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Jahn-Teller effect for Fe^{2+} in III-V semiconductors

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The Jahn-Teller coupling between local vibrations of the host III-V semiconductors and the electronic orbitals of Fe^{2+} substitutional impurities are studied from a theoretical point of view. Coupling to both multiplets resulting after crystal-field splitting is considered. Calculations are performed with just one adjustable parameter, namely, the Jahn-Teller energy (E_{JT}). The compounds GaP:Fe^{2+}, GaAs:Fe^{2+}, and InP:Fe^{2+} are fully discussed, especially the latter. Other III-V semiconductors such as GaSb:Fe^{2+}, InAs:Fe^{2+}, and InSb:Fe^{2+} are referred to for particular applications of the model. The results for the lower multiplet show good agreement for the predicted lines with luminescence spectra; the coupling phonon is identified as belonging to the points TA(L) of the Brillouin zone; values for E_{JT} are about 8 cm^{-1} for this coupling. The coupling to the upper multiplet is described in terms of upper limits as the available infrared-absorption spectra do not show evidence for more than one zero-phonon line. A comparison with similar calculations for II-VI compounds with Fe^{2+} as substitutional impurity is also performed.

I. INTRODUCTION

The manifestation of the Jahn-Teller effect (JTE) for magnetic impurities in binary compounds is a well-known fact.[1] Extensive calculations have been performed for the cases of Ni^{2+} and Fe^{2+} in II-VI semiconductors.[2-6] The general conclusion in these cases is that the magnitude of the vibronic coupling is comparable to the spin-orbit interaction, which means that JTE manifests itself quite clearly in the spectroscopic properties of these systems. In the present paper, we attempt to perform similar calculations for the cases of Fe^{2+} in III-V semiconductors.

It is likely that the same impurity ion would have a similar behavior in the II-VI zinc-blende compounds as in the III-V compounds possessing the same structure. The main purposes of the present article are to explore such a possibility, perform calculations, and compare results both with the available experimental information and with the already mentioned II-VI systems. The theoretical model will be presented in Sec. II.

There is experimental information for some of the III-V compounds with Fe as a substitutional impurity, using both absorption and luminescence techniques. Thus GaP:Fe^{2+},[7-9] GaAs:Fe^{2+},[10] and InP:Fe^{2+},[11-14] have been reported in the literature. There is a general resemblance between the spectra of III-V:Fe^{2+} with respect to those of II-VI:Fe^{2+}. The former shows the following two important characteristics in the optical properties: (a) At very low temperatures there is just one strong zero-phonon line (ZPL) in the absorption spectra corresponding to the infrared range and (b) luminescence and higher-temperature absorption spectra show slight departure from the equally spaced levels within the lower multiplet as predicted by plain crystal-field calculations. A survey of the main experimental information related to the present problem will be included in Sec. III. Special attention is paid to InP, in which there is much interest at present.[12-14]

These two observations point to indicate a weaker JT coupling for iron impurities in III-V compounds as compared with the same ion in II-VI compounds. Some justification for this difference will be given when discussing the results in Sec. IV.

We shall focus our presentation on two different aspects of the problem. First, we discuss the Jahn-Teller coupling dealing with the ^5E electronic functions of the lower multiplet and compare these calculations with the data coming from luminescence experiments. Second, we investigate the possible vibronic coupling with the $^5T_2$ upper electronic multiplet using the low-temperature absorption spectra as experimental information for comparison purposes.

II. THEORETICAL MODEL

The total Hamiltonian H is composed of three terms: the free-ion contribution H_e, the coupling or JT interaction H_{JT}, and the contribution of the vibrational modes coupled to the localized electrons H_v:

$$H = H_e + H_{JT} + H_v \ . \tag{1}$$

H_e describes the ion in terms of the ^5D multiplet, including crystalline field and spin-orbit interaction. H_{JT} is given as a scalar product between a vector in the electronic space **D** and a vector in the vibrational space **Q**. Finally, H_v represents the usual vibrational Hamiltonian in the harmonic approximation.

We follow here the approach of assuming a linear JT Hamiltonian that couples the vibrational field to the electronic field. In principle, a distribution of phonons with different energies could couple. However, not all of these vibrational modes possess the same coupling strength. We suppose here a dominant local mode representative for such a coupling with energy denoted by $\hbar\omega$. From previous treatments for the II-VI compounds that have the same structure and similar lattice dynamics,[5,15,16] we consider here the doubly degenerate modes E only, with creation (annihilation) operators represented by $a_\theta^\dagger$ and $a_\epsilon^\dagger$ (a_θ and a_ϵ). The coupling Hamiltonian can now be written as

$$H_{\mathrm{JT}}=\sqrt{\hbar\omega E_{\mathrm{JT}}}[(a_\theta^\dagger+a_\theta)D_\theta+(a_\epsilon^\dagger+a_\epsilon)D_\epsilon] \ , \tag{2}$$

where E_{JT} is the so-called Jahn-Teller energy and D_θ and D_ϵ are appropriate operators of symmetry E acting on the electronic orbitals.

