Dynamic Jahn-Teller Effect in Octahedrally Coordinated d^1 Impurity Systems*

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We have calculated the effect of first- and second-order spin-orbit, trigonal, and Zeeman interactions within the vibronic states of the d^1 $^2T_2$ term, and also the smaller configurational interaction with the excited ^2E term. A model is used which includes only interactions with vibrational modes having E_g symmetry about the impurity site. It is found that second-order vibronic effects can be very important even though the electron lattice coupling may be relatively weak. The uniform partial quenching of crystal-field splittings, characteristic of a first-order vibronic calculation, is modified in second order. The recently observed far-infrared spectra of Al_2O_3:Ti^{3+} and Al_2O_3:V^{4+} can be explained quantitatively by the inclusion of these second-order terms. Moreover, our calculations explain for the first time the hitherto anomalous ground-state g values of Al_2O_3:Ti^{3+}. For Al_2O_3:V^{4+}, the ground-state spin resonance has not been positively identified, but we predict $g_{\parallel} \approx 1.5$, $g_{\perp} \approx 0$. We find Jahn–Teller energies of 200 and 320 cm^{-1} for Al_2O_3:Ti^{3+} and Al_2O_3:V^{4+}, respectively, and an effective E_g mode frequency of 200 cm^{-1}.

I. INTRODUCTION

ACCORDING to the Jahn-Teller (JT) theorem,[1,2] the non-Kramers degeneracy of an electronic state belonging to a nonlinear complex is lifted by spontaneous asymmetric nuclear displacements. If the coupling between the electrons and the nuclear displacements is very strong, the complex undergoes a distortion to a new configuration of minimum energy (the static JT effect).[3–5] In general, there may be several equivalent configurations which the complex can assume. If a particular complex undergoes transitions among these configurations in a period which is short compared to the time scale of the relevant experimental observation, we have the dynamic JT effect.[5–10] The averaging can occur either by thermal activation over the barrier separating these equivalent configurations or by tunneling. These two averaging mechanisms are not equivalent; the former is random and the latter is selective.

One of the observable consequences of the dynamic JT effect is the partial quenching of the matrix elements of certain orbital operators. This was first recognized by Ham[10] (although special cases of it had been implicitly noted earlier)[11–13] and has been called the Ham effect. The first experimental evidence of such dynamic quenching was furnished by spin-resonance data[14–16] in which great reductions in the orbital contributions to g factors were seen. Recently, Scott and Sturge[17] reported the quenching of spin-orbit and trigonal crystal-field splittings in the excited $^3T_2$ term of Al_2O_3:V^{3+}. Using a model which includes only E_g vibrational modes, they explained their data in terms of a first-order Ham effect plus second-order effects in the static JT or strong-coupling limit.

In this paper we use a similar model to elucidate the consequences of a moderately weak dynamic JT effect. We consider the ground term $^2T_2$ of an octahedrally coordinated $3d^1$ impurity ion, which has a relatively simple electronic structure and for which spectroscopic data have recently been reported.[18,19] We find that the first-order theory is inadequate to account for the results, and that in this region of weak coupling, second-order effects have to be treated in a more exact

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manner than was done previously.[17] The general theory of a second-order JT interaction with excited vibronic states has been outlined by Ham.[10] We have calculated explicitly the effect of this interaction on the $^2T_2$ ground term of $3d^1$ impurity ions in Al_2O_3, also including the small configurational interaction with the excited ^2E term. Inclusion of second-order effects enables us to obtain quantitative agreement with the measured far-infrared spectra[18,19] and with the ground-state g values.[20,21] We find a JT energy of 200 and 320 cm^{-1} for Al_2O_3:Ti^{3+} and Al_2O_3:V^{4+}, respectively, and an effective E_g mode frequency of 200 cm^{-1} for both systems.

In Sec. II we present the conventional crystal-field calculations of octahedrally coordinated $3d^1$ impurity systems including configurational interactions. In Sec. III we calculate the first- and second-order dynamic JT effects for the d^1 $^2T_2$ term coupled to a doubly degenerate E_g vibrational mode. We have obtained analytical expressions for the ground-state g values and the $^2T_2$ splittings. Finally, we discuss the possible application of our results to other systems.

II. CRYSTAL-FIELD CALCULATIONS OF d^1 IMPURITY SYSTEMS

The electronic Hamiltonian for a d^1 impurity ion in a crystal can be written as

$$\mathfrak{IC} = \mathfrak{IC}_{so} + \mathfrak{IC}_{cf}, \qquad (1)$$

where $\mathfrak{IC}_{so}$ is the spin-orbit coupling energy and $\mathfrak{IC}_{cf}$ is the energy due to the crystalline field of the surrounding ligands, which includes V_{cub} and V_{trig}. For Ti^{3+} and V^{4+} in Al_2O_3, $V_{cub} \gg V_{trig}$, $\mathfrak{IC}_{so}$. We therefore choose the zeroth-order Hamiltonian $\mathfrak{IC}_0$ to be V_{cub}, and obtain analytical expressions for the energy by treating the trigonal-field, spin-orbit, and Zeeman interactions as perturbations. The separation of the two cubic terms of d^1 is $\Delta = E(^2E) - E(^2T_2)$. For Al_2O_3:Ti^{3+}, Δ has been measured optically[22] to be around 19 000 cm^{-1}. The corresponding value for Al_2O_3:V^{4+} has not been measured, but it is expected to be somewhat larger. The complex trigonal basis states for the $^2T_2$ and ^2E terms are labelled

$$(\mid \pm\tfrac{1}{2}, x_+ \rangle, \mid \pm\tfrac{1}{2}, x_0 \rangle, \mid \pm\tfrac{1}{2}, x_- \rangle)$$

and

$$(\mid \pm\tfrac{1}{2}, u_+ \rangle, \mid \pm\tfrac{1}{2}, u_- \rangle),$$

respectively. The energy diagram of a d^1 impurity ion in Al_2O_3 is shown in Fig. 1, which also includes the labelling of various term splittings under trigonal-field and spin-orbit perturbations. The diagram is drawn for $v \equiv$
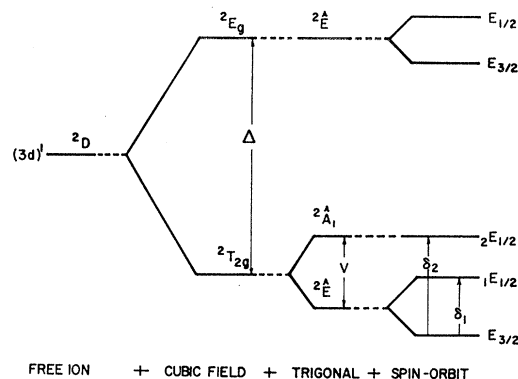
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FIG. 1. Low-lying levels of d^1 impurity systems in corundum.

