curve in Fig. 1. The functional forms of the theoretical and experimental angular dependences show good agreement, but the fitted value of $\tan 2\varphi$ is 1 order of magnitude smaller than the value determined from the g values and the energy levels.[2,3] This discrepancy in $\tan 2\varphi$ may be resolved when a more realistic Jahn-Teller model involving the entire crystal lattice is considered.

In conclusion, we wish to point out that the large angular variation of the Orbach relaxation rate for Ti^{3+} in methylammonium alum, which is absent in crystals free of Jahn-Teller complications, can be interpreted successfully by incorporating the vibronic reduction effect in the spin-phonon interaction. In general, for these dynamic Jahn-Teller systems we expect a similar anisotropy to appear in the Raman relaxation rate while the angular variation of the direct rate would involve this additional anisotropy as well as the usual angular dependence of $H^2\sin^2\theta$. The result reported in this paper appears to be the first demonstration of the vibronic reduction effect on the spin-phonon interaction as a result of dynamic Jahn-Teller coupling. In addition, it supports the Jahn-Teller model for Ti^{3+} in methylammonium alum which involves coupling to Γ_{3g} modes only, as well as suggesting an apparent weakness in the cluster approximation.

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