Superposition-model analyses for the Cr^{3+} $^4A_2$ ground state

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(Received 31 January 1986)

The EPR data for strained ruby have been reanalyzed using a model in which the mixing of five excited multiplets into the ground state are considered. Consistent crystal-field superposition-model parameters were obtained. Tables of the necessary superposition-model "projection" coefficients for both trigonally and tetragonally oriented coordinate systems are provided, making the application of the model to similar systems straightforward. Using this model, the justification for the Müller and Berlinger form of the superposition model for the Cr^{3+} ground state is investigated.

I. INTRODUCTION

The existing situation in regard to the correct superposition-model treatment of the ground-state splitting of the $^4A_2$ ground multiplet of Cr^{3+} is in a state of some confusion. As has been pointed out by Newman,[1] and reiterated by Clare and Devine,[2,3] it is incorrect to assume that the effective spin operators for this state can be transformed as $\mathbb{R}_3$ vectors, because A_2 mixes with the other $L=3$ states under arbitrary transformations. Hence the superposition model of the spin Hamiltonian in the form that has been developed for ions with $L=0$ ground states such as $Mn^{2+}(^6S_{5/2})$ and $Gd^{3+}(^8S_{7/2})$ and $Gd^{3+}(^8S_{7/2})$ (Ref. 4) is not applicable. On the other hand, Müller et al.[5,6] claim considerable success with a model in which just such assumptions *are* made. Even more puzzling is the fact that, although Clare and Devine[2] used the supposedly "correct" approach in applying the superposition model to the crystal field directly, they did not achieve a very good understanding of the experimental results for strained ruby. In particular, the consistency between their superposition-model analysis of the strain parameters and the static parameter D for this system is very poor indeed, and their suggestion that this is due to the operation of different mechanisms in the two cases is unsatisfactory. Besides this, they obtained values of the superposition-model parameters which are inconsistent with those obtained from optical data.

TABLE I. Energy levels of Cr^{3+} in ruby and MgO obtained using parameters B, C, and Δ determined in Refs. 8 and 9. a and b labels distinguish repeated irreducible representations of the octahedral group. States omitted from the Clare and Devine (Ref. 2) analysis are starred. Energies are given in units of 10^3 cm^{-1}.

State	Al_2O_3	MgO
$^4A_2$	0	0
$^4T_2$	18.10	17.60
$_a^2T_2^*$	21.56	21.71
$_a^4T_1$	24.76	24.52
$_b^2T_2^*$	32.17	31.83
$_b^4T_1^*$	39.29	38.60

Müller and Berlinger[5] have suggested that the reason for these inconsistencies is that Clare and Devine[2] used a too restricted set of excited states in their perturbation formalism. This criticism is well founded, because several of the omitted excited states lie no higher in energy than those which were included (see Table I).

The present work aims to achieve three things. We extend the Clare and Devine analysis to see whether a better fit of the model parameters to the experimental data for ruby can be obtained. This calculation is then used to form the basis of a general approach to the superposition-model analysis of ground-state splittings of Cr^{3+} in a near cubic environment. Using this approach we finally examine why the model used by Müller et al.[5,6] apparently works so well.

II. CRYSTAL-FIELD CONTRIBUTIONS TO THE Cr^{3+} $^4A_2$ GROUND-STATE SPLITTING

Contributions to the crystal-field splitting of the $^4A_2$ ground state of Cr^{3+} arise from small admixtures of excited states with orbital degeneracy due to spin-orbit coupling. In contrast to the case of ions with half-filled shell ground states,[4] the one-electron crystal field is not disadvantaged in this process vis-a-vis correlation (or two-electron) contributions. It should therefore only be necessary to consider the crystal-field and spin-orbit operators in constructing the appropriate perturbation expressions. In view of the fact that the previous formalism was incomplete, our first concern will be to include all significant admixtures into the ground state.

The unperturbed Hamiltonian contains, besides the kinetic energy and spherically symmetric one-electron terms, the Coulomb repulsion represented by the Racah parameters B,C and the cubic crystal field represented by $\Delta = 10Dq$. The perturbing Hamiltonian takes the form

$$\mathcal{H} = \zeta \sum_i \mathbf{s}_i \cdot \mathbf{l}_i + \sum_{l,m} B'_{lm} \sum_i C_{lm}(i) , \qquad (1)$$

where the $C_{lm}(i)$ are tensor operators acting on electron i, ζ is the spin-orbit coupling, and B'_{lm} are the C_3 crystal-field parameters. It is presumed that the dominant cubic crystal-field component has been subtracted out from the B'_{lm}, as it is included in the unperturbed Hamiltonian

TABLE II. Nonzero third-order contributions to the ground-state splitting in ruby. For class I, contributions are of the form $\langle ^4A_2 | V_{so} | B \rangle\langle B | V' | C \rangle\langle C | V_{so} | ^4A_2 \rangle /(\Delta E_B \Delta E_C)$. For class II, contributions are of the form $\langle ^4A_2 | V' | B \rangle\langle B | V_{so} | C \rangle \times \langle C | V_{so} | ^4A_2 \rangle /(\Delta E_B \Delta E_C)$.

