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Jahn-Teller effect with the recursion method: Dipole-carrying states and the absorption spectrum of CdTe:Fe^{2+}

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We have theoretically analyzed the Jahn-Teller effect in the near-infrared absorption spectrum of Fe^{2+} ions in CdTe. We have assumed a linear active interaction on the $^5T_2$ levels of the $3d^6$ electrons of the Fe^{2+} impurity; the phonon symmetry taken into account is Γ_3. The spin-orbit interaction has also been included. By means of the recursion method and an appropriate choice of the dipole-carrying initial state, we have calculated in a nonperturbative way the absorption spectrum of Fe^{2+} ions in CdTe, including a large number of phonons. The theoretical absorption spectrum and some temperature-dependent features are discussed and compared with the available experimental data.

I. INTRODUCTION

In recent years there have been several new developments in the traditional fields of electron-phonon interactions and the Jahn-Teller effect. From a theoretical side, the recursion method,[1,2] originally introduced in connection with the electronic problem, has been successfully extended to coupled electron-boson systems; this allows a nonperturbative treatment for the absorption spectra in some typical and interesting vibronic models,[3,4] as well as luminescence spectra of relaxed color centers.[5] Furthermore, the asymptotic study of the continued-fraction coefficients opens a new perspective on this subject. From the experimental point of view, accurate data have been accumulating in a number of systems (impurities, core electrons, surface states), whose quantitative interpretation makes evident the role of interplay between electron and nuclear dynamics.[6-9]

This paper is focused on the Jahn-Teller effect in the infrared-absorption spectrum of CdTe:Fe^{2+}. The spectroscopic studies of substitutional transition-metal ions in cubic crystals have greatly increased the knowledge of the physics of point defects in solids. The CdTe:Fe^{2+} system, however, is so complicated that many features of its absorption spectrum are still unsettled, and conflicting interpretations are given in the literature. The absorption spectrum[10] in the region around 2200–3000 cm^{-1} exhibits a number of sharp lines followed by a rich structure with replicas due to optical and longitudinal phonons. While the first three sharp lines are generally interpreted as zero-phonon lines,[10-12] the other lines are subject to different interpretation.[10,12,13] Also, the temperature dependence has been accounted for in a different way.[10,12]

From a theoretical point of view, the first step for a quantitative study of the Fe^{2+} vibronic system requires the construction of the product space of the electronic and vibrational states. The direct diagonalization of the matrix Hamiltonian in the product space is often practically impossible because of the large number of degrees of freedom. For example, a $^5T_2$ electronic multiplet linearly coupled with a two-dimensional phonon mode leads to a matrix whose dimension is $15\times N^2$, with N the number of phonons included. On the other hand, perturbative approaches can be applied only in the case of reasonably small electron-phonon coupling; when the electron-phonon coupling is stronger, the only workable alternative is to exploit the sparse nature of the matrix to be handled. A sparse matrix can be economically transformed into a tridiagonal form by means of the recursion method; the actual number of recursions to be performed is usually reasonably low, because the relevant information is contained in the first steps of the recursion transformations.

Until now, in the literature[3-5] the use of the recursion method has been confined to vibronic systems with only one dipole-allowed transition (of a given symmetry). Then it is natural to take as the initial state of the recursion this unique dipole-carrying state. The recursion procedure generates a hierarchy of memory states that are orthonormal among themselves, and hence, in particular, to the initial state. Thus all memory states are "dipole free" and the relative intensity of the lines obtained by diagonalizing the tridiagonal matrix is simply given by the projection (modulus square) of the initial state on the corresponding eigenfunctions. A more complicated situation arises in vibronic systems (such as CdTe:Fe^{2+}) with more than one dipole-carrying state. The naive use of the recursion method would be of little help in the calculation of the optical spectrum, since, in general, the memory states of the hierarchy would be dipole coupled to a given initial state; this means that in order to calculate the optical spectrum one should calculate all dipole matrix elements coupling the different memory states and, finally, perform an appropriate unitary transformation. A novelty of this paper is to provide for the first time an elegant and optimized solution to by-pass this complication; it consists of choosing the initial dipole-carrying state so that the chain states generated by the recursion transformation are all dipole free. As an application of our procedure, we have calculated the absorption spectra of Fe^{2+} ions in CdTe, including a large number of phonons, and considering also, for the first time, some aspects of the temperature dependence of the absorption spectrum.

In Sec. II we briefly summarize the relevant feature of the system taken into account and its vibronic Hamiltonian. In Sec. III we illustrate our new procedure, based on the recursion method and on the generation of a hierarchy of non-dipole-carrying states. In Sec. IV we present the results of our calculations, as well as some considerations on hot absorption lines observed in the experimental data.