$+\tfrac{3}{2} \langle t_2 0 \mid V_{trig} \mid t_2 0 \rangle > 0$. The matrix of the Hamiltonian given in Eq. (1) has been calculated in the complex trigonal basis and is given in Appendix A. The Zeeman interactions have also been included. If we consider only interactions within the $^2T_2$ term (which is a good approximation, since $\Delta \gg v$, ζ), the zero magnetic-field energy matrix factorizes into two 2-dimensional and and two 1-dimensional matrices; these have degenerate eigenvalues given by

$$\delta_0(E_{3/2}) = 0,$$

$$\delta_1(_1E_{1/2}) = \tfrac{1}{2}v + \tfrac{3}{4}\zeta - \tfrac{1}{2}[(9/4)\zeta^2 - \zeta v + v^2]^{1/2},$$

$$\delta_2(_2E_{1/2}) = \tfrac{1}{2}v + \tfrac{3}{4}\zeta + \tfrac{1}{2}[(9/4)\zeta^2 - \zeta v + v^2]^{1/2}, \qquad (2)$$

where a constant term $\tfrac{1}{3}v + \tfrac{1}{2}\zeta + \tfrac{2}{5}\Delta$ has been added to the right side of Eq. (2) to make the lowest state $E_{3/2}$ have zero energy. $E_{1/2}$ and $E_{3/2}$ label representations of the C_3 double group. The quantities ζ and v in Eq. (2) are the one-electron spin-orbit and trigonal-field parameters, respectively. The ground-state g values can be obtained in a similar way from Appendix A, and they have the values

$$g_{||} = 2(1 - k),$$

$$g_\perp = 0, \qquad (3)$$

where k is the orbital reduction or covalency factor.[23] We have taken the spin-orbit parameter ζ to be 120 cm^{-1}, which is 80% of the free-ion value. This represents a typical expansion of the $3d$ radial function in the solid. The trigonal-field parameter v is not known for Al_2O_3:Ti^{3+}. However, for four other trivalent $3d^n$ ions in Al_2O_3, v is in the range 700–1000 cm^{-1}.[22,24,25] We take

[23] K. W. H. Stevens, Proc. Roy. Soc. (London) **A219**, 542 (1953).

[24] McClure (Ref. 22) gives $v > 500$ cm^{-1} for Ti^{3+}, $v = 1000$ cm^{-1} for Ni^{3+}, and 1950 cm^{-1} for Mn^{3+}. The optical spectra of these ions are confused by the JT effect in the ground state, and these numbers can only be taken as rough estimates. Co^{3+} has a singlet ground state and McClure's value of 720 cm^{-1} is probably about right. For V^{3+} and Cr^{3+}, Macfarlane (Ref. 25) fits all the optical data, and his value of 800 cm^{-1} for both ions is more accurate than McClure's higher figures.

[25] R. M. Macfarlane, J. Chem. Phys. **39**, 3118 (1963); **40**, 373 (1964).

TABLE I. $^2T_2$ term splittings and ground-state g values of Al_2O_3:Ti^{3+} in the static-crystal-field approximation.

| | Analytical | | Numerical | |
	First order	Second order	First order	Second order
$\delta_1(E_{3/2}\rightarrow_1 E_{1/2})$	$\frac{1}{2}+\frac{3}{4}\zeta-\frac{1}{2}[(9/4)\zeta^2-\zeta v+v^2]^{1/2}$	$-(2\sqrt{2}\zeta v'/\Delta)+(2\zeta^2/\Delta)$	109 cm^{-1}	-11 cm^{-1}
$\delta_2(E_{3/2}\rightarrow_2 E_{1/2})$	$\frac{1}{2}v+\frac{3}{4}\zeta+\frac{1}{2}[(9/4)\zeta^2-\zeta v+v^2]^{1/2}$	$-(\sqrt{2}\zeta v'/\Delta)+(v'^2/\Delta)$ $+\frac{1}{2}(\zeta^2/\Delta)$	771 cm^{-1}	$+19$ cm^{-1}
$g_{||}(E_{3/2})$	$2(1-k)$	$(4k/\Delta)(\sqrt{2}v'-\zeta)$	0.4	$+0.14$
$g_\perp(E_{3/2})$	0	0	0	0

it to be $+700$ cm^{-1}. The positive sign follows from the observation that the ground state is $E_{3/2}$ and has a very anisotropic g value. Putting these values of ζ and v into Eq. (2), we find that the first two excited states of Al_2O_3:Ti^{3+} have energies of 109 and 771 cm^{-1}, respectively. The orbital-reduction factor k for transition-metal ions in the moderately covalent Al_2O_3 typically has a value between 0.7 and 0.8. Taking $k=0.8$ for Al_2O_3:Ti^{3+}, one finds from Eq. (3) $g_{||}=0.4$ and $g_\perp=0$.

Since V^{4+} is isoelectronic with Ti^{3+}, the same expressions apply for the $^2T_2$ term splittings and ground-state g values of Al_2O_3:V^{4+}.

Configurational interactions with the excited ^2E term have also been calculated, and the numerical results together with approximate analytical expressions are summarized in Table I. The numerical corrections were obtained by diagonalizing the d^1 energy matrix including both the $^2T_2$ and ^2E terms. We have taken $\Delta\sim$ 19 000 cm^{-1} and $v'\sim$600 cm^{-1} [26] in this calculation. It was found that these interactions change δ_1 and δ_2 of Eq. (2) by -11 and $+19$ cm^{-1}, respectively, and the correction to the ground state $g_{||}$ is $+0.14$.

The ground-state g values of Al_2O_3:Ti^{3+} have been measured[20,21] to be $g_{||}\approx 1.07$ and $g_\perp<0.1$. In order to explain this anomalous value of $g_{||}$ in terms of static-crystal-field theory, one has to assume an orbital-reduction factor k of 0.5. In the usual covalent theory of the orbital-reduction factor,[23] this would imply complete delocalization of the electron onto the neighboring oxygen ions, which is quite unphysical. No explanation for this anomalous value has previously been offered. The ground-state g value of Al_2O_3:V^{4+} is not known at present,[27] and we will discuss the V^{4+} problem later.