Type	Class I						Class II			
	1	2(a)	2(b)	3	4	5	6(a)	6(b)	7(a)	7(b)
B	$^4T_2$	$^2_aT_2$	$^2_bT_2$	$^2_aT_2$	$^4_aT_1$	$^4_bT_1$	$^4_aT_1$	$^4_aT_1$	$^4_bT_1$	$^4_bT_1$
C	$^4T_2$	$^2_aT_2$	$^2_bT_2$	$^2_bT_2$	$^4T_2$	$^4T_2$	$^2_aT_2$	$^2_bT_2$	$^2_aT_2$	$^2_bT_2$

which defines the basis states.

The low-lying states of Cr^{3+} in ruby and MgO are shown in Table I. Following Macfarlane[7] it is assumed that the contributions from states above $40\,000$ cm^{-1} can be neglected. There are perturbation contributions to the ground-state splitting, as the spin-orbit operator must appear at least twice and the crystal-field operator at least once. Clare and Devine[2] distinguish two classes of contributions [see their Eqs. (5) and (6)], according to whether the crystal field couples to the ground state directly, denoted class II, or whether the crystal field acts between degenerate excited states (as we assumed in Ref. 1), denoted class I. The third-order mechanisms considered in this paper are summarized in Table II.

The main problem in evaluating the matrix elements arises from the doublet excitations, for it is not possible in these cases to separate out the total spin part of the spin-orbit operators as was done previously.[1,2] This is because the operator $\sum_i l_i \cdot s_i$ is only proportional to $\mathbf{L} \cdot \mathbf{S}$ for matrix elements within a given LS term. In order to determine the spin-Hamiltonian parameters it is therefore necessary to compare the perturbation contributions to the ground-state matrix elements directly with the matrix elements of the spin Hamiltonian. Nevertheless, as we wish to make comparisons with the previous formalism and to obtain results that can be used for other Cr^{3+} systems, it is convenient to express our results in terms of factors multiplying the class I and II contributions already determined in Ref. 2. The details of this calculation are described in Sec. III.

III. SUPERPOSITION MODEL
FOR THE Cr^{3+} $^4A_2$ GROUND STATE

It is convenient to introduce the 4×4 energy matrices $\mathcal{H}^T(l,m)$ defined over the $^4A_2$ quartet spin states, where T is a "type" label as defined in Sec. II and l,m describes the crystal-field component. In constructing these matrices we shall omit the energy denominators and the energy operator coefficients ζ, B'_{lm} [see Eq. (1)] from the numerators of the perturbation expressions. The weighted sum of these matrices is given by

$$\mathcal{H}(lm)= \sum_T \mathcal{H}^T(l,m)w_T = \begin{bmatrix} h_1 & h_3 & h_5 & 0 \\ h_4 & h_2 & 0 & h_5 \\ h_6 & 0 & h_2 & -h_3 \\ 0 & h_6 & -h_4 & h_1 \end{bmatrix},$$

$$h_k = h_k(l,m) , \quad (2)$$

where the weighting factors w_T are determined from ratios of the previously omitted energy denominators. It is

clear from Table I that such ratios are effectively constant for different oxygen-coordinated systems. The following relations can be shown to hold:

$$h_k(l,m)=(-1)^m h_k(l,-m) \quad (k=1,2) ,$$

$$h_4(l,m)=(-1)^m h_3(l,-m) ,$$

$$h_6(l,m)=(-1)^m h_5(l,-m) .$$

Values of the $h_k(l,m)$ coefficients have been calculated for both trigonal and tetragonal coordinate systems and are available on request from the authors. These results show that all ten perturbation mechanisms considered in this work give significant contributions to the spin Hamiltonian, except for 7(a) (defined in Table II). We therefore expect our model to give quite different results from those of Clare and Devine.[2]

Using the matrix form of the spin operators we may write

$$\mathcal{H}(l,m)= \sum_{i,j} \langle i(l,m)j \rangle S_i S_j$$

$$= \frac{9}{\theta_l} \sum_{p=1}^{6} a_p S_p^{(2)} , \quad (3)$$

where the Stevens's factors $\theta_2 = \frac{2}{105}$, $\theta_4 = \frac{2}{315}$, and the $S_p^{(2)}$ are given by

$$S_1^{(2)} = S_x^2, \quad S_2^{(2)} = S_y^2, \quad S_3^{(2)} = S_z^2 ,$$

$$S_4^{(2)} = S_y S_z + S_z S_y, \quad S_5^{(2)} = S_z S_x + S_x S_z ,$$

$$S_6^{(2)} = S_x S_y + S_y S_x .$$

Substituting the matrix elements $S_p^{(2)}$ on the right-hand side allows us to determine the coefficients a_p in terms of the matrix elements of $\mathcal{H}(l,m)$. For future convenience we now present these results for both the trigonal and tetragonal coordinate alignments.