II. THE VIBRONIC MODEL FOR THE IMPURITY Fe^{2+} ION IN CUBIC CRYSTALS

The ground state $3d^6$ of the electronic configuration of the Fe^{2+} ion gives rise to a ^5D multiplet (25 times degenerate including spin). When Fe ion substitutes for a Cd ion in a site of tetrahedral symmetry T_d, the lowest free-ion term ^5D is split by the cubic crystalline field into the levels ^5E (10 times degenerate) and $^5T_2$ (15 times degenerate). The standard crystal-field theory predicts that the energy separation between the ground state ^5E and the $^5T_2$ state is $\Delta \simeq 10|Dq|$, where Dq is the one-electron cubic-field parameter.[14] Our attention is thus on the ^5E and $^5T_2$ multiplets and we can safely disregard higher states of Fe^{2+} expected at much higher energy. For convenience, we show in Fig. 1 the level scheme,[15] including the effect of the spin-orbit interaction. The levels are labeled with the notation corresponding to the irreducible representation[16,17] of the group T_d. Notice that in octahedral coordination[18] (point group O_h) the orbital doublet ^5E is higher in energy than the orbital triplet $^5T_2$.

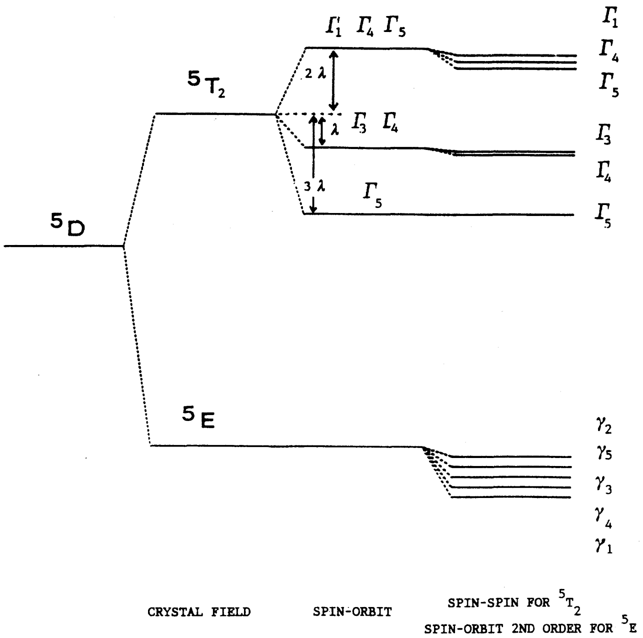

FIG. 1. Scheme of the energy levels of the atomic multiplet ^5D of Fe^{2+} split by the crystal field, by the spin-orbit interaction, and by the spin-spin interaction. The levels are labeled as the irreducible representations of the group T_d.

The structure of the absorption spectrum[10,12] of Fe^{2+} in CdTe has been measured by different authors at low temperature. The broad absorption band between 2200 and 3000 cm^{-1} arises from electronic transitions between spin-orbit levels of the initial ^5E and final $^5T_2$ states of the Fe^{2+} ion. The spectrum contains sharp peaks that can be described as electronic transitions without phonon emission (referred to as the zero-phonon transition) and other peaks that can be interpreted as phonon-assisted transitions in which one or more phonons are emitted together with the electronic transition; of course, this classification is only of qualitative nature, since from the experimental side there is no clear way to identify the type of process to which a given line belongs, and also from a theoretical side one is compelled to adopt simplified models of the phonon dispersion curves (often considering critical points[14] only) as well as of the electron-phonon interaction.

In the CdTe:Fe^{2+} at 3.5 K there are three moderate sharp lines in the energy range of 30 cm^{-1} following the onset of 2282 cm^{-1} and at least two broader lines at higher energy. Notice that at very low temperature when all the atoms are in the γ_1 level the zero-phonon spectrum should consist of only two lines separated by $\approx 5|\lambda|$ in the absence of Jahn-Teller coupling; the importance of the Jahn-Teller effect is thus evident in this impurity center.

Following the literature,[10,12] we designate the optical transitions in the near-infrared spectrum with the (A-B) empirical notation scheme, where $A=1,2,3,4,5$ and $B=6,7,8,\ldots$ identify the sequence of initial and final impurity levels, respectively. In CdTe the transitions (1-6), (1-7), and (1-8) are of comparable strength; there are also two weaker transitions, (1-9) and (1-10), which some authors[10] consider zero-phonon lines and others[12] consider replicas, which is understandable in view of the mentioned difficulties in establishing a demarcation between zero-phonon and phonon-assisted processes.

Experimentally, the temperature dependence has also been studied.[10] When the temperature is increased, other additional lines appear on the low-frequency side of (1-6). The interpretation of the temperature dependence of the near-infrared spectrum is again rather unsatisfactory and, besides experimental uncertainty, other sources of difficulty are the actual energy spacing within the ^5E levels, the fact that "hot" lines (lines starting from excited states populated at finite temperature) overlap partially with "cold" lines, and the observation that final states accessible from the ground and excited states are different. This explains why available theoretical models[13] focus only on the lines originating in the initial ground state γ_1. In this paper we also discuss some features concerning the hot lines, and, in particular, we show the occurrence of final states of new symmetry and moderate strength; however, a thorough and consistent interpretation of the "hot" absorption spectrum requires further efforts from both the experimental and theoretical side.

