

Quasi- Γ_8 Ground State of a Jahn-Teller Ion*

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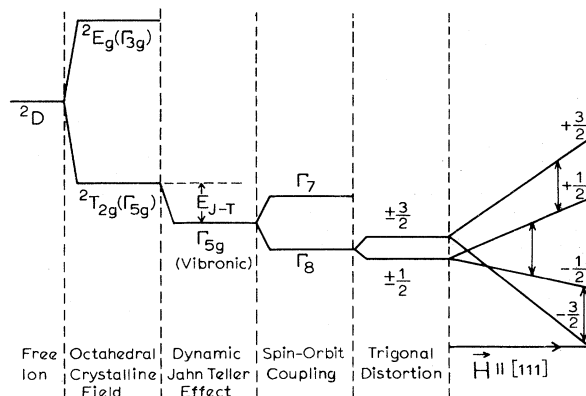
We show that the ground state of Ti^{3+} in CsAl alum is a quasi- Γ_8 state with a very small trigonal splitting. A spin Hamiltonian for this quasi- Γ_8 state is derived and used to describe the experimental EPR anisotropy. The near cancelation of the trigonal splitting is due to the presence of a dynamic Jahn-Teller effect.

The crystal structure of CsAl alum $[CsAl(H_2O)_6 \cdot (SO_4)_2 \cdot H_2O]$ is cubic with space group $Pa\bar{3}$ and four formula units per unit cell.¹ The four $[Al(H_2O)_6]^{3+}$ octahedra are slightly flattened with trigonal symmetry $\bar{3}$. Recent work on Ti^{3+} substituting for Al^{3+} in CH_3NH_3Al alum^{2,3} indicates that the Γ_{5g} ground state of Ti^{3+} in CsAl alum will show a strong Jahn-Teller coupling to the Γ_{3g} vibrational mode. This Letter reports an unusual EPR spectrum and anisotropy for Ti^{3+} as a substitutional impurity for Al in CsAl alum which are interpreted below in terms of a quasi- Γ_8 quartet with a very small trigonal splitting. The trigonal crystal field in CsAl alum is substantial,¹ and the almost complete elimination of the effect of this field is shown to be a direct consequence of the Jahn-Teller coupling of the Γ_{5g} electronic state to the Γ_{3g} vibrational mode. It arises because the trigonal splitting to first order, which is reduced by the vibronic reduction factor,⁴ is comparable with and opposite in sign to the second-order contribution, which involves the excited Γ_{3g} state and is not reduced by any vibronic factor. This Letter also reports the first EPR spectra of and corresponding spin Hamiltonian for a quasi- Γ_8 quartet with trigonal symmetry.

The EPR measurements were performed at 9.46 GHz and 2.5 K on single crystals of CsAl alum doped with 0.1 at. % Ti, which were grown from aqueous solution in an inert atmosphere to prevent the oxidation of Ti^{3+} . Since the spin-lattice relaxation time is short, a good EPR spectrum could only be observed at temperatures below 3 K, and four sets of three lines were identified, each set corresponding to one of the four symmetry-equivalent sites.⁵ A schematic energy-level diagram is shown in Fig. 1 to illustrate the quasi- Γ_8 ground state. The effective trigonal Hamiltonian for a Γ_{5g} triplet coupled to a Γ_{3g} vibrational mode can be written as

$$H_{\text{trig}} = \frac{1}{3}(\gamma v - v'^2/\Delta)[3l_z^2 - l(l+1)], \quad (1)$$

where v is the trigonal splitting of the Γ_{5g} state to first order, γ is the vibronic reduction factor, v' is the admixture of the Γ_{3g} and the Γ_{5g} state by the trigonal field, Δ is the cubic-field splitting, and the orbital angular momentum corresponds to $l=1$.⁶ This equation is identical to Eq. (16) of Abou-Ghantous, Bates, and Stevens⁶ when the third term in their Hamiltonian, which is negligible by comparison with the first two, is omitted. Since the first-order trigonal-field parameter v for Ti^{3+} in CsAl alum is positive and since γv is comparable with v'^2/Δ , there is an almost complete cancelation of the effective trigonal field. The spin-orbit Γ_8 ground state is split slightly by the residual trigonal field, producing a quasi- Γ_8 quartet with three distinct $\Delta M = \pm 1$ EPR transitions. Since the EPR transitions are between vibronic states they will show significant strain broadening, although only the $\pm \frac{3}{2} \leftrightarrow \pm \frac{1}{2}$ transitions will be asymmetrical. Figure 2 is the first-derivative representation of the EPR spectrum of Ti^{3+} in CsAl alum measured with the magnetic field parallel to the $[111]$ axis. The three $\Delta M = \pm 1$ transitions were identified and labeled as A, B, and C which correspond to the

FIG. 1. Schematic energy-level diagram of Ti^{3+} .