It is convenient to remove the trace of $\mathcal{H}$ to obtain a traceless energy matrix $\mathcal{H}'$ as this term does not contribute to the ground-state splitting. For each l,m there are only two nonzero h_k in $\mathcal{H}'$ which, in a trigonal coordinate system, are related to the six a_p as follows.

(i) For $m = 0, \pm3$:

$$a_1 = a_2 = -\tfrac{1}{2} a_3 = \tfrac{1}{6}(h_2 - h_1) ,$$

$$a_4 = a_5 = a_6 = 0 .$$

(ii) For $m = 1, 1\pm3$:

$$a_1 = -a_2 = \frac{h_6}{2\sqrt{3}} = ia_6, \quad a_3 = 0 ,$$

$$a_5 = ia_4 = h_3/2\sqrt{3} .$$

(iii) For $m = -1, -1 \pm 3$:

$$a_1 = -a_2 = ia_6 = h_5/2\sqrt{3}, \quad a_3 = 0,$$

$$a_5 = ia_4 = h_4/2\sqrt{3}.$$

These equations then allow us to relate the perturbation expressions directly to the coefficients of the spin Hamiltonian without separating spin and orbital parts as in Refs. 1 and 2. Hence both excited doublet and quartet contributions can now be included. Table III summarizes the results for a trigonal coordinate system and replaces values of the projection coefficients given in Ref. 1 and Table IV of Ref. 2.

In a tetragonal coordinate system both the values of the elements of the matrix $\mathcal{H}(l,m)$ and the coefficients a_p, $\langle i(l,m)j \rangle$ have different numerical values. The relations between the energy matrix elements and parameters a_p are also rather different. We find for $|m| = 0,4$:

$$a_1 = a_2 = -\tfrac{1}{2}a_3 = \tfrac{1}{6}(h_2 - h_1), \quad a_4 = a_5 = a_6 = 0,$$

for $m = +1, +3$:

$$a_5 = (h_3 + h_4)/2\sqrt{3},$$

$$a_4 = i(h_3 - h_4)/2\sqrt{3},$$

$$a_1 = a_2 = a_3 = a_6 = 0,$$

for $m = -1, -3$:

$$a_5(l,-m) = -a_5(l,m), \quad a_4(l,-m) = a_4(l,m),$$

for $m = +2$:

$$a_1 = -a_2 = (h_5 + h_6)/2\sqrt{3},$$

$$a_6 = i(h_5 - h_6)/2\sqrt{3},$$

$$a_3 = a_4 = a_5 = 0,$$

and for $m = -2$:

$$a_1(l,-2) = -a_2(l,-2) = a_1(l,2),$$

$$a_6(l,-2) = -a_6(l,2).$$

These relations allow us to determine the values of the tetragonal $\langle i(l,m)j \rangle$ parameters from Eq. (3). These have been tabulated and are available from the authors on request.

The energy matrix $\mathcal{H}$ introduced above can be written as a linear expression of the $\mathcal{H}(l,m)$ with the omitted energy factors as coefficients:

$$\mathcal{H} = \left[\frac{\zeta}{3\,\Delta E_2} \right]^2 \sum_{l,m} \mathcal{H}(l,m)\theta_l B_{lm}. \tag{4}$$

Introducing a matrix representation of the spin operators S_i this 4×4 energy matrix can also be expressed in spin-Hamiltonian form as

$$\mathcal{H} = \sum_{i,j} d_{ij} S_i S_j.$$

Comparison of these expressions gives

$$d_{ij} = \left[\frac{\zeta}{3\,\Delta E_2} \right]^2 \sum_l \theta_l \sum_m \tilde{B}_{lm} \langle i(l,m)j \rangle, \tag{5}$$

where

$$\tilde{B}_{lm} = B_{lm} - B_{lm}(\text{cubic})$$

for the static crystal field, and

$$\tilde{B}_{lm} = \sum_{\mu,\nu} \frac{\partial B_{lm}}{\partial \epsilon_{\mu\nu}} \epsilon_{\mu\nu}$$

for the strain tensor $\epsilon_{\mu\nu}$.