Recently, the far-infrared spectra of Al_2O_3:Ti^{3+} and Al_2O_3:V^{4+} have been measured.[18,19] For Al_2O_3:Ti^{3+}, the first two excited states are located at 37.8 and 108.0 cm^{-1}, respectively. The corresponding levels for Al_2O_3:V^{4+} are 28.0 and 52.6 cm^{-1}. These transitions are pure σ polarized as expected for the $E_{3/2}\rightarrow E_{1/2}$ transitions predicted by crystal-field theory (see Fig. 1). These values for the $^2T_2$ term splittings do not agree with crystal-field calculations for any reasonable set of parameters (see Table II). They appear to be very much quenched. It is shown in Sec. III that a

$a_1 = -\frac{1}{2}a_3 + \frac{\sqrt{3}}{2}a_2$

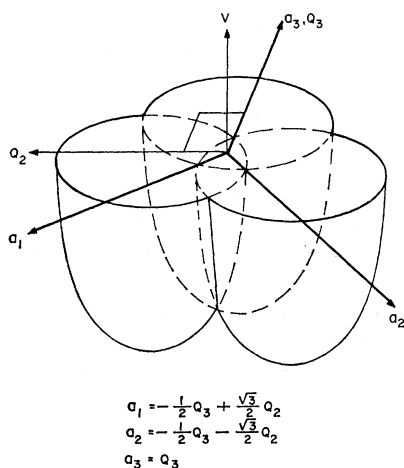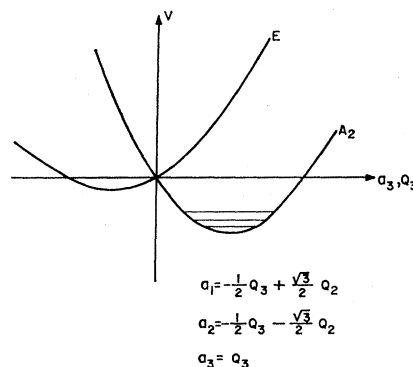$a_2 = -\frac{1}{2}a_3 - \frac{\sqrt{3}}{2}a_2$

$a_3 = a_3$

FIG. 2. Vibronic potential surface $V(Q_2, Q_3)$ for a triply degenerate state interacting with E_g distortions. The electronic states associated with each paraboloid are mutually orthogonal (in a cubic system with zero spin-orbit coupling).

[26] $v' \equiv \langle t_2 x_\pm | V_{trig} | e u_\pm \rangle$. The value of 600 cm^{-1} for v' is typical of transition-metal ions in Al_2O_3.

$a_1 = -\frac{1}{2}a_3 + \frac{\sqrt{3}}{2}Q_2$

$a_2 = -\frac{1}{2}a_3 - \frac{\sqrt{3}}{2}Q_2$

$a_3 = Q_3$

FIG. 3. Section through Fig. 2 along the a_2 axis.

[27] The isotropic spin resonance with $S=\frac{1}{2}$, $g=2$, observed in vanadium-doped corundum at room temperature by J. Lambe and C. Kikuchi, Phys. Rev. **118**, 71 (1960), cannot arise from the same center as the far-infrared spectrum reported in Ref. 19. The infrared data show that the ground state is the $E_{3/2}$ state, which must have $g_\perp=0$. Furthermore, the low-lying excited states would cause rapid spin-lattice relaxation and prevent observation of resonance except at very low temperatures. The spin-resonance spectrum may belong to a VO^{2+} complex: compare, for instance, the data on this complex compiled by K. D. Bowers and J. Owen, Rept. Progr. Phys. **18**, 304 (1955).

TABLE II. Observed and calculated splitting and g factors for the $^2T_2$ ground term of $Al_2O_3:Ti^{3+}$.

	Observed[a]	No JT effect (Sec. II)	Calculated[b] first order[c] (Sec. III A)	First and second order[d] (Sec. III B)
δ_1	37.8 cm^{-1}	98 cm^{-1}	14 cm^{-1}	43 cm^{-1}
δ_2	107.5 cm^{-1}	790 cm^{-1}	195 cm^{-1}	107 cm^{-1}
$g_{||}$	1.07	0.54	1.68	1.14
$g_\perp$	<0.1	0	0	0

[a] References 18, 20, and 21.
[b] Interaction with ^2E is included. The parameters are $\Delta = 19\ 000$ cm^{-1}, $v = 700$ cm^{-1}, $v' = 600$ cm^{-1}, $\zeta = 120$ cm^{-1}, $k = 0.8$.
[c] $\gamma = 0.21$, $f_a = 0$, $f_b = 0$.
[d] $\gamma = 0.21$, $f_a = 0.11$, $f_b = 0.41$.

first-order Ham effect still fails to account for these data. Quantitative agreement with both spin-resonance and far-infrared data is possible only when second-order effects in the dynamic JT or weak-coupling limit are included.

III. DYNAMIC JT EFFECT

A. First Order

In the harmonic approximation, the vibronic Hamiltonian for a complex in which a single E_g mode[28] interacts with a cubic electronic term may be written as

$$\mathcal{H}_{\text{vib}} = \mathcal{H}_0 + (1/2\mu) \sum_{k=2,3} (P_k^2 + \mu^2\omega^2 Q_k^2)$$
$$+ \sum_{k=2,3} (\partial V/\partial Q_k)_0\ Q_k. \quad (4)$$

As in Sec. II, $\mathcal{H}_0$ is the cubic part of the electronic Hamiltonian. $V(Q_k, q_i)$ is the potential energy of the electrons in the field of the nuclei, and is a function of both the electronic coordinate q_i and the normal coordinates Q_k of the E_g mode. The effective mass and angular frequency are denoted by μ and ω, respectively, and P_k are the momenta conjugate to Q_k. The equilibrium configuration of the nuclei in the absence of electron-lattice coupling defines $Q_k = 0$. Only terms linear in Q_k have been retained in the electron-lattice interaction [the last term in Eq. (4)]. If we choose a real tetragonal basis for T_2 and E,[29] then the eigenstates Ψ_i of $\mathcal{H}_{\text{vib}}$ are Born-Oppenheimer products of the electronic components of $^2T_2$ ($|\pm\frac{1}{2}\psi_i\rangle$, $i = 1, 2, 3$) and the eigenstates of a displaced 2-dimensional harmonic oscillator $\phi_{in_2n_3}$.[10] The eigenvalues of $\mathcal{H}_{\text{vib}}$ are given by

