

## Acoustic Paramagnetic Resonance Spectrum of $\text{Cr}^{2+}$ in MgO

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The theory of acoustic paramagnetic resonance (APR) for the  $\text{Cr}^{2+}(3d^4)$  ion at cubic crystal sites with octahedral coordination is developed for comparison with data by Marshall and Rampton for  $\text{Cr}^{2+}$  in MgO. An analytic model that takes explicit account of random strain is obtained and shown to predict in a simple way both the angular dependence of the resonance lines and the asymmetric line shape found experimentally. Although most  $\text{Cr}^{2+}$  ions experience distortions of effectively orthorhombic symmetry, the apparent presence of a tetragonal distortion at the site of the relatively few acoustically active ions is shown to result from the conditions of the experiments, in which the random strain splitting of the  $\text{Cr}^{2+}$  levels is typically larger than the acoustic energy quantum. Using this model, we show that the data for  $\text{Cr}^{2+}$  in MgO may be accounted for quantitatively if the  $\text{Cr}^{2+}$  is subject to a dynamic Jahn-Teller effect for which the tunneling splitting  $3\Gamma$  is large compared with the spin-orbit splitting of the  ${}^5E$  state. This interpretation differs from one proposed previously by Fletcher and Stevens, in which a much smaller value for  $3\Gamma$  was obtained. It is shown that from presently available data one cannot yet determine  $3\Gamma$  or other Jahn-Teller parameters of the system with any certainty. The theory of a dynamic Jahn-Teller effect for a  ${}^5E$  state is developed in a general way to encompass the regime of weak Jahn-Teller coupling, which would be applicable to APR experiments on  $\text{Fe}^{2+}$  in tetrahedral coordination, while also including the limit of strong coupling in which the adiabatic approximation used by Fletcher and Stevens is applicable.

### I. INTRODUCTION

The acoustic paramagnetic resonance (APR) spectrum of the chromous ion ( $\text{Cr}^{2+}$ ) in MgO has been studied by Marshall and Rampton<sup>1</sup> in the liquid-helium and -hydrogen temperature range at 9.46 GHz. Resonance lines were observed below 10° K which appeared to result from a transition within an excited doublet level a few  $\text{cm}^{-1}$  above a nondegenerate ground state. The strong anisotropy of the resonances as a function of the orientation of the magnetic field indicated that the  $\text{Cr}^{2+}$  ions which gave the resonances were situated at tetragonally distorted sites having the fourfold symmetry axis coincident with one of the  $\langle 100 \rangle$  crystal axes. These centers could apparently be aligned along a selected  $\langle 100 \rangle$  axis by application of an external stress. The resonances had a strongly asymmetric line shape. No resonances were observed corresponding to ions on cubic sites.

The  $\text{Cr}^{2+}$  ion in octahedral coordination is a Jahn-Teller (JT) ion, having an orbital doublet ( ${}^5E$ ) ground state in cubic symmetry, and in MgO it should be coupled strongly to the lattice phonons. The resulting dynamic JT effect has been analyzed theoretically by Fletcher and Stevens<sup>2</sup> in the adiabatic approximation.<sup>3,4</sup> The level structure for  $\text{Cr}^{2+}$  perturbed by a small tetragonal compression was shown to be consistent with having acoustically induced resonance transitions within a doublet a few  $\text{cm}^{-1}$  above a singlet ground state. Fletcher and Stevens showed, from a numerical analysis of the splitting of this doublet as a function of magnetic field and

strain, that the observed resonance spectrum could be accounted for qualitatively in terms of a distribution of tetragonal distortions assumed to arise from random strains in the lattice. Using this model, they then obtained from the resonance data a set of values for the parameters characterizing the spin-orbit and JT coupling of  $\text{Cr}^{2+}$  in MgO.

Our purpose, in this paper, is to reexamine the problem of the APR spectrum of  $\text{Cr}^{2+}$  in MgO to try to clarify a number of points that remain unclear in the treatment of Fletcher and Stevens, to try to obtain a more tractable mathematical description of the resonance spectrum, and thereby to obtain a better basis on which to attempt to determine how important the JT effects are in this and related systems. In particular, we have found it possible to obtain an analytic model which predicts in a simple way both the angular dependence of the resonances and the asymmetric line shape found experimentally. Moreover, this model accounts, in a natural way, for the apparent presence of a tetragonal distortion at the site of the active  $\text{Cr}^{2+}$  ions and for the apparent alignment of these centers in an applied stress. This effectively tetragonal distortion is shown to result under the conditions of the experiment from a selection, made by the resonance condition, among all the  $\text{Cr}^{2+}$  ions which are present in the crystal and which, in most cases, see a strain of orthorhombic symmetry. On the basis of this revised model, we can reevaluate the role of the JT coupling in this system. Our conclusion differs somewhat from that of Fletcher and Stevens: We show that  $\text{Cr}^{2+}$  in MgO indeed exhibits a dynamic

JT effect rather than a static JT distortion, but that, from presently available data, we cannot determine the JT parameters, in particular the tunneling splitting  $3\Gamma$ , with any certainty.

The  $\text{Cr}^{2+}$  ion ( $3d^4$ ) is a very interesting one in the study of JT effects, and it provides a marked contrast to the behavior of the  $\text{Fe}^{2+}$  ion ( $3d^6$ ), which has similar electronic states. In tetrahedral coordination,  $\text{Cr}^{2+}$  (ground state  ${}^5T_2$ ) is now known<sup>5</sup> to suffer a static JT distortion at liquid-helium temperature in ZnS, CdS, ZnSe, ZnTe, and CdTe, and in octahedral coordination by analogy with  $\text{Cu}^{2+}$  ( $3d^9$ , ground state  ${}^2E$ ) it would be expected also to show strong JT coupling. In contrast,  $\text{Fe}^{2+}$  in tetrahedral coordination has been found to have sufficiently weak JT coupling in its ground state ( ${}^5E$ ) so that simple crystal field theory seems to provide a good description of this state in most of the crystals in which its spin-orbit splitting has been studied by optical and magnetic methods, namely, ZnS,<sup>6-11</sup> CdS,<sup>10</sup> ZnO,<sup>10</sup> ZnSe,<sup>8,10</sup> CdSe,<sup>10</sup> ZnTe,<sup>8,10</sup> CdTe,<sup>6,8,10,12,13</sup> GaP,<sup>8</sup> GaAs,<sup>8</sup> and  $\text{MgAl}_2\text{O}_4$ .<sup>6</sup> Among these crystals, CdTe is the only one so far in which effects of the JT coupling have been identified in the  ${}^5E$  ground state.<sup>13</sup> For  $\text{Fe}^{2+}$  in MgO, the JT coupling in the  ${}^5T_2$  ground state is again rather weak, although significant departures from the crystal field model have been attributed to a dynamic JT effect.<sup>14</sup> In evaluating the role of JT effects for these ions in various lattices, we would find it of great interest to be able to obtain reliable values for the JT parameters for  $\text{Cr}^{2+}$  in MgO and other crystals with octahedral coordination, and it was in the hope of doing this on the basis of a better understanding of the model proposed by Fletcher and Stevens<sup>2</sup> that the present work was undertaken. Unfortunately, although we have been able to account qualitatively for all of Marshall and Rampton's observations,<sup>1</sup> we conclude that we are not yet in a position to obtain these parameters from the available data and that more experimental measurements and analysis will be necessary. Since APR experiments may also be able to cast more light on the properties of  $\text{Fe}^{2+}$  in fourfold or eightfold coordination, we have included in this paper a general treatment of dynamic JT effects for a  ${}^5E$  state which is applicable over the full range of possible coupling strengths. Our treatment thus includes both the weak-coupling regime appropriate to  $\text{Fe}^{2+}$  as well as the strong-coupling limit to which the work of Fletcher and Stevens, using the adiabatic approximation, is applicable.

We will begin our treatment with a review in Sec. II of the general analysis of the dynamic JT effect<sup>15,16</sup> for an ion in an orbital doublet state in cubic symmetry, in order to establish the connection between the present analysis for a  ${}^5E$  state and that given previously by the author for a  ${}^2E$  state.<sup>16,17</sup>

This treatment also includes the results obtained in the strong-coupling limit by Fletcher and Stevens using the adiabatic approximation. In Sec. III we analyze the APR transitions to be expected from the spin-orbit levels of the  ${}^5E$  term in cubic symmetry, using perturbation theory and taking into account the level splittings caused by the random strains, which, as we will show, are responsible for the unusual line shape. This analysis is extended in Sec. IV to include the effect of the random strains in coupling the different spin-orbit levels. We treat the effect of an externally applied stress in Sec. V, and in Sec. VI the theory is related to the experimental resonance data for  $\text{Cr}^{2+}$  in MgO. An estimate for the JT energy of  $\text{Cr}^{2+}$  in MgO is attempted in Sec. VII. The conclusions are summarized and discussed in Sec. VIII.

## II. DYNAMIC JT EFFECT FOR A ${}^5E$ STATE

### A. General Analysis for an $E$ State

In our treatment of the dynamic JT effect for an ion in a  ${}^5E$  state at a site of cubic symmetry in a crystal, we will use the model<sup>2,17,18</sup> of an orbital doublet electronic state belonging to the irreducible representation  $E$  of the rotation group  $O$  of the cube (or of the tetrahedral group  $T_d$ ), coupled to a degenerate pair of vibrational modes  $Q_g$ ,  $Q_e$  also belonging to  $E$ .<sup>19</sup> This model appears to be a gross oversimplification of the actual situation of an ion in a crystal, where the coupling is with the entire spectrum of lattice phonons as well as with any local modes that are present. Nevertheless, as discussed elsewhere,<sup>11,14,16</sup> we believe this model is really a fairly good representation of the actual situation throughout the full range of possible JT coupling strengths, at least for the spin-orbit levels close to the ground state and with the proviso that the phonons that couple strongly have energies appreciably higher than the excitation energies of these levels. The modes  $Q_g$ ,  $Q_e$  therefore represent, in an average sense, the effect on these lowest spin-orbit levels of JT coupling with these many modes, and appropriate values for the frequency and effective mass for  $Q_g$ ,  $Q_e$  must be chosen accordingly. In the regime of strong coupling,  $Q_g$  and  $Q_e$  may conveniently be thought of as primarily involving the displacements of the cluster of nearest-neighbor ions surrounding the JT ion, in agreement with the cluster model used by Fletcher and Stevens.<sup>2</sup> Although such a mode of the cluster is not a normal mode of the crystal, the effect of the strong JT coupling is to select, as the effective JT mode, a linear combination of normal modes which maximizes the JT coupling.<sup>11</sup> Long-wavelength acoustic modes which are "on speaking terms" with the spin-orbit levels, on the other hand, are relatively ineffective in the JT coupling as far as shifting the energies of the spin-orbit levels or affecting their reduction fac-

tors, as has been shown in the previous work<sup>14</sup> on Fe<sup>2+</sup> in MgO. These modes serve primarily, therefore, to induce transitions among the levels and thus to determine their lifetimes and relaxation behavior, but they may conveniently be omitted from the JT model in determining the vibronic states. Our model, in any case, leads to levels having the correct symmetry, and it is the symmetry properties of the levels on which the critical features of our analysis of the APR spectrum depend.