The coefficient $(\zeta/3\,\Delta E_2)^2$ may be assumed to take the value 9.802×10^{-6}, using the energy $\Delta E_2 = 18\,100$ cm^{-1} quoted in Table I and the ruby spin-orbit parameter $\zeta = 170$ cm^{-1}.[18] (Clare and Devine[2] used the MgO value $\zeta = 138$ cm^{-1}.[19])

The superposition model can then be applied to the $\tilde{B}_{lm}$ of either form. The spin-strain coupling tensor $G_{ij\mu\nu}$ ($\equiv G_{pq}$ in Voigt notation) is defined by

$$d_{ij} = \sum_{\mu,\nu} G_{ij\mu\nu}\epsilon_{\mu\nu},$$

where $\epsilon_{\mu\nu}$ is the (uniform) strain tensor. The spin Hamiltonian can be expressed in terms of a single-parameter D for tetragonal, hexagonal, and trigonal distortions and in terms of two parameters D,E for monoclinic distortions. Remembering that different choices of axes are involved (relative to the orientation of the cube) all of these cases can be expressed in the form

TABLE III. Projection coefficients $\langle i(l,m)j \rangle = (9/\theta_l)a_{ij}$ for all ten contributions using trigonally orientated coordinates.

l,m \ $\begin{matrix}p\\ij\end{matrix}$	1 xx	2 yy	3 zz	4 yz	5 zx	6 xy
2,0	-87.69	-87.69	175.38	0	0	0
2,±1	∓51.02	±51.02	0	$-35.17i$	∓35.17	$51.02i$
2,±2	71.32	-71.32	0	$\mp51.02i$	51.02	$\pm71.32i$
4,0	109.65	109.65	-219.30	0	0	0
4,±1	∓62.41	±62.41	0	$-95.63i$	∓95.63	$62.41i$
4,±2	-31.22	31.22	0	$\mp80.93i$	80.93	$\mp31.22i$
4,±3	±45.87	±46.17	∓91.74	0	0	0
4,±4	-123.86	123.86	0	$\mp19.45i$	-19.45	±123.86

$$\mathcal{H}_s = D[S_z^2 - \tfrac{1}{3}S(S+1)] + E(S_x^2 - S_y^2)$$

$$= \sum_{i,j} d_{ij} S_i S_j$$

so that $d_{xx} = E - \tfrac{1}{3}D$, $d_{yy} = -E - \tfrac{1}{3}D$, and $d_{zz} = \tfrac{2}{3}D$, the off-diagonal elements being zero. Hence

$$D = \tfrac{3}{2}d_{zz} = \left[\frac{\zeta}{3\,\Delta E_2}\right]^2 \sum_l \theta_l \sum_m b_{lm} \tfrac{3}{2}\langle z(l,m)z \rangle \qquad (6)$$

and

$$E = \tfrac{1}{2}(d_{xx} - d_{yy})$$

$$= \left[\frac{\zeta}{3\,\Delta E_2}\right]^2 \sum_l \theta_l \sum_m b_{lm} \tfrac{1}{2}[\langle x(l,m)x \rangle - \langle y(l,m)y \rangle] . \qquad (7)$$

In Eqs. (6) and (7)

$$b_{lm} = B_{lm} - B_{lm}(\text{cubic})$$

$$= \bar{B}_l(R_0)\left[\sum_\alpha \left[\frac{R_0}{R_\alpha}\right]^{t_l} K_l^m(\alpha) - \sum_\alpha K_l^m(\alpha: \text{cubic})\right],$$

where the coordination factors

$$K_l^m(\theta,\phi) = \left[\frac{4\pi}{2l+1}\right]^{1/2} Y_l^{*m}(\theta,\phi) ,$$

and α labels the ligands.

The nonzero cubic sums in the above expression take the form

$$\sum_\alpha K_4^0 = -\tfrac{7}{3} \quad \text{(trigonal frame)} ,$$

$$= \tfrac{7}{2} \quad \text{(tetragonal frame)} ,$$

$$\sum_\alpha K_4^4 = \frac{\sqrt{70}}{2} \quad \text{(tetragonal frame)} ,$$

$$\sum_\alpha K_4^3 = -\frac{\sqrt{70}}{3} \quad \text{(trigonal frame)} .$$

Clare and Devine[3] give a simple demonstration that the coefficients d_{ij} only transform as a tensor for operations R which satisfy $R \mid A_2 \rangle = \pm \mid A_2 \rangle$; i.e., operations in the octahedral group. This makes it clear why the superposition model cannot be applied directly to the spin Hamiltonian, but does not seem to be in accord with their subsequent statement that the "d_{ij} do transform as a Cartesian tensor under rotations of the coordinate frame." The point is that in such a rotation of coordinates the A_2 state is merely reexpressed in terms of the new coordinates, whereas the use of the superposition model requires the identification of A_2 states defined in terms of several different coordinate systems. Hence it is consistent to treat d_{ij} as a Cartesian tensor provided that the description of A_2 is also transformed accordingly.

