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Theory of Crystal Distortion and Zeeman Effects in Rare-Earth Compounds with Zircon Structure

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In some rare-earth crystals there is a second-order phase transition from orthorhombic structure at lower temperatures to tetragonal at higher. A partial theoretical analysis of these materials is given in this paper. The basic idea is to consider the rare-earth ion in a crystal field interacting with a strain mode of the crystal. The temperature dependence of the interactions is assumed. The subjects discussed are the ground-state levels and their g values, the effect of a magnetic field on the transition and on the direction of crystal distortion, and the Zeeman effect for the optical-absorption spectrum.

I. INTRODUCTION

Some of the rare-earth arsenates, phosphates, and vanadates have been found to have remarkable properties. They have the tetragonal zircon structure[1] at high temperature and make a second-order phase transition to an orthorhombic structure at low temperature.[2–7] It has been established[8,9] that the transition is due to a cooperative Jahn–Teller effect as originally suggested by Cooke *et al.*[10] The dominant driving mechanism for the transition is the coupling of the rare-earth ions to the static elastic strain.[11,12] The thermal, spectral, and magnetic properties of the two structures are quite different.[2–25] An applied magnetic field may increase the transition temperature[17,19,20,24] and may even prevent the transition from occurring.[9,12,21,25] The direction of the distortion (from tetragonal to orthorhombic) in the basal plane may be magnetically controllable; application of a magnetic field in the basal plane can cause the orthorhombic axes to switch around through 90°.[10,14,15,19,21,24]

Theoretical models have been proposed by Stevens,[26] Elliott *et al.*[23,27,28] and by Pytte and Stevens.[29] Stevens[26] considers a system with a crystal-field energy contribution, vibrational energy of neighboring ions, and a coupling between. Elliott *et al.*[23,27,28] consider the ion to have just four states having large quadrupole moments with axes in the plane perpendicular to the tetragonal axis and then they couple such ions to the lattice phonons. Pytte and Stevens[29] use the crystal fields in a classical way to suggest the low-lying states of the ion and then couple with a normal mode of the lattice. While these models do not yet give a complete understanding of the phenomena, they agree with the observations as far as they go and they suggest ways to make further progress.

The purpose of this paper is to give a somewhat different model for the properties of the orthorhombic phase especially. It is felt that the model is reliable since it is based on symmetry properties of the material and that it gives a more quantitative understanding of some aspects of the problem.

The basic idea is as follows: (Here we will treat, for example, a tripositive rare-earth ion with an odd number of $4f$ electrons in a crystal field with D_{2d} symmetry.) The deviation of the crystal field from T_d symmetry is regarded as small so that the crystal field can be written as $V(T_d)+V(D_{2d})$, the second term being treated as a perturbation on the first. The electron–lattice-strain interaction is also put in as a perturbation on the same levels. This interaction is proposed to be of the form $V_L Q$, where V_L acts on the electron coordinates and has the symmetry of (x^2-y^2) and where Q is the coordinate for a lattice strain of corresponding symmetry. The lattice vibration energy is taken simply as $\frac{1}{2}\omega^2 Q^2$. It is assumed that there is temperature dependence in $V(D_{2d})$ or V_L or both, as needed to fit the data.

These ideas are appropriate, for example, for $DyVO_4$, $DyPO_4$, and $DyAsO_4$. Each rare-earth ion is surrounded by eight oxygen ions which lie at the corners of two distorted tetrahedrons,[30] thus producing the approximate T_d symmetry. The distortion is along the crystallographic [100] or [010] directions equivalently, indicating the electron–lattice-strain symmetry to use.

The above model gives a natural understanding of some of the properties of the material. The unperturbed crystal-field levels are classified according to the irreducible representations of T_d; these are doublets Γ_6, Γ_7 and a quartet Γ_8. (We use the notation of Koster *et al.*[31]) The perturbations cannot remove the Kramers degeneracy, so we understand that, to have a Jahn–Teller effect, the unperturbed ground state must be the quartet. The splitting of the quartet can be calculated as a function of the lattice-vibration coordinate Q treated classically, and the minimum of the energy as a function of Q determines the ground state. The g values of the states are obtained straightforwardly by introducing the magnetic field interaction as a further perturbation and it is found that they may have the property $g_x \gg g_y, g_z$ as observed in the dysprosium salts. The switching of the distortion by a basal-plane magnetic field and the prevention or promotion of the phase transition by a c-axis magnetic field (as observed in the even-electron $TmVO_4$, $TmAsO_4$ and $TbPO_4$ crystals) are well understood with this model.

A possible experiment which has not yet been done is to observe the intensities of the optical Zeeman lines as a function of the direction of the magnetic field in the basal plane. In earlier analyses[32-34] of the Zeeman effect for ions in crystal fields with C_{3h} symmetry it was found that the energy levels could be classified as type A or type B with the significance that $A \rightarrow A$ and $B \rightarrow B$ transitions have qualitatively different dependence on magnetic field direction than $A \rightarrow B$ and $B \rightarrow A$ transitions. It is shown below that a similar situation applies for these zircon structures with the additional complexity of the domain switching.

II. DESCRIPTION OF THE MODEL

Let the Hamiltonian for the ion in the crystal-field potential, interacting with one vibration mode of its neighbors, be

$$\mathcal{H}_1 = \mathcal{H}_{\text{ion}} + V(T_d) + V(D_{2d}) + V_L Q + \tfrac{1}{2}\omega^2 Q^2 , \qquad (1)$$

where $\mathcal{H}_{\text{ion}}$ is the Hamiltonian for the free rare-earth ion with an odd number of $4f$ electrons.

For calculating energies in the $4f^n$ configuration, only the even part of the crystal field contributes. Since $T_d \times C_i$ is O_h and $D_{2d} \times C_i$ is D_{4h} we write the even parts of $V(T_d)$ and $V(D_{2d})$ as $V(O_h)$ and $V(D_{4h})$, respectively, and consider

$$\mathcal{H}_2 = \mathcal{H}_{\text{ion}} + V(O_h) + V(D_{4h}) + V_L Q + \tfrac{1}{2}\omega^2 Q^2 \qquad (2)$$

for calculating the state functions within $4f^n$. The odd-parity parts are needed in the calculation of electric dipole transition intensities (Sec. VII). The V_L, since it has the symmetry of $(x^2 - y^2)$, already makes an even-parity contribution.

The zero-order Hamiltonian is taken to be $\mathcal{H}_{\text{ion}} + V(O_h) + \frac{1}{2}\omega^2 Q^2$. Also, as part of the model, we assume that it is sensible to restrict the problem to the quartet of zero-order states forming the Γ_8^- representation. Otherwise the above Hamiltonian would give no Jahn–Teller effect. Let these states be written as $\varphi_0(\Gamma_8^-, \gamma)$, where $\gamma = \pm\frac{1}{2}, \pm\frac{3}{2}$, and let the corresponding unperturbed energy be $E_0(\Gamma_8^-) + \frac{1}{2}\omega^2 Q^2$.