Not all the vibrational modes couple with the same strength to the d electrons of the impurity ion; symmetry plays an important selective role.[17] Moreover, local vibrations of the appropriate symmetry (associated to different branches of the phononic spectrum) couple differently to the variety of localized electronic functions. For the sake of simplicity we describe the coupling phonons in the form of just one representative vibrational mode of the surrounding tetrahedron of anions. The appropriate points of the Brillouin zone having E vibrational modes are those represented by TA1(K), TA2(K), and TA(L).[17]

The corresponding vibrational Hamiltonian is given by

$$H_v=\hbar\omega(a_\theta^\dagger a_\theta+a_\epsilon^\dagger a_\epsilon+1) \ . \tag{3}$$

The total Hamiltonian given by previous equations is then diagonalized with respect to a set of functions spanning both the vibrational and electronic spaces, which are referred to as vibronic functions. We choose here to form these functions in the adiabatic limit since E_{JT} is expected to be small. We will present next the way the two vibronic bases needed for the present applications are formed.

Iron substitutes for the cation in III-V compounds and would release three electrons if the bonding would be entirely ionic. In practice, Fe^{2+} is also present in these systems (even Fe^{+} is possible). The local symmetry at the site of the Fe ion is given by the point group T_d.

The six d electrons of the doubly ionized iron atom couple to form a ^5D atomic ground multiplet, which the crystalline field unfolds into a ^5E ground multiplet and a $^5T_2$ excited multiplet, separated by an energy $10|Dq|$. Second-order spin-orbit interaction further splits ^5E giving five equally spaced levels which can be labeled as γ_1, γ_4, γ_3, γ_5, and γ_2 in order of increasing energy. The upper $^5T_2$ multiplet splits into three branches: Γ_{5a} alone, Γ_{4a}, Γ_3 in the second one, and $\Gamma_{5b}, \Gamma_{4b}, \Gamma_1$ in the last one. Further splitting within the branches is due to second-order spin-orbit interaction. A diagram of such an energy-level scheme is presented in Fig. 1.

The details of the treatment of the states corresponding to the $^5T_2$ multiplet were already given in previous papers,[5,6] and will be omitted here. However, we summarize and reformulate the main aspects of the splitting of the lower ^5E multiplet in order to provide the basis for the discussion below.

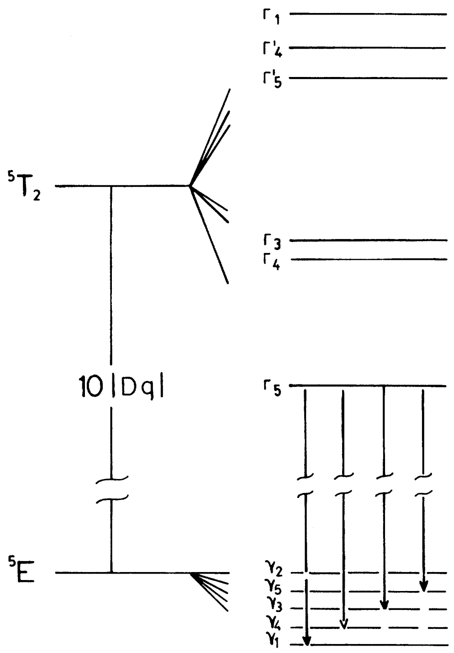

FIG. 1. Energy-level diagram corresponding to the Fe^{2+} substitutional impurity in zinc-blende-structure compounds, up to second-order perturbation theory in spin-orbit interaction.

The energies of the five levels coming from the lower multiplet, up to third-order perturbation theory in spin-orbit interaction, can be expressed in the following way:[7,11]

$$\begin{aligned}&\gamma_2{:}4\sigma[1-2|\lambda|/(10|Dq|)] \ ,\\ &\gamma_5{:}3\sigma[1-3|\lambda|/(10|Dq|)] \ ,\\ &\gamma_3{:}2\sigma[1-5|\lambda|/(10|Dq|)] \ ,\\ &\gamma_4{:}\sigma[1-5|\lambda|/(10|Dq|)] \ ,\\ &\gamma_1{:}0 \ ,\end{aligned} \tag{4}$$

where λ is the spin-orbit parameter and

$$\sigma=6\lambda^2/(10|Dq|) \ . \tag{5}$$

The energy of the true ground state has been defined as zero for convenience.