IV. FIT OF MODEL PARAMETERS TO THE RUBY DATA

The superposition model for the orbit-lattice coupling of Cr^{3+} ions in ruby has been discussed by Clare and De-

vine.[2] Their formulas are, however, not sufficiently general to be used without modification in the present calculation. It is therefore convenient to record the expressions for $\partial B_{lm}/\partial \epsilon_{\mu\nu}$, which have been evaluated using the superposition-model equations for three ions at positions $\phi_j = \eta$, $\eta \pm 120°$ as follows:

$$B_{lm}(R) = \bar{B}_l(R) \sum_{j=1}^{3} K_l^m(\theta_j \phi_j) . \qquad (8)$$

Table IV gives the differentials $\partial B_{lm}/\partial \epsilon_{\mu\nu}$ as coefficients of the intrinsic parameters $\bar{B}_l$ for $\epsilon_{\mu\nu} = \epsilon_{xx}$, ϵ_{zz}, and ϵ_{yz}. The remaining differentials may then be determined from the relationship

$$\frac{\partial B_{lm}}{\partial \epsilon_{yy}} = \begin{cases} \dfrac{\partial B_{lm}}{\partial \epsilon_{xx}} & (m = 0, \pm 3) , \\[2ex] -\dfrac{\partial B_{lm}}{\partial \epsilon_{xx}} & (m = \pm 1, \pm 2, \pm 4) , \end{cases}$$

$$\frac{\partial B_{l,\pm m}}{\partial \epsilon_{xy}} = \begin{cases} 2i\dfrac{\partial B_{l,\pm m}}{\partial \epsilon_{xx}} & (m = 1, 4) , \\[2ex] \mp 2i\dfrac{\partial B_{l,\pm m}}{\partial \epsilon_{xx}} & (m = 2) , \\[2ex] \dfrac{\partial B_{l,m}}{\partial \epsilon_{xx}} = 0 & (m = 0, \pm 3) , \end{cases}$$

$$\frac{\partial B_{l,\pm m}}{\partial \epsilon_{zx}} = \begin{cases} \pm i\dfrac{\partial B_{l,\pm m}}{\partial \epsilon_{yz}} & (m = 1, 4) , \\[2ex] \mp i\dfrac{\partial B_{l,\pm m}}{\partial \epsilon_{yz}} & (m = 2) , \\[2ex] \dfrac{\partial B_{l,m}}{\partial \epsilon_{yz}} = 0 & (m = 0, \pm 3) . \end{cases}$$

A superposition-model fit has been carried out to fit the intrinsic parameters $\bar{B}_2(R_0)$ and $\bar{B}_4(R_0)$ for a fixed ligand distance R_0 and the power-law exponents t_2 and t_4 defined by

$$\bar{B}_l(R) = \bar{B}_l(R_0)\left[\frac{R_0}{R}\right]^{t_l} . \qquad (9)$$

In this fit the coordination angles and distances were corrected for the displacement of the Cr^{3+} position from the Al^{3+} position of 0.0325 Å as determined by McCauley and Gibbs.[10] Clare and Devine[2] have shown that the fitted values of the parameters are not sensitive to this assumption.

The use of crystal-field parameters (rather than spin-Hamiltonian parameters), in the fits is advantageous in that we have some prior expectations regarding their values. In general it is expected that

$$\bar{B}_2 > \bar{B}_4 > 0$$

and

$$t_4 > t_2 > 0 ,$$

where the first inequality is due to the dominance of the

TABLE IV. Values of $\partial B_{lm}/\partial \epsilon_{\mu\nu}$ for C_3 site symmetry ($l = 2, 4$) as coefficients of $\bar{B}_l(R)$. The contributions of three ligands at $\theta = \eta$, $\eta \pm 120°$ are given, $C \equiv \cos\theta$ and $S \equiv \sin\theta$; t_l is the power-law exponent.