III. ENERGIES AND STATE FUNCTIONS

Now consider the splitting of the Γ_8^- level by the $V(D_{4h}) + V_L Q$ perturbation. We follow the organization and notation of Koster *et al.*[31] for handling the matrix elements.

The matrix elements of the perturbation can be taken from the last table on their page 91. The $V(D_{4h})$ is a u_1^3 function and the V_L, which transforms like $x^2 - y^2$, is a u_2^3. The perturbation matrix

$$\langle \varphi_0(\Gamma_8^-, \gamma') \,|\, [V(D_{4h}) + V_L Q] \,|\, \varphi_0(\Gamma_8^-, \gamma)\rangle$$

is then

$$\begin{array}{c} \\ -\frac{3}{2} \\ -\frac{1}{2} \\ \frac{1}{2} \\ \frac{3}{2} \end{array}
\begin{array}{c} \begin{array}{cccc} -\frac{3}{2} \qquad & -\frac{1}{2} \qquad & \frac{1}{2} \qquad & \frac{3}{2} \end{array} \\
\begin{pmatrix} 2^{-1/2}G_1 & 0 & 2^{-1/2}G_2 Q & 0 \\ 0 & -2^{-1/2}G_1 & 0 & 2^{-1/2}G_2 Q \\ 2^{-1/2}G_2 Q & 0 & -2^{-1/2}G_1 & 0 \\ 0 & 2^{-1/2}G_2 Q & 0 & 2^{-1/2}G_1 \end{pmatrix} \end{array} , \qquad (3)$$

where G_1 and G_2 are the appropriate reduced matrix elements of $V(D_{4h})$ and V_L.

As a result of this perturbation the Γ_8^- level splits into two Kramers doublets with perturbed energies given by

$$E(\pm, Q) = E_0(\Gamma_8^-) + \tfrac{1}{2}\omega^2 Q^2 \pm [\tfrac{1}{2}(G_1^2 + G_2^2 Q^2)]^{1/2} . \qquad (4)$$

We consider these $E(\pm, Q)$ as adiabatic potentials of the lattice for the ions in the two possible doublet states. The shapes of the curves $E(\pm, Q)$ are shown in Fig. 1. The shape of the ground-state curve $E(-, Q)$ depends on the size of G_2^4 relative to $2\omega^4 G_1^2$. In case G_2^4 is larger there are minima at finite strains $\pm Q_e$; we suppose this applies in the low-temperature orthorhombic phase. When G_2^4 is smaller there is only the minimum at $Q = 0$; we suppose this applies in the tetragonal phase. Thus in our picture the transition occurs because of temperature dependence in the $V(D_{4h})$ crystal-field component (so G_1 varies with T) or in the electron–lattice-strain interaction (so G_2 varies with T). We will discuss the possible origin of the temperature dependence in Sec. VIII.

There are several remarks to make about the eigenvalue problem in the orthorhombic case. The equilibrium strains, where $E(-, Q)$ is a minimum, are at $\pm Q_e$ where

$$Q_e^2 = (G_2^4 - 2\omega^4 G_1^2)/2\omega^4 G_2^2 . \qquad (5)$$

(One should minimize the free energy rather than the total energy to get the equilibrium strain here. This would lead to considerably more complicated formulas, without much numerical change. In the interest of simplicity, since this is a preliminary treatment of the problem anyway, we minimize the energy.) The two possibilities $\pm Q_e$ correspond to elongation in the [100] direction with contraction in the [010] direction and the opposite. They are equivalent, so we will often consider only the positive value $+Q_e$. The energies at the minimum are

$$E(\pm, Q_e) = E_0(\Gamma_8^-) + \frac{G_2^4 - 2\omega^4 G_1^2}{4\omega^2 G_2^2} \pm \frac{G_2^2}{2\omega^2} . \qquad (6)$$

Thus the energy separation of the two ground doublets at equilibrium is

$$E(+,\ Q_e)-E(-,\ Q_e)=G_2^2/\omega^2\ . \tag{7}$$

The Jahn–Teller energy of the ground level is

$$E(-,0)-E(-,\ Q_e)=(G_2/2\omega)^2\,[1-(2\omega^4 G_1^2/G_2^4)^{1/2}]^2\ . \tag{8}$$

The state functions are given by the eigenvectors of the perturbation matrix at $Q=Q_e$. They are

$$\varphi_{\text{orth+}}(+,\ \tfrac{1}{2})=\cos\theta_e\,\varphi_0(\Gamma_8^-,\ -\tfrac{3}{2})+\sin\theta_e\,\varphi_0(\Gamma_8^-,\ \tfrac{1}{2})\ , \tag{9a}$$

$$\varphi_{\text{orth+}}(+,\ -\tfrac{1}{2})=-\cos\theta_e\,\varphi_0(\Gamma_8^-,\ \tfrac{3}{2})-\sin\theta_e\,\varphi_0(\Gamma_8^-,\ -\tfrac{1}{2})\ , \tag{9b}$$

$$\varphi_{\text{orth+}}(-,\ \tfrac{1}{2})=-\sin\theta_e\,\varphi_0(\Gamma_8^-,\ -\tfrac{3}{2})+\cos\theta_e\,\varphi_0(\Gamma_8^-,\ \tfrac{1}{2})\ , \tag{9c}$$

$$\varphi_{\text{orth+}}(-,\ -\tfrac{1}{2})=\sin\theta_e\,\varphi_0(\Gamma_8^-,\ \tfrac{3}{2})-\cos\theta_e\,\varphi_0(\Gamma_8^-,\ -\tfrac{1}{2})\ . \tag{9d}$$

The notation is that $\varphi_{\text{orth+}}(\pm,\gamma)$ are the eigenfunctions for the orthorhombic phase with strain $+Q_e$ corresponding to the eigenvalues $E(\pm,\ Q_e)$ with $\gamma=\pm\frac{1}{2}$ labelling the degenerate states at each energy. The angle θ_e is given by

$$\tan\theta_e=\frac{G_2}{|G_2|}\left[\frac{1-(2^{1/2}\omega^2 G_1/G_2^2)}{1+(2^{1/2}\omega^2 G_1/G_2^2)}\right]^{1/2}\ , \tag{10}$$

with the understanding that $\pi\geq\theta_e\geq 0$. Relative signs of the functions were chosen here as suggested by the time-reversal convention

$$T\,|j,\ m\rangle=(-1)^{j+m}\,|j,\ -m\rangle\ .$$

The angle θ_e has different ranges, depending on the signs of G_1 and G_2;

if $G_1>0$ and $G_2>0$, then $\frac{1}{4}\pi>\theta_e>0$,

if $G_1<0$ and $G_2>0$, then $\frac{1}{2}\pi>\theta_e>\frac{1}{4}\pi$,

if $G_1<0$ and $G_2<0$, then $\frac{3}{4}\pi>\theta_e>\frac{1}{2}\pi$,

if $G_1>0$ and $G_2<0$, then $\pi>\theta_e>\frac{3}{4}\pi$.

