Synder, Phys. Rev. Letters 4, 274 (1960).

[26] L. R. Walker, G. K. Wertheim, and V. Jaccarino, Phys. Rev. Letters 6, 98 (1961). Referred to as WWJ in this paper.

[27] Y. Y. Chu, O. C. Kistner, A. C. Li, S. Monaro, and M. L. Periman, Phys. Rev. 133, B1361 (1964).

[28] S. Margulies and J. R. Ehrman, Nuclear Inst. and Methods 12, 131 (1961).

[29] S. W. Marshall, J. A. Nelson, and R. M. Wilenzick, Commun. ACM 8, 313 (1965).

[30] A. Abragam and F. Boutron, Compt. Rend. 252, 2404 (1961).

[31] O. G. Folberth, in *Compound Semiconductors*, Vol. I, edited by R. K. Willardson and H. L. Goering (Reinhold, New York, 1961), p. 31.

[32] V. Kothekar, B. Z. Iofa, S. I. Semenov, and V. S. Shpinel, Zh. Eksperim. i Theor. Fiz. 55, 160 (1968) [Soviet Phys. JETP 28, 86 (1969)].

[33] S. L. Ruby and G. K. Shenoy, Phys. Rev. 186, 326 (1969).

[34] J. Lees and P. A. Flinn, Phys. Letters 19, 186 (1965).

[35] J. C. Woolley and B. A. Smith, Proc. Phys. Soc. (London) 72, 214 (1958).

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Dynamic Jahn-Teller Effect in the Orbital ^5E State of Fe^{2+} in CdTe

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A calculation of the ^5E energy levels of Fe^{2+} in CdTe has been performed taking into account coupling between the electron system of the impurity ion and the vibrations of the host lattice. The coupling is approximated to a single pair of E modes corresponding to the TA(L) phonons. We find that even a small electron-phonon coupling not only displaces the energy levels from those of crystal-field theory, but also introduces additional transitions. We get qualitative agreement with the experimental observations for an effective spin-orbit splitting of 20.8 cm^{-1} and a Jahn-Teller energy of 4.2 cm^{-1}. We also find that we get better agreement between theory and experiment if we take spin-spin interactions into account.

I. INTRODUCTION

Low-energy electronic levels of the Fe^{2+} ($3d^6$) ion in sites of tetrahedral symmetry have been detected directly by far-infrared optical absorption in crystals of cubic ZnS[1] and CdTe,[2] in the range below 100 cm^{-1}. For ZnS the number, position, and intensities of the absorption peaks at 4 °K can be accounted for by simple crystal-field theory in terms of the spin-orbit splitting of the ^5E ground state.[1,2] In CdTe, however, the Fe^{2+} spectrum does not fit this theory and in particular exhibits additional lines.[2] The purpose of this paper is to consider a model which can account for this spectrum by augmenting crystal-field theory to include dynamic Jahn-Teller coupling between the ^5E state of the Fe^{2+} ion and a low-frequency vibrational mode of the CdTe lattice.

The crystal lattices of cubic ZnS[3] and CdTe,[4] in common with other II-VI compounds, have the transverse acoustic (TA) branch of the phonon spectrum at a quite low frequency. For cubic ZnS, however, the critical points in this branch are above the energies of the excited levels of the Fe^{2+} ion to which the far-infrared transitions take place. The Jahn-Teller coupling of the ^5E state of the Fe^{2+} ion to these and other vibrational modes is apparently weak,[1] and no definite evidence of a Jahn-Teller effect in the ^5E state of ZnS: Fe^{2+} has been found. For CdTe, on the other hand, the critical points in the TA branch are so low as to lie among these Fe^{2+} levels. Some of these phonons moreover have the correct symmetry to participate in Jahn-Teller coupling with the ^5E state of the substitutional Fe^{2+} ion. As we will show, such a coupling, though weak, nevertheless can appreciably distort the electronic absorption spectrum and can introduce extra lines as found experimentally.

In addition to those phonons which contribute to the Jahn-Teller coupling, other lattice phonons from the TA branch may be optically excited as a result of the electron-phonon coupling with the Fe^{2+} ion, and these may contribute additional structure as side bands to the lines of the electronic absorption spectrum. We will see that there is also evidence for extra absorption of this sort in the experimental spectrum.

In this paper we first review briefly in Sec. II the relevant predictions of crystal-field theory for the Fe^{2+} ion,[1,5] including the effect of spin-spin interaction which heretofore has not been considered. The form of the various types of vibronic coupling is given in Sec. III, and the effect of this coupling on the energy levels of the electron-phonon system and on the optical transition probabilities is then considered. The effect of the Jahn-Teller coupling on the g factor of the lowest excited level, which has been observed to split in a magnetic field,[2] is also obtained. The results of the quantitative calculations and their comparison with the experimental data are presented and discussed in Sec. IV.

II. CRYSTAL-FIELD THEORY

The lowest term, ^5D, of the Fe^{2+} ($3d^6$) free ion is split[6] into an orbital doublet,[7] ^5E, and an orbital triplet, $^5T_2$, by the crystal field of tetrahedral symmetry (point group T_d) when the Fe^{2+} ion substitutes for a Cd ion in the CdTe lattice. The ground state is ^5E, and $^5T_2$ is higher by the cubic-field energy separation $\Delta (= 10|Dq|)$, which in CdTe is found[2,5] to be 2480 cm^{-1}. As Δ is much smaller than the separation of ^5D from higher LS terms in the free ion, we may neglect such higher states for the purposes of this paper (except insofar as they contribute to the effective "spin-spin" interaction within ^5E, see below).