l,m	$\dfrac{\partial B_{lm}}{\partial \epsilon_{xx}}$	$\dfrac{\partial B_{lm}}{\partial \epsilon_{zz}}$	$\dfrac{\partial B_{lm}}{\partial \epsilon_{yz}}$
2,0	$-\dfrac{3}{4}S^2[(t_2+2)(3C^2-1)+2]$	$-\dfrac{3C^2}{2}[(t_2+2)(3C^2-1)-4]$	0
2,±1	$\pm\dfrac{3}{4}\left[\dfrac{3}{2}\right]^{1/2}S^3C(t_2+2)e^{\mp i3\eta}$	0	$-\dfrac{i3}{2}\left[\dfrac{3}{2}\right]^{1/2}[2(t_2+2)S^2C^2-(1+C^2)]$
2,±2	$-\dfrac{3}{8}\left[\dfrac{3}{2}\right]^{1/2}S^2[(t_2+2)S^2-4]$	0	$\mp\dfrac{i3}{2}\left[\dfrac{3}{2}\right]^{1/2}S^3C(t_2+2)e^{\mp i3\eta}$
4,0	$-\dfrac{3S^2}{16}[(t_4+4)(35C^4-30C^2+3)+12(5C^2-1)]$	$-\dfrac{3C^2}{8}[(t_4+4)(35C^4-30C^2+3)+16(3-5C^2)]$	0
4,±1	$\pm\dfrac{3\sqrt{5}}{16}S^3C[(t_4+4)(7C^2-3)+6]e^{\mp i3\eta}$	0	$-\dfrac{i3\sqrt{5}}{8}[2(t_4+4)S^2C^2(7C^2-3)-(5C^4+6C^2-3)]$
4,±2	$-\dfrac{3}{16}\left[\dfrac{5}{2}\right]^{1/2}S^2[(t_4+4)S^2(7C^2-1)+6(1-5C^2)]$	0	$\mp\dfrac{i3}{4}\left[\dfrac{5}{2}\right]^{1/2}S^3C[(t_4+4)(7C^2-1)-5]e^{\mp i3\eta}$
4,±3	$\pm\dfrac{3\sqrt{35}}{8}S^3C[S^2(t_4+4)-3]e^{\mp i3\eta}$	$\pm\dfrac{3\sqrt{35}}{4}S^3C[(t_4+4)C^2-1]e^{\mp i3\eta}$	0
4,±4	$-\dfrac{3}{32}\left[\dfrac{35}{2}\right]^{1/2}S^6(t_4+4)e^{\mp i6\eta}$	0	$\pm\dfrac{i3}{8}\left[\dfrac{35}{2}\right]^{1/2}S^3C[S^2(t_4+4)-4]e^{\mp i3\eta}$

TABLE V. Least-squares fits of superposition-model parameters to D and G_{pq} of Cr^{3+}:Al_2O_3 with corrected values of the coefficients $\langle i(l,m)j \rangle$ (trigonal frame). D is given in cm^{-1}; G_{pq} in cm^{-1}/(unit strain). $\mathscr{D}$ is the weighted sum of square deviations. Note that our fitted values of $\overline{B}_2$ and $\overline{B}_4$ [fit (iii)] correspond to the crystal-field parameter values $v' = 1270$ cm^{-1} and $v = 1440$ cm^{-1}. Parentheses indicate error margins; square brackets are used to indicate that parameter values are fixed.

	Measured values	Stedman[a]	Fit (i)	Fit (ii)	Fit (iii) Total = rank 2 + rank 4
D	$-0.192(1)$	-0.177	-0.168	-0.183	$-0.189 = -0.115 - 0.074$
G_{11}	$3.98(8)$	2.34	4.17	4.13	$4.14 = 3.64 + 0.50$
G_{12}	$-1.57(8)$	-1.30	-1.88	-1.67	$-1.67 = -1.33 - 0.34$
G_{13}	$5.65(7)$	2.76	5.12	5.18	$5.18 = 4.71 + 0.47$
G_{44}	$1.526(35)$	1.365	1.941	1.653	$1.648 = 1.320 + 0.328$
G_{14}	$-0.263(19)$	-0.240	-0.227	-0.247	$-0.237 = -0.217 - 0.020$
G_{41}	$-0.44(6)$	-0.06	-0.06	-0.11	$-0.11 = -0.11 + 0.00$
G_{25}	$-1.45(8)$	-0.61	-1.45	-1.83	$-1.82 = -1.84 + 0.02$
G_{52}	$-1.47(6)$	-0.49	-1.36	-1.73	$-1.73 = -1.75 + 0.02$
G_{16}	$0.0(2)$	-0.30	-0.29	-0.26	$-0.26 = -0.15 - 0.11$
G_{44}	$0.0(3)$	0.15	0.14	0.16	$0.15 = 0.16 - 0.01$
$\overline{B}_2/(10^4$ $cm^{-1})$		$[2.02]$	$3.86(4)$	$4.04(4)$	$3.97(10)$
t_2		$[3]$	$0.6(2)$	$1.3(2)$	$1.24(20)$
$\overline{B}_4/(10^4$ $cm^{-1})$		$[1.17]$	$[1.17]$	$[1.17]$	$1.41(30)$
t_4		$[8.6]$	$[8.6]$	$3.4(5)$	$2.9(6)$
$\mathscr{D}$		2576	274	138	138

[a]Reference 11.

combined overlap, covalency, and electrostatic crystal-field contributions, and the second follows from the expectation that the interaction strength decreases with ligand distance. In the present case, our expectations are even more specific as Stedman[11] has analyzed the optical spectrum using the superposition model.