The sign of G_2 is not such an important property of the material as the sign of G_1, because G_2 only comes into the problem multiplied by the strain-coordinate Q which takes on both positive and negative values equivalently. The Hamiltonian $\mathcal{H}_2$ has the D_{2h} symmetry when Q is not zero; since we are considering an odd number of $4f$ electrons, all the functions $\varphi_{\text{orth+}}(\pm,\ \pm\frac{1}{2})$ belong to the Γ_5^- irreducible representation.

Later we will need the state functions for the orthorhombic phase with strain $-Q_e$. As seen from Eq. (3), changing the sign of Q is the same as changing the sign of G_2 or, according to Eq. (10), changing $\cos\theta_e$ to $-\cos\theta_e$ while leaving $\sin\theta_e$ alone. The ground-state functions are thus written down directly by making this change in Eqs. (9c) and (9d):

$$\varphi_{\text{orth-}}(-,\ \tfrac{1}{2})=-\sin\theta_e\,\varphi_0(\Gamma_8^-,\ -\tfrac{3}{2})-\cos\theta_e\,\varphi_0(\Gamma_8^-,\ \tfrac{1}{2})\ , \tag{11a}$$

$$\varphi_{\text{orth-}}(-,\ -\tfrac{1}{2})=\sin\theta_e\,\varphi_0(\Gamma_8^-,\ \tfrac{3}{2})+\cos\theta_e\,\varphi_0(\Gamma_8^-,\ -\tfrac{1}{2}). \tag{11b}$$

The ground-state energies are the same for both equilibrium strains.

Now consider the eigenvalue problem for the tetragonal phase. The equilibrium strain is at $Q=0$. As seen directly from the perturbation matrix at $Q=0$ the energies are

$$E(\pm,0)=E_0(\Gamma_8^-)\pm 2^{-1/2}\,|\,G_1\,|\ , \tag{12}$$

and the eigenfunctions are

$$\begin{aligned}\varphi_{\text{tet}}(+,\ \pm\tfrac{1}{2})&=\pm\frac{G_2}{|G_2|}\,\varphi_0(\Gamma_8^-,\ \mp\tfrac{3}{2})\quad\text{when } G_1>0\ ,\\ &=\pm\varphi_0(\Gamma_8^-,\ \pm\tfrac{1}{2})\quad\text{when } G_1<0\ ;\end{aligned} \tag{13a}$$

$$\begin{aligned}\varphi_{\text{tet}}(-,\ \pm\tfrac{1}{2})&=\pm\frac{G_2}{|G_2|}\,\varphi_0(\Gamma_8^-,\ \pm\tfrac{1}{2})\quad\text{when } G_1>0\ ,\\ &=\mp\varphi_0(\Gamma_8^-,\ \mp\tfrac{3}{2})\quad\text{when } G_1<0\ .\end{aligned} \tag{13b}$$

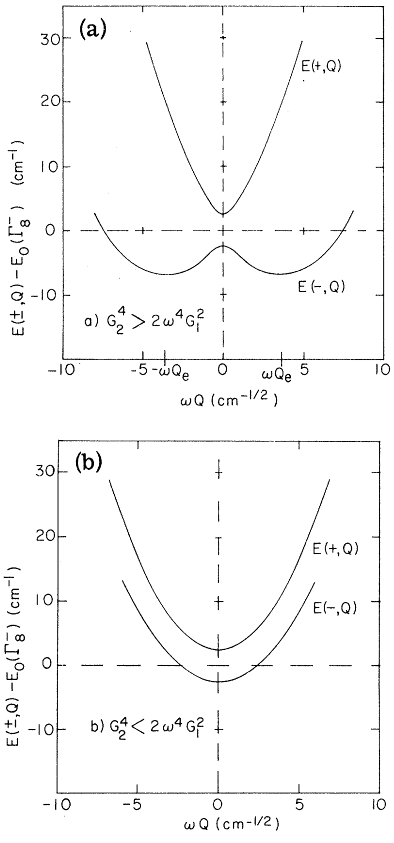

FIG. 1. Adiabatic potentials for the two ground doublets as given by Eq. (4). In case (a), the crystallographic distortion occurs and the equilibrium is at $Q=\pm Q_e$. In (b) there is no distortion and the equilibrium is at $Q=0$.

The signs on the right were chosen to make the functions $\varphi_{\mathrm{orth}+}(\pm, \gamma)$ and $\varphi_{\mathrm{tet}}(\pm, \gamma)$ coincide at the transition where $G_2^4 = 2\omega^4 G_1^2$. The Hamiltonian $\mathcal{H}_2$ has D_{4h} symmetry when $Q=0$; the $\varphi_0(\Gamma_8^-, \pm\frac{3}{2})$ states belong to the Γ_7^- representation and the $\varphi_0(\Gamma_8^-, \pm\frac{1}{2})$ states to the Γ_6^- representation.

Observation of the energy separation of the two ground doublets gives, according to Eq. (7), $(G_2/\omega)^2$ as a function of temperature in the orthorhombic phase and, according to Eq. (12), gives $2^{1/2}|G_1|$ as a function of temperature in the tetragonal phase.

IV. *g*-VALUES OF THE LOWER LEVELS

Once the state functions are established in terms of the unperturbed functions $\varphi_0(\Gamma_8^-, \gamma)$ the g factors can be calculated in terms of properties of the unperturbed functions.

The g factors are defined by

$$g_x(\pm) = 2\langle \varphi(\pm, \tfrac{1}{2}) \,|\, (L_x + 2S_x) \,|\, \varphi(\pm, -\tfrac{1}{2})\rangle ,$$

$$g_y(\pm) = 2i\langle \varphi(\pm, \tfrac{1}{2}) \,|\, (L_y + 2S_y) \,|\, \varphi(\pm, -\tfrac{1}{2})\rangle ,$$

$$g_z(\pm) = 2\langle \varphi(\pm, \tfrac{1}{2}) \,|\, (L_z + 2S_z) \,|\, \varphi(\pm, \tfrac{1}{2})\rangle .$$

Either φ_{orth} or φ_{tet} is to be used on the right and the ± sign indicates the upper or lower level at $E(\pm)$. In terms of these g factors the magnetic contribution to the Hamiltonian $\mu_B \vec{\mathrm{H}} \cdot (\vec{\mathrm{L}} + 2\vec{\mathrm{S}})$ is, effectively for each level,

$$\mathcal{H}_Z = \mu_B (g_x s_x H_x + g_y s_y H_y + g_z s_z H_z) , \tag{14}$$

where $\vec{\mathrm{H}}$ is the applied field, $\vec{\mathrm{s}}$ are spin-$\frac{1}{2}$ matrices acting on the γ label in $\varphi(\pm, \gamma)$, and μ_B is the Bohr magneton.

