PHYSICAL REVIEW B VOLUME 54, NUMBER 11 15 SEPTEMBER 1996-I

Jahn-Teller effect in ZnS:Fe^{2+} revisited with a modified Lanczos-type algorithm

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(Received 18 March 1996)

We study the Jahn-Teller effect in ZnS:Fe^{2+} by means of a modified Lanczos-type algorithm, able to give any excited state of very large quantum systems with good accuracy. The calculations are performed in the energy range of 2945–3580 cm^{-1}, in the framework of a multimode vibronic model. The zero-phonon emission lines (hot lines) are also evaluated. The results are compared with the experimental ones. [S0163-1829(96)08132-5]

I. INTRODUCTION

Many experiments[1,2] have confirmed the role of the Jahn-Teller effect in the infrared absorption spectrum of magnetic impurities in the II-VI compound semiconductors. At the same time, many theoretical vibronic models have been proposed (different for the symmetry and for the number of phonon modes taken into account) and have been treated either by means of perturbation theory,[2] or by direct diagonalization of matrices of rank as large as possible, taking advantage of symmetry-adapted basis states,[3,4] or also of generalized Glauber states.[5]

In Jahn-Teller systems with strong coupling, the main obstacle is the large number of basis functions required in the product space of the electronic and vibrational states. However, the Lanczos-Haydock-Heine-Kelly recursion method,[6] appropriately implemented, has emerged as a very powerful computational procedure.

In the case of the Fe^{2+} impurities in ZnS, the near-infrared-absorption spectrum exhibits a structure more complex than that predicted by the crystal field and spin-orbit interaction. There is a very intense line at 2945 cm^{-1} and there are two weak lines at 2964 and 2984 cm^{-1}, followed by a number of other transitions, qualitatively interpreted as phonon-assisted transitions; so a vibronic Jahn-Teller term must be introduced in the system Hamiltonian. In a previous paper[7] we have proposed a multimode vibronic model, treated with a traditional Lanczos recursion method; however, only a few excited levels could be obtained, because the finite arithmetic precision produces loss of orthogonality among the states of the Lanczos chain. When the basis loses orthogonality, ''good eigenvalues'' should be distinguished from ''ghost eigenvalues'' or ''spurious eigenvalues''; this may limit the accuracy of the procedure (as discussed in detail, for instance, in the prototype example of the Nesbet matrix.[8])

In this paper we revisit the multimode vibronic model with a modified Lanczos-type algorithm,[9] which can give good accuracy. This procedure is illustrated in Sec. II; in Sec. III we will show the results; Sec. IV contains concluding remarks.

II. THEORY

The near-infrared-absorption spectrum of Fe^{2+} in ZnS arises from the electronic transitions between the initial ^5E and the final $^5T_2$ multiplet of Fe^{2+}, obtained from the splitting of the ^5D electronic term (the spin-orbit interaction further splits this multiplet). Moreover, the dynamical Jahn-Teller effect is recognized to play a very important role, because many phonons[10,11] of different energies and symmetries can be coupled with the $^5T_2$ excited states, determining the complex structure of the experimental spectra.

The Jahn-Teller active modes for the $^5T_2$ multiplet (neglecting the breathing Γ_1 mode) are those of symmetry Γ_3 and Γ_5 (the Bethe notation is used for the phonon modes; the correspondig Mulliken notation E and T_2 is reserved for the electronic part). The very high intensity of the first line of the spectrum at low temperature suggests a Jahn-Teller energy weaker or of the same order of the spin-orbit coupling constant.[12]

Calculations made in a cluster model[13] considering as active a single mode of symmetry Γ_3 or Γ_5 (see, for instance, Ref. 14) have given between them very similar results, but they are not able to describe the experimental feature, and in effect only a limited range of the spectrum can be reproduced. So it is necessary to consider a coupling with at least two modes of different energy and, possibly, of different symmetry. Here we recall only some relevant points inherent in the system taken into account and in the procedure.

The total Hamiltonian consists of the sum of the electronic contribution including the spin-orbit interaction, the lattice Hamiltonian, and the linear coupling of the electronic part with two-phonon modes of different frequency and coupling energy.