Table V shows the results of fitting the superposition model simultaneously to the static and strain data. The measured values of the parameters are compared with those calculated using Stedman's values ($v' = 840$ cm^{-1}, $v = 830$ cm^{-1}) (Ref. 11) of the crystal-field parameters determined from optical data, and parameters fitted under several different sets of constraints. It will be seen that the rank 4 contributions (shown separately for the final fit) are not negligible as compared to the rank 2 contributions, especially in those cases where the G_{pq} parameters are well determined experimentally.

The major result of this calculation is to show that both static and strain parameters can be fitted successfully by the same set of superposition-model parameters. The main differences between this set and that originally determined by Stedman is that the rank 2 parameters are twice as large and the power-law exponents t_l are much smaller.

It is also of interest to compare our parameter values with those obtained by Clare and Devine.[2] Their fitted values of the superposition-model parameters were

$$\overline{B}_2 = (9.1 \pm 0.5) \times 10^4 \text{ cm}^{-1} ,$$

$$\overline{B}_4 = (4.7 \pm 2) \times 10^4 \text{ cm}^{-1} ,$$

$$t_2 = -7.6 \pm 0.5 ,$$

$$t_4 = 0.9 \pm 1.0 .$$

All of these values deviate too far from the optical spectroscopic value[11] to be realistic and, in particular, the large negative value of t_2 is unphysical.

If we wish to use the parameters determined for ruby to predict results for other systems it is necessary to keep the following in mind.

(i) The ionicity of O^{2-} varies from crystal to crystal, and this may be expected to affect the values of the intrinsic parameters.

(ii) The t_l values determined for this system are "effective" in that no explicit allowance for local distortion effects has been made.

(iii) The effect of inner elasticity[12] on the strain results has been ignored in defining G_{pq} in terms of uniform strain and hence in our superposition-model analysis. It is possible, therefore, that the parameters (especially the t_l) estimated on the assumption of uniform strain, may not be reliable. Note that inner elasticity and the local distortion at a substituted ion are quite independent phenomena.

Hence the parameters determined for ruby may not be directly applicable to other systems containing Cr^{3+} ions. In particular, as the Cr^{3+} ion is larger than the Al^{3+} ion, the differences between two Cr^{3+}-O^{2-} spacings is expected to be less than that of the Al^{3+}-O^{2-} spacing in the undistorted crystal. This will have the effect of reducing the values of both the fitted exponents t_l by *the same factor*. This is in good agreement with the values quoted in Table V, where the ratios between values obtained in this work and by Stedman[11] are all in the region of 2.5.

V. THE MÜLLER AND BERLINGER MODEL

Müller and Berlinger[5] extended the application of the superposition model to the ground-state splitting of S-state ions (such as Fe^{3+}) to describe the splitting of the $^4A_2$ ground state of Cr^{3+}. We shall henceforth refer to this as the MB model. As explained previously, this extension is technically incorrect, as the effective spin operators do not transform as $\mathbb{R}_3$ tensors and arbitrary rotations do not therefore preserve $\mathbb{R}_3$ ranks. The practical

TABLE VI. Comparison of measured and predicted strain parameters for octahedral Cr^{3+} systems, based on the parameters determined for ruby. Measured values were obtained by Müller and Berlinger (Ref. 5). Errors in the predicted values are due to the uncertainties associated with fitted values of B_l and t_l. G_{pq} is given in cm^{-1}/(unit strain).

| | Cr^{3+}:MgO | | Cr^{3+}:SrTiO$_3$ | |
	Measured	Predicted	Measured	Predicted
G_{11}	0.6 ± 0.6	0.84 ± 0.35	1.13 ± 0.03	0.77 ± 0.32
G_{44}	4.2 ± 0.6	4.34 ± 0.20	4.73 ± 0.07	4.20 ± 0.19

consequences of this have been demonstrated in preceding sections where the second-rank coefficients G_{pq} of the strain spin Hamiltonian have been shown to have rank 4 as well as rank 2 contributions.

The questions that remain to be answered are, why the MB model works so well and whether the deductions of Müller and Berlinger[5] and Müller, Berlinger, and Albers,[6] concerning the structure of the systems they investigated, would also hold in a technically "correct" model?