The matrix elements of $\vec{\mathrm{L}} + 2\vec{\mathrm{S}}$ for the functions $\varphi_0(\Gamma_8^-, \gamma)$ may be expressed in terms of just two real parameters, say K_1 and K_2, and matrix elements given by Koster *et al.*[31] That is, one can let

$$\langle \varphi_0(\Gamma_8^-, \gamma) \,|\, (L+2S)_\alpha \,|\, \varphi_0(\Gamma_8^-, \gamma')\rangle = -iK_1 \langle \psi_\gamma^8 \,|\, u_\alpha^4 \, v_{\gamma'}^8 \rangle - iK_2 \langle \varphi_\gamma^8 \,|\, u_\alpha^4 \, v_{\gamma'}^8 \rangle , \tag{15}$$

where the subscript α indicates x, y, or z and the complex conjugates of the matrix elements on the right are given in the table on p. 93 of Ref. 31.

The g values in the orthorhombic phase with strain $+Q_e$ are found to be

$$g_x(+) = (\tfrac{4}{15})^{1/2}(2K_1 + K_2)\sin\theta_e(\sin\theta_e + \sqrt{3}\cos\theta_e) - (\tfrac{5}{3})^{1/2}K_2 , \tag{16a}$$

$$g_y(+) = (\tfrac{4}{15})^{1/2}(2K_1 + K_2)\sin\theta_e(\sin\theta_e - \sqrt{3}\cos\theta_e) - (\tfrac{5}{3})^{1/2}K_2 , \tag{16b}$$

$$g_z(+) = -(\tfrac{1}{15})^{1/2}(2K_1 + K_2)(\sin^2\theta_e - 3\cos^2\theta_e) - (\tfrac{5}{3})^{1/2}K_2 ; \tag{16c}$$

$$g_x(-) = (\tfrac{4}{15})^{1/2}(2K_1 + K_2)\cos\theta_e(\cos\theta_e - \sqrt{3}\sin\theta_e) - (\tfrac{5}{3})^{1/2}K_2 , \tag{17a}$$

$$g_y(-) = (\tfrac{4}{15})^{1/2}(2K_1 + K_2)\cos\theta_e(\cos\theta_e + \sqrt{3}\sin\theta_e) - (\tfrac{5}{3})^{1/2}K_2 , \tag{17b}$$

$$g_z(-) = -(\tfrac{1}{15})^{1/2}(2K_1 + K_2)(\cos^2\theta_e - 3\sin^2\theta_e) - (\tfrac{5}{3})^{1/2}K_2 . \tag{17c}$$

The g values in the orthorhombic phase with strain $-Q_e$ are found from these results by replacing $\cos\theta_e$ by $-\cos\theta_e$ as discussed before. It is seen that g_x, g_y, and g_z for the ortho+ states are the same as g_y, g_x, and g_z for the ortho− states. As a convention we will use the symbol g_α to mean the ortho+ values only. Thus the ortho+ g values are g_x, g_y, g_z and the ortho− values are g_y, g_x, g_z. Formulas for the tetragonal phase in case $G_1 > 0$ are

$$g_x(+) = g_y(+) = -(\tfrac{5}{3})^{1/2}K_2 , \tag{18a}$$

$$g_z(+) = (\tfrac{4}{15})^{1/2}(3K_1 - K_2) ; \tag{18b}$$

$$g_x(-) = g_y(-) = (\tfrac{1}{15})^{1/2}(4K_1 - 3K_2) , \tag{19a}$$

$$g_z(-) = -(\tfrac{4}{15})^{1/2}(K_1 + 3K_2) . \tag{19b}$$

Similar formulas apply for the tetragonal phase in case $G_1 < 0$ but with $g_\alpha(\mp)$ in place of $g_\alpha(\pm)$.

One consequence of these formulas is that g values of the upper doublet are simply related to those of the lower doublet:

$$g_x(+) = \tfrac{1}{3}[-g_x(-) + 2g_y(-) + 2g_z(-)] , \tag{20a}$$

$$g_y(+) = \tfrac{1}{3}[2g_x(-) - g_y(-) + 2g_z(-)] , \tag{20b}$$

$$g_z(+) = \tfrac{1}{3}[2g_x(-) + 2g_y(-) - g_z(-)] . \tag{20c}$$

This applies in both phases and for either sign of G_1.

It is interesting to consider these results in case $|K_1|$ is large compared to $|K_2|$ because then they imply a large anisotropy. Thus, if the K_2 terms are discarded in Eqs. (17), one has

$$g_x(-) = (\tfrac{4}{15})^{1/2} 2K_1 \cos\theta_e(\cos\theta_e - \sqrt{3}\sin\theta_e) , \tag{21a}$$

$$g_y(-) = (\tfrac{4}{15})^{1/2} 2K_1 \cos\theta_e(\cos\theta_e + \sqrt{3}\sin\theta_e) , \tag{21b}$$

$$g_z(-) = -(\tfrac{1}{15})^{1/2} 2K_1 (\cos^2\theta_e - 3\sin^2\theta_e) . \tag{21c}$$

Therefore, at a temperature such that $\theta_e = \frac{1}{6}\pi$ $[\frac{5}{6}\pi]$, $g_y(-)$ $[g_x(-)]$ is large compared to $g_x(-)$ $[g_y(-)]$ and $g_z(-)$. Evidently a similar extreme anisotropy occurs for the upper level at $\theta_e = +\frac{1}{3}\pi$ or $\frac{2}{3}\pi$. One sees from Eq. (10) that if $G_1 > 0$ then $\theta_e = 0$ or π at the phase transition temperature so the extreme anisotropy in the lower level occurs at a higher temperature than the extreme anisotropy in the higher level. On the other hand, if $G_1 < 0$ then $\theta_e = \frac{1}{2}\pi$ at the transition and the extreme anisotropy in the higher level occurs at the higher temperature. If such anisotropies are observable, the sign of G_1 can be inferred from the data. The sign of G_1 can also be inferred from the g factors in the tetragonal phase. The point is that, if K_2 is small, then $|g_z(-)| \cong \frac{1}{2}|g_x(-)|$ if $G_1 > 0$, whereas $|g_z(-)| \gg |g_x(-)|$ if $G_1 < 0$. Special relations apply among the g values of one level at the temperature at which there is the extreme anisotropy in the other level. For example, if $g_y(-)$ is large compared to $g_x(-)$ and $g_z(-)$, then Eqs. (20) imply that $|g_x(+)| \cong 2|g_y(+)| \cong |g_z(+)| \cong \frac{2}{3}|g_y(-)|$.