The basic vibronic Hamiltonian of our model is

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{JT} + \mathcal{H}_W, \quad (1)$$

where, in the notation<sup>19</sup> used in earlier work,<sup>16,17</sup>

$$\mathcal{H}_0 = (2\mu)^{-1} [P_\theta^2 + P_\epsilon^2 + (\mu\omega)^2(Q_\theta^2 + Q_\epsilon^2)] \mathcal{I} \quad (2)$$

describes the elastic and kinetic energy of the vibrational modes, and

$$\mathcal{H}_{JT} = V(Q_\theta \mathbf{u}_\theta + Q_\epsilon \mathbf{u}_\epsilon) \quad (3)$$

gives the linear JT coupling of the electronic orbital doublet  $|E\theta\rangle$ ,  $|E\epsilon\rangle$ . As in the earlier work,<sup>17</sup>  $\mathcal{I}$ ,  $\alpha_2$ ,  $\mathbf{u}_\theta$ , and  $\mathbf{u}_\epsilon$  denote electronic operators transforming, respectively, as  $A_1$ ,  $A_2$ ,  $E\theta$ , and  $E\epsilon$  and defined as follows:

$$\begin{aligned} \mathcal{I} &= |E\theta\rangle\langle E\theta| + |E\epsilon\rangle\langle E\epsilon|, \\ \alpha_2 &= +i(|E\epsilon\rangle\langle E\theta| - |E\theta\rangle\langle E\epsilon|), \\ \mathbf{u}_\theta &= -|E\theta\rangle\langle E\theta| + |E\epsilon\rangle\langle E\epsilon|, \\ \mathbf{u}_\epsilon &= +|E\theta\rangle\langle E\epsilon| + |E\epsilon\rangle\langle E\theta|. \end{aligned} \quad (4)$$

The JT stabilization energy  $E_{JT}$  obtained for linear coupling alone is

$$E_{JT} = V^2/2\mu\omega^2 \quad (5)$$

and corresponds to all the points in  $Q$  space lying on the circle<sup>20</sup> for which

$$\rho = \rho_0 \equiv |V|/\mu\omega^2, \quad (6)$$

where we define  $\rho$  and  $\theta$  by

$$Q_\theta = \rho \cos\theta, \quad Q_\epsilon = \rho \sin\theta. \quad (7)$$

The final term in Eq. (1) is given<sup>16,21,22</sup> by

$$\mathcal{H}_W = V_a[\mathbf{u}_\theta(Q_\epsilon^2 - Q_\theta^2) + 2\mathbf{u}_\epsilon Q_\epsilon Q_\theta] + V_c Q_\theta(Q_\theta^2 - 3Q_\epsilon^2) \mathcal{I} \quad (8)$$

and describes the higher-order coupling allowed in cubic symmetry. When treated as a weak perturbation on the linear coupling,  $\mathcal{H}_W$  changes the energy at the bottom of the trough in the lower adiabatic potential energy surface of the Hamiltonian (1) by an amount

$$\mathcal{H}_W \sim -\beta \cos 3\theta, \quad (9)$$

where we define

$$\beta = -(\mp V_a \rho_0^2 + V_c \rho_0^3) \quad (10)$$

and take the upper (lower) sign in Eq. (10) for  $V < 0$

( $V > 0$ ).  $\mathcal{H}_W$  therefore destroys the rotational symmetry<sup>20</sup> in this lower surface as a function of  $\theta$  and thereby selects three configurations of minimum energy from the infinite number of energetically equivalent configurations that we had at the bottom of the trough for linear JT coupling alone.

The vibronic ground state of the Hamiltonian (1) is a doublet  $E$  state, and with only linear JT coupling the first excited state is an accidentally degenerate doublet ( $A_1 + A_2$ ), the excitation energy of which is given quite accurately for  $E_{JT}/\hbar\omega \gtrsim 1$  (see Fig. 3 of Ref. 17) by

$$\Delta_1 = 2\alpha, \quad (11)$$

where

$$\alpha = \hbar^2/2\mu\rho_0^2 = \hbar\omega(4E_{JT}/\hbar\omega)^{-1}. \quad (12)$$

This excited state is split by  $\mathcal{H}_W$ , and the lower singlet approaches the ground-state doublet asymptotically as the strength of  $\mathcal{H}_W$  increases. The energy separation  $3\Gamma$  of this singlet from the doublet, which is also called the "tunneling splitting," has been calculated by O'Brien,<sup>3</sup> Williams *et al.*,<sup>23</sup> and Fletcher and Stevens<sup>2</sup> in the adiabatic approximation, in which coupling via the kinetic energy between the upper and lower potential energy surfaces of Eq. (1) is neglected. This approximation should be quite accurate for  $E_{JT}/\hbar\omega \gtrsim 2$ , and a graph showing  $3\Gamma/\alpha$  as a function of  $|A|/\alpha$  has been given by Williams *et al.* (see Fig. 3 of Ref. 23). This lower singlet state belongs to the irreducible representation  $A_1(A_2)$  if  $V$  and  $\beta$  have the same (opposite) sign.

The effect of perturbations in splitting and shifting the electronic orbital doublet  $|E\theta\rangle$ ,  $|E\epsilon\rangle$  may be represented in the general form

$$\mathcal{V} = G_1 \mathcal{I} + G_2 \alpha_2 + G_\theta \mathbf{u}_\theta + G_\epsilon \mathbf{u}_\epsilon, \quad (13)$$

where the  $G$ 's are functions of the components of external perturbations such as magnetic fields and strain, and also of other operators such as electronic or nuclear spin.<sup>24</sup>  $G_1$  is symmetric under cubic transformations of these components,  $G_2$  belongs to the irreducible representation  $A_2$ , and  $G_\theta$  and  $G_\epsilon$  transform as partners belonging to  $E$ . The matrix elements of  $\mathcal{V}$ , with respect to the vibronic  $E$  ground state  $|\Psi_{g\theta}\rangle$ ,  $|\Psi_{g\epsilon}\rangle$ , are then identical with those of

$$\mathcal{V}_g = G_1 \mathcal{I} + p G_2 \alpha_2 + q(G_\theta \mathbf{u}_{g\theta} + G_\epsilon \mathbf{u}_{g\epsilon}), \quad (14)$$

where  $p$  and  $q$  are the reduction factors introduced in the earlier work<sup>17</sup> and defined by

$$q = -\langle \Psi_{g\theta} | \mathbf{u}_\theta | \Psi_{g\theta} \rangle, \quad (15)$$

$$p = +i \langle \Psi_{g\theta} | \alpha_2 | \Psi_{g\epsilon} \rangle,$$

and  $\alpha_{g2}$ ,  $\mathbf{u}_{g\theta}$ , and  $\mathbf{u}_{g\epsilon}$  are operators defined with respect to the vibronic ground state in analogy with Eq. (4), namely,

$$\begin{aligned} \alpha_{g2} &= +i (|\Psi_{g\epsilon}\rangle\langle\Psi_{g\theta}| - |\Psi_{g\theta}\rangle\langle\Psi_{g\epsilon}|), \\ \mathfrak{u}_{g\theta} &= -|\Psi_{g\theta}\rangle\langle\Psi_{g\theta}| + |\Psi_{g\epsilon}\rangle\langle\Psi_{g\epsilon}|, \\ \mathfrak{u}_{g\epsilon} &= +|\Psi_{g\theta}\rangle\langle\Psi_{g\epsilon}| + |\Psi_{g\epsilon}\rangle\langle\Psi_{g\theta}|. \end{aligned} \quad (16)$$

Expressions for  $q$  and  $p$  have been given elsewhere<sup>16,17,23</sup>; for the purposes of this paper it will suffice to know that  $p$  and  $q$  decrease from unity with increasing  $(E_{JT}/\hbar\omega)$ , and that for  $(E_{JT}/\hbar\omega) \gtrsim 2$ ,  $p$  and  $q$  are very close to their limiting values  $p \sim 0$  and  $q \sim \frac{1}{2}$ . We must also introduce a third parameter  $r$  given by the matrix elements of  $\mathfrak{u}_\theta$  and  $\mathfrak{u}_\epsilon$  between the vibronic ground state and the first singlet excited state  $|\Psi_{A1}\rangle$  or  $|\Psi_{A2}\rangle$ . We define this<sup>16</sup> to be

$$r = \langle\Psi_{A1}|\mathfrak{u}_\theta|\Psi_{g\theta}\rangle = \langle\Psi_{A1}|\mathfrak{u}_\epsilon|\Psi_{g\epsilon}\rangle \quad (17a)$$

if the singlet is  $A_1$ , and

$$r = \langle\Psi_{A2}|\mathfrak{u}_\epsilon|\Psi_{g\theta}\rangle = -\langle\Psi_{A2}|\mathfrak{u}_\theta|\Psi_{g\epsilon}\rangle \quad (17b)$$

if the singlet is  $A_2$ .

### B. Spin-Orbit Splitting

For a  ${}^5E$  state we have an electronic spin  $S=2$  and a second-order spin-orbit interaction<sup>25</sup> within this state which can be written in the form of Eq. (13) as

$$\mathfrak{H}_{so} = -\frac{1}{8}K \{ [3S_x^2 - S(S+1)]\mathfrak{u}_\theta + \sqrt{3}(S_x^2 - S_y^2)\mathfrak{u}_\epsilon \}. \quad (18)$$

For  $\text{Cr}^{2+}$  or  $\text{Fe}^{2+}$  ions, this expression serves to describe not only the effect of spin-orbit coupling among the states derived from the  ${}^5D$  term of the free ion [for which  $\lambda(\vec{L} \cdot \vec{S})$  gives the spin-orbit coupling, and for which the cubic-field splitting is  $\Delta = 10|Dq|$ ], but it also describes the effective spin-spin interaction,<sup>26</sup> which includes the effect of spin-orbit coupling to higher states with  $S=1$ . The coefficient  $K$  is given<sup>13</sup> when  ${}^5E$  is the ground state by

$$K = 6[(\lambda^2/\Delta) + \rho], \quad (19)$$

where  $\rho$  is the effective spin-spin interaction parameter,<sup>26</sup> and, of course,  $\lambda$  and  $\rho$  may both be changed from their free-atom values by the crystalline environment.

The effect of the JT coupling on the spin-orbit splitting of the vibronic  $E$  ground state, then, is to replace the effective interaction coefficient  $K$  by

$$K' = qK, \quad (20)$$

in accord with Eq. (14). If the nearest excited state has an excitation energy much larger than the spin-orbit splitting, namely,  $3\Gamma \gg 4K$ , the splitting of the ground state is the same as in the crystal field model except for the reduced size of the splitting. The five spin-orbit levels are then uniformly spaced,<sup>6,25</sup> the separation of adjacent levels being  $K'$ . The order of the levels is  $\Gamma_1, \Gamma_4, \Gamma_3, \Gamma_5$ , and

$\Gamma_2$ , with  $\Gamma_1$  the ground state if  $K > 0$ . However, if  $3\Gamma$  is not large compared to  $4K$ , we must include the spin-orbit coupling to the excited states. If only the lowest singlet is low enough in energy to be important, there are then two additional spin-orbit levels to be considered; these are  $\Gamma_3$  and  $\Gamma_5$  if the singlet is  $A_1$  (since the spin states with  $S=2$  span  $\Gamma_3 + \Gamma_5$ ), and  $\Gamma_3$  and  $\Gamma_4$  if the singlet is  $A_2$ . The relative energies of the  $\Gamma_1, \Gamma_2$ , and  $\Gamma_3$  levels are independent of whichever singlet is lower and are given by

$$\Gamma_1: E = -2Kq, \quad (21a)$$

$$\Gamma_2: E = +2Kq, \quad (21b)$$

$$\Gamma_3: E^{(*)} = \frac{3}{2}\Gamma \pm [(\frac{3}{2}\Gamma)^2 + 2K^2r^2]^{1/2}. \quad (21c)$$

When the lower singlet is  $A_1$ , the energies for  $\Gamma_4$  and  $\Gamma_5$  are given by

$$\Gamma_4: E = -Kq, \quad (21d)$$

$$\Gamma_5: E^{(*)} = \frac{3}{2}\Gamma + \frac{1}{2}Kq \pm [(\frac{3}{2}\Gamma - \frac{1}{2}Kq)^2 + K^2r^2]^{1/2}, \quad (21e)$$

or, when the lower singlet is  $A_2$ , by

$$\Gamma_4: E^{(*)} = \frac{3}{2}\Gamma - \frac{1}{2}Kq \pm [(\frac{3}{2}\Gamma + \frac{1}{2}Kq)^2 + K^2r^2]^{1/2}, \quad (21d')$$

$$\Gamma_5: E = +Kq. \quad (21e')$$

These results agree with those obtained by Fletcher and Stevens<sup>2</sup> for the adiabatic approximation in the strong-coupling limit,<sup>27</sup> whereas for  $3\Gamma \gg 4K$  the lower five levels from Eqs. (21) are uniformly spaced, as found earlier, with a separation  $K'$ , agreeing with Eq. (20). It is, in fact, a good approximation for most values of the JT coupling parameters to replace  $r^2$  in Eqs. (21) by its limiting value<sup>16,23</sup> for large  $|\beta|/\alpha$  in the adiabatic approximation, namely,  $r^2 \sim 2q^2$ . The resulting energy levels are plotted as functions of  $3\Gamma/Kq$  in Fig. 1. The limit as  $3\Gamma/Kq \rightarrow 0$  of course corresponds to the static JT effect, in which it may be shown that only the five spin states of  $S=2$  corresponding to each of the three tetragonally distorted configurations are coupled strongly by perturbations such as magnetic fields or strains. This limit is attained in practice<sup>16</sup> when the random strain splittings of the levels (see Secs. IID and IV) are larger than  $3\Gamma$ , and in this limit the spin levels belonging to each distorted configuration are displaced as a group by an additional strain. In this limit, therefore, the fluctuating strain associated with an acoustic wave cannot, to a first approximation, induce transitions either among the spin levels of a single distorted configuration or between spin levels of the different configurations. In the static JT limit, therefore, the vibronic levels behave in the same way as spin states ( $S=2$ ) associated with three static tetragonally distorted centers, and the APR absorption would be very weak compared to what is