We introduce now a unit of energy which will be convenient for the discussion of the unequal energy differences among the five levels:

$$\delta=\sigma[1-5|\lambda|/(10|Dq|)] \ . \tag{6}$$

It is possible now to reformulate the set of equations (4) in the following way:

$$\begin{aligned}&\gamma_2{:}4\delta+12\sigma|\lambda|/(10|Dq|)\ ,\\&\gamma_5{:}3\delta+6\sigma|\lambda|/(10|Dq|)\ ,\\&\gamma_3{:}2\delta\ ,\\&\gamma_4{:}\delta\ ,\\&\gamma_1{:}0\ .\end{aligned} \tag{7}$$

It is now obvious that the two low-lying differences, namely, $\gamma_3-\gamma_4$ and $\gamma_4-\gamma_1$, should be exactly the same and slightly smaller than the next possible difference $\gamma_5-\gamma_3$. A departure from this result is an indication for a Jahn-Teller effect.

Level γ_2 is not considered in the analysis since it does not show up in luminescence spectra. Since the symmetry of the low-lying level of the upper multiplet is Γ_5 and the electric dipole transition is represented by a Γ_5 operator, the selection rules allow for connection only with the levels contained in the Kronecker product:

$$\Gamma_5\otimes\Gamma_5=\gamma_1+\gamma_3+\gamma_4+\gamma_5\ . \tag{8}$$

If n and m are the occupancy numbers of modes θ and ϵ, respectively, then the total occupancy number is N, given by

$$N=n+m\ . \tag{9}$$

Vibronic functions can now be formed in the Born-Oppenheimer approximation. The maximum number of vibrational quanta N considered in the construction of the vibronic basis can be increased up to the limit that the computational facilities allow. However, we have found that stable solutions for the energies of the four expected lines (variations of less than 1%) are reached for $N=5$ which we will use in the remainder of the calculations involving states of the lower electronic multiplet.

Vibronic functions are constructed for each one of the electronic levels γ_i, considering the symmetric powers of the irreducible representation associated to the vibrational functions. This can be illustrated in the following way:

$$\gamma_i\otimes E^0,\ \ \gamma_i\otimes E^1,\ \ \gamma_i\otimes E^2,\ldots,\ \text{and}\ \ \gamma_i\otimes E^N\ . \tag{10}$$

Sorting the resulting vibronic functions according to the symmetry properties, it is possible to break down the Hamiltonian matrix into submatrices for an easier diagonalization.

We can form the basis of vibronic functions corresponding to the upper multiplet in a similar way, which has been already presented in quite a detailed manner.[5,6] We briefly summarize here the main aspects of the corresponding basis in order to set up the notation.

The zeroth-order vibronic functions for the upper $^5T_2$ level can be denoted by $|\tilde{\Gamma}_i(\Gamma_j,N),s\rangle$, where N is the total number of vibrational quanta given by Eq. (9), Γ_j represents the electronic level, while $\tilde{\Gamma}_i$ represents the final irreducible representation of the vibronic functions with component s. We can form the vibronic functions for the lower multiplet by means of a similar procedure. In this case we adopt the same notation except for the use of lower-case Greek letters, namely, $|\tilde{\gamma}_i(\gamma_j,N),s\rangle$.

The diagonalization of these two different Hamiltonian matrices is performed with the following considerations. In both cases the crystal-field parameter $10|Dq|$ and spin-orbit parameter $|\lambda|$ are kept fixed. The latter is taken as the free-ion value, namely, 100 cm^{-1}. The crystal-field parameter is adjusted so as to give the threshold transition $\Gamma_{5a}-\gamma_1$ without any further adjustment for a particular system. The energy of the coupling phonon can be taken as a variable; however, it must correspond to one of the phonons possessing local modes of symmetry E. The Jahn-Teller energy is then the only true adjustable parameter in the diagonalization processes.

III. REVIEW OF EXPERIMENTAL RESULTS

The energies of the possible phonons having local component E are given in Table I for the three semiconductors under consideration.[18-22] The presence of the impurity can modify the frequency of the local modes; however, the approximate values of the coupling modes and their relative magnitudes as going from one compound to the other should follow the experimental data given in Table I.

However, we must separate the vibronic coupling to the upper multiplet with respect to the coupling to the lower one. The electronic functions are different in these two cases, which means that the we must consider two different coupling phonons as well. Since the charge distribution is also different in these two coupling mechanisms, the magnitude of the coupling (hence, E_{JT}) can vary from one multiplet to the other one.