As the spin functions for $S = 2$ span the irreducible representations $\Gamma_3 + \Gamma_5$ of T_d and we have the reduction of the direct product[8]

$$\Gamma_3 \times (\Gamma_3 + \Gamma_5) = \Gamma_1 + \Gamma_2 + \Gamma_3 + \Gamma_4 + \Gamma_5, \qquad (1)$$

we expect the ^5E state, in general, to split into five spin-orbit levels in tetrahedral symmetry. The spin-orbit interaction, described by $\lambda_0(\vec{L}\cdot\vec{S})$ within the ^5D free-ion states with $\lambda_0 \approx -(100 \pm 10)$ cm^{-1}, causes no first-order splitting of ^5E but does cause a second-order splitting as a result of the coupling between ^5E and $^5T_2$. To the accuracy of second-order perturbation theory this splitting is equivalent to that produced by the effective spin-orbit operator

$$\mathcal{H}_{SO} = -\tfrac{1}{6}K\{[3S_Z^2 - S(S+1)]U_\theta + \sqrt{3}[S_X^2 - S_Y^2]U_\epsilon\} \qquad (2)$$

acting within ^5E. Here $\hbar\vec{S}$ is the spin operator with components S_X, S_Y, S_Z referred to the cubic (fourfold) axes, and U_θ, U_ϵ are orbital operators[9] transforming[10] as $\Gamma_{3\theta}$, $\Gamma_{3\epsilon}$ under T_d and defined to have matrix elements with respect to the orbital electronic states Ψ_θ, Ψ_ϵ of ^5E given by

$$U_\theta = \begin{pmatrix} -1 & 0 \\ 0 & +1 \end{pmatrix}, \quad U_\epsilon = \begin{pmatrix} 0 & +1 \\ +1 & 0 \end{pmatrix} \qquad (3)$$

[i.e., $\langle \Psi_\theta | U_\theta | \Psi_\theta \rangle = -1$, etc.]. The coefficient K in Eq. (2) has the value

$$K = +6\lambda^2/\Delta, \qquad (4)$$

where $\lambda(\vec{L}\cdot\vec{S})$ represents the effective spin-orbit interaction between ^5E and $^5T_2$, and λ may depart from the free-ion value λ_0 because of covalency and other effects of the crystalline environment. The splitting of ^5E as given by $\mathcal{H}_{SO}$ in Eq. (2) is then shown in Fig. 1(A): The five levels are spaced[6] uniformly[11] with a separation $\delta = K$, in the order Γ_1, Γ_4, Γ_3, Γ_5, Γ_2, with the Γ_1 singlet the ground state. The explicit wave functions for these levels, given as linear combinations of products of the spin functions with the orbital states Ψ_θ and Ψ_ϵ, are uniquely determined from the tables[8] of coupling coefficients for the group T_d.

These spin-orbit levels of ^5E, arranged as in Fig. 1(A) with a suitable value of δ, provide the model which has been used successfully[1] to interpret the far-infrared absorption spectrum of ZnS: Fe^{2+} on the basis of simple crystal-field theory, but which fails[2] to account for the data on CdTe: Fe^{2+}.

A. Spin-Spin Interaction

The magnetic spin-spin interaction among the electrons of an ion is equivalent within an LS term to the operator

$$\mathcal{H}_{SS} = -\rho\,[(\vec{L}\cdot\vec{S})^2 + \tfrac{1}{2}(\vec{L}\cdot\vec{S}) - \tfrac{1}{3}L(L+1)S(S+1)], \qquad (5)$$

where $\hbar\vec{L}$ is the orbital angular momentum operator. Pryce[12] inferred the value

$$\rho = +0.95 \pm 0.1\ cm^{-1} \qquad (6)$$

for the ^5D term of Fe^{2+} from spectroscopic data for the free ion by considering departures from the Landé interval rule. Trees[13] subsequently noted that spin-orbit coupling between different LS terms provides an important additional interaction having

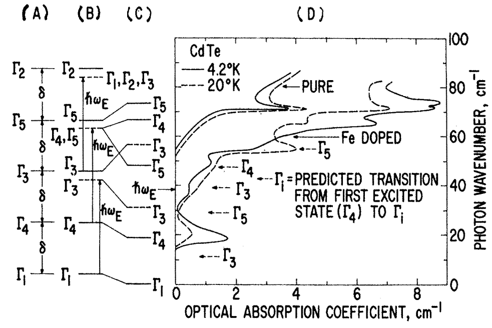

FIG. 1. (A) Electronic energy levels for Fe^{2+} in CdTe as predicted from simple crystal-field theory. (B) Vibronic energy levels originating from the electronic ^5E states of Fe^{2+} in CdTe with no Jahn-Teller coupling ($\mathcal{H}_{JT} = 0$). (C) Vibronic energy levels originating from the electronic ^5E states of Fe^{2+} in CdTe with Jahn-Teller coupling ($\mathcal{H}_{JT} \neq 0$). (D) Experimental results (from Ref. 2) of the optical absorption coefficient versus photon wave number for Fe-doped CdTe.

exactly the same form as Eq. (5), when this coupling is treated by second-order perturbation theory. The value (6) for the coefficient ρ inferred from spectroscopic data thus represents the combined effect on the ^5D term of both the true spin-spin interaction and the spin-orbit interaction to the higher terms of the $3d^6$ configuration having $S=1$. Watson and Blume[14] have more recently calculated the coefficient in Eq. (5) for the true spin-spin interaction, using free-ion Hartree-Fock wave functions, to be $\rho_0=+0.18\ \text{cm}^{-1}$ for the ^5D term of Fe^{2+}, a value estimated to be accurate to 5%. The balance of Pryce's value (6) must therefore result from the spin-orbit interaction.