In a cluster model,[6] commonly adopted in the literature, the vibrational lattice modes useful for the electron $^5T_2$ functions mixing are those of Γ_3 and Γ_5 symmetries (elsewhere called E and T_2, respectively). Following the literature concerning the Jahn-Teller effect in the infrared-absorption spectrum of this and similar systems,[13,19,20] we take into account only the coupling with lattice vibrations of Γ_3 symmetry. This is also done in consideration of the fact that model calculations available in the literature (see, for example, Ref. 4) show that the interaction with modes of Γ_5 symmetry do not exhibit drastically different effects. However, we note that our treatment, if necessary, could be easily applied to interactions other than the Γ_3 interaction.

The total Hamiltonian H considered for the impurity Fe^{2+} ion in the $^5T_2$ state can be written in the following form:

$$H = H_e + H_{\mathrm{s.o.}} + H_L + H_{e\text{-}L} \ , \tag{1}$$

where $H_e + H_{\mathrm{s.o.}}$ is the electron Hamiltonian including the spin-orbit interaction $\lambda\mathbf{S}\cdot\mathbf{L}$, whose explicit form can be obtained with a standard method.[21] H_L and $H_{e\text{-}L}$ are the lattice Hamiltonian and electron-lattice interaction. In terms of creation and annihilation operators a_θ, $a_\theta^\dagger$, a_ε, and $a_\varepsilon^\dagger$ (θ and ε indicate the partner rows of the two-dimensional mode of Γ_3 symmetry and $\hbar\omega$ energy), H_L has the form

$$H_L = \hbar\omega(a_\theta^\dagger a_\theta + a_\varepsilon^\dagger a_\varepsilon + 1) \ . \tag{2}$$

The linear contribution $H_{e\text{-}L}$ to the electron-phonon interaction is obtained by using the general procedure of the paper of Sturge[6] and the Clebsch-Gordan coefficients for the tetrahedral group;[17] its expression is

$$H_{eL} = K[(a_\theta^\dagger + a_\theta)D_\theta + (a_\varepsilon^\dagger + a_\varepsilon)D_\varepsilon] \ ,$$
$$D_\theta = \begin{bmatrix} -\frac{1}{2} & 0 & 0 \\ 0 & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix}, \quad D_\varepsilon = \begin{bmatrix} \sqrt{3}/2 & 0 & 0 \\ 0 & -\sqrt{3}/2 & 0 \\ 0 & 0 & 0 \end{bmatrix} , \tag{3}$$

taking the T_2 electronic functions as basis functions. K is the linear coupling constant related to the Jahn-Teller energy E_{JT} and to the Huang-Rhys factor S by the relations $E_{\mathrm{JT}} = K^2/\hbar\omega = S\hbar\omega$. We examine now the method of solution of the vibronic Hamiltonian (1), when the number of phonons to be included in the basis set is so high as to prevent the possibility of direct diagonalization.

III. THE RECURSION METHOD AND THE "SPECIAL" DIPOLE-FREE HIERARCHY OF STATES

The recursion method is particularly suitable to treat vibronic models when the coupling between electrons and phonons is large. This is the case of CdTe:Fe^{2+}, where the Huang-Rhys factor $S \approx 6$ is expected from the values of the phonon energies according to the lattice dynamics of CdTe (Ref. 22) and from the Jahn-Teller energies estimated in previous works.[10–13]

Since the Hamiltonian that expresses displacement operators on the basis of oscillator occupation number is in a "sparse" form, the vibronic model becomes a natural candidate for the application of the recursion method.[2,7] The initial and large sparse matrix can be transformed into a manageable tridiagonal one, whose dimension is the number of iterations performed. From a formal point of view the recursion method is closely linked both to the Lanczös[23] method and to the renormalization-group technique.[24]

For convenience we briefly summarize the recursion procedure for our model Hamiltonian. Let $|u_0\rangle, |u_1\rangle, \ldots, |u_\nu\rangle$ indicate the first $\nu+1$ normalized functions of the recursion hierarchy; let $|U_{\nu+1}\rangle$ be the (unnormalized) function defined as

$$|U_{\nu+1}\rangle = H|u_\nu\rangle - a_\nu|u_\nu\rangle - b_\nu|u_{\nu-1}\rangle \ . \tag{4}$$

The next pair of parameters $b_{\nu+1}$ and $a_{\nu+1}$ is given by the normalization and the expectation value of the Hamiltonian on the state $|U_{\nu+1}\rangle$, namely

$$\begin{aligned} b_{\nu+1}^2 &= \langle U_{\nu+1}|U_{\nu+1}\rangle \ , \\ a_{\nu+1} &= \langle U_{\nu+1}|H|U_{\nu+1}\rangle / \langle U_{\nu+1}|U_{\nu+1}\rangle \ . \end{aligned} \tag{5}$$

After determining $b_{\nu+1}^2$, we construct the normalized function $|u_{\nu+1}\rangle$,

$$|u_{\nu+1}\rangle = |U_{\nu+1}\rangle / b_{\nu+1} \ ,$$

and we start with a new iteration.