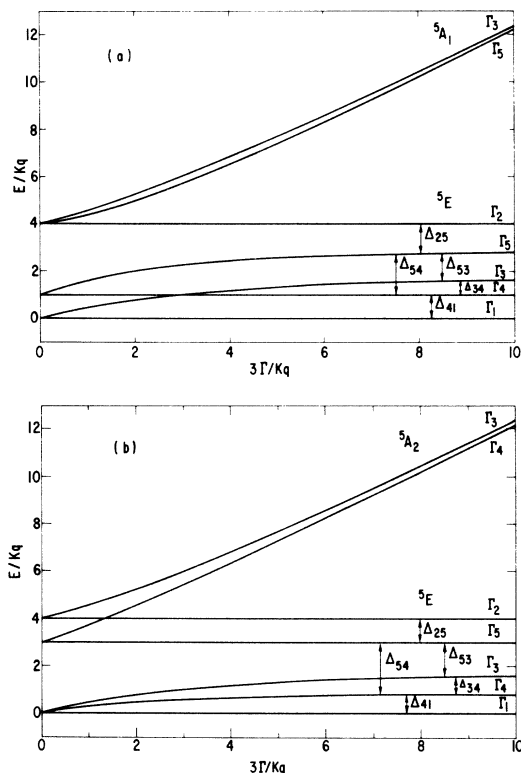


FIG. 1. Relative energies of spin-orbit levels ( $S=2$ ) derived from an orbital doublet  ${}^5E$  electronic state in cubic symmetry for a strong JT coupling, showing the approach to the limit of a static JT effect (after Bates and Dixon, Ref. 41). The levels shown include those derived from the lowest orbital singlet tunneling level (a)  ${}^5A_1$  or (b)  ${}^5A_2$ . Energies are given relative to the  $\Gamma_1$  ground state in units of the reduced spin-orbit parameter  $Kq$ , as a function of the tunneling splitting  $3\Gamma$  [see Eqs. (21) in text, where the approximation  $r^2=2q^2$  has been used in plotting the curves].

found in the dynamic JT regime with which our analysis in this paper is principally concerned.

### C. Zeeman Splitting

In a  ${}^5E$  electronic state in cubic symmetry, the linear coupling of the spin to a magnetic field  $\vec{H}$  has the same general form as that derived<sup>17</sup> for a  ${}^2E$  state; we have

$$\mathcal{H}_H = g_1 \mu_B (\vec{S} \cdot \vec{H}) + \frac{1}{2} g_2 \mu_B \{ [3S_x H_x - (\vec{S} \cdot \vec{H})] u_0 + \sqrt{3} [S_x H_x - S_y H_y] u_1 \}, \quad (22)$$

where  $\mu_B = (e\hbar/2mc)$  is the Bohr magneton. For  $\text{Cr}^{2+}$  or  $\text{Fe}^{2+}$  with  ${}^5E$  the ground state,  $g_1$  and  $g_2$  are given to first order in the spin-orbit interaction by

$$\begin{aligned} g_1 &= 2 - (4\lambda/\Delta), \\ g_2 &= -(4\lambda/\Delta). \end{aligned} \quad (23)$$

The effect of the JT coupling on the matrix elements of  $\mathcal{H}_H$  among the states derived from the vibronic  $E$  ground state is then to introduce the reduction factor  $q$  into the anisotropic terms of Eq. (22), in accord with Eqs. (14).

We shall be particularly interested in obtaining the  $g$  factors which describe the linear splitting of each of the spin-orbit triplet levels  $\Gamma_4$  and  $\Gamma_5$ , from Eqs. (21), in a magnetic field. From symmetry considerations, the  $\Gamma_1$  and  $\Gamma_2$  singlets and the  $\Gamma_3$  doublets are not affected by a magnetic field to first order in  $H$ , while for each  $\Gamma_4$  or  $\Gamma_5$  triplet the Zeeman splitting must be isotropic and is given by

$$\mathcal{H}_{gH} = g \mu_B (\vec{\mathcal{J}}' \cdot \vec{H}). \quad (24)$$

Here  $g$  is the  $g$  factor for the particular spin-orbit triplet, while  $\vec{\mathcal{J}}'$  is an effective spin operator ( $\mathcal{J}'=1$ ) acting within that triplet alone and defined with respect to the states  $|\Gamma_4 x\rangle$ ,  $|\Gamma_4 y\rangle$ ,  $|\Gamma_4 z\rangle$  or  $|\Gamma_5 \xi\rangle$ ,  $|\Gamma_5 \eta\rangle$ ,  $|\Gamma_5 \zeta\rangle$  of the particular vibronic triplet by

$$\mathcal{J}'_x = +i(|\Gamma_4 y\rangle\langle\Gamma_4 x| - |\Gamma_4 x\rangle\langle\Gamma_4 y|) \quad (25a)$$

or

$$\mathcal{J}'_x = +i(|\Gamma_5 \eta\rangle\langle\Gamma_5 \xi| - |\Gamma_5 \xi\rangle\langle\Gamma_5 \eta|), \quad (25b)$$

etc. From the wave functions obtained for the levels of Eqs. (21), using Eqs. (14) and (17), we obtain for the case in which the lower singlet is  $A_1$  the following  $g$  factors<sup>28</sup>:

$$\Gamma_4: \quad g = \frac{1}{2} g_1 - q g_2, \quad (26a)$$

$$\Gamma_5^{(-)}: \quad g = \frac{1}{2} g_1 (1 - 3 \sin^2 \beta_1) + q g_2 \cos^2 \beta_1 - r g_2 \sin \beta_1 \cos \beta_1, \quad (26b)$$

$$\Gamma_5^{(+)}: \quad g = -g_1 (1 - \frac{3}{2} \sin^2 \beta_1) + q g_2 \sin^2 \beta_1 + r g_2 \sin \beta_1 \cos \beta_1. \quad (26c)$$

Here  $\Gamma_5^{(-)}$  and  $\Gamma_5^{(+)}$  denote the lower and higher  $\Gamma_5$  levels from Eq. (21e), respectively, and we have

$$\tan 2\beta_1 = -2rK/(3\Gamma - Kq). \quad (27)$$

When the lower singlet is  $A_2$  we have instead

$$\Gamma_5: \quad g = \frac{1}{2} g_1 + q g_2, \quad (28a)$$

$$\Gamma_4^{(-)}: \quad g = \frac{1}{2} g_1 (1 - 3 \sin^2 \beta_2) - q g_2 \cos^2 \beta_2 - r g_2 \sin \beta_2 \cos \beta_2, \quad (28b)$$

$$\Gamma_4^{(+)}: \quad g = -g_1 (1 - \frac{3}{2} \sin^2 \beta_2) - q g_2 \sin^2 \beta_2 + r g_2 \sin \beta_2 \cos \beta_2, \quad (28c)$$

where

$$\tan 2\beta_2 = -2rK/(3\Gamma + Kq). \quad (29)$$

These results [Eqs. (26)–(29)] again agree with those obtained by Fletcher and Stevens<sup>2</sup> in the adiabatic approximation.<sup>27</sup>

#### D. Strain Splitting

The splitting of the electronic orbital  $E$  doublet, as a result of a strain in the crystal described by

$$e_\theta = e_{xx} - \frac{1}{2}(e_{xx} + e_{yy}), \quad (30)$$

$$e_\epsilon = \frac{1}{2}\sqrt{3}(e_{xx} - e_{yy}),$$

where

$$e_{ij} = \frac{1}{2} \left( \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right) \quad (31)$$

is a component of the strain tensor, may be represented by

$$\mathcal{H}_S = V_2(e_\theta \mathbf{u}_\theta + e_\epsilon \mathbf{u}_\epsilon), \quad (32)$$

where  $V_2$  is the strain coupling coefficient. (The strains  $e_{xy}$ ,  $e_{yz}$ , and  $e_{zx}$  do not affect the doublet if we neglect spin-orbit coupling, and their effect,<sup>16,17</sup> even with spin-orbit coupling, is quenched by the JT interaction via the reduction factor  $b$ .) In the form of Eq. (32), the strain coupling appears as a direct splitting of the electronic degeneracy as a result of the deformation of the crystal; we may alternatively view the effect of strain to be that of shifting the equilibrium position of the active modes  $Q_\theta$ ,  $Q_\epsilon$  from  $Q_\theta = Q_\epsilon = 0$  in the elastic energy in Eq. (2) to

$$Q_\theta^0 = De_\theta, \quad (33)$$

$$Q_\epsilon^0 = De_\epsilon,$$

where  $D$  is an appropriate coefficient. However, as proved elsewhere<sup>14,16</sup> by a simple change of variable, the effect of this change on the states of the JT system is identical to that of Eq. (32) if  $V_2$  is given the value

$$V_2 = DV, \quad (34)$$

where  $V$  is the JT coupling coefficient.  $\mathcal{H}_S$  as given by Eq. (32) therefore suffices as a general phenomenological expression for the effect of strain on the system.

We shall be particularly concerned with the first-order strain splitting of the  $\Gamma_4$  and  $\Gamma_5$  spin-orbit triplet levels of the JT system, whose unperturbed energies are given by Eqs. (21). Within each such triplet, the effect of  $\mathcal{H}_S$  in Eq. (32) is equivalent to that of

$$\mathcal{H}_S(\Gamma_i) = V_S[\mathcal{G}'_\theta e_\theta + \mathcal{G}'_\epsilon e_\epsilon], \quad (35)$$

where in terms of  $\vec{\mathcal{G}}'$  from Eq. (25) for the same triplet we define

$$\begin{aligned} \mathcal{G}'_\theta &= \mathcal{G}'_x{}^2 - \frac{1}{2}(\mathcal{G}'_x{}^2 + \mathcal{G}'_y{}^2), \\ \mathcal{G}'_\epsilon &= \frac{1}{2}\sqrt{3}(\mathcal{G}'_x{}^2 - \mathcal{G}'_y{}^2). \end{aligned} \quad (36)$$

Thus, for example, for one of the  $\Gamma_4$  levels, we have

$$\begin{aligned} \mathcal{G}'_\theta &= -|\Gamma_4 z\rangle\langle\Gamma_4 z| + \frac{1}{2}|\Gamma_4 x\rangle\langle\Gamma_4 x| + \frac{1}{2}|\Gamma_4 y\rangle\langle\Gamma_4 y|, \\ \mathcal{G}'_\epsilon &= \frac{1}{2}\sqrt{3}(-|\Gamma_4 x\rangle\langle\Gamma_4 x| + |\Gamma_4 y\rangle\langle\Gamma_4 y|). \end{aligned} \quad (37)$$

In the notation of Eqs. (26)–(29), we find, then, for these strain coupling coefficients when the  $A_1$  singlet is lower,

$$\begin{aligned} \Gamma_4: \quad V_S &= -qV_2, \\ \Gamma_5^{(-)}: \quad V_S &= +qV_2 \cos^2\beta_1 + 2rV_2 \sin\beta_1 \cos\beta_1, \\ \Gamma_5^{(+)}: \quad V_S &= +qV_2 \sin^2\beta_1 - 2rV_2 \sin\beta_1 \cos\beta_1, \end{aligned} \quad (38)$$

and when the  $A_2$  singlet is lower,

$$\begin{aligned} \Gamma_5: \quad V_S &= +qV_2, \\ \Gamma_4^{(-)}: \quad V_S &= -qV_2 \cos^2\beta_2 + 2rV_2 \sin\beta_2 \cos\beta_2, \\ \Gamma_4^{(+)}: \quad V_S &= -qV_2 \sin^2\beta_2 - 2rV_2 \sin\beta_2 \cos\beta_2. \end{aligned} \quad (39)$$

### III. APR SPECTRUM FOR A ${}^5E$ STATE

Let us now consider the APR absorption spectrum to be expected from transitions within one of the  $\Gamma_4$  or  $\Gamma_5$  spin-orbit triplets, in the presence of a small crystal strain characterized by values of  $e_\theta$ ,  $e_\epsilon$  from Eqs. (30) which are taken to vary at random among the chromium sites. The probability distribution  $p(e_\theta, e_\epsilon)$  for  $e_\theta$  and  $e_\epsilon$  presumably looks somewhat similar to that in Fig. 2(a) for a cubic crystal with no externally applied stress; this distribution is not necessarily independent of the azimuthal angle  $\psi$  in the  $(e_\theta, e_\epsilon)$  plane, where we have

$$\begin{aligned} e_\theta &= (e_\theta^2 + e_\epsilon^2)^{1/2} \cos\psi, \\ e_\epsilon &= (e_\theta^2 + e_\epsilon^2)^{1/2} \sin\psi; \end{aligned} \quad (40)$$

but to satisfy the requirements of cubic symmetry  $p(e_\theta, e_\epsilon)$  must be invariant to a rotation in  $\psi$  by  $\pm \frac{2}{3}\pi$  and must be symmetric under reflection in the  $e_\theta$  axis ( $\psi \rightarrow -\psi$ ). We assume, moreover, that the typical strain splitting of our triplet is appreciably larger than the energy quantum  $h\nu$  of the incident acoustic wave. We believe this assumption should be appropriate in the experimental situation of Marshall and Rampton<sup>1</sup> because their frequency 9.46 GHz ( $0.315 \text{ cm}^{-1}$ ) is smaller than our estimate of  $\sim 1 \text{ cm}^{-1}$  for typical strain splittings (see Sec. VI). In order to simplify our discussion in this section, we will assume for now that, despite these rather large splittings, we may nevertheless ignore strain coupling between the different spin-orbit levels of Eqs. (21), so that we may treat each triplet separately. This assumption will be removed in Sec. IV, where the necessary modifications of the theory appropriate to a more realistic analysis of the case of  $\text{Cr}^{2+}$  in  $\text{MgO}$  will be given.

