

## Vibronic coupling for substitutional iron impurities in ZnTe

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Theoretical calculations based on a linear Jahn-Teller Hamiltonian are performed for the case of ZnTe:Fe<sup>2+</sup>. The results show a clear and rather strong vibronic coupling, which allows a good interpretation of the available experimental results. A brief study of the line shape calls for experiments with slightly better resolution than presently available from the literature. The reported values for both the Jahn-Teller energy and the frequency of the coupling phonons are in good agreement with those calculated for similar systems. Vibronic functions with vibrational quanta  $N$  up to 14 were used in order to study the stability of the solutions. This analysis is also extended to CdTe, ZnS, and ZnSe with iron impurities where results with only  $N = 10$  were available.

### INTRODUCTION

Infrared spectra of Fe<sup>2+</sup> in several II-VI-compound semiconductors have been recently interpreted as a manifestation of a dynamic Jahn-Teller effect.<sup>1,2</sup> The case of ZnTe has remained without quantitative approach due to the existence of just one reported spectrum. Moreover, such a spectrum does not possess the appropriate resolution in order to perform the adjustment of both the energy levels and absorption intensities.<sup>3</sup> In the present article we propose a way to by-pass the lack of enough experimental information in order to calculate and report the Jahn-Teller energy ( $E_{JT}$ ) and the energy of the coupling phonon ( $\hbar\omega$ ).

The electronic states of the iron impurity are coupled to the vibrational states of the host crystal by means of a linear Jahn-Teller Hamiltonian, namely

$$H_{JT} = K[(a_{\theta}^{\dagger} + a_{\theta})D_{\theta} + (a_{\varepsilon}^{\dagger} + a_{\varepsilon})D_{\varepsilon}], \quad (1)$$

where  $D_{\theta}$  and  $D_{\varepsilon}$  are electronic operators, and  $a_{\theta}^{\dagger}$  and  $a_{\varepsilon}^{\dagger}$  ( $a_{\theta}$  and  $a_{\varepsilon}$ ) are creation (annihilation) operators for vibrational modes  $\theta$  and  $\varepsilon$  corresponding to the irreducible representation  $E$  of the point group  $T_d$ . The coupling constant  $K$  can be expressed as

$$K = (\hbar\omega E_{JT})^{1/2}. \quad (2)$$

The total Hamiltonian comprises, as well, the harmonic vibrational contribution and the pure electronic term due to the free ion plus the crystalline field.

The zeroth-order vibronic functions can be constructed in the Born-Oppenheimer limit and denoted by  $|\Gamma_i(\Gamma_j, N), s\rangle$ , where  $N$  is the total number of vibrational quanta,  $\Gamma_j$  corresponds to the irreducible representation associated to the electronic functions coupled to  $N$  quanta; and  $\Gamma_i$  indicates the group properties of the resulting vibronic functions, while  $s$  selects one of them.

More details about the approach and the computation-

al techniques employed were already reported<sup>1</sup> so we will omit these aspects here, aiming mainly towards the results.

### DISCUSSION AND RESULTS

As a starting point of the discussion, let us quickly review the main characteristics of the system. The infrared-absorption spectrum of ZnTe:Fe<sup>2+</sup> shows a sharp rise at about 2475 cm<sup>-1</sup> and a descent of 2510 cm<sup>-1</sup> with an absolute maximum at 2491 cm<sup>-1</sup> showing one shoulder on each side. These three lines are indicated clearly, although the experimental resolution does not allow one to read the actual energy values directly from the spectrum. As for the intensities, they should all be of the same order of magnitude in order to show the structure already described. The method used so far<sup>1,2</sup> makes use of four experimental results (two energy differences

TABLE I. Phonon energies corresponding to particular states possessing  $E$ -type symmetry for several zinc-blende compounds. The value for  $\hbar\omega$  found for the case of Fe<sup>2+</sup> in each of these compounds is also included. It follows that the states  $TA_1(K)$  have the appropriate frequencies. (All energies in cm<sup>-1</sup>.)

Compound	TA(L)	TA <sub>1</sub> (K)	TA <sub>2</sub> (K)	$\hbar\omega$
CdTe	30 <sup>a</sup>	37 <sup>a</sup>	50 <sup>a</sup>	40 <sup>d</sup>
ZnS	74 <sup>b</sup>	90 <sup>b</sup>	115 <sup>b</sup>	100 <sup>d</sup>
ZnSe	56 <sup>c</sup>	70 <sup>c</sup>	93 <sup>c</sup>	65 <sup>c</sup>
ZnTe	42 <sup>b</sup>	54 <sup>b</sup>	75 <sup>b</sup>	50 <sup>f</sup>

<sup>a</sup>Reference 5.