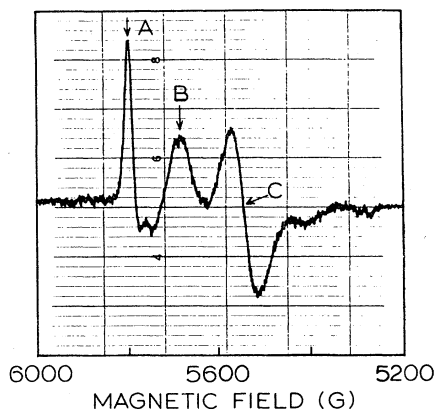


FIG. 2. First-derivative representation of EPR spectrum of Ti^{3+} in CsAl alum measured at 9.46 GHz and 2.5 K with \vec{H} along a $[111]$ axis. The labels are A: $-\frac{3}{2} \leftrightarrow -\frac{1}{2}$; B: $+\frac{3}{2} \leftrightarrow +\frac{1}{2}$; C: $+\frac{1}{2} \leftrightarrow -\frac{1}{2}$.

$-\frac{3}{2} \leftrightarrow -\frac{1}{2}$, $+\frac{3}{2} \leftrightarrow +\frac{1}{2}$, and $+\frac{1}{2} \leftrightarrow -\frac{1}{2}$ transitions, respectively. The identification of the $-\frac{3}{2} \leftrightarrow -\frac{1}{2}$ transition was made by considering the relative intensity increase at lower temperatures. Because of the asymmetrical line shape the extrema of lines A and B as indicated in Fig. 2 were employed to locate their positions; the position of the symmetric line C was located by the zero crossing. Although lines A and B show the expected asymmetrical line shapes, the structure of the spectrum is complex because of the presence of weak unidentified transitions. The weak transitions on the low-field side do not correspond to the $\Delta M = \pm 2$ and ± 3 transitions. Figure 3 shows the experimental angular EPR spectra measured in a $\{110\}$ plane. The examination of the angular spectra measured in $\{111\}$ and $\{110\}$

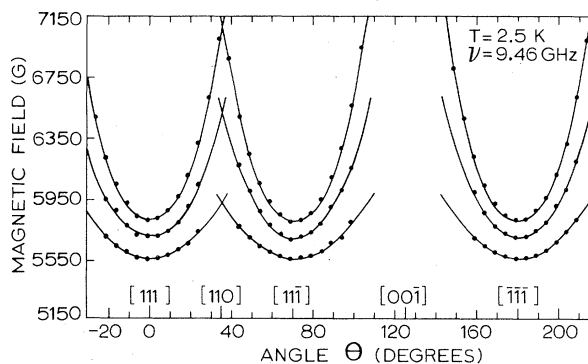


FIG. 3. Experimental angular EPR spectra with \vec{H} in $\{110\}$ showing equivalent sites of Ti^{3+} in CsAl alum.

planes confirmed the presence of four symmetry-equivalent sites with the symmetry axes along $\langle 111 \rangle$ directions. Because of the weak intensities, the EPR spectra for any site could only be traced in the angular range of $+30^\circ$ to -30° with respect to the symmetry axis.

Bleaney first employed a group-theoretical argument to introduce an augmented spin Hamiltonian⁷ for a Γ_8 quartet which, in addition to the usual Zeeman term $g\mu_B\vec{H}\cdot\vec{S}$, included a third-order spin-angular-momentum term $f\mu_B(H_x S_x^3 + H_y S_y^3 + H_z S_z^3)$. The importance of this third-order term in describing the EPR anisotropy for a Γ_8 quartet has been demonstrated for Co^{2+} in cubic and tetrahedral coordination⁸ and Re^{4+} in octahedral coordination.⁹ The generalized spin Hamiltonian for a quasi- Γ_8 state in a trigonal lattice can be derived by using the tensor decomposition method¹⁰ and the requirement of symmetry invariance. With an effective spin $S = \frac{3}{2}$, this generalized spin Hamiltonian, which includes terms linear in H , has the form

$$H_s = D_{20}T_{20}(\vec{S}) + g_{\parallel}\mu_B H_z T_{10}(\vec{S}) + \sqrt{\frac{1}{2}}g_{\perp}\mu_B H_x [T_{1-1}(\vec{S}) - T_{11}(\vec{S})] + f_{\parallel}\mu_B H_z T_{30}(\vec{S}) + \sqrt{\frac{1}{2}}f_{\perp}\mu_B H_x [T_{3-1}(\vec{S}) - T_{31}(\vec{S})] + h\mu_B [H_z [T_{33}(\vec{S}) - T_{3-3}(\vec{S})] - \sqrt{\frac{1}{2}}H_x [T_{32}(\vec{S}) + T_{3-2}(\vec{S})]], \quad (2)$$