In the case of our vibronic model we have

$$|U_\nu\rangle = \sum_{\substack{i=1,3 \\ j=1,5 \\ l,m=0,\infty}} c_{ijlm}^{(\nu)} |F_i S_j; lm\rangle \ .$$

Here, $|F_i\rangle$ ($i=1,2,3$) are the many-electron wave-function partners for the irreducible representations $^5T_2$ of the group T_d (usually labeled d_{yz}, d_{xz}, d_{xy}; F_4 and F_5 concern the ^5E states $d_{3z^2-r^2}$ and $d_{x^2-y^2}$); $|S_j\rangle$ are appropriate corresponding combinations of spin functions for $S=2$ and S_z from $+2$ to -2; l,m are the occupation numbers for the partner modes θ and ε. Using the Hamiltonian (1), we have obtained after standard algebraic manipulations the iterative relations for the coefficients $c_{ijlm}^{(\nu)}$; the expressions are explicitly reported in Ref. 21.

Now the problem arises of which state to take as the initial state of the recursion procedure. In principle, any state is possible, and from the evaluation of the imaginary part of the Green's function one obtains the density of states projected on the chosen initial state $|u_0\rangle$. However, the projected density of states provides directly the relative strength of the optical-absorption spectrum only in the special situation in which all the states of the hierarchy, but the initial seed state, are dipole forbidden. An elegant and manageable procedure to achieve this purpose is provided in the following.

Consider first the impurity center Fe^{2+} of $T=0$, i.e., in its lowest γ_1 sublevel of the ^5E multiplet. Consider the linear combination of states $|F_iS_j\rangle$ constructed as follows:

$$|U_0\rangle=\sum_{\substack{i=1,3\\j=1,5}}|F_iS_j\rangle\langle F_iS_j|\mu_x|\gamma_1\rangle\ , \tag{6}$$

where μ_x is the dipole operator, for instance, say, the electric dipole operator along the x axis. The state $|\gamma_1\rangle$ of symmetry Γ_1, given by standard group theory,[17,13] is

$$|\gamma_1\rangle=\frac{1}{\sqrt{2}}(|F_4S_4\rangle+|F_5S_5\rangle)\ . \tag{7}$$

The special linear combination (6) becomes, after explicit calculation and normalization,

$$|u_0\rangle=-\tfrac{1}{2}|F_1S_4\rangle+\frac{\sqrt{3}}{2}|F_1S_5\rangle\ . \tag{8}$$

We call this the "dipole-carrying state" when the transition starts from the γ_1 fundamental state. We can, in fact, demonstrate that the hierarchy of states generated by $|u_0\rangle$ does not carry a dipole, i.e., $\langle\gamma_1|\mu_x|u_\nu\rangle=0$. Let us consider a state $|u_\nu\rangle$ of the hierarchy generated starting from $|u_0\rangle$; quite generally we can write

$$|u_\nu\rangle=\sum_{\substack{i,j\\l,m}}c_{ijlm}^{(\nu)}|F_iS_j;lm\rangle\ . \tag{9}$$

Separating from the sum $\sum_{i,j,l,m}$ the terms $|F_1S_4;00\rangle$ and $|F_1S_5;00\rangle$ (indicated, for brevity, by $|F_1S_4\rangle$ and $|F_1S_5\rangle$), we can write

$$|u_\nu\rangle=\alpha|F_1S_4\rangle+\beta|F_1S_5\rangle+\sum{}''c_{ijlm}^{(\nu)}|F_iS_j;lm\rangle\ .$$

Hence,

$$\langle\gamma_1|\mu_x|u_\nu\rangle=\alpha\langle F_1|\mu_x|F_4\rangle+\beta\langle F_1|\mu_x|F_5\rangle\ . \tag{10}$$

From the well-known orthonormality properties of the states of the hierarchy, we have, in particular,

$$\begin{aligned}0&=\langle u_0|u_\nu\rangle\\&=\alpha\langle F_1|\mu_x|F_4\rangle+\beta\langle F_1|\mu_x|F_5\rangle\ .\end{aligned} \tag{11}$$

Then it follows that $\langle\gamma_1|\mu_x|u_\nu\rangle=0$, which means that the only dipole-carrying state of the hierarchy is the special state $|u_0\rangle$ itself. This entails a far-reaching consequence: when we calculate the Green's-function expansion in continued fractions (or, equivalently, diagonalize the small tridiagonal matrix), the projected density of states is proportional to the absorption spectrum originating from ions in the γ_1 state.