Since under our assumptions both  $e_\theta$  and  $e_\epsilon$  are

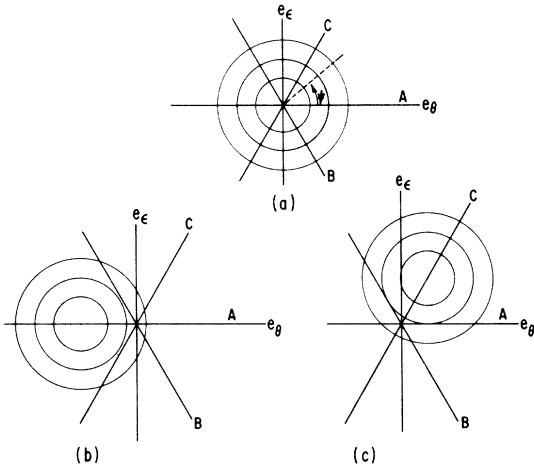


FIG. 2. Contours of equal probability (schematic) as given by the probability distribution  $p(e_\theta, e_\epsilon)$  for the components  $e_\theta, e_\epsilon$  of the total strain at  $\text{Cr}^{2+}$  sites in a cubic MgO crystal: (a) local random strain with no externally applied stress; (b) local random strain plus a uniform uniaxial compression along [001]; (c) local random strain plus a uniform uniaxial compression along [010]. Lines A, B, and C are the loci of points for which the local strain has tetragonal symmetry with respect to the [001], [100], and [010] crystal axes, respectively.

typically nonzero for most of the chromium ions in the crystal, for most of these ions all three levels of our triplet are separated from each other by more than  $h\nu$ , the effective site symmetry is orthorhombic, and no resonance absorption is possible. There are a few ions, however, for which  $e_\theta$  and  $e_\epsilon$  happen to lie close enough to the lines A, B, and C in Fig. 2(a) [defined by (A)  $\psi = 0$  or  $\pi$ , (B)  $\psi = +\frac{2}{3}\pi$  or  $-\frac{1}{3}\pi$ , and (C)  $\psi = -\frac{2}{3}\pi$  or  $+\frac{1}{3}\pi$ ] so that two of the triplet levels are separated by less than  $h\nu$  from each other according to Eq. (35). These ions then see a nearly tetragonal strain (a compression for  $\psi = \pm\frac{1}{3}\pi$  or  $\pi$ , an elongation for  $\psi = 0$  or  $\pm\frac{2}{3}\pi$ ) having the tetragonal axis along the (A) [001], (B) [100], or (C) [010] directions. For most of the ions in each of these three sets, the third level is well separated from the other two, and we may treat the possible resonance transition as occurring within this isolated pair, the separation of which depends both on the applied magnetic field and on the part of the local strain which represents the departure from perfect tetragonal symmetry. Only when  $e_\theta$  and  $e_\epsilon$  are both near zero are all three levels of the triplet close together; under our assumptions, such ions constitute a small fraction of those in our three sets A, B, and C, so that we will ignore them. Further justification for this assumption will be apparent later in our treatment.

We now consider the dependence on the magnetic field of the separation of the pair of states  $|\Gamma_4x\rangle$

and  $|\Gamma_4y\rangle$  for an ion in the set A, for which  $e_\epsilon$  is small and  $e_\theta$  large (for definiteness we take our triplet to be  $\Gamma_4$ ; the analysis for a  $\Gamma_5$  triplet is identical, with  $|\Gamma_5\xi\rangle, |\Gamma_5\eta\rangle, |\Gamma_5\xi\rangle$  replacing  $|\Gamma_4x\rangle, |\Gamma_4y\rangle, |\Gamma_4z\rangle$ ). The separation of the third state  $|\Gamma_4z\rangle$  from the mean energy of the pair is then

$$W = -\frac{3}{2} V_S e_\theta \quad (41)$$

from Eq. (35), and we will take account of the magnetic coupling between this state and our pair by perturbation theory. Before doing this, however, let us consider the terms of order  $H^2$  which result in cubic symmetry from the second-order coupling of our triplet, via the magnetic field, to the other spin-orbit levels of Eqs. (21). Their general form may be written down from symmetry considerations as follows:

$$\begin{aligned} \mathcal{H}_H^{(2)}(\Gamma_{4\text{ or }5}) = & -a'[\mathcal{G}'_\theta(3H_x^2 - H^2) + \mathcal{G}'_\epsilon\sqrt{3}(H_x^2 - H_y^2)] \\ & -b'[\mathcal{T}'_\zeta H_y H_x + \mathcal{T}'_\eta H_x H_x + \mathcal{T}'_\zeta H_x H_y] - c'H^2, \end{aligned} \quad (42)$$

where in addition to the operators  $\mathcal{G}'_\theta, \mathcal{G}'_\epsilon$ , which transform as E and were defined in Eqs. (37), we have introduced  $T_2$  operators  $\mathcal{T}'_\zeta, \mathcal{T}'_\eta, \mathcal{T}'_\zeta$  defined as

$$\mathcal{T}'_\zeta = \mathcal{J}'_x \mathcal{J}'_y + \mathcal{J}'_y \mathcal{J}'_x = -|\Gamma_4x\rangle\langle\Gamma_4y| - |\Gamma_4y\rangle\langle\Gamma_4x|, \quad (43)$$

etc. The coefficients  $a', b', c'$  will be given later for the particular triplet levels of interest. Assuming for now that these coefficients giving the effect of the distant levels on the states  $|\Gamma_4x\rangle, |\Gamma_4y\rangle$  are not significantly changed by the local strain, we obtain the effective Hamiltonian for this pair, to second order in  $H$  and including the strain, from the matrix elements of Eqs. (24), (35), and (42) with respect to these states. To this we add the second-order corrections resulting from the magnetic coupling via Eq. (24) to  $|\Gamma_4z\rangle$ ; the result may be expressed in operator form as

$$\mathcal{H}_{\text{eff}} = g\mu_B\sigma_2 H_x + [a(H_x^2 - H_y^2) - \frac{1}{2}\sqrt{3}V_S e_\epsilon]\sigma_3 + b\sigma_1 H_x H_y, \quad (44)$$

where for simplicity we have omitted terms that shift the center of gravity of the pair without affecting its splitting. In Eq. (44)  $\sigma_1, \sigma_2, \sigma_3$  are the Pauli matrices defined with respect to the pair states as follows:

$$\begin{aligned} \sigma_1 &= |\Gamma_4x\rangle\langle\Gamma_4y| + |\Gamma_4y\rangle\langle\Gamma_4x|, \\ \sigma_2 &= -i|\Gamma_4x\rangle\langle\Gamma_4y| + i|\Gamma_4y\rangle\langle\Gamma_4x|, \\ \sigma_3 &= |\Gamma_4x\rangle\langle\Gamma_4x| - |\Gamma_4y\rangle\langle\Gamma_4y|, \end{aligned} \quad (45)$$

and we have for the coefficients

$$\begin{aligned} a &= \frac{1}{2}(g^2\mu_B^2/W) + \frac{3}{2}a', \\ b &= (g^2\mu_B^2/W) + b'. \end{aligned} \quad (46)$$

The eigenvalues of  $\mathcal{H}_{\text{eff}}$  from Eq. (44) are easily found to be  $\pm \frac{1}{2} \Delta E$ , where

$$\Delta E = \left\{ \left[ \sqrt{3} V_S e_\epsilon - 2a(H_x^2 - H_y^2) \right]^2 + 4g^2 \mu_B^2 H_x^2 + 4b^2 H_x^2 H_y^2 \right\}^{1/2}. \quad (47)$$

The separation of these two states in a given magnetic field, therefore, has a minimum value as a function of  $e_\epsilon$  given by

$$\Delta E_{\text{min}} = \left[ 4g^2 \mu_B^2 H_x^2 + 4b^2 H_x^2 H_y^2 \right]^{1/2}, \quad (48)$$

which is attained for those ions for which

$$\sqrt{3} V_S e_\epsilon - 2a(H_x^2 - H_y^2) = 0. \quad (49)$$

In the experiments of Marshall and Rampton,<sup>1</sup> a longitudinal acoustic wave was propagated along the [100] axis of the crystal, thereby modulating the strain at the chromium sites by

$$\begin{aligned} \delta e_\theta &= S \cos(2\pi\nu t), \\ \delta e_\epsilon &= -\sqrt{3} S \cos(2\pi\nu t). \end{aligned} \quad (50)$$

It follows from Eq. (35) that this perturbation has diagonal matrix elements with respect to  $|\Gamma_4 x\rangle$ ,  $|\Gamma_4 y\rangle$  given by

$$\begin{aligned} \langle \Gamma_4 x | \mathcal{H}'_S | \Gamma_4 x \rangle &= +2V_S S \cos(2\pi\nu t), \\ \langle \Gamma_4 y | \mathcal{H}'_S | \Gamma_4 y \rangle &= -V_S S \cos(2\pi\nu t). \end{aligned} \quad (51)$$

Since the off-diagonal matrix elements are zero, the acoustic wave cannot in any case induce transitions between the strain-split states  $|\Gamma_4 x\rangle$  and  $|\Gamma_4 y\rangle$  in zero magnetic field. The magnetic field, however, serves to mix these states, via the terms involving  $\sigma_1$  and  $\sigma_2$  in Eq. (44), thereby making such acoustically induced transitions possible when the resonance condition  $h\nu = \Delta E$  is satisfied. Using Eq. (51), we find that the square of the absolute value of this acoustic matrix element between the eigenstates of Eq. (44) is proportional to

$$M^2 = V_S^2 S^2 (g^2 \mu_B^2 H_x^2 + b^2 H_x^2 H_y^2) / (\Delta E)^2, \quad (52)$$

which for a fixed  $\Delta E$  thus increases as the second or fourth power of  $H$ . A second factor affecting the shape of the APR spectrum is the probability (per unit energy) that  $\Delta E$  in Eq. (47) satisfies the resonance condition. Weighting  $M^2$  with this probability, we find that the resonance absorption should be proportional to

$$G(H, \nu) = \int_C \frac{M^2 p(e_\theta, e_\epsilon) ds_e}{|\text{grad}_e \Delta E|}, \quad (53)$$

where the line integral is taken along the contour  $C$  in the  $(e_\theta, e_\epsilon)$  plane on which  $\Delta E = h\nu$ , and  $\text{grad}_e \Delta E$  is the gradient of  $\Delta E$  with respect to  $e_\theta, e_\epsilon$ . If we can neglect the dependence of  $\Delta E$  in Eq. (47) on  $e_\theta$  through that of  $a$  and  $b$ , we have

$$|\text{grad}_e \Delta E|^{-1}_{\Delta E = h\nu} = \frac{\Delta E}{\sqrt{3} |V_S| (h^2 \nu^2 - 4g^2 \mu_B^2 H_x^2 - 4b^2 H_x^2 H_y^2)^{1/2}} \quad (54)$$

for  $h\nu > \Delta E_{\text{min}}$ . This factor therefore also contributes to an increasing absorption with increasing  $H$ , until a field is reached at which

$$h\nu = (4g^2 \mu_B^2 H_x^2 + 4b^2 H_x^2 H_y^2)^{1/2}. \quad (55)$$

At higher fields the absorption is zero because the resonance condition cannot be satisfied, since  $\Delta E_{\text{min}}$  is then larger than  $h\nu$  according to Eq. (48). The absorption should therefore rise to a peak at a field given by Eq. (55), and then fall sharply to zero.