<sup>b</sup>Reference 9.

<sup>c</sup>Reference 12.

<sup>d</sup>Reference 1.

<sup>e</sup>Reference 2.

<sup>f</sup>Proposed here.

plus two intensity ratios) in order to adjust the two free parameters ( $E_{JT}$ ,  $\hbar\omega$ ). Unfortunately, for ZnTe:Fe<sup>2+</sup> the information presently available does not allow one to give individual numerical values to all four experimental conditions.

We propose here that from earlier theoretical approaches,<sup>4</sup> as well as from the experience obtained from CdTe:Fe<sup>2+</sup>,<sup>1</sup> ZnS:Fe<sup>2+</sup>,<sup>1</sup> and ZnSe:Fe<sup>2+</sup>,<sup>2</sup> the energy of the coupling phonon can be identified from the vibrational dispersion curves of the host crystal. In these cases  $E$  modes ( $\theta$  and  $\epsilon$ ) suffice in order to explain the high-resolution absorption spectra. Three points from the Brillouin zone meet the requirement of describing phonons with an  $E$  component from the point of view of the iron impurity surrounded by the four Te atoms: TA( $L$ ), TA<sub>1</sub>( $K$ ), and TA<sub>2</sub>( $K$ ). In Table I we summarize the properties of CdTe,<sup>5-8</sup> ZnS,<sup>7,9-11</sup> ZnSe,<sup>6,7,10-12</sup> and ZnTe.<sup>8,9,13</sup> It follows from here that the energy of the coupling phonon is close to the frequency of the TA<sub>1</sub>( $K$ ) point, which allows one to "guess" that  $\hbar\omega = 50 \text{ cm}^{-1}$  is a good value for ZnTe. We shall use this value from now on.

We performed diagonalizations of the total Hamiltonian varying the only free parameter left: the Jahn-Teller energy. For values of  $E_{JT} = 250 \text{ cm}^{-1}$  or slightly higher, good agreement with the main characteristics of the absorption spectrum is obtained. Figure 1 shows the energy differences  $\Delta_i$  of the vibronic levels as a function of  $E_{JT}$ .

A very interesting result is obtained when the stability of the solutions is studied. Figure 2 represents the convergence of the energy differences as functions of  $(N-1)/N$ , which is a convenient way of representing the number of vibrational quanta. It is clear that we have to increase  $N$  up to 11 in order to reach convergence. This feature, along with previous results,<sup>1,2</sup> allows one to draw a conclusion about the relationship between  $E_{JT}$  and  $N_m$ , the minimum number of vibrational quanta needed in order to reach stability.

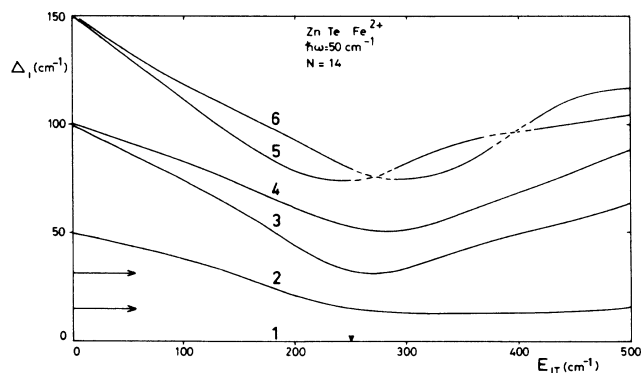


FIG. 1. Energy differences  $\Delta_i$  corresponding to the vibronic levels of the  $T_2$  multiplet of Fe<sup>2+</sup> in ZnTe referred to the lowest one among them, as functions of the Jahn-Teller Energy  $E_{JT}$ . Actual experimental energy of the lowest level ( $\Delta_1$ ) is  $2476 \text{ cm}^{-1}$ . Arrows indicate the expected levels as read from the experiment (Ref. 3). The solid inverted triangle indicates the value for  $E_{JT}$  reported here.

We define  $N_m$  as the minimum  $N$  such that the variation of the splitting between the first two levels of the  $T_2$  multiplet ( $\Delta_1$ ) is less than 1%. Namely, when the following condition is satisfied:

$$\frac{\Delta_1(N_m) - \Delta_1(N_m - 1)}{\Delta_1(N_m - 1)} < 0.01 .$$

In order to obtain reliable values for  $N_m$  throughout the already mentioned compounds, we performed calculations up to  $N = 14$ . This extends previous treatments for Fe<sup>2+</sup> in CdTe, ZnS, and ZnSe beyond  $N = 10$ .<sup>1,2</sup> The values of  $N_m$  for the different compounds and their relation with  $E_{JT}$  are listed in Table II. Clearly stronger Jahn-Teller coupling needs a more complete set of vibronic functions based on vibrational functions with higher numbers of quanta,  $N$ .