$$E_{n_2n_3} = E_0 + (n_2 + n_3 + 1)\hbar\omega - E_{\text{JT}}, \quad (5)$$

where

$$E_{\text{JT}} = (\langle T_2 || \partial V/\partial Q_k || T_2\rangle^2/2\mu\omega^2)$$
$$= (C^2/2\mu\omega^2) \quad (6)$$

is the JT stabilization energy. The vibronic potential surface in (Q_2, Q_3) space consists of three disjoint paraboloids,[5,30] one for each component of T_2 (see Fig. 2). Without any perturbation terms in $\mathcal{H}_{\text{vib}}$, the complexes in the crystal would randomly occupy one of the three paraboloids and undergo a tetragonal distortion (the static JT effect). The T_2 term is split into an E and an A_2 (of D_{4h}) as shown in Fig. 3. The dynamic JT effect arises when a particular complex undergoes transitions among these paraboloids in a period which is short compared to the time scale of the relevant experimental observation. Since ψ_i are orthogonal, transitions from one paraboloid to another can only occur via terms not included in Eq. (4). In the present case, such terms can be the trigonal-field, the spin-orbit interaction, and the orbital part of the Zeeman interaction (we will show later that T_{2g} vibrations are not important). We will regard these three terms as perturbations ($\mathcal{H}_{\text{pert}}$) on $\mathcal{H}_{\text{vib}}$.

Now we consider the evaluation of the matrix elements of $\mathcal{H}_{\text{pert}}$ in the zeroth-order vibronic basis $|\Psi_{in_2n_3}\rangle = |\pm\frac{1}{2}\psi_i\rangle |\phi_{in_2n_3}\rangle$. In a tetragonal representation, the trigonal-field spin-orbit coupling and orbital angular momentum have only off-diagonal matrix elements within the $^2T_2$ term. Since these perturbation operators are independent of the Q_k, the off-diagonal matrix elements of $\mathcal{H}_{\text{pert}}$ are given by

$$\langle\Psi_{in_2n_3} | \mathcal{H}_{\text{pert}} | \Psi_{jn_2'n_3'}\rangle$$
$$= \langle\pm\frac{1}{2}\psi_i | \mathcal{H}_{\text{pert}} | \pm\frac{1}{2}\psi_j\rangle\langle\phi_{in_2n_3} | \phi_{jn_2'n_3'}\rangle. \quad (7)$$

The electronic matrix element is multiplied by a factor $\gamma = \langle\phi_{in_2n_3} | \phi_{jn_2'n_3'}\rangle < 1$, which is the overlap integral between vibrational wave functions corresponding to the different components of $^2T_2$. These functions are not orthogonal, since they belong to displaced oscillators

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[28] In a real crystal the impurity ion interacts with a continuum of vibrational modes, not just one. Ham (Ref. 10) has shown that, as far as first-order effects are concerned, the same results are obtained for a continuum as for a single mode. We will assume that this is also true for the second-order effects considered in this paper.

[29] That is, for T_2 (ξ, η, ζ) transforming under O as (yz, zx, xy) and for $E(u, v)$ as $[(3z^2 - r^2), (x^2 - y^2)]$.
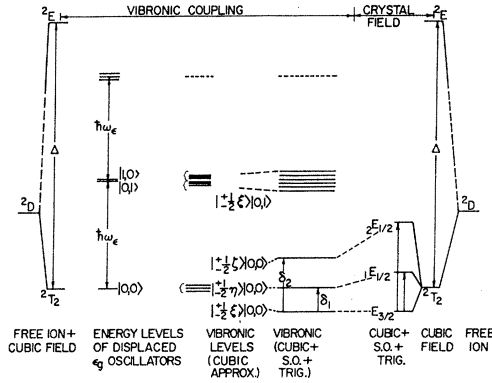
[30] A. D. Liehr, J. Phys. Chem. **67**, 389, 471 (1963).

FIG. 4. Vibronic energy levels of d^1 impurity systems in corundum.

with different origins. For the lowest vibronic levels, $\gamma = \exp(-3E_{\rm JT}/2\hbar\omega)$. This quenching of off-diagonal operators is known as the Ham effect.

To obtain the first-order correction to the energy of the $^2T_2$ term, we must diagonalize the energy matrix of $\mathcal{K}_{\rm pert}$ among the states $|\Psi_{i00}\rangle$, since the latter are degenerate. Although the qualitative splitting pattern of the $^2T_2$ term due to $\mathcal{K}_{\rm pert}$ remains the same as in the absence of the JT coupling, the magnitudes of the splittings are reduced. The discrepancy between crystal-field calculations and the measured far-infrared spectra in the $^2T_2$ term splittings of $3d^1$ impurity ions in corundum has been mentioned in Sec. II (see Table II). It seems

reasonable to attribute the reduction of these splittings to a Ham effect. However, according to Eq. (7), matrix elements of all operators which are off-diagonal in this tetragonal representation (i.e., all operators included in $\mathcal{K}_{\rm pert}$) are reduced by the same factor γ. Thus δ_1, δ_2, and k should be reduced by the same factor. Clearly this is not the case experimentally; δ_1 is reduced by a factor of roughly 0.35, δ_2 by 0.14, and k by 0.6. We will find that by going to the next order of perturbation theory we can account for this difference.

B. Second Order

We now consider second-order interaction within $^2\mathfrak{Z}_2$ and between $^2\mathfrak{Z}_2$ and $^2\mathcal{E}$.[31] The latter interaction is rather small, and we can neglect "nondiagonal" second-order contributions (i.e., contributions from perturbation loops beginning and ending on different electronic components of $^2T_2$), since these are reduced by a factor γ relative to the "diagonal" contributions. The latter are unquenched and may be calculated using electronic matrix elements in a trigonal basis, in exactly the same way as in static-crystal-field theory (Sec. II). We neglect the correction ($\approx E_{\rm JT}$) to the energy denominators Δ, since $E_{\rm JT} \ll \Delta$.