It may be shown from the Wigner-Eckart theorem that the direct effect of the operator in Eq. (5) within the ^5E state must be equivalent to that of an operator identical in form with $\mathcal{H}_{SO}$ in Eq. (2). From a simple calculation we find that this equivalence to Eq. (5) is achieved if we replace the coefficient $(-\frac{1}{6}K)$ in Eq. (2) by $|-p|$. We recognize, therefore, that the combined effect of the spin-spin and spin-orbit interactions in splitting the ^5E state, including the effect of spin-orbit coupling to the higher terms with $S=1$, is thus given by our previous discussion of the effect of the spin-orbit coupling between ^5E and $^5T_2$, except that the separation of the spin-orbit levels in Fig. 1(A) is now given by

$$\delta=K+6\rho=6(\lambda^2/\Delta+\rho). \tag{7}$$

Since K is positive when ^5E is the ground state, and since ρ as given by Eq. (6) is also positive, we conclude that the effective spin-spin interaction given by Eq. (5) acts to increase the spin-orbit splitting of the ^5E state for Fe^{2+} in tetrahedral coordination. Although the proper value of ρ for use in Eq. (4) may be changed somewhat in the crystal because of the splitting of the higher $S=1$ terms in the crystal field and because of covalency, we will use Pryce's value (6) in our present work since we do not know the energies of these higher terms and therefore have not attempted to calculate this correction, and since in CdTe the cubic-field splitting Δ is in any case much smaller than the energies of these higher levels in the free ion.[15]

III. VIBRONIC COUPLING

A. General Form of Coupling

Interaction between the electrons of the Fe^{2+} impurity and lattice vibrations of the crystal results from the changes in the crystal field induced by displacements of the ions. This coupling must take the form

$$\mathcal{H}_v=\sum_{p,i} V_p(i)\sum_q U_q^p(i)Q_q^p(i) \tag{8}$$

to first order in the various independent (real) linear combinations of the ion displacements, which we denote by $Q_q^p(i)$ and which we classify according to the row q of the irreducible representation Γ_p by which each transforms under the symmetry operations of the point group (T_d) of the Fe^{2+} site. The $U_q^p(i)$ are real Hermitian operators acting on the electronic states and having the same transformation behavior as the $Q_q^p(i)$, while the $V_p(i)$ are real coefficients. $\mathcal{H}_v$ as given by Eq. (8) is invariant under time reversal and under the full point group T_d when the symmetry transformations are applied simultaneously to the electron and ion coordinates.

B. Jahn-Teller Coupling

Of the many displacements $Q_q^p(i)$ appearing in Eq. (8) only those transforming as Γ_3 contribute to the Jahn-Teller coupling[16] with an orbital doublet $E(\Gamma_3)$ state, that is, to a splitting of the doublet linear in the Q.[17] Since the strongest coupling should be with the displacements of the four Te ions which are nearest neighbors of the Fe^{2+}, and as there is but one Γ_3 mode that can be formed from these displacements, it should suffice for many purposes to assume that the Jahn-Teller coupling with the ^5E state of the Fe^{2+} may be described by a single pair of terms from Eq. (8), which we may put in the form[9]

$$\mathcal{H}_{JT}=V[Q_\theta U_\theta+Q_\epsilon U_\epsilon], \tag{9}$$

using the operators defined in Eq. (3). Although these displacements of the nearest neighbors are not normal modes of vibration of the crystal, it is often assumed in treating Jahn-Teller problems in crystals[18] that it is a good approximation to take these to be normal modes with elastic energy given by

$$\mathcal{H}_{el}=\tfrac{1}{2}\kappa(Q_\theta^2+Q_\epsilon^2). \tag{10}$$

The justification of this approximation has been discussed recently by Ham, Schwarz, and O'Brien[19] for the case in which the phonons of the crystal, with which the principal Jahn-Teller coupling occurs, have frequencies appreciably higher than the energies of the electronic states of interest (the lowest $^5T_{2g}$ spin-orbit levels of symmetry Γ_{3g}, Γ_{4g}, and Γ_{5g} of MgO: Fe^{2+} in the case studied by Ham *et al.*[19]), which are displaced as a result of the vibronic coupling. However, in the present case the critical points in the TA branch of CdTe are so low as to place these phonons among the ^5E spin-orbit levels of the Fe^{2+}. We might expect therefore that the distribution of vibronic states arising from these ^5E electronic states as a result of the Jahn-Teller coupling might reflect the structure of the critical points in the TA branch, if the phonons at these points have the correct symmetry to participate in the coupling. The symmetry of the phonons in the zinc-blende lattice has been worked out by Loudon,[20] who finds that at the centers X and L of the Brillouin zone face in the ⟨100⟩ and ⟨111⟩ directions, respectively, the TA phonons (which comprise the basis for an irreducible representation of the space group) provide a basis for the following representations of the point group (T_d) at a lattice site:

$$\begin{aligned} &\mathrm{TA}(X): \quad \Gamma_4+\Gamma_5 \\ &\mathrm{TA}(L): \quad \Gamma_3+\Gamma_4+\Gamma_5. \end{aligned} \tag{11}$$

We see that only TA(L) contributes a Γ_3 mode, so that phonons at TA(X) do not participate in the Jahn-Teller coupling for an E state. While this argument does not exclude the likelihood that phonons over a considerable range *inside* the Brillouin zone, as well as those at points other than X on its surface, contribute to the Jahn-Teller coupling, it does suggest that a model for the ^5E state of CdTe: Fe^{2+} may nevertheless suffice in which the Jahn-Teller coupling is taken with a single Γ_3 mode, as in Eq. (9), having an effective frequency ω_E near TA(L). This is the model we will use in our calculations. Its usefulness must, of course, ultimately be judged on the extent to which it succeeds in providing a basis for the interpretation of the data.