The parameter  $b$ , of course, depends on the strain  $e_\theta$  through the energy denominator  $W$  in the first term of Eq. (46). The absorption spectrum is therefore the superposition of asymmetric lines corresponding to the various values of  $e_\theta$  lying within the strain distribution; each component line has its peak and high-field absorption edge at a field given by Eq. (55). The absorption edge of the full absorption spectrum will, accordingly, be broadened by the variation in  $b$  (if both  $H_x$  and  $H_y$  are not zero). Nevertheless, if the range of  $e_\theta$  over which  $b$  varies significantly is only a small portion of the extent of the strain distribution, a well-defined asymmetric peak should still occur at a field given by the value of  $b$  appropriate to the majority of ions. Such a case is illustrated in Fig. 3, where  $b$  is plotted from Eqs. (46) using a value for  $b'$  roughly appropriate to what we might expect for  $\text{Cr}^{2+}$  in  $\text{MgO}$  (however, see Sec. IV, where the effect of strain coupling between different levels is included).

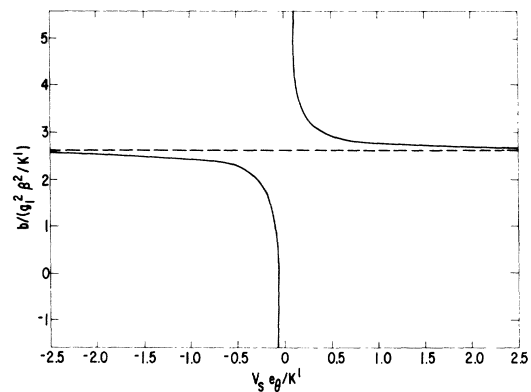


FIG. 3. Value of the parameter  $b$  for a  $\Gamma_4$  or  $\Gamma_5$  triplet level as a function of the splitting of the triplet by a tetragonal strain, as given by Eqs. (41) and (46) of the text, neglecting any strain coupling of the triplet to other levels. The fixed parameter  $b'$  giving the asymptotic limit of  $b$  for large splitting (dashed line) is taken from Eq. (60) of the text. The figure illustrates the fact that under these assumptions  $b$  would be very nearly equal to  $b'$  for all the tetragonally distorted ions, with the exception of those for which the strain splitting is close to zero.



We see that the absorption line shape predicted by our model if  $b$  is constant, namely,

$$G(H, \nu) \propto \frac{g^2 \mu_B^2 H_x^2 + b^2 H_x^2 H_y^2}{(h^2 \nu^2 - 4g^2 \mu_B^2 H_x^2 - 4b^2 H_x^2 H_y^2)^{1/2}}, \quad (56)$$

does not require any very special form for the strain distribution. This shape should be found under rather broad conditions if  $b$  does not depend strongly on  $e_\theta$ , and if the spread in the zero-field separation of the states  $|\Gamma_4 x\rangle$  and  $|\Gamma_4 y\rangle$  (resulting from the component  $e_\epsilon$  of the random strain) is sufficiently large compared with  $h\nu$  so that the ions contributing to the resonance absorption lie within the central portion of the strain distribution where  $p(e_\theta, e_\epsilon)$  does not depend strongly on  $e_\epsilon$ . On the other hand, if this spread should be smaller than  $h\nu$ , the line shape would depend strongly on the form of the strain distribution with respect to  $e_\epsilon$ . In particular, if we assumed the "random" strains to be strictly tetragonal so that  $e_\epsilon = 0$ , as in the case treated by Fletcher and Stevens,<sup>2</sup> we would obtain from Eq. (47) an absorption peak at a field given, not by Eq. (55), but by

$$h\nu = [4g^2 \mu_B^2 H_x^2 + 4a^2 (H_x^2 - H_y^2)^2 + 4b^2 H_x^2 H_y^2]^{1/2}, \quad (57)$$

and there would be no absorption on the low-field side of this peak, except for what results from the broadening of the peak through the dependence of  $a$  and  $b$  on  $e_\theta$ .

We have so far considered only the resonance spectrum due to ions from the set  $A$ , and we may expect similar peaks from sets  $B$  and  $C$  corresponding to suitable permutations of  $H_x$ ,  $H_y$ , and  $H_z$  in Eqs. (55) and (56), for example. For set  $B$  having its tetragonal axis along the  $[100]$  direction, however, a longitudinal wave along  $[100]$  affects both states  $|\Gamma_4 y\rangle$  and  $|\Gamma_4 z\rangle$  identically, in contrast to Eqs. (51), so that such a wave has vanishing matrix elements between all orthogonal linear combinations of these states. Thus, as noted also by Marshall and Rampton, under the conditions of their experiments, ions in set  $B$  should not contribute to the absorption. Ions in set  $C$ , on the other hand, should give an absorption identical to what we have found for set  $A$  but with the role of  $H_y$  and  $H_z$  interchanged. The resonance peak for this set therefore occurs at

$$h\nu = (4g^2 \mu_B^2 H_y^2 + 4b^2 H_x^2 H_z^2)^{1/2}. \quad (58)$$

In low magnetic fields the APR spectrum for an ion with a  ${}^5E$  ground state should result from transitions within the  $\Gamma_4$  and  $\Gamma_5$  triplets only, since the  $\Gamma_1$  and  $\Gamma_2$  singlets and the  $\Gamma_3$  doublets are nonmagnetic and are not mixed with the triplets by the strains  $e_\theta$  and  $e_\epsilon$ . Of the three triplets from Eqs. (21) or Fig. 1, the lowest  $\Gamma_4$  will have the greatest probability of being populated at temperatures of a few degrees Kelvin and should be the most important level in determining the APR spec-

trum at these temperatures. To complete our general analysis we should therefore obtain the parameters  $a'$  and  $b'$  for this level, which fix the size of the second-order magnetic perturbations of the triplet in Eq. (42) and thus determine the parameters  $a$  and  $b$  from Eqs. (46). In obtaining these, we will neglect the small terms involving  $g_2$  in the Zeeman interaction (22), and we will treat only the case for which the tunneling splitting  $3\Gamma$  is sufficiently large so that it is a good approximation to neglect the mixing of the  ${}^5A_1$  or  ${}^5A_2$  states with  ${}^5E$  via the spin-orbit interaction (18). The isotropic Zeeman interaction  $g_1 \mu_B (\vec{S} \cdot \vec{H})$ , then, does not couple  ${}^5E$  with  ${}^5A_1$  or  ${}^5A_2$ , so that we obtain for  $a'$  and  $b'$  of the lowest  $\Gamma_4$  triplet simply

$$a' = +g_1^2 \mu_B^2 \left( \frac{2}{3} \Delta_{41}^{-1} - \frac{2}{3} \Delta_{34}^{-1} + \frac{1}{4} \Delta_{54}^{-1} \right), \quad (59a)$$

$$b' = +g_1^2 \mu_B^2 \left( 2\Delta_{41}^{-1} + \Delta_{34}^{-1} - \frac{3}{4} \Delta_{54}^{-1} \right), \quad (59b)$$

where  $\Delta_{ij} = [E(\Gamma_i) - E(\Gamma_j)]$  denotes the energy-level separations indicated in Fig. 1. When  $3\Gamma \gg 4K$ , so that the lowest five spin-orbit levels have a uniform spacing  $K' = qK$ , we have simply

$$a' = g_1^2 \mu_B^2 / 8K', \quad (60)$$

$$b' = +21 g_1^2 \mu_B^2 / 8K',$$

the small value for  $a'$  resulting from the cancellation of the first two terms in Eq. (59a) under these conditions.

We may also show that for the lowest  $\Gamma_5$  triplet, under the same conditions for which Eqs. (59) hold, we have

$$a' = -g_1^2 \mu_B^2 \left( \frac{2}{3} \Delta_{25}^{-1} - \frac{2}{3} \Delta_{53}^{-1} + \frac{1}{4} \Delta_{54}^{-1} \right), \quad (61)$$

$$b' = -g_1^2 \mu_B^2 \left( 2\Delta_{25}^{-1} + \Delta_{53}^{-1} - \frac{3}{4} \Delta_{54}^{-1} \right),$$

or, with uniform separation, the negative of the values (60).

#### IV. APR SPECTRUM INCLUDING STRAIN MIXING OF LEVELS

The treatment of Sec. III is not yet quantitatively applicable to an interpretation of Marshall and Rampton's<sup>1</sup> results for  $\text{Cr}^{2+}$  in  $\text{MgO}$ , because we have so far neglected the strain mixing of the different spin-orbit levels of Eqs. (21). When the strain splitting of these levels, as given by Eqs. (38) and (39), is comparable with their separation, this mixing causes the parameters  $a$ ,  $b$ , and  $g$  in Eq. (44) to depend on the strain in a more complicated way than indicated by Eqs. (46) or Fig. 3. Since for  $\text{Cr}^{2+}$  in  $\text{MgO}$  the separation of the levels is only about  $2 \text{ cm}^{-1}$  while we believe that the random strain splittings are  $\sim 1 \text{ cm}^{-1}$ , we clearly must take this dependence into account.

Taking the strain coupling as given by Eq. (32), it is a straightforward computation to obtain the

energies and wave functions of the eigenstates derived from those of Eqs. (21) for ions in the set  $A$ , for which  $e_\epsilon$  is small and may be taken equal to zero, as a function of  $e_\theta$ . From these wave functions and energy differences we may then calculate  $a$ ,  $b$ , and  $g$  in Eq. (44) for the lowest doublet level (derived from the lowest  $\Gamma_4$  level), using second-order perturbation theory to treat the magnetic interaction. Fletcher and Stevens<sup>2</sup> have described some of the results of such a calculation, in which they included the coupling with the levels derived from the higher orbital singlet state. In our calculations, for simplicity, we have assumed  $3\Gamma \gg 4K$ , so that we consider coupling only among the  ${}^5E$  levels; in this case the strain coupling for nonzero  $e_\theta$  occurs only between the pairs of states ( $\Gamma_4x$ ,  $\Gamma_5\xi$ ), ( $\Gamma_4y$ ,  $\Gamma_5\eta$ ), ( $\Gamma_1$ ,  $\Gamma_3\theta$ ), and ( $\Gamma_2$ ,  $\Gamma_3\epsilon$ ), so that the resulting secular equations are easily solved analytically. We find for the lowest doublet the result

$$g = g_1(1 + 2x)[(2+x)^2 + 3x^2]^{-1/2}, \quad (62)$$

where we have neglected  $g_2$  and have set

$$x = qV_2e_\theta/K' = V_2e_\theta/K. \quad (63)$$

For  $b$  for this doublet we obtain the result shown in Fig. 4.

We see, therefore, that the parameters  $b$  and  $g$ , which determine the positions of the APR absorption peaks found in Sec. III and given by Eqs. (55) and (58), may be expected to vary quite significantly as a function of the strain. Since over the range  $x = -\frac{1}{2}$  to  $+\frac{1}{2}$ ,  $g$  varies from 0 to  $\sim +1.5$ , we may expect that an absorption peak determined primarily by the value of  $g$  [for example, Eq. (58) if  $H_x = 0$ ] would be greatly broadened by a strain distribution extending over this range, and that this broadening would probably erase most of the pronounced asymmetry of the line expected on the basis of Eq. (56). On the other hand, the value of  $b$  given in Fig. 4 for positive values of  $x$  has a broad minimum at

$$(b)_{\min} = 3.4(g_1^2\mu_B^2/K'). \quad (64)$$

According to our analysis in Sec. III leading to Eq. (55), ions having  $x > 0$  and contributing to a peak depending primarily on the value of  $b$  [for example, Eq. (55) if  $H_x = 0$ ] should all have their absorption on the low-field side of the field obtained from Eq. (55) by substituting the minimum value of  $b$  from Eq. (64). If the strain distribution is broad enough, ions having  $x > 0$  should therefore contribute an absorption having a sharp edge at this field and extending to lower fields, and the position of this edge should be independent of the details of the strain distribution. Ions for which the local strain corresponds to  $x < 0$ , on the other hand, should contribute to a broad absorption having no well-defined structure and extending on both sides of the edge.

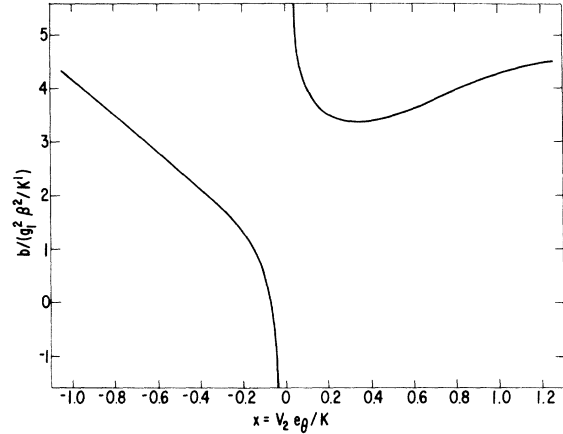


FIG. 4. Value of the parameter  $b$  for the lowest  $\Gamma_4$  triplet level of the  ${}^5E$  state of  $\text{Cr}^{2+}$  at a cubic site as a function of a tetragonal strain. The curve takes into account the strain mixing of the different spin-orbit levels and is appropriate to the case of a large tunneling splitting,  $3\Gamma \gg 4K$ .