V. DEPENDENCE OF THE TRANSITION ON MAGNETIC FIELD APPLIED ALONG THE *c* AXIS

The model shows how a c-axis magnetic field may influence the transition. One reconsiders the splitting of the Γ_8^- level, Sec. III, in case there is a Zeeman term

$$\mathcal{H}_Z = \mu_B H(L_z + 2S_z) \tag{22}$$

present also. This gives field-dependent formulas for the energy levels and field-dependent conditions for the distortion to be stable.

The matrix to be considered now is that of Eq. (3) with, in addition, the elements

$$\langle \varphi_0(\Gamma_8^-, \gamma') | \mathcal{H}_Z | \varphi_0(\Gamma_8^-, \gamma) \rangle .$$

These are given by Eq. (15); the nonzero entries are

$$\langle \varphi_0(\Gamma_8^-, \pm\tfrac{3}{2}) | \mathcal{H}_Z | \varphi_0(\Gamma_8^-, \pm\tfrac{3}{2}) \rangle = \mp(\tfrac{1}{15})^{1/2}(3K_1 - K_2)\,\mu_B H ,$$

$$\langle \varphi_0(\Gamma_8^-, \pm\tfrac{1}{2}) | \mathcal{H}_Z | \varphi_0(\Gamma_8^-, \pm\tfrac{1}{2}) \rangle = \mp(\tfrac{1}{15})^{1/2}(K_1 + 3K_2)\mu_B H .$$

The degeneracy is now completely removed. The matrix still reduces to two 2×2 components, but they are no longer equivalent. The Γ_8^- level is split into four with energies

$$E(\zeta, \eta, Q, H) = E_0(\Gamma_8^-) + \tfrac{1}{2}\omega^2 Q^2 + \eta(\tfrac{1}{15})^{1/2}(2K_2 - K_1)\,\mu_B H + \zeta\{\tfrac{1}{2}[G_1 - \eta(\tfrac{2}{15})^{1/2}(2K_1 + K_2)\,\mu_B H]^2 + \tfrac{1}{2}G_2^2 Q^2\}^{1/2} . \tag{23}$$

Here, ζ and η may independently be plus or minus one, giving the four energies.

The effect of the field is to shift the energies by $\eta(\frac{1}{15})^{1/2}(2K_2 - K_1)\,\mu_B H$ and to replace G_1 by $G_1 - \eta(\frac{2}{15})^{1/2}(2K_1 + K_2)\,\mu_B H$. Consequently, as argued following Eq. (4), the lower levels, $E(-1, \eta, Q, H)$, have minima at finite strains in case

$$G_2^4 > 2\omega^4[G_1 - \eta(\tfrac{2}{15})^{1/2}(2K_1 + K_2)\,\mu_B H]^2 \tag{24}$$

and otherwise the minima are at $Q = 0$. When inequality (24) holds, the energies at the minima are

$$E(-1, \eta, Q_e, H) = E_0(\Gamma_8^-) - G_2^2/4\omega^2 + \eta(\tfrac{1}{15})^{1/2}(2K_2 - K_1)\,\mu_B H - (\omega^2/2G_2^2)[G_1 - \eta(\tfrac{2}{15})^{1/2}(2K_1 + K_2)\,\mu_B H]^2 , \tag{25}$$

as may be inferred from Eq. (6).

Many things can happen here depending on the signs and sizes of the various parameters. Suppose for example that $G_2^4 > 2\omega^4 G_1^2$ and that $2K_2 - K_1 > 0$. At zero field there is the Jahn–Teller distortion and the crystal is orthorhombic. At finite field values the $\eta(2K_2 - K_1)$ term in Eq. (25) probably dominates the $\eta(2K_1 + K_2)$ term because the latter has an $\omega^2 G_1/G_2^2$ factor; consequently, we suppose that $\eta = -1$ gives the ground state.

If, on the one hand, $G_1/(2K_1 + K_2) > 0$, Eq. (24) implies that, as the field is increased at constant temperature, the material makes the transition to tetragonal at the value

$$H_{c1} = (\tfrac{15}{2})^{1/2}\,\frac{1}{|2K_1 + K_2|}\,\frac{1}{\mu_B}\left(\frac{G_2^2}{2^{1/2}\omega^2} - |G_1|\right) . \tag{26}$$

The right side of Eq. (24) increases monotonically with H so an applied field decreases the transition temperature. In a field greater than $H_{c1}(T = 0)$ the orthorhombic phase does not exist.

If on the other hand $G_1/(2K_1 + K_2) < 0$, Eq. (24) implies that, as the field is increased at constant temperature, the material makes the transition to tetragonal at the value

$$H_{c2} = (\tfrac{15}{2})^{1/2}\,\frac{1}{|2K_1 + K_2|}\,\frac{1}{\mu_B}\left(\frac{G_2^2}{2^{1/2}\omega^2} + |G_1|\right) . \tag{27}$$

The right side of Eq. (24) decreases as H increases until the value

$$H_{c3} = (\tfrac{15}{2})^{1/2}\,\frac{|G_1|}{|2K_1 + K_2|}\,\frac{1}{\mu_B} \tag{28}$$

and then increases monotonically afterward. Consequently, the effect of a magnetic field is at first to stabilize the transition and increase the transition temperature but, for high enough field, the transition temperature is lowered. In a field greater than $H_{c2}(T = 0)$ the orthorhombic phase does not exist.

This model also indicates that a substance with no zero-field Jahn–Teller effect ($G_2^4 < 2\omega^4 G_1^2$) but with $G_1/(2K_1 + K_2) < 0$ would nevertheless have the phase transition with c-axis magnetic fields in the range

$$|G_1| - G_2^2/2^{1/2}\omega^2 < (\tfrac{2}{15})^{1/2}|2K_1 + K_2|\mu_B H < |G_1| + G_2^2/2^{1/2}\omega^2 . \tag{29}$$

The extreme field values here are the limiting values for inequality (24) in case $\eta = -1$.

VI. SWITCHING OF DOMAINS BY A MAGNETIC FIELD APPLIED IN THE BASAL PLANE

We consider now what the model implies about the stability of the domains under an applied magnetic field.