C. Energy Levels of Jahn-Teller Model

The vibrational Hamiltonian for the two-dimensional harmonic oscillator with which the Jahn-Teller coupling (9) takes place in our model is obtained by adding to the elastic energy (10) the corresponding kinetic energy, so that we obtain

$$\mathcal{H}_{\mathrm{vib}}=(1/2\mu)\left[P_\theta^2+P_\epsilon^2+\mu^2\omega_E^2\left(Q_\theta^2+Q_\epsilon^2\right)\right], \tag{12}$$

where P_θ and P_ϵ are momenta conjugate to Q_θ and Q_ϵ, and μ is the effective mass of the mode. The vibrational eigenfunctions of (12) are the products $F_\theta^n F_\epsilon^m$ of the simple harmonic oscillator wave functions $F_\theta^n \equiv F^n(Q_\theta)$, $F_\epsilon^m \equiv F^m(Q_\epsilon)$, which have the properties

$$\langle F_i^n | F_j^m \rangle = \delta_{ij}\delta_{nm}, \tag{13}$$

$$\langle F_i^n | Q_i | F_j^m \rangle = \delta_{ij} \times \begin{cases} (1/\alpha)\left[\tfrac{1}{2}(n+1)\right]^{1/2}, & m=n+1 \\ (1/\alpha)\left(\tfrac{1}{2}n\right)^{1/2}, & m=n-1 \\ 0, & \text{otherwise} \end{cases} \tag{14}$$

$$\mathcal{H}_{\mathrm{vib}} F_\theta^n F_\theta^m = \hbar\omega_E (n+m+1) F_\theta^n F_\epsilon^m. \tag{15}$$

[α is a constant characteristic for the harmonic oscillator considered and defined as $\alpha=(\mu\omega_E/\hbar)^{1/2}$.]

The unperturbed vibronic energy levels of the ^5E state of the Fe^{2+} are then the eigenstates of

$$\mathcal{H}_0=\mathcal{H}_{\mathrm{SO}}+\mathcal{H}_{\mathrm{vib}}, \tag{16}$$

where in taking the spin-orbit interaction (2) we replace K in the coefficient by δ as given in Eq. (7), to include the effective spin-spin interaction. The eigenenergies of Eq. (16) [Fig. 1 (b)] are just the sum of the electronic energies of $\mathcal{H}_{\mathrm{SO}}$ [Fig. 1(A)] and the vibrational energies of Eq. (15). The corresponding wave functions are products of eigenstates of $\mathcal{H}_{\mathrm{SO}}$ and $\mathcal{H}_{\mathrm{vib}}$. We have obtained these wave functions and their transformation properties by using the tables of Koster *et al.* (Table I).[8] From Table I and Eq. (13) we note that transitions can only occur between states with the same number of phonons excited. Therefore only electronic energy levels are observed and $\mathcal{H}_{\mathrm{vib}}$ is of no practical importance.

When $\mathcal{H}_{\mathrm{JT}} \neq 0$ we have to consider the Hamiltonian

$$\mathcal{H}=\mathcal{H}_{\mathrm{SO}}+\mathcal{H}_{\mathrm{vib}}+\mathcal{H}_{\mathrm{JT}}. \tag{17}$$

According to Eq. (9) and Eq. (14) we will now have a coupling between states differing by one vibrational quantum. Thus this coupling not only displaces the energy levels but also admixes the states and thereby makes possible additional optical transitions.

In order to calculate the matrix elements of the Hamiltonian in the presence of a Jahn-Teller effect we observe the following: (a) The spin-orbit mixing of $^5T_2$ and ^5E wave functions is small and can be neglected in evaluating the matrix elements of $\mathcal{H}_{\mathrm{JT}}$; (b) according to group theory a totally symmetric operator only couples wave functions belonging to the same row of the same irreducible representation.[21]

Neglecting the unimportant shifts in energies of the ^5E states due to the crystal-field and zero-point motion of the lattice we obtain, for instance,

$$\langle \Gamma_1 | \mathcal{H} | \Gamma_1 \rangle = \begin{pmatrix} 0 & V/\alpha \\ V/\alpha & 2\delta+\hbar\omega_E \end{pmatrix}. \tag{18}$$

These are the matrix elements of $\mathcal{H}$ with regard to the two lowest-lying vibronic Γ_1 states. These states originate from the Γ_1 spin-orbit split state with no phonon excited and from the Γ_3 state with one phonon excited. There are, of course, higher Γ_1 vibronic states involving two or more phonons excited. However these states influence the zero-phonon ground state Γ_1 only by higher-order processes and can be neglected [relation (14)]. Corresponding matrices are obtained for the other symmetry states. Table I includes all states considered in calculating the energy levels.

Fletcher and Stevens[22] have also treated the Jahn-Teller problem of an ^5E state coupled to a Γ_3 vibrational mode (Cr^{2+} in MgO). However, these authors considered the case of strong coupling $\mathcal{H}_{\mathrm{JT}} \gg \mathcal{H}_{\mathrm{SO}}$, while in the present work the Jahn-Teller coupling is very weak and is treated as a modest perturbation on the eigenstates of (16).

TABLE I. Vibronic wave functions for $\mathcal{H}_{JT}=0$, originating from the electronic ^5E states of Fe^{2+} in CdTe.