Since, however, for  $x < 0$  the doublet derived from the lower  $\Gamma_4$  triplet lies *above* the split-off singlet and has had its excitation energy relative to the ground state *increased* by the strain, the doublet is relatively less likely to be populated at low temperatures in proportion to the appropriate Boltzmann factor. The population distribution at a few degrees Kelvin, therefore, favors having absorption from those ions with  $x > 0$ , for which the doublet is not only below the split-off  $\Gamma_4$  singlet but also close to the singlet ground state. Despite the random strain distribution, therefore, we should expect to see a sharp asymmetric peak in the absorption spectrum at the field given by Eq. (55) for the value  $(b)_{\min}$  from Eq. (64).

Fletcher and Stevens<sup>2</sup> have also identified some of the absorption peaks in Marshall and Rampton's data<sup>1</sup> with extrema in the distribution of resonance fields as a function of tetragonal strain, so that our interpretation is in qualitative agreement with theirs on this point. We will defer a more detailed comparison with their conclusions until Sec. VI.

#### V. EFFECT OF APPLIED STRESS ON THE APR SPECTRUM

The effect of an applied stress on the APR spectrum may now be obtained easily, since such a stress simply superimposes a uniform strain on the random strains already present at the chromium sites. The effect on the distribution for the resulting total strain given by  $e_\theta$ ,  $e_\epsilon$  is, therefore, simply to shift the distribution of Fig. 2(a) by the amount of the uniform strain. For example, a uniaxial compression along [001] will shift the distribution to that of Fig. 2(b), or a compression along [010] to that of Fig. 2(c). The resonance spectrum is,

however, obtained just as in Secs. III and IV, but the analysis must now be applied to the shifted strain distribution. All those ions for which the point  $(e_\theta, e_\epsilon)$  lies within a narrow band along the  $e_\theta$  axis (line A) in Fig. 2 continue to contribute to the absorption having its peak given by Eq. (55) and its line shape given by Eq. (56), at least to the extent that these ions have the lowest doublet level thermally populated. Since the value of  $g$  depends on the value of  $e_\theta$  along line A as described by Eq. (62), we may expect the mean value of  $g$ , appropriate to this set of ions, to shift in proportion to the amount by which the uniform strain displaces the distribution along line A. The value of  $b$  corresponding to the extremum in Fig. 4 is, however, independent of the applied stress, so that the position of the resonance peak (or edge) corresponding to  $(b)_{\min}$  should be unaffected. The intensity of this peak depends, on the other hand, on the value of the strain distribution near the extremum; this should be nearly independent of the applied stress so long as the uniform strain remains less than the mean value of the random strain, provided, of course, that the random strain distribution extends well beyond the position of the extremum and is relatively smooth. Once the applied stress begins to displace the distribution away from the extremum, on the other hand, the intensity of the peak will be diminished. Since for a [001] stress [Fig. 2(b)] line A continues to be a diameter of the shifted strain distribution while for lines B and C this is no longer true, the number of ions satisfying the resonance condition for sets B and C is reduced relative to that of set A, and we may expect the integrated intensities of the absorption associated with these sets to vary accordingly. Alternatively, if the stress is applied along [010] as in Fig. 2(c), the total resonance absorption from sets A and B should be reduced in intensity relative to that of set C. The intensities of these several contributions to the absorption spectrum are, of course, also influenced by the Boltzmann factor for the doublet level in each set and how this is changed by the applied stress. If the latter has a sense tending to reduce the doublet excitation energy relative to the ground state, the stress will tend to enhance the intensity of the absorption for that set, while for the opposite sense it will tend to be diminished.

We may note that if the original random strain distribution was not more or less independent of the azimuthal angle  $\psi$ , as assumed in drawing Fig. 2, but was instead composed of a distribution of strictly tetragonal strains lying along the lines A, B, and C as assumed by Fletcher and Stevens,<sup>2</sup> then the application of a moderate stress parallel to [001] would carry the ions originally on lines B and C sufficiently far from these lines so that their zero-field splitting would be larger than  $h\nu$  and they would

be unable to contribute to the resonance spectrum at all. We would expect the resonance peak of set C to vanish at a considerably lower applied stress, in this case, than it would if the original strain distribution were independent of  $\psi$ . We note also that the resonance of set C is lost, not because the ions originally in this set are reoriented by the applied stress to have the same alignment as set A, but because their symmetry is reduced to orthorhombic and their levels split by more than  $h\nu$ , so that they cannot contribute to the resonance.

#### VI. APPLICATION TO THE APR SPECTRUM OF $\text{Cr}^{2+}$ IN MgO

In the geometry of Marshall and Rampton's experiments,<sup>1</sup> the orientation of the magnetic field with respect to the crystal defined angles  $\theta$  and  $\varphi$  such that

$$\begin{aligned} H_x &= H \cos \theta, \\ H_y &= H \sin \theta \cos \varphi, \\ H_z &= H \sin \theta \sin \varphi, \end{aligned} \quad (65)$$

while the longitudinal acoustic wave propagated in the  $x$  direction [100]. Two resonance lines attributed to  $\text{Cr}^{2+}$  were observed which, from their dependence on  $\theta$  and  $\varphi$ , were judged to result from a transition within a doublet level for two sets of ions situated in tetragonally distorted sites, one set having its axis along [010] and the other along [001]. From the temperature dependence of the intensity of these lines, it was concluded that the doublet level was a few  $\text{cm}^{-1}$  above a singlet ground state. One of these lines (line C) had a  $\theta$  dependence for  $\varphi = 0$  given by

$$H = h\nu/g_{\parallel}\mu_B \sin \theta, \quad (66)$$

while the other (line U) was given by

$$H = H''/(\sin 2\theta)^{1/2}. \quad (67)$$

Lines C and U became coincident for  $\varphi = 45^\circ$ .

Comparing the expressions (66) and (67) with the theory developed in Sec. III, we find that the angular variation of line C agrees with that of the absorption peak of our set C [Eq. (58)] if we take

$$g = \frac{1}{2}g_{\parallel}, \quad (68)$$

while line U agrees with Eq. (55) (set A) if

$$|b| = h\nu/(H'')^2. \quad (69)$$

Both lines C and U were found to be asymmetric (see Fig. 2 of Ref. 1); line U, in particular, showed a very sharp edge on the high-field side, in agreement with the line shape we have predicted for the random strain distribution. Line C is also steeper on the high-field side, as our theory leads us to expect, but less so than line U. Since the position of line C was found to vary from sample to sample

more than did that of line *U*, this behavior and the reduced asymmetry are therefore consistent with the strong strain dependence of *g* found in Sec. IV.

Marshall and Rampton's observations thus appear to be consistent with the theory we have described if the resonance occurs within a triplet level a few  $\text{cm}^{-1}$  above the ground state. The lowest such triplet should be  $\Gamma_4$  according to Eqs. (21) and Fig. 1 and, in agreement with the conclusion of Fletcher and Stevens,<sup>2</sup> we believe that the absorption is the result of resonant transitions within this triplet, as split by the random strain. Our conclusion differs from that of Fletcher and Stevens, however, in that we do not have to postulate that all the naturally occurring random strains have tetragonal symmetry. Indeed, the unusual line shape with the extended tail on the low-field side of the resonance peak can be explained as the result of having a broad distribution with respect to the nontetragonal component of the strain. As we have shown, the fact that the ions contributing to the resonance appear to be in sites of nearly tetragonal symmetry has a simple explanation if the acoustic energy quantum  $h\nu$  is small compared with the mean splitting of the triplet level by the random strain: Most of the  $\text{Cr}^{2+}$  ions are indeed in sites with a more pronounced departure from tetragonal symmetry, but for these all three levels of the triplet are separated by more than  $h\nu$ , and these ions are unable to contribute to the resonance absorption.

Marshall and Rampton obtained a value for  $g_{\parallel}$  in Eq. (68) in the range 1.9–2.3 from the position of the line *C* which, as we have already noted, varied somewhat from one sample to another. From Eq. (68) we conclude that  $|g|$  for the responsible triplet level must be between 0.95 and 1.15. Comparing with Eqs. (26) and (28), we see that this result is indeed consistent with having the resonance within the lowest  $\Gamma_4$  triplet, for which we should have  $g \sim 1$  under a rather broad range of conditions. Since  $g_2$  is small, we would indeed have  $g(\Gamma_4) \sim 1$  from Eq. (26a) for all values of  $3\Gamma/K$  if the orbital singlet is  $A_1$ , while if the singlet is  $A_2$  we obtain this result from Eq. (28b), provided the ratio  $3\Gamma/K$  is sufficiently large. If we had  $3\Gamma/K < 2$  in the latter case, we would have  $g < 0.80$  from Eq. (28b), so that the data show that we must have  $3\Gamma \gtrsim 2K$  if the singlet is  $A_2$ . We note that the variation in the position of the line *C* is consistent with the strain dependence of *g* given by Eq. (62), for although the random strain distribution is probably roughly symmetrical about  $x=0$  as in Fig. 2(a), the Boltzmann factor for the doublet level weights the resonance line in favor of ions having  $x > 0$ . Such ions have *g* values shifted to larger values by the strain, in agreement with the observation that part of the line *C* must correspond to ions with *g* appreciably larger than unity. The latter result would not have been explicable on

the basis of Eq. (26a) or (28b) in the absence of the strain effects.

The data of Marshall and Rampton also give the value  $H'' = 5.16$  kG from line *U* and Eq. (67), and this value was found to change by only  $\pm 1\%$  from one sample to another. Relating  $H''$  to our parameter *b* via Eq. (69), we see that *b* must then not be sensitive to the state of strain in the various samples. This result is explained if the value of *b* corresponding to the peak *U* represents an extremum with respect to the distribution of tetragonal strain, as discussed in Sec. IV. If we equate this value for *b* to the minimum value given by Eq. (64), we obtain for  $K'$  the estimate

$$K' \approx 3.4(g_1\mu_B H'')^2/h\nu = 2.5 \text{ cm}^{-1}. \quad (70)$$

This would therefore be our estimate, as obtained from Marshall and Rampton's data,<sup>1</sup> for the separation  $K' = qK$  of the spin-orbit levels of  $\text{Cr}^{2+}$  in MgO for perfect cubic symmetry, if we could assume the ratio  $3\Gamma/K$  to be sufficiently large so that the five  ${}^5E$  levels are spaced approximately uniformly. We note also from Fig. 4 that the point at  $x = x_m \approx +0.35$  at which the minimum occurs must be well within the distribution of random strains even in the most perfect samples used by Marshall and Rampton, so that from the definition (63) for  $x$  and the estimate (70) for  $K'$  we would find that the typical strain splitting  $\frac{3}{2}(qV_2e_g)$  of the  $\Gamma_4$  triplet would be at least  $\frac{3}{2}(K'x_m) = 1.2 \text{ cm}^{-1}$ .