If the lattice is distorted so that the strain is $+Q_e$, the ground-state energy and wave functions are given by Eqs. (6) and (9c) and (9d). If the magnetic field is applied in the basal plane at angle ϕ_m with the x axis, the effective contribution to the Hamiltonian is

$$\mathcal{H}_Z = \mu_B H(g_x s_x \cos\phi_m + g_y s_y \sin\phi_m) , \qquad (30)$$

the g factors to be found from Eqs. (17a) and (17b). The eigenvalues of this matrix give the perturbations on the energy

$$\Delta E(+Q_e) = \pm \mu_B H \left(\frac{g_x^2+g_y^2}{8}\right)^{1/2} \times \left(1+\frac{g_x^2-g_y^2}{g_x^2+g_y^2}\cos 2\phi_m\right)^{1/2} . \qquad (31)$$

On the other hand, if the lattice is distorted so that the strain is $-Q_e$, the energy is still given by Eq. (6) but the wave functions now by Eqs. (11). The g factors are now different and the magnetic contribution to the Hamiltonian is

$$\mathcal{H}_Z = \mu_B H(g_y s_x \cos\phi_m + g_x s_y \sin\phi_m) . \qquad (32)$$

The eigenvalues of this matrix are

$$\Delta E(-Q_e) = \pm \mu_B H \left(\frac{g_x^2+g_y^2}{8}\right)^{1/2} \times \left(1+\frac{g_y^2-g_x^2}{g_x^2+g_y^2}\cos 2\phi_m\right)^{1/2} . \qquad (33)$$

Suppose the system stays at minimum energy as the field direction ϕ_m is varied. Regardless of the relative size of g_y and g_x, the minimum energy is attained by switching from strain $\pm Q_e$ to the opposite strain $\mp Q_e$ at angles $\phi_m = \pm\frac{1}{4}\pi$, $\pm\frac{3}{4}\pi$, $\pm\frac{5}{4}\pi$, etc. It is necessary that g_x^2 and g_y^2 be unequal or else the energy difference between the two strains would be zero.

VII. LINE INTENSITIES IN ZEEMAN PATTERNS

In this section we discuss optical-absorption intensities for the rare-earth ion in the distorted lattice and with magnetic field applied in the basal plane.

The absorption intensity for an electric dipole transition from an initial state ψ_i to a final state ψ_f is proportional in the closure approximation to $|\langle \psi_f | V^o P_\alpha | \psi_i \rangle|^2$. Here V^o is the odd-parity part of $V(T_d) + V(D_{2d})$ in Eq. (1) and P_α is the electric dipole moment operator in the direction of polarization of the incident radiation.

If $g_x^2 > g_y^2$ then, according to Eqs. (31) and (33), strain $+Q_e$ is stable when $\frac{1}{4}\pi > \varphi_m > -\frac{1}{4}\pi$ or $\frac{5}{4}\pi > \varphi_m > \frac{3}{4}\pi$ and strain $-Q_e$ is stable otherwise. If $g_y^2 > g_x^2$, the opposite situation occurs. With strain $+Q_e$ stable, the state functions are $\varphi_{\text{orth}+}(-, \gamma)$ perturbed by the $\mathcal{H}_Z$ of Eq. (30). As a convenient notation we will write this Hamiltonian as

$$\mathcal{H}_Z = \tfrac{1}{2}\mu_B H(g_x^2\cos^2\phi_m + g_y^2\sin^2\phi_m)^{1/2}\begin{pmatrix} 0 & e^{-i\chi_+} \\ e^{i\chi_+} & 0 \end{pmatrix}, \qquad (34)$$

where χ_+ is defined by

$$e^{-i\chi_+} = \frac{g_x\cos\phi_m - i g_y \sin\phi_m}{(g_x^2\cos^2\phi_m + g_y^2\sin^2\phi_m)^{1/2}} . \qquad (35)$$

For the lower level the state function is then

$$\psi_i = 2^{-1/2}[e^{-i\chi_+/2}\varphi_{\text{orth}+}(-, \tfrac{1}{2}) - e^{i\chi_+/2}\varphi_{\text{orth}+}(-, -\tfrac{1}{2})] . \qquad (36)$$

On the other hand, with strain $-Q_e$ stable, the state functions are $\varphi_{\text{orth}-}(-, \gamma)$ perturbed by the $\mathcal{H}_Z$ of Eq. (32). One defines χ_- by

$$e^{-i\chi_-} = \frac{g_y\cos\phi_m - i g_x \sin\phi_m}{(g_y^2\cos^2\phi_m + g_x^2\sin^2\phi_m)^{1/2}} , \qquad (37)$$

and the state function for the lower level is

$$\psi_i = 2^{-1/2}[e^{-i\chi_-/2}\varphi_{\text{orth}-}(-, \tfrac{1}{2}) - e^{i\chi_-/2}\varphi_{\text{orth}-}(-, -\tfrac{1}{2})] . \qquad (38)$$

The φ_m dependence of the energies of these states is given in Eqs. (31) and (33), the negative signs to be used.

We will suppose that the final states in the absorption process came from Γ_6^- or Γ_7^- representations of $\mathcal{H}_{\text{ion}} + V(O_h) + \frac{1}{2}\omega^2 Q_e^2$, say $\varphi_0(\Gamma_n^-, \gamma)$, where $\gamma = \pm\frac{1}{2}$ and n is 6 or 7. The perturbation $V(D_{4h}) + V_L Q_e$ does not affect these states in the first order. They have just one g factor defined by

$$g_n \langle \gamma | \vec{s} | \gamma' \rangle = \langle \varphi_0(\Gamma_n^-, \gamma) | (\vec{L} + 2\vec{S}) | \varphi_0(\Gamma_n^-, \gamma') \rangle , \qquad (39)$$

so for them the magnetic contribution to the Hamiltonian is

$$\mathcal{H}_Z = \mu_B g_n \vec{s} \cdot \vec{H} . \qquad (40)$$

With the magnetic field at angle ϕ_m in the basal plane, this matrix can be written as

$$\mathcal{H}_Z = \tfrac{1}{2}\mu_B g_n H \begin{pmatrix} 0 & e^{-i\phi_m} \\ e^{i\phi_m} & 0 \end{pmatrix}, \qquad (41)$$

and so the final states in the transition are

$$\psi_f = 2^{-1/2}[e^{-1/2 i\phi_m}\varphi_0(\Gamma_n^-, \tfrac{1}{2}) + \eta_n e^{1/2 i\phi_m}\varphi_0(\Gamma_n^-, -\tfrac{1}{2})] , \qquad (42)$$

with energies

$$E_f = E_0(\Gamma_n^-) + (G_2^4 - 2\omega^4 G_1^2)/4\omega^2 G_2^2 + \eta_n \tfrac{1}{2}\mu_B g_n H . \qquad (43)$$

Here $\eta_n = \pm 1$ labels the two states. Which state is lower depends on the sign of g_n.

The ϕ_m dependence of the transition energy comes only from the ground level so is of the form

$$\delta E(+Q_e) = \delta E(H=0) + \tfrac{1}{2}\mu_B H[\eta_n g_n + (g_x^2\cos^2\varphi_m + g_y^2\sin^2\varphi_m)^{1/2}] , \qquad (44a)$$

$$\delta E(-Q_e) = \delta E(H=0) + \tfrac{1}{2}\mu_B H[\eta_n g_n + (g_y^2\cos^2\varphi_m + g_x^2\sin^2\varphi_m)^{1/2}] . \qquad (44b)$$

Figure 2 shows how this transition energy looks, as a function of ϕ_m, allowing for the domain switching.