The most important part of the optical spectra comprises all of the $\gamma_i \Longrightarrow \Gamma_{5a}$ transitions ($i=1,4,3,5$) allowed via electric dipole interaction. In luminescence spectra these four lines are clearly present and the equal separation among the γ levels can be readily tested.[8] The main experimental results are summarized in Table II. It is clear that the spacing among the lines is not equal, which provides evidence for a weak Jahn-Teller coupling.

The system InP:Fe^{2+} is the one that has been most studied among the cases under consideration.[11-13] Recent information includes mixed systems of the kind $In_{1-x}Ga_xP$.[14] We will choose InP:Fe^{2+} in order to illustrate in a detailed manner the calculations to be reported in Sec. IV. Let us review this system in a more complete way. Far from some small discrepancies among the experiments,[11-13] four lines are unequally spaced. The successive separations would be 14–15, 24–26, and 42–43

TABLE I. Vibrational energies (in cm^{-1}) of phonons with local component E for three III-V semiconductors.

	GaP[a]	GaAs[b]	InP[c]
TA1(K)	130	120	105
TA2(K)	104	79	68
TA(L)	83	62	55

[a] Reference 18.

[b] Reference 19.

[c] Reference 20.

TABLE II. Calculated energies (in cm^{-1}) of the first three excited states for the three indicated semiconductors. In parentheses we give the experimental values as taken from the references quoted in the text. The values (in cm^{-1}) for the vibrational quanta and Jahn-Teller energy used in the present calculations are listed in the last two rows.

	GaP[a,b]	GaAs[c]	InP[d,c,e]
$E(\gamma_4)$	13 (13)	14 (14)	15 (15) (13.7) (15)
$E(\gamma_3)$	24 (24)	24 (23)	25 (25) (24.3) (26)
$E(\gamma_5)$	40 (40)	41 (40)	43 (43) (42.3) (43)
$\hbar\omega$ TA(L)	83	62	55
E_{JT}	8	8	7

[a] Reference 7.
[b] Reference 8.
[c] Reference 12.
[d] Reference 11.
[e] Reference 13.

cm^{-1}, showing a slightly enhanced effect of the unequal energy difference as compared to GaP:Fe^{2+} or GaAs:Fe^{2+}. Another interesting feature of the luminescence spectrum of InP:Fe^{2+} is that beyond the leading four lines there is a broad band between 60 to 85 cm^{-1} approximately.[11] Between 90 to 95 cm^{-1} there is a clear absence of emitted lines while over 100 cm^{-1} there arises a second band which is broader and weaker than the former.

Not given in Table II are the intensities of the lines. For all of these three systems the characteristics of luminescence spectra are the following: there is one dominant line ($\Gamma_{5a}-\gamma_4$) with intensity about three times the intensity of the other three lines ($\Gamma_{5a}-\gamma_1$, $\Gamma_{5a}-\gamma_3$, $\Gamma_{5a}-\gamma_5$) which have comparable intensities among themselves.

On the other hand, infrared-absorption experiments will connect the same γ levels with all the vibronic states originating in the Γ levels of the upper multiplet. These spectra are very sensitive to temperature as the upper γ levels have to be populated in order to produce an absorption. At very low temperatures (less than the separation of about 20 K between consecutive pairs of γ levels), only absorptions originating from the ground state γ_1 can be expected. Special attention to the ZPL will be paid as they contain information about the admixture of states originated in the vibronic coupling.

The absorption spectra of Fe^{2+} in II-VI compounds differ appreciably from the above description, CdTe:Fe^{2+} being the best-known example.[5,23,24] In this system up to three ZPL connecting $\gamma_1 \Longrightarrow \Gamma_{5a}$ are observed at liquid-helium temperature.

The known infrared-absorption spectra of Fe^{2+} in GaAs, GaP and InP (Refs. 7–14) do not show evidence for more than one quite strong ZPL. This is an indication for a weak coupling. It is clear that no definite numerical values for E_{JT} can be obtained from this rather qualitative experimental information. However, we will try to propose an upper limit for E_{JT} consistent with the experimental observation of just one strong ZPL in the absorption spectra.

IV. RESULTS AND DISCUSSION

Parameters $10|Dq|$ for the crystalline fields of the different compounds are taken from spectroscopic data, while $|\lambda|$ for the spin-orbit interaction is taken as the free-ion value, namely, 100 cm^{-1}.