Wave function[a]	Energy
$\lvert \Gamma_1 \rangle_0 = (1/\sqrt{2})(\lvert \theta\theta \rangle + \lvert \epsilon\epsilon \rangle) F_\theta^0 F_\epsilon^0$	0
$\lvert \Gamma_4 Z \rangle_0 = \lvert \epsilon\zeta \rangle F_\theta^0 F_\epsilon^0$	δ
$\lvert \Gamma_3 \theta \rangle_1 = (1/\sqrt{2})(\lvert \theta\theta \rangle + \lvert \epsilon\epsilon \rangle) F_\theta^1 F_\epsilon^0$	$\hbar\omega_E$
$\lvert \Gamma_3 \theta \rangle_0 = (1/\sqrt{2})(-\lvert \theta\theta \rangle + \lvert \epsilon\epsilon \rangle) F_\theta^0 F_\epsilon^0$	2δ
$\lvert \Gamma_4 Z \rangle_1 = -\lvert \epsilon\zeta \rangle F_\theta^1 F_\epsilon^0$	$\delta + \hbar\omega_E$
$\lvert \Gamma_5 \zeta \rangle_1 = \lvert \epsilon\zeta \rangle F_\epsilon^1 F_\theta^0$	$\delta + \hbar\omega_E$
$\lvert \Gamma_5 \zeta \rangle_0 = -\lvert \theta\zeta \rangle F_\theta^0 F_\epsilon^0$	3δ
$\lvert \Gamma_1 \rangle_1 = \frac{1}{2}[(-\lvert \theta\theta \rangle + \lvert \epsilon\epsilon \rangle) F_\theta^1 F_\epsilon^0 + (\lvert \epsilon\theta \rangle + \lvert \theta\epsilon \rangle) F_\epsilon^1 F_\theta^0]$	$2\delta + \hbar\omega_E$
$\lvert \Gamma_4 Z \rangle_2 = (1/\sqrt{2}) \lvert \epsilon\zeta \rangle (F_\theta^2 F_\epsilon^0 + F_\theta^0 F_\epsilon^2)$	$\delta + 2\hbar\omega_E$
$\lvert \Gamma_4 Z \rangle_{2'} = (1/\sqrt{2}) \lvert \epsilon\zeta \rangle (F_\theta^2 F_\epsilon^0 - F_\theta^0 F_\epsilon^2)$	$\delta + 2\hbar\omega_E$
$\lvert \Gamma_5 \zeta \rangle_2 = \lvert \epsilon\zeta \rangle F_\theta^1 F_\epsilon^1$	$\delta + 2\hbar\omega_E$
$\lvert \Gamma_4 Z \rangle_{1'} = -\lvert \theta\zeta \rangle F_\epsilon^1 F_\theta^0$	$3\delta + \hbar\omega_E$
$\lvert \Gamma_5 \zeta \rangle_{1'} = \lvert \theta\zeta \rangle F_\theta^1 F_\epsilon^0$	$3\delta + \hbar\omega_E$

[a] The kets on the right-hand side denote the electronic wave functions as products of orbital and spin functions. The first label in each ket denotes the orbital function, the second the spin function.

D. Optical Transition Probabilities in Jahn-Teller Model

To demonstrate the effect the Jahn-Teller coupling has on transition probabilities we will consider a simple example. Let us assume that when $\mathcal{H}_{JT}=0$ we have two electronic states, the ground state Γ_i, and the excited state Γ_f. The transition probability is proportional to $P_0 = \hbar\omega_0 \lvert\langle \Gamma_f \lvert O \rvert \Gamma_i \rangle\rvert^2$. O is the operator causing the transition and $\hbar\omega_0$ is the energy difference between Γ_i and Γ_f. Let us further assume that an excited vibronic state Γ_v has the same symmetry properties as the no-phonon vibronic state of $\Gamma_f = \Gamma_{f0}$ (but different from Γ_i), and that these two states interact through a linear Jahn-Teller coupling. We now obtain the eigenfunctions for $\mathcal{H}_{JT} \neq 0$, $\Psi_1 = a\Gamma_{f0} + b\Gamma_v$ and $\Psi_2 = b\Gamma_{f0} - a\Gamma_v$ with $a^2 + b^2 = 1$. We now have two possible final states with transition probabilities proportional to

$$P_1 = \hbar\omega_1 \lvert \langle \Psi_1 \lvert O \rvert \Gamma_{i0} \rangle^2$$

and

$$P_2 = \hbar\omega_2 \lvert \langle \Psi_2 \lvert O \rvert \Gamma_{i0} \rangle \rvert^2 .$$

$\hbar\omega_j$ is the energy difference between the initial state Γ_{i0} and the excited state Ψ_j. Because O is an electronic operator it will only couple vibronic states containing the same vibrational part. We therefore obtain $P_1 = (\omega_1/\omega_0)a^2 P_0$ and $P_2 = (\omega_2/\omega_0) \times b^2 P_0$. If we define the nth moment M_n for the transitions as

$$M_n = \sum_i (\hbar\omega_i)^{n-1} P_i \ , \tag{19}$$

one can show that M_0, as well as M_1, is independent of $\mathcal{H}_{JT}$ as long as Γ_{i0} is unaffected by the Jahn-Teller coupling and as long as the coupling is linear.[23] As we showed in Sec. III C the ground state *is* affected by the Jahn-Teller coupling (Eq. 18). However, in calculating transition probabilities from the ground state in CdTe: Fe^{2+} we find that the corrections due to this coupling are small and can be neglected. This simple example thus demonstrates how the pure electronic transition is shared between different vibronic states when a linear Jahn-Teller coupling is present.

E. Additional Far-Infrared Absorption Including Simultaneous Phonon Emission

In addition to the far-infrared absorption lines corresponding to transitions between the Jahn-Teller energy levels, as considered in Sec. III D, there is, of course, also the possibility that excitation of the Jahn-Teller system may be accompanied by the simultaneous emission (or, at sufficiently high temperatures, absorption) of a lattice phonon. Selection rules for optical transitions in tetrahedral symmetry indeed permit such processes, at least in principle, for phonons at both TA(X) and TA(L), accompanying a transition between any pair of levels of our Jahn-Teller system. Such absorptions may become weakly allowed as electric dipole processes by borrowing intensity, via terms in the vibronic interaction (8) involving such non-Jahn-Teller phonons as those of Γ_4 or Γ_5 symmetry in (11), from allowed electronic transitions of the covalent Fe^{2+} complex. Absorption lines of this sort may therefore occur at energies displaced by that of one (or more than one) lattice phonon from the energy difference of the corresponding pair of levels of the Jahn-Teller system (including processes in which the initial and final levels of the Jahn-Teller systems are the same). Intensities for some of these absorptions may be weakened by spin selection rules; for example, the electronic spin-orbit states Γ_1, Γ_3, and Γ_2 of the ^5E state are made up from the Γ_3 spin states of $S=2$, while the Γ_4 and Γ_5 spin-orbit states are made up from the Γ_5 spin states, so that electric dipole transitions between vibronic states derived from these different sets of states are allowed only because of the spin-orbit interaction.