The number of basis functions, a product of electronic and vibrational functions, can become so large as to make difficult or hopeless any direct diagonalization of the Hamiltonian. The Lanczos recursion method presents a fundamental difficulty that makes this method unstable: due to finite arithmetic precision, the functions constructed with the three-term iterative relation lose orthogonality rather soon (about 20–30 steps) and ''spurious states'' or ''ghost states''

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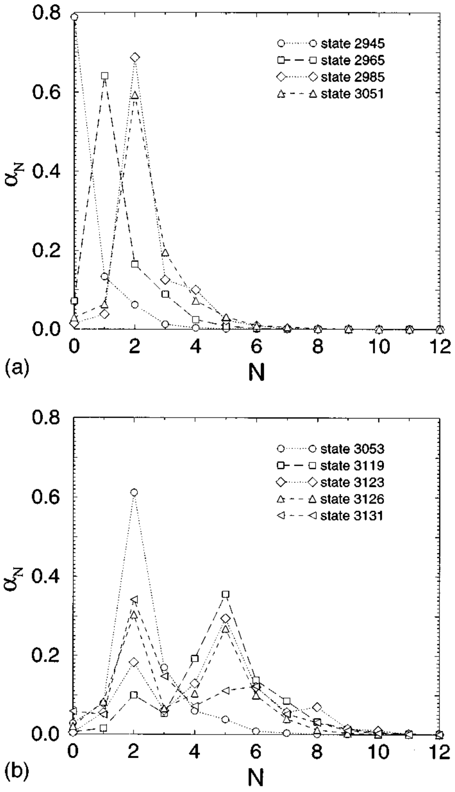

FIG. 1. Behavior of α_N for some states whose energy is given in cm^{-1}. The calculations are made within the modified Lanczos procedure and with $\lambda = -100\ \mathrm{cm}^{-1}$, $10|Dq| = 3136\ \mathrm{cm}^{-1}$, $\hbar\omega_1 = 25\ \mathrm{cm}^{-1}$, $E_{\mathrm{JT}1} = 50\ \mathrm{cm}^{-1}$; $\hbar\omega_2 = 125\ \mathrm{cm}^{-1}$, $E_{\mathrm{JT}2} = 130\ \mathrm{cm}^{-1}$.

appear in the diagonalization procedure.

To override these difficulties, and to obtain any excited state with the desired accuracy, we have previously proposed a new iterative technique,[9] which leads to determination, within the Lanczos algorithm, of the ground state of the auxiliary operator $A = (H - E_t)^2$, and hence the eigenvalue of H nearest in energy to E_t, where E_t is any chosen trial energy in the range of interest. For more details, see Ref. 9. The iterative process alternates the diagonalization of 2×2 Lanczos matrices to a two-pass Lanczos procedure of suitable small dimension.

Concerning the details of calculations, we notice that the Lanczos chain coefficient b_1 is the most important indicator of the accuracy of the calculation. Hence it will be used to determine at what level to stop the global iterative cycle. In fact, let $|\psi_0^M\rangle$ be the normalized ground state after M cycles; at the next step we have

$$b_1^M = \langle \psi_0^M | H | \psi_1^M \rangle = \| H|\psi_0^M\rangle - a_0|\psi_0^M\rangle \|$$

$$\text{with } a_0 = \langle \psi_0^M | H | \psi_0^M \rangle .$$

Thus, in this formalism, when the procedure converges, $|\psi_0^M\rangle$ is an eigenstate of H and b_1^M is approaching zero ($b_1^M \neq 0$ imply again a component in the orthogonal space). In practice, b_1 is chosen to be smaller than a suitable precision parameter ϵ. In the vibronic system taken into account, for $\epsilon \approx 10^{-2}$, the relative accuracy of the eigenvalues is 10^{-8}–10^{-9}.