A. Coupling to the lower multiplet

Let us tackle the problem of Jahn-Teller coupling for the E lower multiplet in the first place. As we do not have any indication for the possible energy of the coupling phonon, we shall use three different values for each system in accordance with the experimental values given in Table I. The Jahn-Teller energy is left out as the only adjustable parameter. For each tetrad ($10|Dq|,\lambda,\hbar\omega,E_{\mathrm{JT}}$), a complete diagonalization of the Hamiltonian is performed on a vibronic basis defined up to N vibrational quanta. The energies of the levels are then compared with the level scheme that can be obtained from experiment. The resulting wave functions lead to the calculation of the intensities of the four observed lines. Once agreement is found for a large enough value of the total vibrational quantum number, this is brought down to a value N where the first energy difference ($\gamma_4-\gamma_1$) does not vary more than 1% with respect to the value for $N+1$. We then say that the solutions are already stable for N. For all the results concerning the lower multiplet, N will be 5.

The diagonalization procedure just described was performed for the systems GaP:Fe^{2+}, GaAs:Fe^{2+}, and InP:Fe^{2+}. We shall use the last one of these cases to do a more detailed discussion. Actually, the situation of the other two is quite similar to the one of InP:Fe^{2+}. The main results for the three systems are summarized in Table II.

The energies of the lowest four vibronic levels with maximal zero-phonon component for the case of InP:Fe^{2+} are plotted in Fig. 2 as a function of the Jahn-Teller energy. The energy of the ground state (γ_1 at $E_{\mathrm{JT}}=0$) is defined as zero through all of this paper. The three different phonon energies given in Table I were considered in the analysis.

By simple inspection of these graphics, it is possible to realize that JTE implies that the second energy difference is always smaller than the first one. The phonon energy and or the magnitude of the coupling can make this difference noticeable.

In Fig. 2 the position of the levels according to the spectroscopic data is represented by means of three different horizontal straight lines in accordance with the experimental values reported in Table II.[11–13] We have drawn circles at the intersection of our calculated results and one of the lines representing the experimental results (we have chosen the values of Koschel *et al.* since they are sort of an average of the three experiments). No circles are drawn for the second line due to the large error that would be introduced depending on the experimental