The most important contributions come from interactions within $^2\mathfrak{Z}_2$, these being absent when there is no vibronic coupling (see Fig. 4). The general expression for the second-order correction to the lowest vibronic level is

$$\langle ^2\mathfrak{Z}_2 i00 \mid \mathcal{K}_{pp'} \mid ^2\mathfrak{Z}_2 j00 \rangle = -\sum_{k \neq i,j} \sum_{n,m \neq 0} \frac{\langle ^2\mathfrak{Z}_2 i00 \mid \mathcal{K}_p \mid ^2\mathfrak{Z}_2 knm \rangle \langle ^2\mathfrak{Z}_2 knm \mid \mathcal{K}_{p'} \mid ^2\mathfrak{Z}_2 j00 \rangle}{(n+m)\hbar\omega}. \tag{8}$$

Here $\mathcal{K}_p$ and $\mathcal{K}_{p'}$ are operators in $\mathcal{K}_{\rm sert}$. Since these are electronic operators, the vibrational part of the matrix elements can be integrated out. The vibrational integrals have been evaluated by Ham,[10] and we may write the result as

$$M_{ij} = \langle ^2\mathfrak{Z}_2 i00 \mid \mathcal{K}_{pp'} \mid ^2\mathfrak{Z}_2 j00 \rangle$$

$$= -(\hbar\omega)^{-1}\Big[\sum_{k \neq i,j} \langle ^2T_2 i \mid \mathcal{K}_p \mid ^2T_2 k \rangle \langle ^2T_2 k \mid \mathcal{K}_{p'} \mid ^2T_2 j \rangle\Big][\delta_{ij}f_b + (1-\delta_{ij})f_a], \tag{9}$$

where

$$f_b = e^{-x}G(x), \qquad f_a = e^{-x}G(\tfrac{1}{2}x),$$

and

$$G(x) = \sum_{n=1}^{\infty} [x^n/(n \times n!)].$$

The numerical values of the quenching factors γ (see Sec. III A), f_b, and f_a as a function of $x = 3E_{\rm JT}/\hbar\omega$ have been tabulated,[10] and a plot is shown in Fig. 5. Note that in the limit of strong JT effect, γ and f_a fall off as $\exp(-x/2)$ or faster, while f_b only goes as $1/x$. Terms in f_b represent the second-order effects which survive in the static JT case; these were the only second-order terms included in previous calculations (see, for instance, Ref. 17).

Matrix elements of $\mathcal{K}_{\rm pert}$ within $^2T_2$ in a real tetragonal basis[32] were obtained by transforming the $^2T_2$ block of $\mathcal{K}_{\rm pert}$ given in Appendix A (superscripts on N and M indicate the basis used to calculate the matrix

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[31] $^2\mathfrak{Z}_2$ denotes the manifold of vibronic energy levels derived from the $^2T_2$ electronic term (and $^2\mathcal{E}$ that of ^2E). The first-order effects discussed in Sec. III A are within the lowest three levels of $^2\mathfrak{Z}_2$, these being degenerate in the absence of $\mathcal{K}_{\rm pert}$.

[32] The reason for expressing $\mathcal{K}_{\rm pert}$ in a real tetragonal basis is for convenience in introducing the quenching factors f_b and f_a. Ultimately we will transform back to a trigonal basis to get analytical expressions for the g values. In the case of the spin-orbit and trigonal terms (i.e., the part of $\mathcal{K}_{\rm pert}$ which yields the energy levels but not the g values), we can work directly in the trigonal basis. This is because the coefficient of f_b is a multiple of the unit matrix (i.e., $\tilde{M}_{ii}^{\rm tet}$ is the same for $i=1, 2, \cdots, 6$) and is unaffected by the transformation.

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elements):

$$\tilde{N}_{ij}{}^{\text{tet}} \equiv \gamma \langle {}^2T_2 i \mid \mathcal{3C}_{\text{pert}} \mid {}^2T_2 j \rangle$$

$$= U_{i\alpha}\gamma \langle {}^2T_2 \alpha \mid \mathcal{3C}_{\text{pert}} \mid {}^2T_2 \beta \rangle U_{j\beta}{}^*$$

$$\equiv U_{i\alpha}\tilde{N}_{\alpha\beta}{}^{\text{trig}}U_{j\beta}{}^*. \qquad (10)$$

The real tetragonal components of ${}^2T_2$ are labeled $i\cdots$ and the complex trigonal components $\alpha\cdots$. The unitary transformation matrix U between trigonal and tetragonal bases is given in Appendix B. These matrix elements were used to evaluate the second-order matrix $\tilde{M}^{\text{tet}}$ using Eq. (9). At this point we could diagonalize $\tilde{N}^{\text{tet}}+\tilde{M}^{\text{tet}}$ to get the energies and g values of the lowest vibronic triplet of ${}^2\mathfrak{J}_2$, and this was subsequently done as a check. A more elegant method is to transform the matrix $\tilde{N}^{\text{tet}}+\tilde{M}^{\text{tet}}$ to a trigonal basis

$$U_{\alpha i}{}^*(\tilde{N}^{\text{tet}}+\tilde{M}^{\text{tet}}) U_{\beta j}=\tilde{N}^{\text{trig}}+\tilde{M}^{\text{trig}}, \qquad (11)$$

where $\tilde{N}^{\text{trig}}+\tilde{M}^{\text{trig}}$ is now expressed in reduced form comprising three 2-dimensional matrices,[33] and we can obtain analytical expressions for the energy levels and g values by solving the quadratic secular equations. We find

$$\delta_1=\gamma(\tfrac{1}{2}v+\tfrac{3}{4}\zeta)+(f_a/\hbar\omega)(-\tfrac{3}{8}\zeta^2+\tfrac{1}{2}\zeta v-\tfrac{1}{6}v^2)-\tfrac{1}{2}A, \quad (12a)$$

$$\delta_2=\gamma(\tfrac{1}{2}v+\tfrac{3}{4}\zeta)+(f_a/\hbar\omega)(-\tfrac{3}{8}\zeta^2+\tfrac{1}{2}\zeta v-\tfrac{1}{6}v^2)+\tfrac{1}{2}A, \quad (12b)$$

where

$$A^2=\gamma^2(v^2-\zeta v+\tfrac{9}{4}\zeta^2)$$

$$+(f_a/\hbar\omega)^2(\tfrac{1}{9}v^4+\tfrac{2}{9}v^3\zeta+\tfrac{1}{6}\zeta^2v^2+\tfrac{1}{2}\zeta^3v+\tfrac{9}{16}\zeta^4)$$

$$-(\gamma f_a/\hbar\omega)(\tfrac{2}{3}v^3+\tfrac{1}{3}v^2\zeta+\tfrac{1}{2}\zeta^2v+\tfrac{9}{4}\zeta^3).$$

The ground-state $(E_{3/2})$ g values are[34]

$$g_\perp \equiv 0 \text{ (by symmetry)},$$

$$g_{\|}=2-(2k/\hbar\omega)(a^2+b^2)^{1/2}, \qquad (13)$$

where

$$a=-(2/9)\zeta f_b-(7/9)\zeta f_a-\tfrac{2}{3}vf_a-\gamma\hbar\omega$$

and

$$b=\tfrac{1}{9}\sqrt{2}\zeta(f_b-f_a).$$

While f_b appears in the expression for the g factor, it drops out of δ_1 and δ_2. In the static limit the spin-orbit and trigonal splitting of the ground vibronic state go to zero, as they must since this state is then a Kramers' doublet.