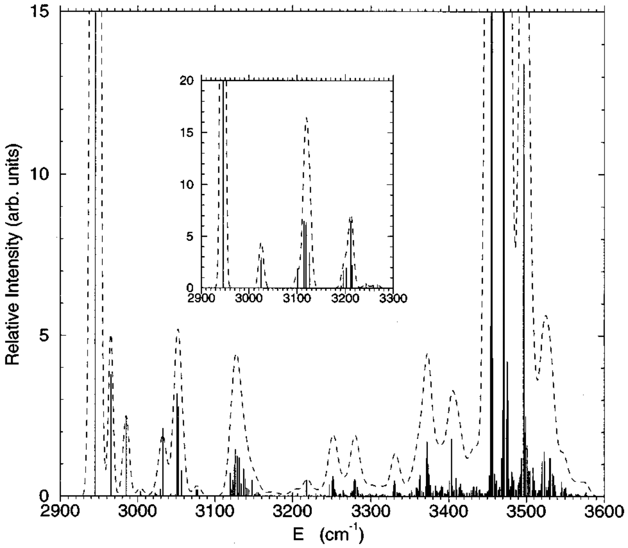

FIG. 2. Relative intensities, in arbitrary units, of the transitions from the ground state to the vibronic states associated to the ${}^5T_2$ multiplet; histogram and convolution with a Gaussian function (half-width of $4\ \mathrm{cm}^{-1}$). The phonon energies and the Jahn-Teller energies are the same as in Fig. 1. In the inset, the phonon and the Jahn-Teller energies are $\hbar\omega_1 = 125\ \mathrm{cm}^{-1}$, $E_{\mathrm{JT}1} = 130\ \mathrm{cm}^{-1}$; $\hbar\omega_2 = 295\ \mathrm{cm}^{-1}$, $E_{\mathrm{JT}2} = 50\ \mathrm{cm}^{-1}$.

For what concerns the more convenient number of 2×2 relaxation steps, we have noticed that the technique is efficient if b_1 is monotonically decreasing. When this characteristic is lost, it is useful to alternate a two-pass Lanczos procedure with a number of steps not higher than ten, to safely avoid the ghost states.

III. RESULTS

The infrared-absorption spectrum[1] at low temperature of Fe^{2+} in ZnS presents a strong line at $2945\ \mathrm{cm}^{-1}$ (referred to as L_0), followed by two weak lines at 2964 and 2984 cm^{-1} (L_1 and L_2). There are then four rather broad lines at 3051, 3129, 3182, and 3241 cm^{-1} (L_3, L_4, L_5, and L_6); after some other structure, at $3500\ \mathrm{cm}^{-1}$ the spin-orbit partner band begins. When the temperature increases other transitions are observed (hot lines or zero-phonon emission lines), of decreasing intensity, at 2930, 2919, 2899, and 2882 cm^{-1}.

In a previous paper[7] we have considered a two-phonon vibronic model, both of Γ_3 symmetry. For the sake of scrupulosity, the studies of the two-mode vibronic model ${}^5T_2\otimes(\Gamma_3+\Gamma_5)$ have been performed, but the results are not satisfactory, particularly as far as the possibility of reproducing both the energies and the intensities of the transitions is concerned. Thus we remain at the two-mode vibronic model ${}^5T_2\otimes(\Gamma_3+\Gamma_3)$. The number of basis functions is now $4(N_1+1)^2(N_2+1)^2$, because here the formalism of the "dipole-carrying" state[12] and the symmetry involved allows us to work in an invariant subspace of H of reduced dimension.[14] In the calculations we have used the crystal-field parameter $10|Dq| = 3136\ \mathrm{cm}^{-1}$ (to reproduce the first L_0 line), the free-ion spin-orbit coupling constant[15]

TABLE I. Energies and peak intensities of the relevant transitions from the ground state calculated with the modified Lanczos procedure and with $\lambda = -100$ cm^{-1}, $10|Dq| = 3136$ cm^{-1}, $\hbar\omega_1 = 25$ cm^{-1}, $E_{\mathrm{JT}1} = 50$ cm^{-1}; $\hbar\omega_2 = 125$ cm^{-1}, $E_{\mathrm{JT}2} = 130$ cm^{-1} and compared with experimental values.[1] The numbers in parentheses give the calculated total intensity of the groups of states around the levels of energy 3051 and 3129 cm^{-1}.