Similar considerations can be repeated at higher temperature. At temperature $T\neq0$ higher states of the ${}^5E$ multiplet become populated in agreement with the Boltzmann distribution. At temperatures in the range $T=10$–15 K, we have to consider also transitions from the γ_4 state. Following the same procedure, it is easily seen that the dipole-carrying state corresponding to the initial γ_4 state of the ${}^5E$ multiplet is either

$$|u_0\rangle=|F_1S_2\rangle\quad\text{or}\quad|u_0\rangle=|F_1S_3\rangle\ ,$$

depending on the chosen partner function of the γ_4 irreducible representation. We thus have a technique (very simple when compared to the methods of calculations available in the literature) for calculating the properties of the impurity vibronic model.

IV. RESULTS AND COMPARISON WITH EXPERIMENTAL DATA

We first discuss the results related to allowed electric dipole transitions from the ground γ_1 state of the ${}^5E$ multiplet to Γ_5 final states of the ${}^5T_2$ multiplet, including spin-orbit and Jahn-Teller interactions. The initial seed state $|u_0\rangle$ is the linear combination expressed by Eq. (8) (or any other of its partners in the Γ_5 irreducible representation). About 50 iterations were found to be more than sufficient to obtain good convergence in the 100-cm^{-1} energy range at the onset of the near-infrared-absorption spectrum. To avoid over-recursions, the number of iterations done also corresponds to the number of phonons involved in each direction; thus, the order of the original vibronic matrix was the large number $(15)\times(50^2)=37\,500$. Whenever necessary, for checking purposes, even larger clusters, up to 15×100^2 basis functions, were considered.

The energies quoted in Table I are calculated with the following choice of the parameters: the crystal-field pa-

TABLE I. Energies and intensities of relevant transitions calculated with the recursion method. Experimental data are also reported for comparison. The calculation is made with the following choice of parameters: $\lambda=-100\ \text{cm}^{-1}$, $\hbar\omega=36\ \text{cm}^{-1}$, $|Dq|=258.5\ \text{cm}^{-1}$, and $E_{\text{JT}}=232\ \text{cm}^{-1}$. (a) Reference energy is the γ_1 level, and (b) reference energy is the γ_4 level (the difference $\gamma_1-\gamma_4$ is selected at 20 cm^{-1}).

Cold-line transitions	Energy (cm^{-1}) Calc.[a]	Expt.[b]	Intensity (arb. units)	Hot-line transitions	Energy (cm^{-1}) (a)	(b)	Intensity (arb. units)
(1-6)	2282	2282	0.106	(2-6)	2282	2262	0.052
(1-7)	2295	2294	0.112	(2-7)	2295	2275	0.111
(1-8)	2306	2309	0.081	(2-8)	2304	2284	0.024
(1-9)	2320	2318	0.040		2309	2289	0.022
(1-10)	2334	2334	0.029	(2-9)	2321	2301	0.068

[a] Our reference energy is the γ_1 level.

[b] Reference 10.