The convergence of the intensities for ZnTe are shown in Fig. 3. Again, good stability is reached for  $N = 11$ , with relative intensities  $f_1:f_2:f_3 \approx 2:1:2$  for the first three lines. Predicted intensities for other lines are negligible as compared with the three leading ones. In Fig. 4 two

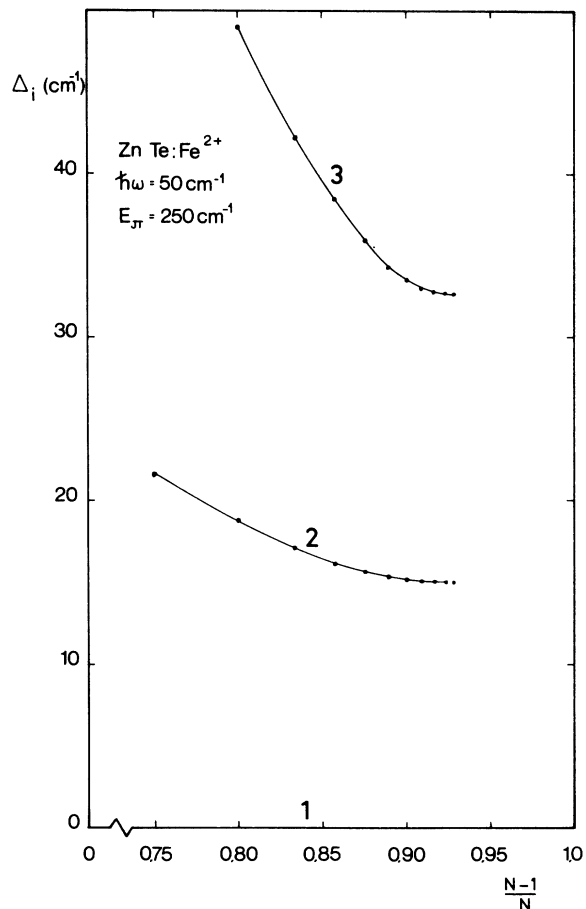


FIG. 2. Energy differences corresponding to the three leading vibronic levels with orbital symmetry  $T_2$  as a function of the total number of vibrational quanta,  $N$ , considered in the diagonalization. Calculated energies are represented by dots joined by auxiliary lines.

TABLE II. Jahn-Teller energies and minimum number of vibrational quanta,  $N_m$ , needed in order to obtain stable solutions for four zinc-blende II-IV compounds with  $\text{Fe}^{2+}$ , substitutional impurities.

	ZnS	ZnSe	CdTe	ZnTe
$E_{JT}$ ( $\text{cm}^{-1}$ )	200 <sup>a</sup>	230 <sup>b</sup>	240 <sup>a</sup>	250 <sup>c</sup>
$N_m$	7	9	11	11

<sup>a</sup>Reference 1.

<sup>b</sup>Reference 2.

<sup>c</sup>Present article.

different line shapes are shown in order to realize the importance of the experimental resolutions. Each individual absorption is assumed to be Gaussian. The superposition of the first three lines defines an amplitude  $A(E)$  which, in arbitrary units, can be expressed as

$$A(E) = \sum_{i=1}^3 \frac{f_i}{\delta_i} \exp[-(E - E_i)^2 / (\delta_i)^2],$$

where  $E_i$  is the energy at the center of the  $i$ th line of relative oscillator strength  $f_i$  and width  $2\delta_i$ . The energies  $E_i$  are obtained from Fig. 2, namely 2476, 2491, and 2507