The estimate (70) for  $K'$  is, in fact, very reasonable. For the free  $\text{Cr}^{2+}$  ion, we have from a least-squares fitting of the spin-orbit splitting<sup>29</sup> of the  ${}^5D$  term the values

$$\begin{aligned} \lambda_0 &= +57 \text{ cm}^{-1}, \\ \rho_0 &= +0.47 \text{ cm}^{-1}, \end{aligned} \quad (71)$$

where  $\lambda_0$  and  $\rho_0$  are the free-ion values for the spin-orbit and effective spin-spin parameters (the latter combining the true spin-spin coupling with the effect of spin-orbit coupling to the excited states with  $S=1$ ). Taking  $\lambda_0$  and  $\rho_0$  to calculate  $K$  from Eq. (19), and assuming  $\Delta = 14000 \text{ cm}^{-1}$ ,<sup>30,31</sup> we obtain  $K = 4.2 \text{ cm}^{-1}$ . Accordingly, taking  $K' = qK$  with  $q = \frac{1}{2}$ , the value appropriate to *q* for all but rather weak JT coupling, we would expect to find  $K' = 2.1 \text{ cm}^{-1}$ , a value in fairly good agreement with the value (70) in view of the uncertainty as to the value for  $\rho$  which is appropriate to the ion in the crystal. Our estimate for  $K'$  is also roughly consistent with an experimental value for  $|D| = \frac{1}{2}K = 2.24 \text{ cm}^{-1}$  obtained from electron spin resonance for  $\text{Cr}^{2+}$  in  $\text{CrSO}_4 \cdot 5\text{H}_2\text{O}$  and cited by Griffith.<sup>31</sup>

We have, of course, no *a priori* reason for assuming that the ratio  $3\Gamma/K$  is large, and, indeed, it would be our expectation, based on experience with the  $\text{Cu}^{2+}$  ion, that this ratio might be  $\sim 1$  or

smaller. In most crystals in which  $\text{Cu}^{2+}$  has been studied in cubic or trigonal symmetry and octahedral coordination,<sup>16</sup> the  ${}^2E$  ground state undergoes a static JT effect, indicating that the tunneling splitting  $3\Gamma$  is less than typical strain splittings which are estimated to be a few  $\text{cm}^{-1}$ .<sup>16</sup> In  $\text{MgO}$ ,  $\text{Cu}^{2+}$  has been shown by Coffman<sup>32</sup> to exhibit a dynamic JT effect, but even here there is evidence<sup>16,33</sup> from the asymmetric broadening of the EPR spectrum that the  ${}^2A_2$  orbital singlet level is close enough to significantly perturb the  ${}^2E$  ground state through the effects of random strain. We may guess that for  $\text{MgO}:\text{Cu}^{2+}$   $3\Gamma$  is not larger than  $\sim 10 \text{ cm}^{-1}$ , and we would expect a similar or smaller value for  $\text{Cr}^{2+}$  since the  $3d$  orbitals of  $\text{Cr}^{2+}$  are more extended spatially than those of  $\text{Cu}^{2+}$ . It is therefore really a surprise that our simple calculation, which ignores the orbital singlet, appears to describe Marshall and Rampton's data as well as it does, as judged particularly from the reasonable value for  $K'$  obtained in Eq. (70). This estimate for  $K'$  should be increased somewhat if we do have  $3\Gamma/K \gg 1$  but take the coupling to the orbital singlet into account. As seen from Fig. 1, the proximity of the singlet causes the separation  $\Delta_{34}$  of the  $\Gamma_3$  and  $\Gamma_4$  levels to be smaller than  $K'$ , and if it is the  $A_2$  singlet that is lower [Fig. 1(b)], the separation  $\Delta_{41}$  of the  $\Gamma_4$  and  $\Gamma_1$  levels is also reduced. This reduction of the energy denominators in the expression (59b) for  $b'$  outweighs the reduction in the matrix elements of  $\vec{S}$  due to the mixing of the wave functions, at least for a sufficiently large value of  $3\Gamma/K$ . Our theoretical value of  $b'$  is therefore increased, this increasing the value of  $(b)_{\text{min}}$  from that given in Eq. (64).

Fletcher and Stevens,<sup>2</sup> on the other hand, have also been able to fit the peak positions in Marshall and Rampton's results using a model with the  ${}^5A_1$  singlet lower and  $K' = 2.02 \text{ cm}^{-1}$  and  $3\Gamma = 7.6 \text{ cm}^{-1}$ , values which are certainly very reasonable. On the basis of a series of computer calculations to locate the extrema in the resonance field as a function of the tetragonal strain, they have asserted that this is the only choice of the parameters that is consistent with the data. This conclusion is based on identifying line  $U$  with one extremum and, in addition, identifying a further peak, which was not described in Marshall and Rampton's paper<sup>1</sup> but is said to be more prominent in samples containing a higher concentration of impurities, with a second extremum in the resonance field which Fletcher and Stevens obtained for larger strain. In view of the possibility of the occurrence of associated impurity complexes, etc., in the less pure samples, it is difficult to know with what confidence one can accept Fletcher and Stevens's identification of this additional peak, and this question should be investigated experimentally in more detail. If Fletcher

and Stevens's interpretation is the correct one, then a further interesting difference between  $\text{MgO}:\text{Cr}^{2+}$  and the results for  $\text{Cu}^{2+}$  is that in all cases involving octahedrally coordinated  $\text{Cu}^{2+}$  in which a JT effect has been found, it is the  $A_2$  orbital singlet that is lowest,<sup>16</sup> and the distorted configuration that is stabilized by the static JT effect represents an elongation along the tetragonal axis [that is, we have  $\beta > 0$  in Eqs. (9) and (10)]. The  $A_2$  singlet is also known to be lowest for  $\text{MgO}:\text{Cu}^{2+}$ .<sup>16</sup> In contrast, Fletcher and Stevens concluded that the  $A_1$  singlet was lowest in their interpretation, so that if this is correct we must have  $\beta < 0$  for  $\text{MgO}:\text{Cr}^{2+}$ .

Since in our work we have not attempted detailed calculations of the strain mixing of the levels taking account of the orbital singlet, we cannot claim to have shown that our simple model in which  $3\Gamma$  is taken to be  $\gg K$  provides the best fit to the data. What we do assert, however, is that this simple model does suffice to account in a reasonable way for Marshall and Rampton's published data. Thus, more experimental data are needed to enable us to distinguish between this model, the interpretation proposed by Fletcher and Stevens, and other cases in which the coupling to the singlet is important. The accurate determination of the JT parameters, such as  $3\Gamma$ , for this system would be very interesting, for these are not yet known for most JT ions, and, in particular,  $3\Gamma$  has not yet been determined accurately for  $\text{Cu}^{2+}$  in any crystal.

Marshall and Rampton also performed experiments to study the effect of applied stress on the APR spectrum, and their results appear to be consistent with our discussion in Sec. V. Under compression along the  $[001]$  ( $Z$ ) axis, line  $C$  was reduced in intensity while line  $U$  was increased. Since this corresponds to the situation shown in Fig. 2(b) with the shift in the direction of positive  $x$  [since  $V_2$  should be negative for  $\text{Cr}^{2+}$  while  $e_\theta < 0$  for compression, we have  $x > 0$  from Eq. (63)], the Boltzmann factor favors an increase in the intensity of line  $U$ . The shift carries the strain distribution away from the line marked  $C$  in Fig. 2, so that the number of ions that are able to contribute to the resonance of line  $C$  is correspondingly reduced, as observed. Under compression along  $[010]$  ( $Y$ ), the reverse change occurred, with line  $C$  increased and line  $U$  reduced, again as expected from Fig. 2(c). In this case the shift in line  $C$  to smaller fields is consistent with the increase in  $g$  for increasing axial compression given by Eq. (62). The fact that in both cases the line that was reduced in intensity remained at the same field is also consistent with the model of Fig. 2.

It was noted by Marshall and Rampton<sup>1</sup> that a term of the form of the term  $4a^2(H_x^2 - H_y^2)^2$  in our Eq. (57) was allowed by symmetry in the expression for the resonance frequency, but was not found ex-

perimentally, the parameter they called  $H'$  evidently being so large that  $1/H'$  could be neglected. It is interesting to note in our present theory how this term is eliminated by the small nontetragonal component of the strain. The peak in the APR line occurs when  $h\nu$  equals the minimum separation  $\Delta E_{\text{min}}$  of the pair states, and by Eq. (47) this minimum occurs when Eq. (49) is satisfied rather than when  $e_\epsilon = 0$ . We therefore obtain Eq. (55) instead of (57) as the condition for the resonance peak.

#### VII. JT ENERGY

In view of our conclusion that a model having the tunneling splitting  $3\Gamma$  much larger than the spin-orbit parameter  $K$  can account for Marshall and Rampton's APR data, it is of interest to attempt to estimate the JT energy for  $\text{Cu}^{2+}$  in MgO and thereby to determine if such a value for  $3\Gamma$  is at all plausible. We may do this, using a procedure that has led to values for  $E_{\text{JT}}$  of the correct order of magnitude for  $\text{Fe}^{2+}$  in MgO<sup>14</sup> and a few other cases,<sup>16</sup> if we relate the JT coupling coefficient  $V$  to the strain coefficient  $V_2$  by Eq. (34) and take

$$D = (2/\sqrt{3})R, \quad (72)$$

the value appropriate<sup>16,17</sup> if the JT active mode is the distortion mode of the cluster of six nearest-neighbor oxygen ions and if the local elastic constants near the  $\text{Cr}^{2+}$  defect are the same as in the bulk. Here  $R$  is the nearest-neighbor distance, and under these assumptions we take for the effective mass of the mode<sup>17</sup>

$$\mu = M, \quad (73)$$

where  $M$  is the mass of a single oxygen atom.  $E_{\text{JT}}$  is then found from Eq. (5) to be given by

$$E_{\text{JT}} = 0.176(V_2/\hbar\omega)^2 \quad (\text{in cm}^{-1}), \quad (74)$$

where we must choose  $\omega$  such that  $\mu\omega^2$  gives the spring constant of the local mode. In the absence of better information for this mode, we will simply take  $\omega$  in the range (300–400  $\text{cm}^{-1}$ ) of the principal peaks of the phonon frequency distribution for MgO, as done in the work<sup>14</sup> on  $\text{Fe}^{2+}$  in MgO.

Since we do not as yet have an experimental value for the strain coefficient  $V_2$ , we may estimate it using the simplest possible model, that of the point-ion approximation to crystal field theory. This model, which ignores covalency, often gives the strain coefficients to a fairly good approximation,<sup>34–37</sup> and it has been found<sup>14</sup> to give the size of these coefficients correctly for  $\text{Fe}^{2+}$  in MgO (although, curiously, the sign is apparently wrong<sup>14</sup>). Considering electrostatic coupling to the nearest-neighbor oxygens only, we obtain for  $V_2$  in Eq. (32) for  $\text{Cr}^{2+}$  in MgO the result

$$V_2 = -e^2 \left( \frac{27}{7} \frac{\langle r^2 \rangle}{R^3} + \frac{50}{21} \frac{\langle r^4 \rangle}{R^5} \right), \quad (75)$$

where  $-e$  is the electron charge. Or, taking account of the coupling to more distant atoms as well, we obtain from the lattice sums given by Kanamori<sup>38</sup> the slightly larger result

$$V_2 = -e^2 \left( \frac{(23.84)}{7} \frac{\langle r^2 \rangle}{R^3} + \frac{(66.44)}{21} \frac{\langle r^4 \rangle}{R^5} \right). \quad (76)$$

Using  $R = 3.98$  a. u. for MgO and  $\langle r^2 \rangle = 1.760$  a. u.,  $\langle r^4 \rangle = 7.003$  a. u. for  $\text{Cr}^{2+}$ ,<sup>39</sup> we find

$$V_2 = -24\,600 \text{ cm}^{-1} \quad (77)$$

from Eq. (74), or  $-25\,700 \text{ cm}^{-1}$  from Eq. (75).

Using the value for  $V_2$  given by Eq. (77) in Eq. (74), we therefore obtain the estimate

$$E_{\text{JT}} = 1180 \text{ cm}^{-1} \quad (665 \text{ cm}^{-1}) \quad (78)$$

and

$$(E_{\text{JT}}/\hbar\omega) = 3.94 \quad (1.66) \quad (79)$$

for  $\hbar\omega = 300 \text{ cm}^{-1}$  (400  $\text{cm}^{-1}$ ). Referring to Eq. (12), we accordingly have for the energy parameter  $\alpha$  the value

$$\alpha = 19.0 \text{ cm}^{-1} \quad (60.5 \text{ cm}^{-1}). \quad (80)$$

The excitation energy  $3\Gamma$  of the first excited state would be  $2\alpha$  from Eq. (11) for linear JT coupling only, but this is reduced further if the warping parameter  $\beta$  in Eqs. (9) and (10) is appreciable. We find, for example, that for  $|\beta|/\alpha = 10$  we have  $3\Gamma \cong 0.2\alpha$ .<sup>23</sup> On the basis of the estimates given by Eqs. (77)–(80), therefore, we might well expect to find a value for the ratio  $3\Gamma/K$  larger than unity and possibly  $\gg 1$ . Alternatively, if our estimate for  $E_{\text{JT}}$  in Eq. (78) should prove to be too small and/or if we should have  $|\beta|/\alpha \gtrsim 10$ , a much smaller value for  $3\Gamma$  may be expected. These results are hardly conclusive, but they do support the possibility that an interpretation of the APR data with  $3\Gamma/K \gg 1$  could be correct.

#### VIII. DISCUSSION

We have succeeded in showing, in some generality, how APR within a triplet level broadened by random strain can lead to a spectrum of the type observed by Marshall and Rampton, provided the strain coupling is predominantly with the strain components  $e_\theta$  and  $e_\epsilon$ . Our model predicts the orientation dependence of the observed lines as well as their broad and asymmetric line shape. Moreover, our model makes it unnecessary to postulate that the random strains are predominately tetragonal, in that it shows for the conditions of the experiments that with a truly random distribution of strains only those ions can contribute to the reso-

nance absorption that are in sites for which  $e_\theta$  and  $e_\epsilon$  give a nearly tetragonal distortion. The small nontetragonal component of the strain at these sites indeed has been shown to play a crucial role in determining the line shape.