In addition, direct excitation of a Γ_5 phonon with no excitation of the Jahn-Teller system may occur in an ionic crystal such as CdTe simply as a result of the direct coupling of the light to the ionic displacements. The selection rule on the k vector that would normally prevent the excitation of one phonon at the zone boundary such as TA(L) or TA(X), in the perfect crystal, may be broken[20] because of the mass defect or difference in force constants associated with the Fe^{2+} impurity, or because the effective charge of the Fe^{2+} differs from that of the Cd it replaces.

F. *g* Factor of First Excited State

The Zeeman interaction in the ${}^5E$ state of Fe^{2+} in a magnetic field H, as given by crystal-field theory in cubic or tetrahedral symmetry, may be expressed[9] in terms of the operators (3) as

$$\mathcal{H}_z = g_1\beta(\vec{\mathrm{S}}\cdot\vec{\mathrm{H}}) + (\tfrac{1}{2}g_2\beta)\{[3S_Z H_Z - (\vec{\mathrm{S}}\cdot\vec{\mathrm{H}})]U_\theta + \sqrt{3}\,[S_X H_X - S_Y H_Y]U_\epsilon\}\,, \tag{20}$$

where g_1, g_2 are given by

$$g_1 = 2 - (4\lambda/\Delta), \quad g_2 = -(4\lambda/\Delta)$$

to first order in the spin-orbit coupling between ${}^5E$ and ${}^5T_2$. We will use Eq. (2) to obtain the g factor of the lowest excited state (Γ_4), as it is affected by the Jahn-Teller coupling.

The vibronic eigenfunctions for the lowest Γ_4 level, as obtained from the analysis of Sec. III C to the accuracy of including the admixture of states with one phonon excited, are given by

$$\Psi_i = a\Phi_{40i} = b\Phi_{41i} + c\Phi_{41'i}, \tag{21}$$

where the Φ_{kji} are the vibronic functions given in Table I,[24] and a, b, and c are real coefficients satisfying the normalization condition

$$a^2 + b^2 + c^2 = 1. \tag{22}$$

Since the linear splitting of a Γ_4 triplet in a magnetic field may be described in terms of an effective spin $\vec{\mathcal{J}}(\vec{\mathcal{J}}=1)$ by the isotropic effective interaction

$$\mathcal{H}_z(\Gamma_4) = g\beta(\vec{\mathcal{J}}\cdot\vec{\mathrm{H}}), \tag{23}$$

we can evaluate the g factor by equating the matrix elements of (23) within a spin-1 manifold with those of (20) among the states (21). We obtain the result that

$$g = a^2 g_{40} + b^2 g_{41} + c^2 g_{41'} + 2bc\, g_{41,41'}, \tag{24}$$

where g_{40}, g_{41}, and $g_{41'}$ are the g factors of the corresponding vibronic states in the absence of Jahn-Teller coupling. One easily finds that $g_{40} = \frac{1}{2}(g_1 - 2g_2)$, $g_{41} = -\frac{1}{4}(g_1 - 2g_2)$, $g_{41'} = -\frac{1}{4}(g_1 + 2g_2)$. $g_{41,41'}$ is due to the magnetic coupling between Φ_{41} and $\Phi_{41'}$ and one finds that $g_{41,41'} = \frac{3}{4}g_1$.

IV. RESULTS AND DISCUSSION

In calculating the energy levels we assume that perturbation theory can be used except for the close-lying Γ_3 and Γ_5 states [Fig. 1(B)]. For these states we solve the eigenvalue problem exactly. The advantage of using perturbation theory is that analytic expressions for the energies are obtained and therefore the experimental data can be fitted much more easily.

The experimental results[2] for the optical absorption in the far infrared [Fig. 1(D)] for CdTe : Fe^{2+} show at 4 °K prominent absorption peaks at 18.6, 36, 49, 67, and 73 cm^{-1}, and some structure at 55 cm^{-1}. The absorption line at 18.6 cm^{-1} is assigned to a $\Gamma_1 - \Gamma_4$ transition and the line at 73 cm^{-1} to a $\Gamma_1 \rightarrow \Gamma_5$ transition.[2] The line at 36 cm^{-1}, we believe, is due to a one-phonon excitation of TA(L), as discussed in Sec. III E. This is the mode we have chosen as our E mode. although we set $\hbar\omega_E = 38\ \mathrm{cm}^{-1}$ to get better agreement with the experimental results.

The terms δ and V/α are then determined so that we get energy levels at 18.6 and 73 cm^{-1} (relative to the ground state) in agreement with experiment. This gives $\delta = 20.8\ \mathrm{cm}^{-1}$ and $V/\alpha = 17.9\ \mathrm{cm}^{-1}$. This corresponds to a value of 93 cm^{-1} for the effective spin-orbit parameter if we use Eq. (4). This value is slightly lower than the free-ion value of 100 cm^{-1}. We obtain a still lower value, 79 cm^{-1}, if part of the splitting is due to spin-spin coupling [Eq. (7) with $\rho = 0.95\ \mathrm{cm}^{-1}$]. The V/α value corresponds to a Jahn-Teller energy ($= V^2/2\alpha^2\hbar\omega_E$) of 4.2 cm^{-1}.

We also obtain the following energy levels [Fig. 1(C)]: $\Gamma_3 = 31.0$ and 56.6 cm^{-1}, $\Gamma_4 = 67\ \mathrm{cm}^{-1}$, and $\Gamma_5 = 47.8\ \mathrm{cm}^{-1}$. These predictions are consistent with the experimental observations because at low temperatures only the ground state (Γ_1) is heavily populated and transitions from this state are allowed only to states of Γ_4 symmetry (magnetic dipole) and Γ_5 symmetry (electric dipole). We therefore assign the absorption peak at 49 cm^{-1} to a $\Gamma_1 \rightarrow \Gamma_5$ transition. The structure at 55 cm^{-1} is most likely a transition from the first excited state (Γ_4) to the state 73 cm^{-1} above the ground state (Γ_5) because its intensity increases with temperature.