where the parallel direction is along the trigonal $[111]$ axis and $T_{lm}(\vec{S})$ are tensor operator equivalents of rank l expressed in terms of the spin angular momentum \vec{S} . These operator equivalents are related to the Stevens operator equivalents and are defined as irreducible tensors which possess the convenient transformation properties.¹¹ The last term in Eq. (2) can give rise to $\Delta M = \pm 2$ and ± 3 transitions when the magnetic field is along a $[111]$ axis. Since only $\Delta M = \pm 1$ transitions are observed experimentally, this term will be omitted in the analysis; the omission is fully justified by the very good agreement between theory and experiment as shown below. By diagonalizing the dominant g term, the $\Delta M = \pm 1$ EPR transitions within the quasi- Γ_8 quartet are given to first order for $+\frac{1}{2} \leftrightarrow -\frac{1}{2}$ transitions by

$$h\nu = g\mu_B H - \frac{9}{10}\sqrt{\frac{5}{2}}\mu_B H \left\{ (f_{\parallel}g_{\parallel}/g) \cos^2\theta [5(g_{\parallel}^2/g^2) \cos^2\theta - 3] + \sqrt{\frac{3}{2}}(f_{\perp}g_{\perp}/g) \sin^2\theta [5(g_{\parallel}^2/g^2) \cos^2\theta - 1] \right\}, \quad (3)$$

and for $\pm \frac{3}{2} \leftrightarrow \pm \frac{1}{2}$ transitions by

$$h\nu = g\mu_B H + \frac{6}{10}\sqrt{\frac{3}{2}}\mu_B H \left\{ (f_{\parallel}g_{\parallel}/g) \cos^2\theta [5(g_{\parallel}^2/g^2) \cos^2\theta - 3] + \sqrt{\frac{3}{2}}(f_{\perp}g_{\perp}/g) \sin^2\theta [5(g_{\parallel}^2/g^2) \cos^2\theta - 1] \right\} \pm \sqrt{\frac{3}{2}}D [3(g_{\parallel}^2/g^2) \cos^2\theta - 1], \quad (4)$$

where θ is the angle between the magnetic field \vec{H} and the [111] axis, and $g^2 = g_{\parallel}^2 \cos^2\theta + g_{\perp}^2 \sin^2\theta$.

The experimental anisotropic EPR spectra of Ti^{3+} in CsAl alum can be described successfully by using the generalized spin Hamiltonian of Eq. (2) for a quasi- Γ_8 state with trigonal symmetry. The spin-Hamiltonian parameters were determined by fitting these angular spectra with Eqs. (3) and (4), and were found to be

$$g_{\parallel} = 1.1937 \pm 0.001, \quad g_{\perp} = 0.6673 \pm 0.005,$$

$$u_{\parallel} = -0.0144 \pm 0.002, \quad u_{\perp} = -0.0868 \pm 0.005,$$

$$D = 39.3 \pm 1.0 \text{ MHz},$$

where $u_{\parallel, \perp} = \sqrt{\frac{3}{2}}f_{\parallel, \perp}$. A comparison of the calculated angular EPR spectra using these spin-Hamiltonian parameters and the corresponding experimental parameters is presented in Fig. 4, where dots are experimental data and curves are calculated angular spectra. Since the zero-field splitting parameter D given above is very small, we estimate using Eq. (1) that γ equals approximately 0.03.¹² Thus the excited Γ_7 spin-orbit level, which has an energy $\frac{3}{2}\gamma\lambda$, is approximately 6 cm^{-1} above the ground state. A spin-lattice re-

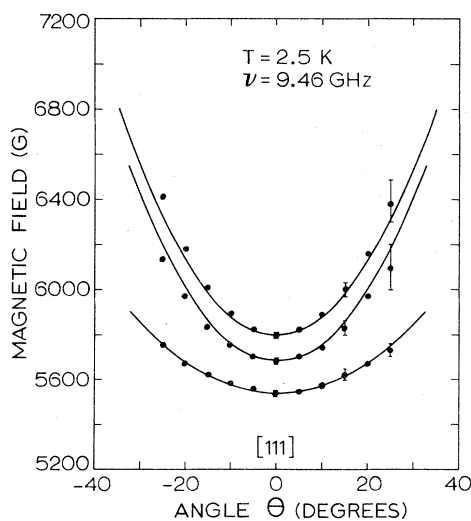


FIG. 4. Calculated and experimental angular EPR spectra of Ti^{3+} in CsAl alum. Dots are experimental data; solid lines are calculated spectra.

laxation study is underway to confirm the Γ_7 energy level.

It has been shown that the ground state of Ti^{3+} as a dilute impurity in CsAl alum is a quasi- Γ_8 state with a small zero-field splitting. This is the first demonstration of a quasi- Γ_8 ground state with trigonal site symmetry. This unique situation arises because the trigonal splitting to first order, which is reduced by the vibronic reduction factor, is comparable with and opposite in sign to the second-order contribution, which is not reduced by any vibronic factor. A spin Hamiltonian is derived for the quasi- Γ_8 state, and the agreement between the calculated and experimental angular spectra is shown to be very good. With a vibronic reduction factor γ of approximately 0.03, the excited Γ_7 state is estimated to be 6 cm^{-1} above the ground state.

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