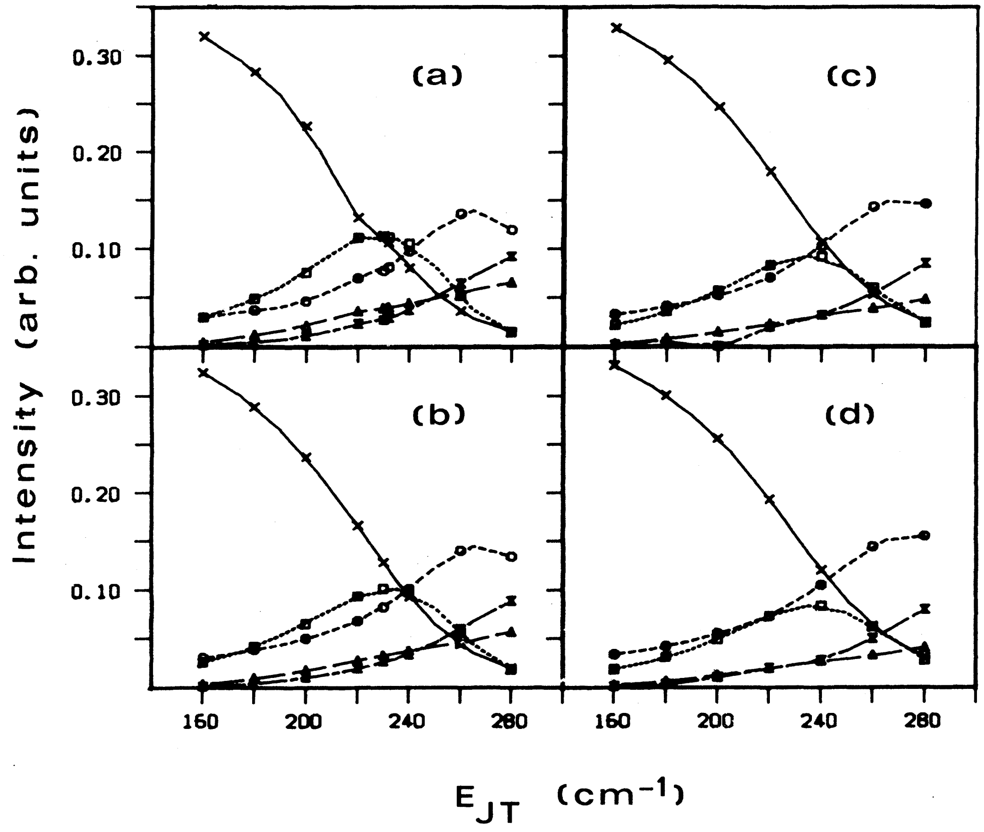

FIG. 2. Intensities of the lowest five lines as a function of the Jahn-Teller energy (E_{JT}) for different phonon coupling energies. Case (a), $\hbar\omega=36$ cm^{-1}; case (b), $\hbar\omega=38$ cm^{-1}; case (c), $\hbar\omega=40$ cm^{-1}; case (d), $\hbar\omega=42$ cm^{-1}. For all cases, $\lambda=-100$ cm^{-1}. ×,□,○,△, ⧗ label the first five lines in increasing energy order.

rameter $|Dq|$ is chosen equal to 258.5 cm^{-1} (a value only slightly different from that given in the literature) to reproduce the first spectral line at 2282 cm^{-1}. This parameter is the least important of the model, since its effect is merely to shift rigidly all the transition energies. The spin-orbit coupling is that of the free ion[25] ($\lambda=-100$ cm^{-1}). The energy $\hbar\omega$ of the coupling phonons is taken to be equal to 36 cm^{-1}, a value intermediate between the phonon energies of the acoustic branches. The Jahn-Teller energy E_{JT} is chosen to be equal to 232 cm^{-1}, taking into account the behavior of the intensities of the lowest lines versus E_{JT}, shown in Fig. 2. This behavior is quite complicated, but in the region around 230–240 cm^{-1} the intensities of the first three lines are comparable with the experimental results at 3.5 K. We notice that, with this choice, the phonon contribution $S(\hbar\omega)^2$ to the second moment of the ^5E-$^5T_2$ absorption spectrum is about 10% of the spin-orbit contribution $6\lambda^2$. This fact seems to be compatible with the general discussion of Ref. 19.

In Fig. 3 we show the energies of the first absorption lines versus the E_{JT} parameter with the phonon energy equal to 36 cm^{-1} and the same previous choices of λ and $|Dq|$. The differences between the eigenvalues are much less influenced by the variation of E_{JT} than the intensities

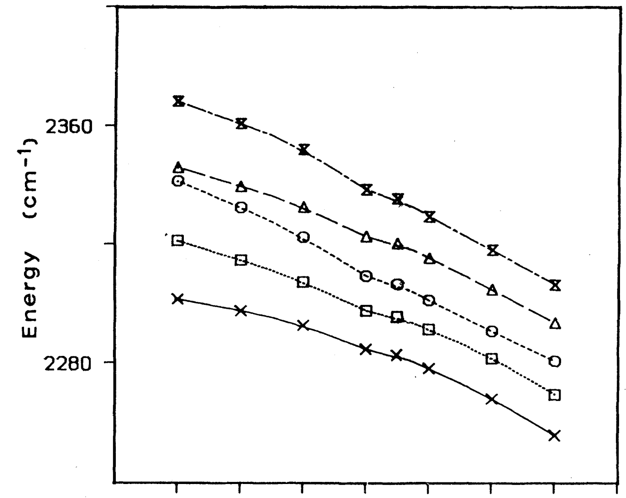

FIG. 3. Energy of the lowest five lines as a function of the Jahn-Teller energy (E_{JT}), with the following choice of parameters: $\lambda=-100$ cm^{-1}, $|Dq|=258.5$ cm^{-1}, and $\hbar\omega=36$ cm^{-1}. ×,□,○,△, ⧗ label the first five lines in increasing energy order.

of the lines; notice also that the Jahn-Teller energy shifts down, by only about 40 cm^{-1}, the position of the $\Gamma_5(1)$ level $(10|Dq|-3|\lambda|)$, since the overall spin-orbit separation $(\simeq 5|\lambda|)$ is somewhat higher compared to the Jahn-Teller energy.