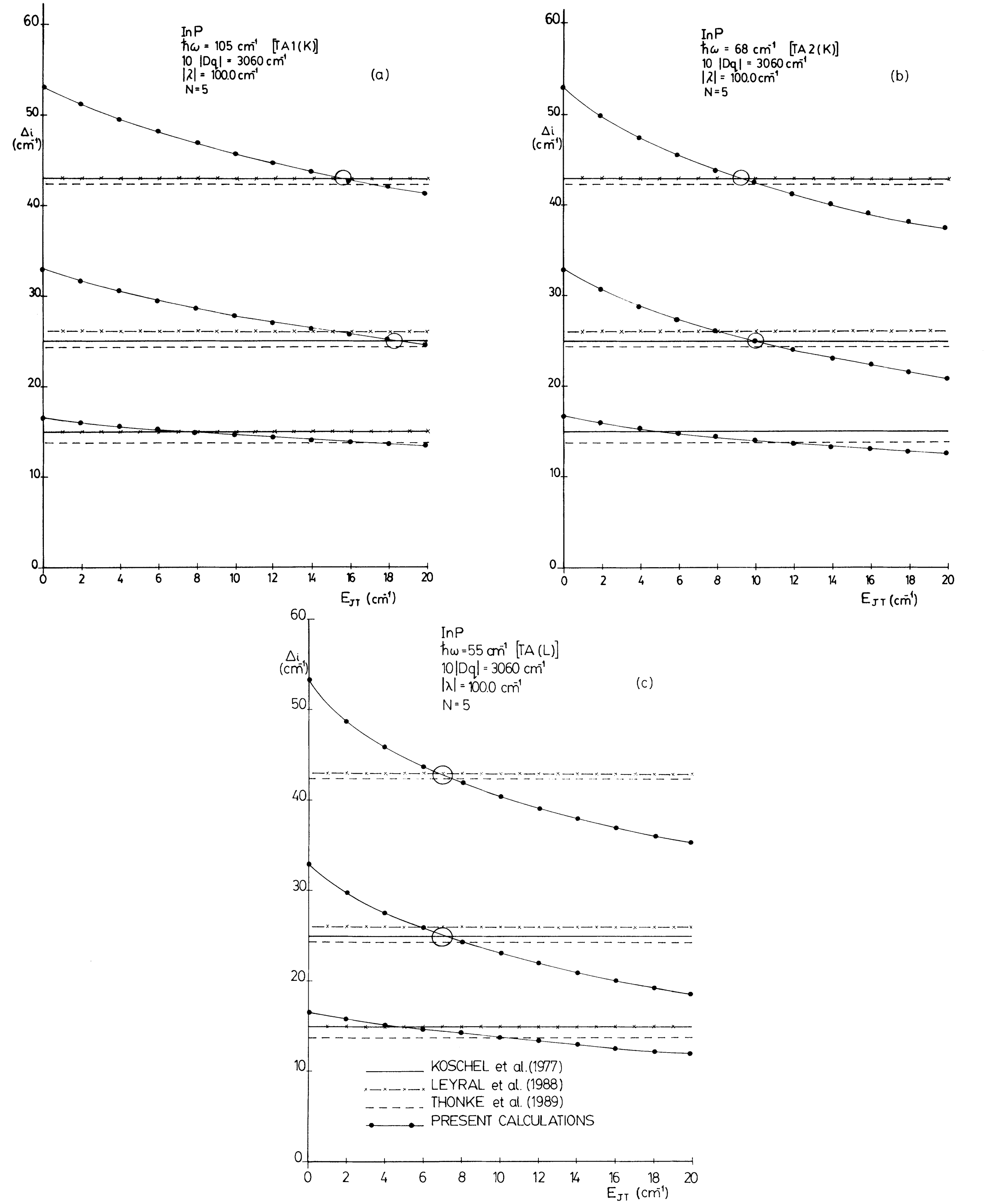

FIG. 2. Energy differences among the four low-lying vibronic levels corresponding to the ^5E multiplet. Experimental values for InP:Fe^{2+} are shown by means of horizontal lines. Three different vibrational energies are reported: (a) phonon TA1(K) with $\hbar\omega = 105$ cm^{-1}; (b) phonon TA2(K) with $\hbar\omega = 68$ cm^{-1}; and (c) phonon TA(L) with $\hbar\omega = 55$ cm^{-1}. A better simultaneous coincidence is reached for the latter at about $E_{JT} = 7$ cm^{-1}.

value chosen for the actual comparison. Of course, the explanation would be satisfactory if the other two intersections occur at the same value for E_{JT}. This goal is achieved as the frequency of the coupling phonon diminishes. Actually, for the case of $\hbar\omega = 55$ cm^{-1} [corresponding to the points TA(L) of the phononic spectrum for InP], the agreement is quite good within the approximations of our theoretical model.

A similar analysis was performed for GaP:Fe^{2+} and GaAs:Fe^{2+}. Again, no adjustment is possible for the higher phononic energies, while the energies corresponding to the points TA(L) of the corresponding lattice dy-