On the basis of this analysis, we have shown that it is possible to account quantitatively in all respects for Marshall and Rampton's published data<sup>1</sup> on their purer samples of MgO containing Cr<sup>2+</sup>, using a model in which the Cr<sup>2+</sup> exhibits a dynamic JT effect but has the tunneling splitting  $3\Gamma$  large compared to the spin-orbit splitting  $4K' = 4qK \sim 2K \sim 10 \text{ cm}^{-1}$  of the  ${}^5E$  ground state. We have also shown that this model is not inconsistent with a theoretical estimate of the JT energy based on the point-ion approximation, and with the resulting estimate of the range in which  $3\Gamma$  may lie. On the other hand, Fletcher and Stevens<sup>2</sup> have shown that one can also account for the observed data on the basis of an equally satisfactory model for which  $3\Gamma = 7.6 \text{ cm}^{-1}$ ,  $K' = \frac{1}{2}K = 2.02 \text{ cm}^{-1}$ , and the lower orbital singlet is  ${}^5A_1$ , so that one is very near the point in Fig. 1(a) at which the  $\Gamma_3$  level crosses  $\Gamma_4$ . From presently available data we cannot distinguish between these two possibilities or between these and others that may fit the data equally well. It thus remains for further investigation to settle the question of the actual role of the JT coupling for Cr<sup>2+</sup> in MgO and, in particular, to determine  $3\Gamma$ . If Fletcher and Stevens's interpretation is sustained by further experimental work, then our present analysis will supplement theirs to show why the resonant ions appear to be tetragonally distorted despite the presumably random nature of the strains, and also to exhibit the role of the nontetragonal strain component in determining the asymmetric line shape. We should emphasize that one or more extrema in the value of the parameter  $b$ , which thus should correspond to resonance peaks in the APR absorption, occur not only in the case we have considered and in that treated by Fletcher and Stevens, but presumably over a broad range in the possible values for the ratio  $3\Gamma/K$ , and that the analysis we have presented may be generalized to apply to any such situation which further experiments and analysis of the data may suggest is relevant.

We have estimated from our interpretation of Marshall and Rampton's data that the splitting of the  $\Gamma_4$  level in their samples as a result of random strains must have been at least  $1 \text{ cm}^{-1}$ . Using Eqs. (38) and (39) with  $q = \frac{1}{2}$ , and taking our estimate (77) for the strain coefficient  $V_2$ , we find that we

must then have typical local strains  $(e_\theta^2 + e_\epsilon^2)^{1/2} > 5 \times 10^{-5}$ . This conclusion is consistent with estimates of Schawlow *et al.*<sup>34</sup> from the fluorescence linewidth of Cr<sup>3+</sup>, and those of Stoneham<sup>40</sup> from an analysis of EPR linewidths, that good crystals of MgO have residual strains  $\sim 2 \times 10^{-4}$ .

The splitting of the levels of Cr<sup>2+</sup> in MgO by the random strains is accordingly large, being comparable with the separation  $K'$  of the  ${}^5E$  levels caused by the spin-orbit interaction. The interpretation of the APR spectrum is therefore complicated by these strain effects, and, indeed, at first sight it seems remarkable in this situation that well-defined resonance lines occur at all. Similar complications undoubtedly occur also in the case of Cr<sup>2+</sup> in Al<sub>2</sub>O<sub>3</sub>, which has been considered recently by Bates and Dixon<sup>41</sup> and by Challis and DeGoër.<sup>42</sup> It would clearly be desirable to be able to study this system in a sufficiently perfect crystal such that the strain splitting is a small fraction of  $K'$ . While it may not yet be possible to attain such crystal perfection for Cr<sup>2+</sup> in MgO, in view of the small value  $K' \sim 2.5 \text{ cm}^{-1}$  for Cr<sup>2+</sup>, we can achieve this desired situation for Fe<sup>2+</sup> in some of the crystals<sup>6-13</sup> in which it has been studied in tetrahedral symmetry, since  $K'$  in these cases lies typically in the range  $10-20 \text{ cm}^{-1}$ . APR experiments on Fe<sup>2+</sup> in such crystals, therefore, would clearly be of interest. For Fe<sup>2+</sup> in ZnS,<sup>7,9</sup> for example, we have  $K' = 15.0 \pm 0.1 \text{ cm}^{-1}$ , while from the width of the far-infrared  $\Gamma_1 - \Gamma_4$  absorption line we can conclude that the mean strain splitting of  $\Gamma_4$  in the crystals used in the optical studies was  $\sim 2 \text{ cm}^{-1}$ . The linewidth was found to be even smaller for Fe<sup>2+</sup> in CdTe, for which  $K' = 18.6 \text{ cm}^{-1}$ .<sup>12</sup> Of course, with the larger value of  $K'$  we should have a rather small value of  $b'$  from Eqs. (60), so that the parameter  $b$  in Eqs. (46) will be dominated by the contribution from within the triplet and will accordingly depend strongly on the strain. The line  $U$  may therefore not be seen as a well-defined peak in these systems. Line  $C$ , depending on  $g(\cong 1)$ , should still be observed, however, and since the strain mixing of the states is less, it should show less strain broadening and have a more pronounced asymmetry of the form given by Eq. (56) than for Cr<sup>2+</sup> in MgO. One would expect that the interpretation of APR data for such systems, including data on the effects of applied stress, would therefore be much more straightforward for Fe<sup>2+</sup> in these tetrahedral systems than for Cr<sup>2+</sup> in MgO. Such data would be very interesting since they should further clarify the role of the JT coupling in these systems.

<sup>1</sup>F. G. Marshall and V. W. Rampton, *J. Phys. C* **1**, 594 (1968).

<sup>2</sup>J. R. Fletcher and K. W. H. Stevens, *J. Phys. C* **2**, 444 (1969).

<sup>3</sup>M. C. M. O'Brien, *Proc. Roy. Soc. (London)* **A281**, 323 (1964).

<sup>4</sup>C. A. Bates, J. M. Dixon, J. R. Fletcher, and K. W. H. Stevens, *J. Phys. C* **1**, 859 (1968).

- <sup>5</sup>J. T. Vallin and G. D. Watkins, *Solid State Commun.* **9**, 953 (1971).
- <sup>6</sup>G. A. Slack, F. S. Ham, and R. M. Chrenko, *Phys. Rev.* **152**, 376 (1966).
- <sup>7</sup>G. A. Slack, S. Roberts, and F. S. Ham, *Phys. Rev.* **155**, 170 (1967).
- <sup>8</sup>J. M. Baranowski, J. W. Allen, and G. L. Pearson, *Phys. Rev.* **160**, 627 (1967).
- <sup>9</sup>J. T. Vallin, G. A. Slack, and C. C. Bradley, *Phys. Rev. B* **2**, 4406 (1970).
- <sup>10</sup>J. P. Mahoney, C. C. Lin, W. H. Brumage, and F. Dorman, *J. Chem. Phys.* **53**, 4286 (1970).
- <sup>11</sup>F. S. Ham and G. A. Slack, *Phys. Rev. B* **4**, 777 (1971).
- <sup>12</sup>G. A. Slack, S. Roberts, and J. T. Vallin, *Phys. Rev.* **187**, 511 (1969).
- <sup>13</sup>J. T. Vallin, *Phys. Rev. B* **2**, 2390 (1970).
- <sup>14</sup>F. S. Ham, W. M. Schwarz, and M. C. M. O'Brien, *Phys. Rev.* **185**, 548 (1969).
- <sup>15</sup>A general review of the present understanding of the dynamic and static JT effect of point defects in crystals is given in Ref. 16.
- <sup>16</sup>F. S. Ham, in *Electron Paramagnetic Resonance*, edited by S. Geschwind (Plenum, New York, 1971).
- <sup>17</sup>F. S. Ham, *Phys. Rev.* **166**, 307 (1968).
- <sup>18</sup>H. C. Longuet-Higgins, U. Opik, M. H. L. Pryce, and R. A. Sack, *Proc. Roy. Soc. (London)* **A244**, 1 (1958).
- <sup>19</sup>We use interchangeably the notation of Mulliken  $A_1$ ,  $A_2$ ,  $E$ ,  $T_1$ ,  $T_2$  [R. S. Mulliken, *Phys. Rev.* **43**, 279 (1933)] and that of Bethe  $\Gamma_1$ ,  $\Gamma_2$ ,  $\Gamma_3$ ,  $\Gamma_4$ ,  $\Gamma_5$  [H. A. Bethe, *Ann. Physik* **3**, 133 (1929)] to denote the irreducible representations of the symmetry group  $O$  of the rotations of a cube or the tetrahedral group  $T_d$ . We use the former to label orbital states, the latter for spin-orbit states. The labels  $\theta$  and  $\epsilon$  are used to designate any two partners which belong to  $E(\Gamma_3)$  and transform as  $(3z^2 - r^2)$  and  $\sqrt{3}(x^2 - y^2)$ , respectively, where  $x$ ,  $y$ ,  $z$  denote Cartesian coordinates with respect to the fourfold axes of the cube. The labels  $\xi$ ,  $\eta$ , and  $\zeta$  are used for three partners belonging to  $T_2(\Gamma_3)$  and transforming as  $yz$ ,  $zx$ , and  $xy$ , while  $x$ ,  $y$ , and  $z$  label partners belonging to  $T_1(\Gamma_4)$  and transforming as angular momentum components  $L_x$ ,  $L_y$ , and  $L_z$ .
- <sup>20</sup>J. H. Van Vleck, *J. Chem. Phys.* **7**, 72 (1939).
- <sup>21</sup>U. Opik and M. H. L. Pryce, *Proc. Roy. Soc. (London)* **A238**, 425 (1957).
- <sup>22</sup>A. D. Liehr and C. J. Ballhausen, *Ann. Phys. (N.Y.)* **3**, 304 (1958).
- <sup>23</sup>F. I. B. Williams, D. C. Krupka, and D. P. Breen, *Phys. Rev.* **179**, 255 (1969).
- <sup>24</sup>We assume in this paper that the  $G$ 's are not functions of the vibrational operators  $Q_\theta$ ,  $Q_\epsilon$ , although a generalization to this case could easily be made.
- <sup>25</sup>W. Low and M. Weger, *Phys. Rev.* **118**, 1119 (1960).
- <sup>26</sup>M. H. L. Pryce, *Phys. Rev.* **80**, 1107 (1950).
- <sup>27</sup>In the adiabatic approximation the correspondence between our notation for the parameters in Eqs. (21) and that used by Fletcher and Stevens is the following:  $q = \frac{1}{2}f_1$ ,  $3\Gamma = \delta$ ,  $K = 2D$ , and  $r = -\frac{1}{2}f_2$ .
- <sup>28</sup>When  $3\Gamma = 0$ , the levels belonging to different  $\Gamma_i$  are degenerate (Fig. 1), and matrix elements of  $\mathcal{H}$  between states belonging to different  $\Gamma_i$  contribute to the linear splitting of these levels. The  $g$  factors of Eqs. (26) and (28) give the level splittings only if the magnetic splittings are small compared to the separation of the levels in Eqs. (21).
- <sup>29</sup>*Atomic Energy Levels*, edited by C. E. Moore, Natl. Bur. Std. (U. S.) Circ. No. 467 (U. S. GPO, Washington, D. C., 1952), Vol. 2, p. 14.
- <sup>30</sup>D. S. McClure, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1959), Vol. 9, p. 399.
- <sup>31</sup>J. S. Griffith, *The Theory of Transition Metal Ions* (Cambridge U. P., Cambridge, England, 1961), p. 354.
- <sup>32</sup>R. E. Coffman, *J. Chem. Phys.* **48**, 609 (1968).
- <sup>33</sup>L. L. Chase, *Phys. Rev. B* **2**, 2308 (1970).
- <sup>34</sup>A. L. Schawlow, A. H. Piksis, and S. Sugano, *Phys. Rev.* **122**, 1469 (1961).
- <sup>35</sup>M. D. Sturge, *Phys. Rev.* **131**, 1456 (1963).
- <sup>36</sup>R. M. Macfarlane, *Phys. Rev.* **158**, 252 (1967).
- <sup>37</sup>K. Zdansky, *Phys. Rev.* **159**, 201 (1967).
- <sup>38</sup>J. Kanamori, *Progr. Theoret. Phys. (Kyoto)* **17**, 197 (1956).
- <sup>39</sup>F. M. O. Michel-Calendrini and M. R. Kibler, *Theoret. Chim. Acta* **10**, 367 (1968).
- <sup>40</sup>A. M. Stoneham, *Proc. Phys. Soc. (London)* **89**, 909 (1966).
- <sup>41</sup>C. A. Bates and J. M. Dixon, *J. Phys. C* **2**, 2209 (1969).
- <sup>42</sup>L. J. Challis and A. M. De Góer, *Phys. Letters* **31A**, 463 (1970).