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[33] This is guaranteed since the over-all symmetry of the Hamiltonian is trigonal.
[34] The fact that the g values may sometimes agree with those predicted by static-crystal-field theory does not necessarily mean that the vibronic effects are unimportant. The static-crystal-field g values can be reproduced even with substantial JT quenching because of the complicated way that second-order terms come in.
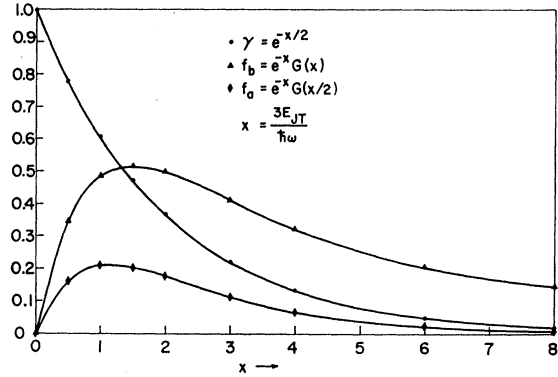

FIG. 5. Values of γ, f_a, and f_b as a function of x. (The quantities γ, f_a, f_b, and x are defined in the text.)

Substituting into Eqs. (12) and (13) the crystal-field parameters for $Al_2O_3:Ti^{3+}$ as discussed in Sec. II, viz., $v=700$ cm^{-1}, $v'=600$ cm^{-1}, $\zeta=120$ cm^{-1}, $k=0.8$, the JT quenching factors $\gamma=0.21$, $f_b=0.41$, $f_a=0.11$,[35] and an effective E_g mode frequency $\hbar\omega=200$ cm^{-1} (note that the values of f_b and f_a are fixed by the choice of γ), we get

$$\delta_1=43 \text{ cm}^{-1}, \qquad \delta_2=107 \text{ cm}^{-1},$$

$$g_{\|}=1.14, \qquad g_\perp=0,$$

where the second-order interactions with the excited ${}^2E$ term (see Sec. II) have been included.

IV. DISCUSSION

We have shown in Sec. III B that a model in which only E_g vibrations are considered to interact with the d^1 electronic system gives a satisfactory quantitative explanation of the low-lying levels and ground-state g values of $Al_2O_3:Ti^{3+}$. There are several other reasons why we restrict our attention to E_g modes. Firstly, only even-parity modes will interact with d-like functions. The symmetric A_{1g} mode produces no vibronic splittings and so has not been considered. The justification for neglecting the T_{2g} mode is more difficult. Including it would lead to a much more complicated calculation, since the Born-Oppenheimer products $\mid {}^2T_2, T_{2g}n_4n_5n_6\rangle$ would no longer diagonalize the vibronic Hamiltonian [Eq. (4)]. Also, further parameters would be required, and there are insufficient experimental data to determine them. However, there is also some physical justification for restricting our attention to the E_g modes. The observed spectrum indicates that there is comparable quenching of spin-orbit and trigonal splittings (the latter is in fact quenched somewhat more strongly). The trigonal field is a T_{2g} operator, and coupling to the T_{2g} modes should be quenched by the

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[35] The corresponding numbers for the ${}^3T_2$ term of $Al_2O_3:V^{3+}$ (Ref. 17) are 0.023, 0.156, and 0.007, respectively.

same factor (about 1/7) as is the trigonal field. Furthermore, coupling to T_{2g} modes would tend to quench the spin-orbit interaction much more strongly than the trigonal field.[10] In fact, we find that the latter is quenched more than the former, and we can safely conclude that T_{2g} coupling is not important.

It is interesting to discuss the transition from the static to the dynamic limit. When the last term in Eq. (5) is neglected (no vibronic coupling), the Hamiltonian is invariant under operations of the cubic group O_h applied separately to the electronic and nuclear coordinates. In the presence of vibronic coupling, it is invariant under operations of O_h applied simultaneously to the electronic and nuclear coordinates. There are always spin-orbit terms present as perturbations, and these provide a mechanism for the system to tunnel among the equivalent distorted configurations (Sec. III A). In the case where the system is observed in a time which is long compared to the tunneling period, an individual complex exhibits the full cubic symmetry of the Hamiltonian when averaged over the observation *time* (dynamic effect). If the tunneling period is very long compared to the observation time, it is possible to observe the system "frozen" into one of the distorted configurations. An individual complex may assume any of the equivalent configurations with equal probability, so that a spatial average yields a system with cubic symmetry (static effect). In the static limit the lowest vibronic state of $^2T_2$ is effectively a Kramers' doublet, $^2A_2$ of D_{4h}, and cannot be split except by a magnetic field. (This was not true, of course, of the $^3T_2$ term considered in Ref. 17.) There is still a second-order contribution to the g factor, arising from magnetic interaction with the upper JT branch (^2E of D_{4h}).

The calculation that we have performed does several things. It shows that the second-order vibronic interactions can be important even in the case of relatively weak coupling between the lattice and the electrons. It provides useful expressions for the vibronic energy levels and g values of single d-electron systems for the case of an E_g vibrational mode interacting with a cubic T_2 level, and we are able to show that the introduction of vibronic coupling modifies the crystal-field predictions in a way that gives quantitative agreement with the observed spectrum of Al_2O_3:Ti^{3+}.