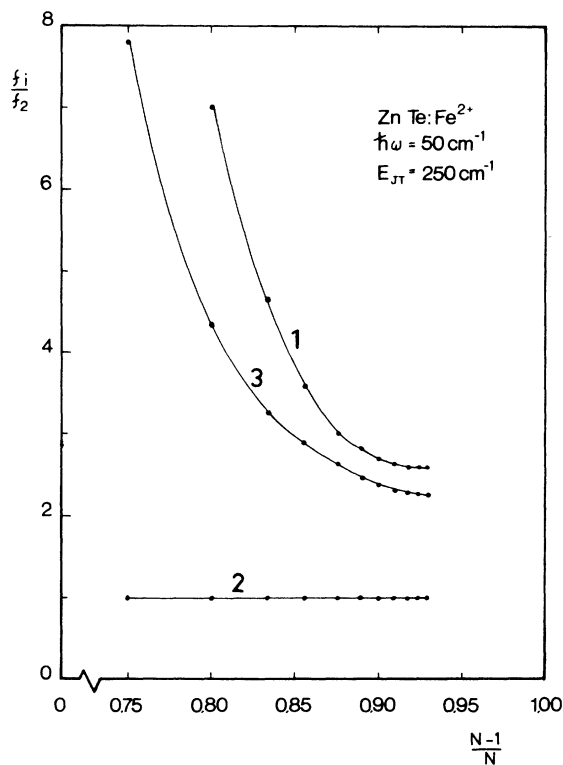


FIG. 3. Relative oscillator strengths for electric dipole absorptions between the ground state and the three levels defined in Fig. 2. Calculated intensities are represented by dots joined by auxiliary lines.

$\text{cm}^{-1}$ , while the relative oscillator strengths were already given. When half-widths of 14, 8, and  $14 \text{ cm}^{-1}$  are used for the first three lines, we obtain the solid curve in Fig. 4, which is quite similar to the experimental one given by Baranowski, Allen, and Pearson.<sup>3</sup> On the other hand, if the experimental resolution can be improved, the values of  $\delta_i$  can be reduced to 8, 4, and  $8 \text{ cm}^{-1}$ , respectively; then, the discontinuous line shape would be obtained.

## CONCLUSIONS

From the previous analysis we conclude that the infrared-absorption spectrum of  $\text{Fe}^{2+}$  in ZnTe shows evidence of a vibronic coupling between the electronic states

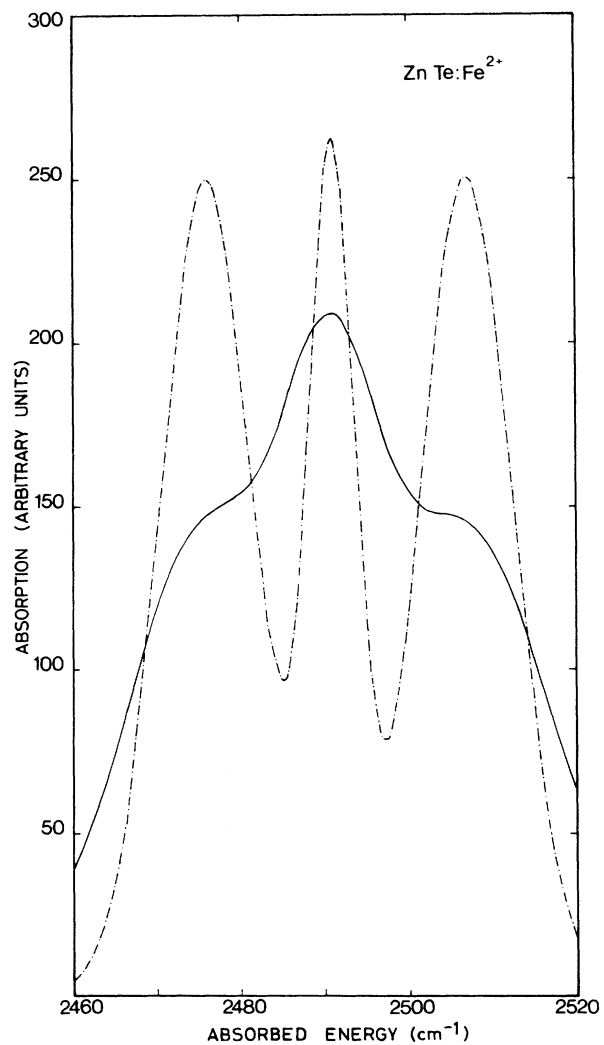


FIG. 4. Two different line shapes corresponding to the calculated absorption intensities of the three leading lines of  $\text{ZnTe:Fe}^{2+}$ . The solid curve corresponds to rather poor resolution with half-widths of 14, 8, and  $14 \text{ cm}^{-1}$ , while the dashed curve corresponds to a case of improved resolution with half-widths of 8, 4, and  $8 \text{ cm}^{-1}$ , respectively.

of the magnetic impurity and phonons of  $\hbar\omega = 50 \text{ cm}^{-1}$  with a strength given by  $E_{JT} = 250 \text{ cm}^{-1}$ .

The possible extensions of the present work are the following: (a) to obtain higher-resolution infrared-absorption spectra, (b) to review all four compounds in both Tables I and II fixing  $\hbar\omega$  in the way proposed above and attempting a line-shape analysis, and (c) to perform Jahn-Teller calculations using wave functions constructed in the strong-limit case,<sup>14</sup> and applying them to the case of ZnTe, which shows the largest value for  $E_{JT}$  among the system analyzed in this paper.

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