A comparison between measured and predicted strain results, using previously derived values of the super-position-model parameters, for Cr^{3+} in MgO and SrTiO$_3$ is given in Table VI. It will be immediately apparent that the experimental data are reasonably consistent with the model developed in using approximately determined parameters and extrapolating to different systems. Why, then, does the MB model seem to work so well? Basically this seems to be due to the fact that the first attempts to test any parametrization must be carried out without much idea as to what values of the parameters can reasonably be expected, so that any values are likely to be accepted.

We begin with the superposition-model expressions for the strain parameters G_{44}^c and G_{11}^c for cubic systems:

$$G_{44}^c = \left[\frac{\zeta}{3\,\Delta E_2}\right]^2 [9.899\bar{B}_2 + (0.0559t_4 + 3.379)\bar{B}_4] \quad (10)$$

$$= 2\bar{b}_2 \quad (11)$$

(according to Müller and Berlinger[5]),

$$G_{11}^c = -2(G_{11}^t + 3G_{12}^t)$$

$$= \left[\frac{\zeta}{3\,\Delta E_2}\right]^2 [0.1343t_2\bar{B}_2 + (1.390t_4 - 0.149)\bar{B}_4]$$

$$\simeq 1.39t_4\bar{B}_4 \left[\frac{\zeta}{3\,\Delta E_2}\right]^2 \quad (12)$$

$$= -\tfrac{4}{3}\tilde{t}_2\bar{b}_2 \quad (13)$$

(according to Müller and Berlinger[5]), where the tilde has been inserted to distinguish the power-law exponent used in Ref. 5 from ours. The stable values of G_{44}^c may thus be interpreted as being due to the effective independence of this parameter on the exponents t_2 and t_4 as well as the absence of cancellations. Comparison with the above equations shows that the ratio

$$\frac{G_{11}^c}{G_{44}^c} \simeq \frac{1.39t_4}{9.899(\bar{B}_2/\bar{B}_4)+3.379} \simeq 0.140\frac{\bar{B}_4}{\bar{B}_2}t_4 \quad (14)$$

is interpreted in the MB model as $-\tfrac{4}{3}\tilde{t}_2$. Our formalism thus predicts definitely that this ratio is small and positive while such a ratio leads to a small *negative* $\tilde{t}_2$ in the MB model. The small and sometimes negative values of t_2 which appear, for example, in the case of the Gd^{3+} ground-state splitting, are the result of strongly cancelling contributions to the spin-Hamiltonian parameters. We see no reason to expect such effects in the $^4A_2$ ground state of Cr^{3+}. It appears from the above equations that the small negative $\tilde{t}_2$ values obtained in the MB model are an artifact of the model.

The more recent work of Müller et al.[6] uses the Müller and Berlinger[5] model to determine the position of the Cr^{3+} ion in the orthorhombic phase of BaTiO$_3$. The interest in this system arose from earlier work on Fe^{3+}:BaTiO$_3$ (Ref. 13), where it was found that the Fe^{3+} ions are significantly displaced from that of the Ti^{4+} ion they replace, in the sense that the Fe^{3+} ions are more "centered" with respect to the surrounding oxygen ions than the Ti^{4+} ions. Because of the problems encountered in determining reliable values of the t_l from ruby data, we have used Stedman's[11] superposition model to determine the superposition-model values of the spin-Hamiltonian parameters D and E from Eqs. (6) and (7). Our results (for the two alternative sites) are given in Table VII. They suggest that the conclusions obtained in Ref. 6 are correct: the Cr^{3+} ion, just like Fe^{3+}, is centered with respect to the surrounding ligands.

TABLE VII. Predicted and experimental values of the spin-Hamiltonian parameters for Cr^{3+}:BaTiO$_3$ (orthorhombic phase).

	Experimental	Predicted (centered)	Predicted (Ti^{4+} position)
D (10^{-4} cm^{-1})	185	148	1336
E (10^{-4} cm^{-1})	32	83	196

VI. SUMMARY AND CONCLUSIONS

We have shown that the inclusion of a larger number of excited states results in a superposition model for the levels of the $^4A_2$ ground multiplet of Cr^{3+} in ruby which provides satisfactory agreement with *both* the static and strain data using the same parameters. This model has been formulated for both trigonally and tetragonally orientated coordinate systems in order to make it generally useful. The calculated projection coefficients $\langle i(l,m)j \rangle$ are insensitive to the small changes in energy levels expected for systems with octahedral oxygen coordination. At the same time it has been emphasized that the values of the superposition-model parameters obtained for ruby may not simply be used to predict results for other systems.

The success of the MB model[5,6] has been explained as a consequence of the stability of the ratio $\bar{B}_4/\bar{B}_2$, together with the acceptance of small negative values of their parameters $\bar{t}_2$ as being realistic. In our reinterpretation of the experimental data, parameter values are obtained which are reasonably consistent with optical values.[11] This has provided an important additional check on our results.

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