The present discussion is also relevant to the case of Al_2O_3:V^{4+}, which is isoelectronic with Al_2O_3:Ti^{3+}. As mentioned in Sec. II, the spin-resonance spectrum of Al_2O_3:V^{4+} has not been positively identified at present.[27] The positions of the low-lying levels of this system as obtained from the far-infrared spectrum[17] ($\delta_1 = 28.1$ cm^{-1}, $\delta_2 = 52.8$ cm^{-1}) do not agree with static-crystal-field theory. We have performed a similar calculation on this system using the crystal-field parameters $\Delta = 20,000$ cm^{-1}, $v = 700$ cm^{-1}, $v' = 600$ cm^{-1}, $\zeta = 200$ cm^{-1}, and $k_z = 0.8$, and obtained quantitative fit to the experimental data with $E_{JT} = 320$ cm^{-1} and $\hbar\omega = 200$ cm^{-1}. The ground-state ($E_{3/2}$) g values with this set of

parameters are predicted to be $g_{||} \approx 1.5$ and $g_\perp = 0$ (by symmetry).[36]

Note that the number of parameters describing the crystal-field, spin-orbit, and vibronic interactions is greater than the number of experimental data available. However, we should stress that this does not imply that a fit to the data is meaningless, since most of the parameters are constrained to a relatively narrow range of values. We arrived at these values as follows. The cubic parameter Δ is obtained from the position of the excited ^2E term measured by optical spectroscopy,[22] and v and v' were fixed by extrapolating the values found for other d^n ions in corundum.[24,25] (Δ and v' have only a small effect on the $^2T_2$ splittings.) The spin-orbit parameter is taken to be about 80% of its free-ion value ζ_0, which corresponds to a very reasonable expansion of the $3d$ radial wave functions in a solid. The expectation value of orbital angular momentum has been reduced in the same ratio, viz., ζ/ζ_0. For the two and three d-electron systems in corundum (V^{3+}, Cr^{3+}), it has been observed that transitions to JT distorted states couple strongly to a vibrational mode of $\sim$200 cm^{-1}.[22,37] We note that static-crystal-field theory cannot give a fit to the data for any physically reasonable set of parameters. A further test of the model that we propose here would be to measure the g values of the $_{1,2}E_{1/2}$ levels of Al_2O_3:Ti^{3+} at 37.8 and 108.5 cm^{-1}, respectively. We have calculated these numerically for the set of parameters in Sec. III B, and find $g_{||}(_1E_{1/2}) = -2.5$, $g_\perp(_1E_{1/2}) \lesssim 0.2$; $g_{||}(_2E_{1/2}) = 1.9$, $g_\perp(_2E_{1/2}) \approx 2$.

In a recent paper Moser et al.[38] argue that the far-infrared lines in Al_2O_3:Ti^{3+} are not associated with Ti^{3+}. However, the evidence for the assignment to Ti^{3+} is fairly conclusive. The first infrared transition at 37.8 cm^{-1} corresponds very closely to the activation energy for Orbach relaxation observed in spin resonance.[20,21] Recent experimental results[39] indicate that the 38 cm^{-1} line splits in a magnetic field, and that $g_{||} \gg g_\perp$. This is consistent with our theoretical prediction but inconsistent with its assignment as a localized vibrational mode. The Ti^{3+} spectrum does not appear in all Ti-doped samples because Ti^{4+} is the most stable charge state and Ti^{3+} is only obtained under controlled conditions. Correlations with chemical analyses can be misleading for this reason. While Moser et al.[38] report that they obtained the same infrared spectrum in a sample containing less than 20 ppm Ti, it would appear from the anomalous dependence on a sample thickness that they have a surface effect, and it may be that the sur-

[36] Resonances of vanadium ions in Al_2O_3 with g values in this region have recently been measured by F. R. Merritt (private communication) and by J. D. Castle, Jr. (private communication).

[37] M. H. L. Pryce and W. A. Runciman, Discussions Faraday Soc. **26**, 34 (1958); B. N. Grechushnikov and P. O. Feofilov, Zh. Eksperim. i Teor. Fiz. **29**, 384 (1955) [English transl.: Soviet Phys.—JETP **2**, 330 (1956)].

[38] J.-F. Moser, W. Zingg, H. Steffen, and F. K. Kneubühl, Phys. Letters **24A**, 411 (1967).

[39] P. L. Richards and R. Joyce (private communications).

TABLE III. d^1 energy matrix in complex trigonal basis.

	$^2T_2(t_2)$						$^2E(e)$			
	$\frac{1}{2}x_+$	$-\frac{1}{2}x_+$	$\frac{1}{2}x_-$	$-\frac{1}{2}x_-$	$\frac{1}{2}x_0$	$-\frac{1}{2}x_0$	$\frac{1}{2}u_+$	$-\frac{1}{2}u_+$	$\frac{1}{2}u_-$	$-\frac{1}{2}u_-$
$^2T_2(t_2)$										
$\frac{1}{2}x_+$	$-\frac{2}{5}\Delta-\frac{1}{3}v$ $-\frac{1}{2}\zeta-kH_z$ $+\frac{1}{2}gH_z$									
$-\frac{1}{2}x_+$	$\frac{1}{2}gH_z$	$-\frac{2}{5}\Delta-\frac{1}{3}v$ $+\frac{1}{2}\zeta-kH_z$ $-\frac{1}{2}gH_z$								
$\frac{1}{2}x_-$	0	0	$-\frac{2}{5}\Delta-\frac{1}{3}v$ $+\frac{1}{2}\zeta+kH_z$ $+\frac{1}{2}gH_z$							
$-\frac{1}{2}x_-$	0	0	$\frac{1}{2}gH_z$	$-\frac{2}{5}\Delta-\frac{1}{3}v$ $-\frac{1}{2}\zeta+kH_z$ $-\frac{1}{2}gH_z$						
$\frac{1}{2}x_0$	$-\frac{1}{2}\sqrt{2}kH_z$	$-\frac{1}{2}\sqrt{2}\zeta$	$-\frac{1}{2}\sqrt{2}kH_z$	0	$-\frac{2}{5}\Delta+\frac{2}{3}v$ $+\frac{1}{2}gH_z$					
$-\frac{1}{2}x_0$	0	$-\frac{1}{2}\sqrt{2}kH_z$	$-\frac{1}{2}\sqrt{2}\zeta$	$-\frac{1}{2}\sqrt{2}kH_z$	$\frac{1}{2}gH_z$	$-\frac{2}{5}\Delta+\frac{2}{3}v$ $-\frac{1}{2}gH_z$				
$^2E(e)$										
$\frac{1}{2}u_+$	$v'-\frac{1}{2}\sqrt{2}\zeta$ $-\sqrt{2}kH_z$	0	kH_z	ζ	kH_z	0	$\frac{3}{5}\Delta$ $+\frac{1}{2}gH_z$			
$-\frac{1}{2}u_+$	$v'+\frac{1}{2}\sqrt{2}\zeta$ $-\sqrt{2}kH_z$	0	0	kH_z	ζ	kH_z	$\frac{1}{2}gH_z$	$\frac{3}{5}\Delta$ $-\frac{1}{2}gH_z$		
$\frac{1}{2}u_-$	$-kH_z$	0	$v'+\frac{1}{2}\sqrt{2}\zeta$ $+\sqrt{2}kH_z$	0	kH_z	ζ	0	0	$\frac{3}{5}\Delta$ $+\frac{1}{2}gH_z$	
$-\frac{1}{2}u_-$	$-\zeta$	$-kH_z$	0	$v'-\frac{1}{2}\sqrt{2}\zeta$ $+\sqrt{2}kH_z$	0	kH_z	0	0	$\frac{1}{2}gH_z$	$\frac{3}{5}\Delta$ $-\frac{1}{2}gH_z$

face concentration of Ti^{3+} was quite high in this particular sample.