In order to better understand the reason for the complicated behavior of the curves of Fig. 2, and to better exhibit the interplay of λ and E_{JT} parameters of comparable size, we have also analyzed the behavior of the intensity of the first lowest lines as a function of the spin-orbit coupling constant $|\lambda|$. In Fig. 4 we show the results obtained for the first five lines using $\hbar\omega=36\ \mathrm{cm}^{-1}$ and $E_{\mathrm{JT}}=232\ \mathrm{cm}^{-1}$. We have verified that for $\lambda=0$ (i.e., when the Jahn-Teller interaction is dominant) the intensity of the lines follows the Poisson distribution $S^n e^{-S}/n!$ with average S (the Huang-Rhys factor) about $\simeq 6$; so the more intense line is the sixth. As $|\lambda|$ increases and the spin-orbit interaction eventually becomes dominant with respect to the Jahn-Teller separation, the more intense line is the first, and the order of the intensities is reversed with respect to the case of $\lambda=0$.

On the left-hand side of Table I we report the energy and intensities of the lowest five lines, compared with the experimental ones, computed with the following choice of parameters: $\lambda=-100\ \mathrm{cm}^{-1}$, $\hbar\omega=36\ \mathrm{cm}^{-1}$, $|Dq|=258.5\ \mathrm{cm}^{-1}$, and $E_{\mathrm{JT}}=232\ \mathrm{cm}^{-1}$. All of the calculated spectrum is normalized to 1; the sum of the intensities of the first five lines is 0.38. From Table I we can see reasonably good agreement of the vibronic model when compared with the experimental transitions denoted (1-6), . . . , (1-10); at higher energies the situation is complicated by the presence of phonon-assisted replicas.

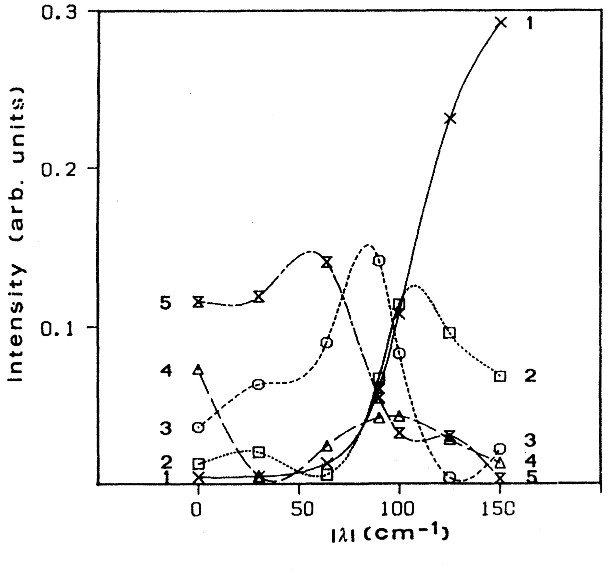

FIG. 4. Intensity of the lowest lines as a function of the spin-orbit coupling constant. The other parameters of the vibronic model are $\hbar\omega=36\ \mathrm{cm}^{-1}$ and $E_{\mathrm{JT}}=232\ \mathrm{cm}^{-1}$.

Concerning the temperature effects on the near-infrared-absorption spectrum, very little experimental information is available;[10] also, different interpretations of the peaks appearing at 14–16 K at 2273, 2264, and 2250 cm^{-1} are made,[10,12] relating to different values for the far-infrared transition γ_1-γ_4.[12,26,27]

Now that we have established reasonably well the parameters of our vibronic model, we have attempted a preliminary analysis of the temperature dependence of the absorption lines, despite the numerous implications discussed at the beginning of Sec. II. Considering the special seed state, appropriate for transitions originating from the γ_4 level, we have calculated the energies and intensities of the corresponding optical transition. In Table I we show our results—the energies and intensities of the lowest "hot" lines due to the transition from the γ_4 level. In the column labeled (a) the origin of the energy is the γ_1 level; in the column labeled (b) the energies are referred to the γ_4 level, assuming a difference of about 20 cm^{-1} between γ_1 and γ_4 levels, according to experimental data. We notice that the first two hot lines are in reasonably good agreement with the experimental results. The higher hot lines occur in an energy range that overlaps with the previously discussed cold lines; however, experimentally, no appearance of new extra lines has been observed. Among possible reasons for difficulty in experimental detection (whose resolution is $\simeq 4\ \mathrm{cm}^{-1}$) could be the fact that transitions from the γ_4 state of ^5E are allowed not only to final Γ_5 states, but also to $\Gamma_2,\Gamma_3,\Gamma_4$ states. In particular, for instance, we see from Table I that the calculated line at 2309 cm^{-1} is a new transition, of moderate strength, that involves a final state of Γ_4 symmetry (degenerate with Γ_3 if spin-spin interactions are neglected). This new line could well experimentally overlap with the nearby (2-8) line involving a final state of Γ_5 symmetry, but a conclusive interpretation of hot lines at higher energy calls for further investigations.

V. CONCLUSIONS

In this paper we have applied for the first time the recursion method for the calculation of the absorption spectrum in complicated vibronic systems that exhibit a number of dipole-allowed final states. We have considered explicitly the case of the doubly ionized Fe transition metal in CdTe, a situation where the standard diagonalization becomes unwieldy because of the strong Jahn-Teller coupling. A nice feature of the recursion method is the possibility of creating the special hierarchy of no dipole-carrying states. This elegant and still workable technique allows one to introduce a large number of phonons and to obtain good convergence for the energies and intensities of the absorption spectrum. The successful application of the procedure to the relatively complicated Fe^{2+} ions opens interesting perspectives on a nonperturbative treatment of the Jahn-Teller effect in many other transition-metal impurities as well as other classes of impurities.