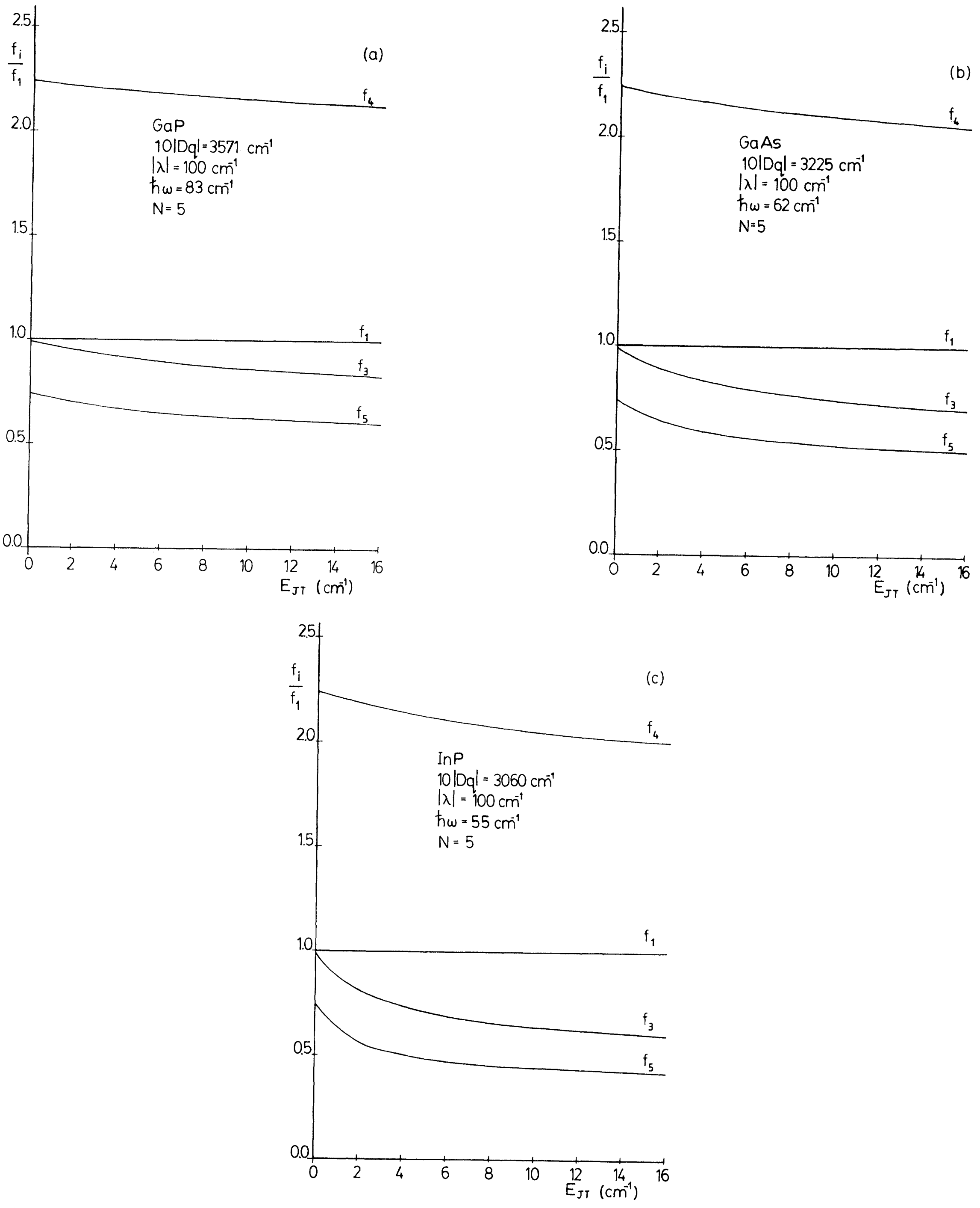

FIG. 3. Relative oscillator strengths f_i/f_1 corresponding to transitions $\Gamma_{5a} \Rightarrow \gamma_i$ as a function of the Jahn-Teller energy for the systems: GaP:Fe^{2+} in (a), GaAs:Fe^{2+} in (b), and InP:Fe^{2+} in (c). The effect is clearly more important as the energy of the coupling phonon diminishes.

namics lead to good adjustment for one value of E_{JT} in each case.

In Table II we summarize the numerical results. We would like to stress the generality of the treatment, dealing with different phonon energies and different spectroscopic data. However, the three found values for the Jahn-Teller energies are very similar among themselves. This tends to indicate that the vibronic coupling is primarily related to the impurity ion and its surrounding symmetry. A similar result was observed for the vibronic coupling within the upper multiplet of II-VI compounds.[25]

We now turn our attention towards the intensity of the luminescence lines connecting the lower level of the upper multiplet with the four levels under consideration. In Fig. 3 we represent the relative oscillator strength f_i/f_1 of the four possible lines $\Gamma_{5a} \Longrightarrow \gamma_i$ for the three systems under consideration. We have used here the values of E_{JT} that lead to a good adjustment for the energy differences in accordance with Table II. We report relative intensities choosing transition $(\Gamma_{5a}\text{-}\gamma_1)$ as a unit to express the intensity of the other lines.

Let us go back to the particular system InP:Fe^{2+}. In Fig. 4 we give a diagram of the vibronic energy levels. Arrows of appropriate width represent the relative intensities after including the JT coupling. It follows from Fig. 4 that the band between 60 and 85 cm^{-1}, the absence of emission as we increase in energy, and the appearance of a weak and broad band over 100 cm^{-1} can be explained at least qualitatively from the calculations reported here.

It is clear that the calculated relative intensities agree well with the experimental result for InP:Fe^{2+} that gives one dominant line (the second one), three slightly weaker lines with similar intensity, a band due to superposition of several weak lines, and a region without emissions followed by a second band weaker and broader than the first one. The comment concerning the four lines holds for each of the three cases where it is possible to obtain spectroscopic information: GaP:Fe^{2+}, GaAs:Fe^{2+}, and InP:Fe^{2+}. No bands have been reported in the available spectra for GaP:Fe^{2+} and GaAs:Fe^{2+}. Our calculations give a weak indication for a first band in the case of GaAs:Fe^{2+} and none for the case of GaP:Fe^{2+}.