V. CONCLUSION

We have investigated the interaction between an E_g vibrational mode and the $^2T_2$ electronic term of the d^1 configuration. Such interaction gives rise to the JT effect. The theory proposed by Ham has been applied to this case, and analytical expressions were obtained for the energies of the lowest vibronic levels and the ground-state g values of single d-electron systems. We find that second-order interactions within the lowest vibronic multiplet are important even in the case of relatively weak coupling to the lattice, and we are able to obtain quantitative agreement with observed levels and g values in $Al_2O_3:Ti^{3+}$.

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APPENDIX A

We give in Table III the d^1 electronic energy matrix without the electron-lattice interaction terms. The parameters are defined as follows: $\Delta \equiv -\frac{5}{2} \langle t_2 \mid V_{\text{cub}} \mid t_2 \rangle$, $v \equiv +\frac{3}{2} \langle t_2 0 \mid V_{\text{trig}} \mid t_2 0 \rangle$, $v' \equiv \langle t_2 x_\pm \mid V_{\text{trig}} \mid e u_\pm \rangle$, and ζ is the one-electron spin-orbit parameter; k is the orbital-reduction factor (assumed to be isotropic); $g = 2.0023$ is the spin-only spectroscopic splitting factor. The magnetic field is expressed in units of $1/\beta$, and lies in the (x, z) plane. Note that if $H_x = 0$, the $^2T_2$ block of the energy matrix can be rearranged into two 2-dimensional and two 1-dimensional matrices. (The latter two are

connected in second order via ^2E). The energies and g values of $E_{3/2}(\frac{1}{2}x_+, -\frac{1}{2}x_-)$, $_1E_{1/2}(-\frac{1}{2}x_+, \frac{1}{2}x_-)$, and $_2E_{1/2}(\frac{1}{2}x_0, -\frac{1}{2}x_0)$ of $^2T_2$ can be obtained by solving the quadratic secular equations.

APPENDIX B

In Sec. III B we require the matrix

$$U_{i\alpha} = \langle M_s \gamma (\gamma \equiv \xi, \eta, \zeta) \mid M_s' \gamma' (\gamma' \equiv x_+, x_0, x_-) \rangle,$$

which transforms the six components of the $^2T_2$ term from a complex trigonal $(\gamma \equiv x_+, x_0, x_-)$ to a real tetragonal $(\gamma \equiv \xi, \eta, \zeta)$ basis. The spin components are labelled by $M_s = \pm\frac{1}{2}$, the orbital components by γ, and the transformation is carried out in the coupled (spin and orbit) space. The matrix U can most readily be obtained as a product of two 6×6 matrices, $U = U_1 U_2$. U_2 is the transformation from a complex trigonal to a complex tetragonal basis and is given by a direct product of two rotation matrices[40]:

$$U_2 = D^{(1/2)}(\theta_1, \theta_2, \theta_3) \otimes D^{(1)}(\theta_1, \theta_2, \theta_3), \quad (B1)$$

where the Eulerian angles which rotate the (100) axis into the (111) axis are $\theta_1 = \pi/4$, $\theta_2 = \cos^{-1} \frac{1}{3}\sqrt{3}$, and $\theta_3 = \pi$. The choice $\theta_3 = \pi$ is made to conform to Griffith's[41] convention for the definition of the complex bases. Now the transformation matrix between real and complex tetragonal bases is given by

$$U_1 = D^{(1/2)}(0, 0, 0) \otimes \begin{bmatrix} -\frac{1}{2}i\sqrt{2} & 0 & \frac{1}{2}i\sqrt{2} \\ \frac{1}{2}\sqrt{2} & 0 & \frac{1}{2}\sqrt{2} \\ 0 & i & 0 \end{bmatrix}, \quad (B2)$$

so that we get

$$\begin{bmatrix} \mid -\frac{1}{2}\xi \rangle \\ \mid +\frac{1}{2}\xi \rangle \\ \mid -\frac{1}{2}\eta \rangle \\ \mid +\frac{1}{2}\eta \rangle \\ \mid -\frac{1}{2}\zeta \rangle \\ \mid +\frac{1}{2}\zeta \rangle \end{bmatrix} = i\sqrt{2} \begin{bmatrix} \omega\alpha^* & -\omega\beta^* & \alpha^* & -\beta^* & -\omega^*\alpha^* & \omega^*\beta^* \\ \omega\beta & \omega\alpha & \beta & \alpha & -\omega^*\beta & -\omega^*\alpha \\ \omega^*\alpha^* & -\omega^*\beta^* & \alpha^* & -\beta^* & -\omega\alpha^* & \omega\beta^* \\ \omega^*\beta & \omega^*\alpha & \beta & \alpha & -\omega\beta & -\omega\alpha \\ \alpha^* & -\beta^* & \alpha^* & -\beta^* & -\alpha^* & \beta^* \\ \beta & \alpha & \beta & \alpha & -\beta & -\alpha \end{bmatrix} \begin{bmatrix} \mid -\frac{1}{2}x_+ \rangle \\ \mid +\frac{1}{2}x_+ \rangle \\ \mid -\frac{1}{2}x_0 \rangle \\ \mid +\frac{1}{2}x_0 \rangle \\ \mid -\frac{1}{2}x_- \rangle \\ \mid +\frac{1}{2}x_- \rangle \end{bmatrix}, \quad (B3)$$

where $\omega = \exp[i(2\pi/3)]$, $\alpha = \exp[-i(\pi/8)] \cos[\frac{1}{2} \cos^{-1} \frac{1}{3}\sqrt{3}]$, $\beta = -\exp[-i(\pi/8)] \sin[\frac{1}{2} \cos^{-1} \frac{1}{3}\sqrt{3}]$, and ω^*, α^*, and β^* are complex conjugates of ω, α, and β, respectively.

[40] See e.g., M. Tinkham, *Group Theory and Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1964).
[41] J. S. Griffith, *The Irreducible Tensor Method for Molecular Symmetry Groups* (Prentice-Hall, Inc., Englewood Cliffs, N.J., 1962).