

Energy splittings of the 2T_2 vibronic state Ti^{3+} in methylammonium alum

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The two excited doublets of the 2T_2 vibronic state are found to be at 9.4 ± 0.5 and 28.9 ± 0.5 cm^{-1} using accurate electron spin-lattice relaxation measurements. The experimental g values of the ground-state doublet are $g_{\parallel} = 1.400 \pm 0.005$ and $g_{\perp} = 1.606 \pm 0.005$. The Jahn-Teller energy is 515 cm^{-1} and the E_g -mode energy is 371 cm^{-1} .

The electron paramagnetic resonance (EPR) and spin-lattice relaxation of Ti^{3+} as an impurity in methylammonium alum was recently reported by us¹ to be consistent with a Jahn-Teller model which considers the 2T_2 electronic ground state of the Ti^{3+} ion to interact with an E_g mode of vibration only. The spin-orbit coupling plus the trigonal electric field (both reduced by Ham vibronic reduction factor²) split the resulting 2T_2 vibronic level into three doublets. From the two-Orbach relaxation process, which described the EPR recovery to equilibrium of the ground doublet after pulse saturation at X-band frequencies, the energy levels of the two excited doublets were obtained. However, the Orbach relaxation process to the first excited doublet dominated the EPR recovery, and the energy of the higher doublet could only be predicted from the deviation from a straight line of the Arrhenius plot of the temperature dependence of the spin-lattice relaxation. We wish to emphasize that the relaxation rate reported here cannot be fitted to a T^9 Raman process as was the case for the previously reported rate.¹ It was also mentioned that there appeared to be considerable anisotropy in the relaxation rate. Indeed, the ratio of the relaxation rate for the dc magnetic field H parallel and perpendicular to the trigonal axis is

TABLE I. Observed and calculated splittings and g factors for the 2T_2 ground term of $Al(CH_3NH_3)(SO_4)_2 \cdot 12H_2O : Ti^{3+}$.

	Observed	Calculated ^a
First excited doublet	9.4 ± 0.5 cm^{-1}	9.4 cm^{-1} ^b
Second excited doublet	28.9 ± 0.5 cm^{-1}	28.9 cm^{-1} ^b
Ground doublet g_{\parallel}	1.400 ± 0.005	1.40
Ground doublet g_{\perp}	1.606 ± 0.005	1.62
$\hbar\omega$...	370 cm^{-1}
E_{JT}	...	515 cm^{-1}

^aParameters are $v = -\frac{5}{8}\lambda$, $\lambda = 135$ cm^{-1} , $k = 0.9$, $\gamma = 0.125$, $f_a = 0.063$, and $f_b = 0.314$.

^bFor a definite value of $x = 3E_{JT}/\hbar\omega$, γ , f_a , and f_b are fixed. The value of x is obtained by fitting the theoretical splittings to the experimental values. See Ref. 1.

greater than an order of magnitude. The theoretical explanation for this unexpected result has appeared in another publication.³

In this note we report the spin-lattice relaxation for H parallel to the trigonal axis, where the relaxation time is sufficiently long to determine unambiguously the energy level of the higher doublet. Figure 1 shows the measured relaxation time τ versus temperature together with the corresponding theoretical fit by the two-Orbach relaxation process. We note that the energy level of the lower doublet agrees with the former measurements¹ (after correcting 10.5 ± 0.5 cm^{-1} to read 10.1 ± 0.5 cm^{-1}) within the experimental errors. The value of $x = 3E_{JT}/\hbar\omega$ as well as the vibronic reduction factors γ , f_a , and f_b , are obtained by equating the theoretical splittings, Eq. (3) of Ref. 1, to the experimental values obtained from the theoretical fit in Fig. 1. From these parameters the g values of the ground doublet are calculated, and

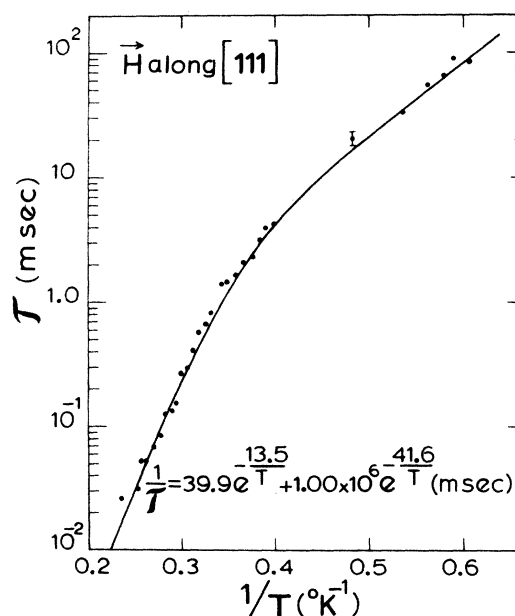


FIG. 1. Arrhenius plot of spin-lattice relaxation time.

are shown in Table I to be in excellent agreement with our latest experimental g values. Table I

also gives the corresponding Jahn-Teller stabilization energy E_{JT} and the E_g -mode energy $\hbar\omega$.

¹N. Rumin, C. Vincent, and D. Walsh, Phys. Rev. B 7, 1811 (1973).

³Y. H. Shing, C. Vincent, and D. Walsh, Phys. Rev. Lett. 31, 1036 (1973).

²F. S. Ham, Phys. Rev. 138, A1727 (1965).