In calculating the transition probability for electric dipole induced transitions among the ${}^5E$ states the spin-orbit mixing between the ${}^5E$ and the ${}^5T_2$ states has to be considered. Actually this mixing is responsible for the electric dipole transitions because electric dipole transitions between pure orbital E states is forbidden by symmetry. The allowed optical transitions from the ground state (Γ_1) and the first excited state (Γ_4) together with their relative oscillator strengths are given in Fig. 2. The relative oscillator strengths are given in units of the parameters p_e and p_m as defined by Slack *et al.*[1] The oscillator strength is then obtained as $f_i(A, B)=p_i(A, B)C_i$ [Eqs. (13), (14), and (17) of Ref. 1]. Taking[2] $n=3.1$ and $(\epsilon/\epsilon_{eff})=3.9$ (see definitions below) and $\lambda=93$ cm^{-1} we obtain $c_e=5\times10^{-9}$ and $c_m=2\times10^{-9}$.

Experimentally the oscillator strength $f(A,B)$ for the transition $A\rightarrow B$ is given by [25,5]:

$$f(A,B)=\frac{4mn\mu}{e^2\mu_0 N}\left(\frac{\epsilon}{\epsilon_{eff}}\right)^2\frac{Z\exp(E_A/kT)}{d_A}\int\alpha(\bar{\nu})\,d\bar{\nu}\,. \tag{25}$$

Using SI units N is the number of point defects per unit volume, e and m the electron charge and mass, n the real part of the index of refraction, ϵ_{eff}/ϵ the ratio of the effective electric field at the site of the impurity ion to the macroscopic field in the crystal, μ_0 is the permeability of free space, and $Z=\sum_i d_i\exp(-E_i/kT)$ with d_i being the degeneracy of state i with energy E_i. $\alpha(\bar{\nu})$ is the optical absorption coefficient at $\bar{\nu}$ wave number.

TABLE II. Calculated and observed oscillator strengths in the far infrared for Fe^{2+} in CdTe.

$\hbar\omega$(cm^{-1})	Transition		$10^8\times$(oscillator strength) Experiment	Theory
18.6	Γ_1-Γ_4	(M^a)	1.5 ± 0.2	0.8
48	Γ_1-Γ_5	(E^b)	1.5 ± 1	3.5
67	Γ_1-Γ_4	(M)	1.5 ± 1	0.5
73	Γ_1-Γ_5	(E)	1.5 ± 1	5.4
54	Γ_4-Γ_5	($E+M$)	1.5 ± 1	0.7

[a] M is the magnetic dipole transitions.

[b] E is the electric dipole transitions.

In Table II a comparison between the experimental and theoretical results is made. We find a quantitative agreement for the magnetic dipole transitions. The discrepancy for the electric dipole transitions may indicate that the spin-orbit coupling between the ^5E and $^5T_2$ states is smaller than estimated from the effective spin-orbit splitting of the ^5E states [Eq. (4)]. This would mean that part of the splitting is due to some other mechanism, for instance spin-spin coupling. Using Eq. (7) with $\rho=0.95$ cm^{-1} the theoretical values for the electric dipole transitions in Table II will be reduced by 30%. At higher temperatures the lowest Γ_4 state will be thermally populated, and transitions from this excited state, so called hot lines, are allowed to Γ_3, Γ_4, and Γ_5 states (electric and magnetic dipole), to Γ_1 (magnetic dipole), and to Γ_2 (electric dipole). The relative oscillator strengths for the hot lines (arbitrary units) as obtained from theory are: Γ_3(12 cm^{-1}) = 3; Γ_3(38 cm^{-1}) = 13; Γ_4 (48 cm^{-1}) = 2; and Γ_5(55 cm^{-1}) = 13. This is in good quantitative agreement with the experiment [Fig. 1(D), 20 °K].

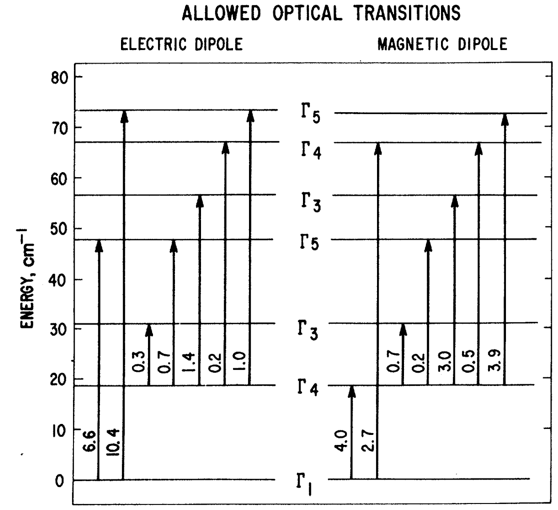

FIG. 2. Calculated relative oscillator strengths in units of p_e and p_m (Ref. 5) for the allowed optical transitions from the ground state and the first excited state.

In the presence of a magnetic field it is found[2] that the Γ_4 (18.6 cm^{-1}) states split with a g value of 1.02 ± 0.04. This is to be compared with a g value of 0.97 obtained [Eq. (24) with $a=0.94$, $b=0.31$, $c=0.15$] with a Jahn-Teller coupling but no spin-orbit mixing of the ^5E and $^5T_2$ wave functions, which means that $g_1=2$ and $g_2=0$. Slack *et al.*[2] calculated a g value of 0.92 by including the ^5E-$^5T_2$ mixing, but neglecting Jahn-Teller effects and renormalization of the wave function. We have made a calculation including all these effects and obtain a g value of 0.91.