[1] R. Haydock, V. Heine, and M. J. Kelly, J. Phys. C **5**, 2845 (1972); **8**, 2591 (1975). See also the volume by D. W. Bullet, R. Haydock, V. Heine, and M. J. Kelly, in *Solid State Physics,* edited by H. Erhenreich, F. Seitz, and D. Turnbull (Academic, New York, 1980), Vol. 35.

[2] G. Grosso and G. Pastori Parravicini, Adv. Chem. Phys. **62**, 81 (1975); **62**, 133 (1985), and references therein.

[3] M. C. M. O'Brien and S. N. Evangelou, J. Phys. C **13**, 611 (1980); Solid State Commun. **36**, 29 (1980); M. C. M. O'Brien, J. Phys. C **16**, 85 (1983); **16**, 6345 (1983); **19**, 4963 (1985).

[4] L. Martinelli and G. Pastori Parravicini, Phys. Rev. B **37**, 10 612 (1988).

[5] L. Martinelli, G. Pastori Parravicini, and P. L. Soriani, Phys. Rev. B **32**, 4106 (1985).

[6] M. D. Sturge, in *Solid State Physics,* edited by F. Seitz, D. Turnbull, and H. Ehrenreich (Academic, New York, 1967), Vol. 20.

[7] *The Dynamical Jahn-Teller Effect in Localized Systems,* Vol. 7 of *Modern Problems in Condensed Matter,* edited by Yu. E. Perlin and M. Wagner (North-Holland, Amsterdam, 1984) (see, in particular, the article of D. R. Pooler, p. 199).

[8] G. Chiarotti, in Proceedings of the Seventh General Conference of the Condensed Matter Division of the European Physical Society, edited by F. Bassani, G. Grosso, G. Pastori Parravicini, and M. P. Tosi [Phys. Scr. T **19**, 387 (1987)], and references quoted therein.

[9] M. Cini and A. D'Andrea, J. Phys. C **21**, 193 (1988).

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

[11] J. M. Baranowski, J. W. Allen, and G. L. Pearson, Phys. Rev. **160**, 627 (1967).

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

[13] J. Rivera-Iratchet, M. A. De Orúe, and E. E. Vogel, Phys. Rev. B **34**, 3992 (1986).

[14] F. Bassani and G. Pastori Parravicini, *Electronic States and Optical Transition in Solids* (Pergamon, Oxford, 1975; Nauka, Moscow, 1982), and references quoted therein.

[15] W. Gehlhoff and W. Ulrici, Phys. Status Solidi B **102**, 11 (1980).

[16] As commonly done in the literature, we adopt indifferently either the notations of Mulliken ($A_1A_2ET_1T_2$) [R. S. Mulliken, Phys. Rev. **43**, 279 (1933)] or the notations of Bethe ($\Gamma_1\Gamma_2\Gamma_3\Gamma_4\Gamma_5$) [H. E. Bethe, Ann. Phys. (Leipzig) **3**, 133 (1929)].

[17] G. F. Koster, J. O. Dimmock, R. G. Wheeler, and H. Statz, *Properties of the Third-two Point Group* (MIT University Press, Cambridge, MA, 1963).

[18] A. Hjortsberg, J. T. Vallin, and F. S. Ham, Phys. Rev. B **37**, 3196 (1988).

[19] F. S. Ham and G. A. Slack, Phys. Rev. B **4**, 777 (1971).

[20] H. Maier and U. Scherz, Phys. Status Solidi B **62**, 153 (1974).

[21] M. Passaro, thesis, University of Naples, 1988.

[22] J. M. Rowe, R. M. Nicklow, D. L. Price, and K. Zanio, Phys. Rev. B **10**, 671 (1974).

[23] C. Lanczös, J. Res. Nat. Bur. Stand. (U.S.) **45**, 255 (1950); **49**, 33 (1952); *Applied Analysis* (Prentice-Hall, Englewood Cliffs, NJ, 1956).

[24] P. Giannozzi, G. Grosso, S. Moroni, and G. Pastori Parravicini, Appl. Num. Math. **4**, 273 (1988).

[25] C. E. Moore, *Atomic Energy Levels,* Nat. Bur. Stand. (U.S.) Circ. No. 467 (U.S. GPO, Washington, D.C., 1949), Vol. I; Vol. II (1952); Vol. III (1958).

[26] J. T. Vallin, Phys. Rev. B **2**, 2390 (1970).

[27] E. E. Vogel and J. Rivera-Iratchet, Phys. Rev. B **22**, 4511 (1980).