To simplify the matrix elements $\langle\psi_f | V^o P_\alpha | \psi_i\rangle$, one regards $\varphi_0(\Gamma_n^-, \gamma)$, V^o, P_x, P_y, P_z, and $\varphi_{\mathrm{orth}}(-, \gamma)$ as bases of the Γ_5, Γ_1, Γ_4, Γ_2, Γ_3, Γ_5 representations of D_2. The matrix elements are then given by the tables on p. 37 of Koster *et al.*[31] in terms of a few parameters, say,

$$\alpha_\pm = \langle\varphi_0(\Gamma_n^-, -\tfrac{1}{2}) | V^o P_x | \varphi_{\mathrm{orth}\pm}(-, \tfrac{1}{2})\rangle , \tag{45a}$$

$$\beta_\pm = \langle\varphi_0(\Gamma_n^-, -\tfrac{1}{2}) | V^o P_y | \varphi_{\mathrm{orth}\pm}(-, \tfrac{1}{2})\rangle , \tag{45b}$$

$$\gamma_\pm = \langle\varphi_0(\Gamma_n^-, \tfrac{1}{2}) | V^o P_z | \varphi_{\mathrm{orth}\pm}(-, \tfrac{1}{2})\rangle . \tag{45c}$$

For the intensities $I_{\alpha\pm}$, of absorption of light polarized in the α direction from states of strain $\pm Q_e$ to states η_n, one finds

$$I_{x\pm} \propto \tfrac{1}{2}[1 - \eta_n \cos(\phi_m + \chi_\pm)] | \alpha_\pm |^2 , \tag{46a}$$

$$I_{y\pm} \propto \tfrac{1}{2}[1 + \eta_n \cos(\phi_m + \chi_\pm)] | \beta_\pm |^2 , \tag{46b}$$

$$I_{z\pm} \propto \tfrac{1}{2}[1 + \eta_n \cos(\phi_m - \chi_\pm)] | \gamma_\pm |^2 . \tag{46c}$$

The right-hand sides here are just the absolute squares of the matrix elements $\langle\psi_f | V^o P_\alpha | \psi_i\rangle$. The dependence on ϕ_m can be written out explicitly since Eqs. (35) and (37) give the sine and cosine of $\chi_\pm$. That is,

$$\cos(\phi_m \pm \chi_+) = \frac{g_x \cos^2\phi_m \mp g_y \sin^2\phi_m}{(g_x^2 \cos^2\phi_m + g_y^2 \sin^2\phi_m)^{1/2}} . \tag{47}$$

The formulas for χ_- are the same except with g_x and g_y interchanged.

Sketches of typical intensity patterns in some of the possible cases are given in Figs. 3–6.

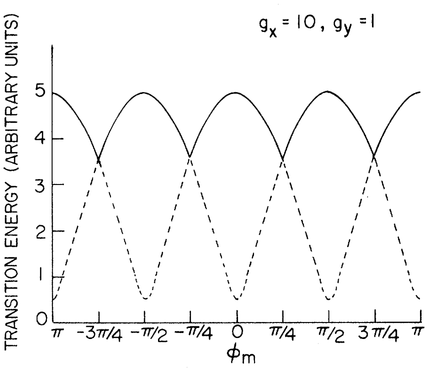

FIG. 2. Typical transition energy δE as a function of the angle ϕ_m at which a magnetic field is applied in the basal plane, measured from the x axis. The formulas for the curves are Eqs. (44). The case $g_x^2 > g_y^2$ is considered so that strain $+Q_e$ is stable when $\frac{1}{4}\pi > \phi_m > -\frac{1}{4}\pi$ or $\frac{5}{4}\pi > \phi_m > \frac{3}{4}\pi$ and strain $-Q_e$ is stable otherwise. The solid line shows the energy of transition from the stable distortion, the dotted from the unstable distortion.

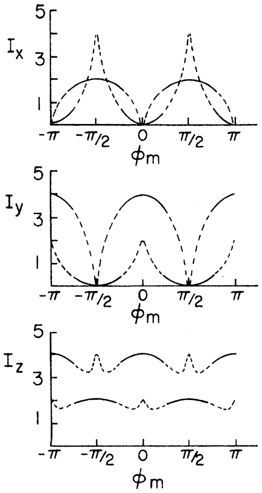

FIG. 3. Typical intensities I_α of absorption lines as a function of the angle ϕ_m at which a magnetic field is applied in the basal plane. The formulas for the curves are Eqs. (46) and (47). The case $g_x^2 > g_y^2$ (so that strain $+Q_e$ is stable when $\frac{1}{4}\pi > \phi_m > -\frac{1}{4}\pi$ or $\frac{5}{4}\pi > \phi_m > \frac{3}{4}\pi$ and strain $-Q_e$ is stable otherwise), g_x and g_y both positive (so that the transition is type A to type A), $\eta_n = +1$ is considered. The solid lines are for transitions from the stable distortion, the dotted for transitions from the unstable distortion.

A remarkable feature of the intensity patterns is that when the domain switching effect is disregarded, the continuous curves $I_\alpha(\phi_m)$ (partly solid and partly dotted lines) either oscillate considerably like I_x and I_y in Fig. 4 or oscillate only weakly like I_z in Fig. 3 and Fig. 4. These qualitatively different behaviors are related to the types of levels involved in the transition. As suggested by the earlier work on C_{3h} symmetry,[32–34] we define the level $\psi_i(\phi_m)$ or $\psi_f(\phi_m)$ to be type A if the level forms the same representation of C_{2h} about the x axis when the magnetic field is along the x axis as of C_{2h} about the y axis when the magnetic field is along the y axis. We define the level to be type B if these representations are different. In deciding which representations occur, it is only necessary to watch C_{2x} or C_{2y} since all the functions have the same inversion property. It is straightforward to find the C_2 characters using

$$C_{2x}\,\varphi(\pm\tfrac{1}{2}) = i\,\varphi(\mp\tfrac{1}{2}) , \qquad C_{2y}\,\varphi(\pm\tfrac{1}{2}) = \mp\varphi(\mp\tfrac{1}{2}) .$$

Thus from Eq. (42) one finds

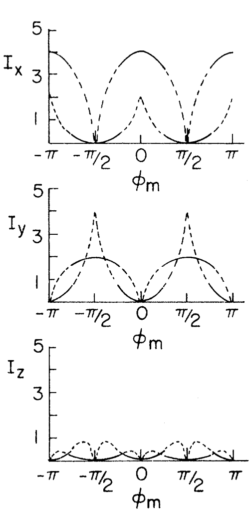

FIG. 4. Typical intensities of absorption lines, the same as Fig. 3, except for the case $g_x^2 > g_y^2$, g_x and g_y both positive, $\eta_n = -1$.