As for the transition probabilities, part of the discrepancies (~10%) between experiment and theory for the g factor could be accounted for if the ^5E-$^5T_2$ spin-orbit coupling is smaller than that obtained from the splitting of the ^5E levels using Eq. (4). The g values calculated above are for the zero-field limit. For fields of the order of 10 kG used in determining the g factor experimentally, second-order terms in the magnetic field will become important. These terms arise from the magnetic interaction between vibronic states of different symmetry, and the effective g factor will increase. Calculations for 10-kG fields give an effective g value of 0.95.

V. CONCLUSIONS

The aim of this paper has been to present a possible explanation for the extra lines observed in the optical absorption spectrum of Fe-doped CdTe and not accounted for by simple crystal-field theory. We have found that a small linear Jahn-Teller coupling in a quantitative way accounts for the extra lines and their oscillator strengths as well as the *g* factor. It is, however, difficult to make a complete analysis of the experimental data because it is hard to separate the pure phonon spectrum and the vibronic transitions due to Fe^{2+}.

Finally, we have observed that a better agreement between theory and experiment is obtained when spin-spin interactions are also taken into account.

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[1] G. A. Slack, S. Roberts, and F. S. Ham, Phys. Rev. 155, 170 (1967).

[2] G. A. Slack, S. Roberts, and J. Vallin, Phys. Rev. 187, 511 (1969).

[3] L. A. Feldkamp, G. Venkataraman, and J. S. King, Solid State Commun. 7, 1571 (1969).

[4] C. T. Spennett, D. R. Bosomworth, W. Hayes, and A. R. L. Spray, J. Phys. C 2, 1137 (1969).

[5] G. A. Slack, F. S. Ham, and R. M. Chrenko, Phys. Rev. 152, 376 (1966).

[6] W. Low and M. Weger, Phys. Rev. 118, 1119 (1960).

[7] We use interchangeably the notation (A_1, A_2, E, T_1, T_2) of Mulliken [R. S. Mulliken, Phys. Rev. 43, 279 (1933)] and the notation (Γ_1, Γ_2, Γ_3, Γ_4, Γ_5) of Bethe [H. E. Bethe, Ann. Physik 3, 133 (1929); see also Ref. 8, pp. 88–101] to denote the irreducible representations of T_d. We use Mulliken's notation in particular for orbital electronic states.

[8] G. F. Koster, J. O. Dimmock, R. G. Wheeler, and H. Statz, *Properties of the Thirty-Two Point Groups* (The MIT Press, Cambridge, Mass., 1963).

[9] F. S. Ham, Phys. Rev. 166, 307 (1968).

[10] Throughout the paper the notation θ, ϵ is used to designate partner functions (or operators) belonging to Γ_3 and transforming, respectively, as $[2z^2-(x^2+y^2)]$ and $\sqrt{3}\,(x^2-y^2)$, while ξ, η, ζ designate those belonging to Γ_5 and transforming as yz, zx, xy (or equivalently under T_d as x, y, z), and X, Y, Z designate partners belonging to Γ_4 and transforming like the angular momentum components L_X, L_Y, L_Z.

[11] Small departures from this uniform spacing were obtained for the crystal-field calculation in Ref. 2 by treating the spin-orbit coupling exactly instead of by second-order perturbation theory. Such corrections would require only slight adjustments to the model proposed here, and for simplicity we have ignored them in the present paper.

[12] M. H. L. Pryce, Phys. Rev. 80, 1107 (1950).

[13] R. E. Trees, Phys. Rev. 82, 683 (1951).

[14] R. E. Watson and M. Blume, Phys. Rev. 139, A1209 (1965); 184, 606(E) (1969).

[15] The effective spin-spin interaction was not considered in the work on ZnS : Fe^{2+} in Refs. 1 and 5 when the separation δ was used to obtain an estimate for $|\lambda|$. Revising this estimate in accord with Eq. (7), using the values $\delta=15.2\ \mathrm{cm}^{-1}$, $\rho=0.95\ \mathrm{cm}^{-1}$, $\Delta=3400\ \mathrm{cm}^{-1}$, one obtains $|\lambda|=73\ \mathrm{cm}^{-1}$ in place of the earlier estimate of 93 cm^{-1}.

[16] H. A. Jahn and E. Teller, Proc. Roy. Soc. (London) A161, 220 (1937).

[17] Since the symmetrized direct product $(\Gamma_3\times\Gamma_3)$ reduces to $\Gamma_1+\Gamma_3$, the only real Hermitian operators $Uq^{P}(i)$ having nonvanishing matrix elements within a Γ_3 state are those belonging to Γ_1 or Γ_3. A totally symmetric operator belonging to Γ_1 does not, however, split the doublet.

[18] Reviews of the Jahn-Teller effect of impurity ions in crystals have been given by M. D. Sturge, in *Solid State Physics*, edited by F. Seitz, D. Turnbull, and H. Ehrenreich (Academic, New York, 1967), Vol. 20, p. 91; F. S. Ham, in *Electron Paramagnetic Resonance*, edited by S. Geschwind (Plenum, New York, 1970).

[19] F. S. Ham, W. M. Schwarz, and M. C. M. O'Brien, Phys. Rev. 185, 548 (1969).

[20] R. Loudon, Proc. Phys. Soc. (London) 84, 379 (1964).

[21] M. Tinkham, *Group Theory and Quantum Mechanics* (McGraw-Hill, New York, 1964), p. 80.

[22] J. R. Fletcher and K. W. H. Stevens, J. Phys. C 2, 444 (1969).

[23] C. H. Henry, S. E. Schnatterly, and C. P. Slichter, Phys. Rev. 137, A583 (1965).

[24] Only the Z components of the states are given explicitly in Table I; the X and Y components may be obtained from these using tables[8] of the coupling coefficients.

[25] D. L. Dexter, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1959), Vol. 6, p. 353.