Experimental data		Results of this work	
E_i (cm^{-1})	I_i^{rel}	E_i (cm^{-1})	I_i^{rel}
2945	100	2945.2	100
2965	4	2964.5	3.8
2985	1	2984.0	2.6
3051	12	3050.9	3.2 (9)
3129	25	3128.4	1.25 (9)

$\lambda = -100$ cm^{-1}, the phonon energies $\hbar\omega_1 = 25$ cm^{-1}, $\hbar\omega_2 = 125$ cm^{-1}; the Jahn-Teller energies $E_{\mathrm{JT}1} = 50$ cm^{-1} and $E_{\mathrm{JT}2} = 130$ cm^{-1}, these last chosen to reproduce the energies and the intensities of the experimental lines.

The maximum number $\mathcal{M}$ of phonons for each degree of freedom has been determined working with one phonon mode at time and changing $\mathcal{M}$ at fixed S (the Huang-Rhys factor, that is, the Jahn-Teller energy in units of the phonon energy). The results have shown that $\mathcal{M} \approx 2S+1$ assures a relative accuracy at least of 10^{-4} in the eigenvalues and of 10^{-2} in the eigenvectors (the accuracy is better for the lower-lying states).

This rule remains valid also for the two-mode vibronic model, as confirmed by the calculation of the contribution (called α_N) of the basis functions with a fixed *total* phonon number N, to the projection modulus square of chain eigenstate. In Fig. 1 we show the behavior of α_N for some levels of interest. It can be seen that α_N is almost zero for any state already for $N \geqslant 10$, and its maximum value occurs at $N \leqslant 7$.

With the procedure discussed, we have explored a large energy range, up to 3580 cm^{-1}. In Fig. 2 we give the histogram of the energies and the intensities for the transitions from the ground zero-phonon state (γ_1 level in the ^5E multiplet) to the vibronic $^5T_2$ levels. As expected, the first three lines agree well with the experimental ones. At higher energies we obtain many eigenstates very near one another, separated by less than the experimental resolution; if we associate to each transition a Gaussian function, with half-width of the order of the experimental resolution (4 cm^{-1}), we obtain the dashed line shown in Fig. 2 superimposed on the palisade. In the inset of the same figure, we show what was obtained with two interacting modes of intermediate and high energy, that is, $\hbar\omega_1 = 125$ cm^{-1}, $\hbar\omega_2 = 295$ cm^{-1}; Jahn-Teller energies $E_{\mathrm{JT}1} = 130$ cm^{-1} and $E_{\mathrm{JT}2} = 50$ cm^{-1}. As expected, the L_4 line is enhanced and a new transition appears at about 3200 cm^{-1}, corresponding to the L_5 transition line. In Table I we give the relevant eigenvalues compared with the experimental data.

TABLE II. Energy separations and intensities of the hot lines calculated with the same parameters as in Table I and compared with the experimental values.

i	$\delta E_i^{\mathrm{calc}}$ (cm^{-1})	I_i^{calc}	$\delta E_i^{\mathrm{expt}}$ (cm^{-1})	I_i^{expt}
4	16	130	15 ± 2	100
3	32	100	26 ± 2	120
5	52	130	46 ± 2	60

The transitions observed at higher temperature, hot lines (or equivalently the emission zero-phonon lines), involve as initial states (final states) the higher levels γ_i ($i = 3,4,5$) of the multiplet ^5E and are below the first line at 2945 cm^{-1} by the quantity $\delta E_i = E_{\gamma_i} - E_{\gamma_1}$. The energies can be satisfactorily calculated taking into account the crystal-field and the spin-orbit interaction at all the orders. To calculate the peak intensity, however, we need to know the vibronic ground state of the $^5T_2$ multiplet.

The energies and the line intensities, shown in Table II, agree with the experimental results given in Ref. 1 within the experimental uncertainties of the order of a factor of 2.

IV. CONCLUSIONS

We have applied our recently developed Lanczos-type algorithm to a multimode vibronic model for studying the Jahn-Teller effect on Fe^{2+} impurities in ZnS. The technique proposed, differently from the ordinary Lanczos procedure, has allowed us to span accurately a very large energy range. Also, the knowledge of the vibronic wave functions has allowed us to find very easily the hot lines. The increased numerical accuracy allows us to better define the physical model considered, including the limits of the model. So we have found that the more convenient symmetry for the phonon coupling is the Γ_3 symmetry, and that more phonons are needed to reproduce all the rich stucture of the experimental spectra.

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