$$C_{2x}\,\psi_f\,(\phi_m=0)=i\,\eta_n\,\psi_f\,(\phi_m=0)\ ,$$

$$C_{2y}\,\psi_f\,(\phi_m=\tfrac{1}{2}\pi)=i\,\eta_n\,\psi_f(\phi_m=\tfrac{1}{2}\pi)\ ,$$

so the final states ψ_f are type A. For ψ_i with strain $+Q_e$, using Eqs. (35) and (36), one calculates

$$C_{2x}\,\psi_i\,(\phi_m=0)=-\,i\,(g_x/|g_x|)\,\psi_i(\phi_m=0)\ ,$$

$$C_{2y}\,\psi_i\,(\phi_m=\tfrac{1}{2}\pi)=-\,i\,(g_y/|g_y|)\psi_i(\phi_m=\tfrac{1}{2}\pi)\ .$$

These states are therefore type A if g_x and g_y are the same sign, type B if g_x and g_y are of opposite sign. The same result holds for ψ_i with strain $-Q_e$. In an A → A transition $I_x(\phi_m)$ and $I_y(\phi_m)$ must oscillate strongly because the C_2 selection rule on the matrix element acts differently at $\phi_m=0$ than at $\phi_m=\frac{1}{2}\pi$. Also $I_z(\phi_m)$ must oscillate weakly because the selection rule acts the same at the two angles. On the other hand, in a B → A transition I_x and I_y must oscillate weakly and I_z must oscillate strongly. These are evident features of the intensity patterns, Figs. 3–6. In addition to these considerations, the domain switching gives additional complexity to the observed intensity patterns.

VIII. DISCUSSION

The model presented here gives a satisfactory account of many of the properties of $DyVO_4$, $DyPO_4$, and $DyAsO_4$ crystals in the orthorhombic and tetragonal phases. It allows for the phase transition as long as $V(D_{4h})$ or V_L has the proper temperature dependence. If K_2/K_1 is small and there is enough temperature dependence, it requires that $g_x(-)$ $[g_y(-)]$ be large compared to $g_y(-)$ $[g_x(-)]$ and $g_z(-)$ at a certain temperature in the orthorhombic phase. The model accounts for the switching of domains by a basal-plane magnetic field. Also, it suggests that the phase transition temperature will be strongly influenced by a magnetic field applied in the c-axis direction, as has been observed for $TmVO_4$,[9,12,25] $TmAsO_4$,[21,25] and $TbPO_4$,[19,24] but not reported so far for the dysprosium crystals.

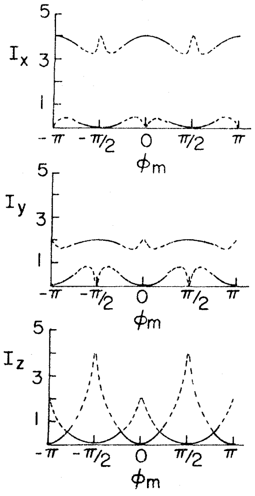

FIG. 5. Typical intensities of absorption lines, the same as Fig. 3, except for the case $g_x^2>g_y^2$, g_x negative and g_y positive (so that the transition is type B to type A), $\eta_n=+1$.

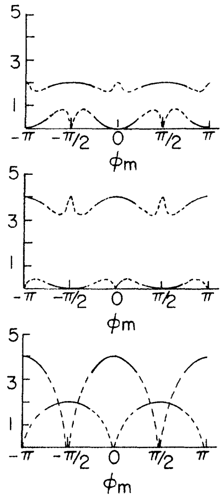

FIG. 6. Typical intensities of absorption lines, the same as Fig. 3, except for the case $g_x^2>g_y^2$, g_x negative and g_y positive, $\eta_n=-1$.

The model makes many definite predictions which will be interesting to compare with experimental results as new data become available.

As concluded at the end of Sec. III, the energy separation of the two ground doublets is $(G_2/\omega)^2$ in the orthorhombic phase, $2^{1/2}\,|\,G_1\,|$ in the tetragonal phase. In all the crystals that have the orthorhombic-tetragonal phase transition, the splittings of the levels are temperature-dependent in the orthorhombic phase. Thus the temperature dependence is in the electron–lattice-strain interaction term, G_2 is temperature dependent, and G_1 is not. One knows both $|\,G_2/\omega\,|$ and $|\,G_1\,|$ in the orthorhombic phase from the energy separation of the ground doublets; $|\,G_2/\omega\,|$ from the separation in the orthorhombic phase and $|\,G_1\,|$ from the separation in the tetragonal phase. The sign of G_1 must be inferred somehow, perhaps by one of the methods discussed at the end of Sec. IV, but then $\theta_e(T)$ is known from Eq. (10) and the relative sizes of all the g factors are predicted, in case K_2/K_1 is small, by Eqs. (21).

One can start to make a numerical comparison for $DyVO_4$. The observed separations of the two ground doublets in the distorted and undistorted phases are about 27 and 5 cm^{-1}, respectively.[16–18] The observed g values are $|\,g_x(-)\,|\cong 0$, $|\,g_y(-)\,|\cong 19$, $|\,g_z(-)\,|\cong 0.5$.[10,16] One can find $\tan\theta_e$ independently from these two types of observation and make a comparison. The level separations give $(G_2/\omega)^2=27$ cm^{-1}, $2^{1/2}G_1=\pm 5$ cm^{-1} and then Eq. (10) implies (taking G_2 positive) that $\tan\theta_e$ is 0.69 or 1.45. The g factors give the ratio $g_y(-)/g_z(-)=\pm 38$. This ratio determines $\tan\theta_e$ by way of Eqs. (21a) and (21c). The result here is that $\tan\theta_e$ is 0.61 or 0.55. There is rough agreement with the level-separation result for positive G_1.

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Symmetry-Dependent Effective Force-Constant Changes around Impurities in Ionic Crystals*

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The lattice relaxation and effective force-constant changes for even symmetry modes around substitutional impurities in ionic crystals are studied in terms of a simple classical ionic-crystal model for the potential energy. It is shown that Coulomb and second-neighbor repulsive interactions can make large contributions to the effective force-constant changes. These contributions are symmetry dependent, and may even yield, for example, A_{1g} and E_g effective force-constant changes which have opposite signs, contrary to what has been frequently assumed in the literature. Illustrative results are presented for the Raman scattering of substitutional Ag^+ ions in sodium chloride.

I. INTRODUCTION

To obtain quantitative agreement with experimental data on substitutional impurities in ionic crystals, it is generally necessary to include changes in force constants as well as in mass in the theoretical treatment. Furthermore, although the major force-constant changes are localized around the defect, it is often not sufficient to restrict these changes to first neighbors only; the work of several authors on the substitutional H^- ion (U center) in the alkali halides[1-4] provides a good illustration of this point. For example, the model of Gethins, Timusk, and Woll[2] for the U center permits changes in the force constants between the impurity ion and its first neighbors, and in those linking ions in the first and fourth shells, since these should be most strongly affected by the relaxation about the defect. Although perhaps surprising at first, it is easy to show that small lattice