It is tempting to extend our calculations to the other III-V semiconductors where there is no experimental information due mainly to their narrow energy gaps: GaSb:Fe^{2+}, InAs:Fe^{2+}, and InSb:Fe^{2+}.[26] We can use the frequencies of the TA(L) phonons to be consistent with the calculations and discussions above. The energies of these phonons have been taken from the literature,[21,22,27–29] and the values are 46 cm^{-1} for GaSb, 44 cm^{-1} for InAs, and 33 cm^{-1} for InSb. We have used 8 cm^{-1} for E_{JT} common to these three systems, which is consistent with Table II and subsequent discussion. It is interesting to notice that a value of 7 cm^{-1} has been reported for the same kind of coupling in the isostructural compound ZnS:Fe^{2+}.[30] In Fig. 5 we report the calculat-

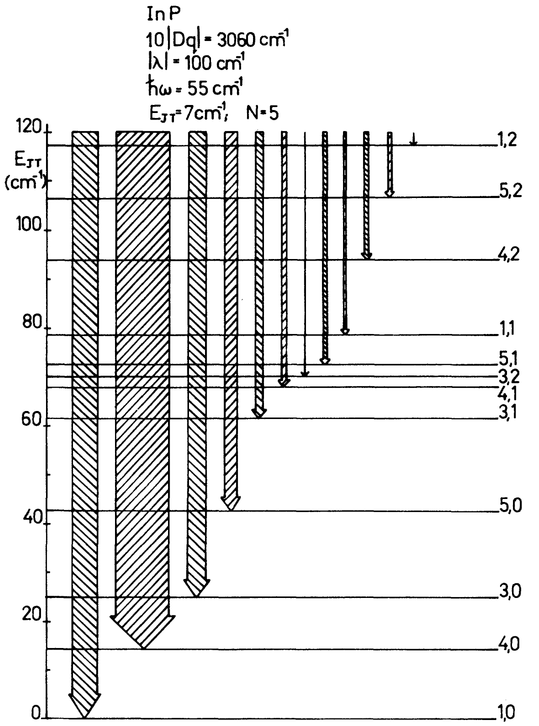

FIG. 4. Energy-level scheme corresponding to InP:Fe^{2+}. Levels are denoted by means of j,N in correspondence with the notation $|\tilde{\gamma}_i(\gamma_j,N),s\rangle$ defined in the text. Arrows illustrate the transitions from the excited Γ_{5a} level; the widths of the arrows are proportional to the calculated intensities.

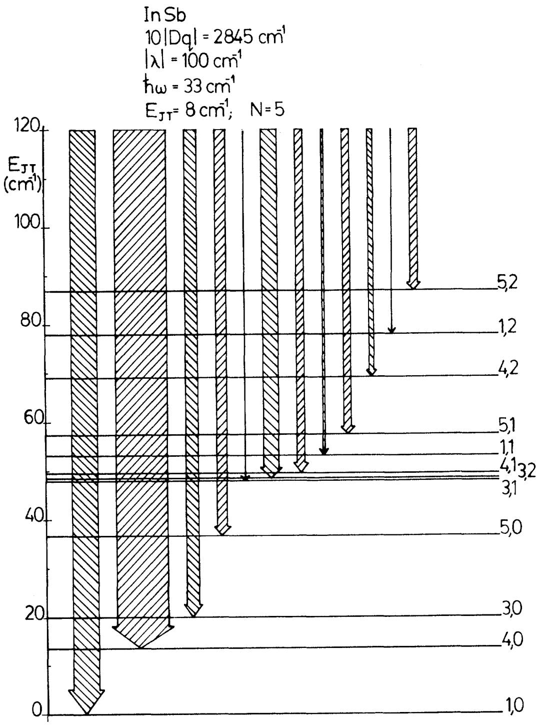

FIG. 5. Energy-level scheme corresponding to InSb:Fe^{2+} using plausible values for the physical parameters. Notation and conventions are the same as defined in Fig. 4.

ed values for both the energy differences and the relative intensities of the luminescence lines associated to the system InSb:Fe^{2+}. That is to say, if the interband luminescence could be subtracted from the experimental data, the possible lines to be observed would be those represented in Fig. 5. It is clear that more lines and bands would appear showing the importance of the JT coupling in this system. A situation quite similar to the one described here was found for CdTe:Fe^{2+} where both the unequal difference among lines and the presence of extra ZPL were interpreted as clear indication of a detectable JT coupling.[4,27]

B. Coupling to the upper multiplet

The action of the JTE on the Γ levels is better shown in low-temperature absorption spectra. However, the available experimental information shows that only one ZPL is possible, namely, $|\tilde{\gamma}_1(\gamma_1,0),a\rangle \Longrightarrow |\tilde{\Gamma}_5(\Gamma_{5a},0),k\rangle$, where k runs over the three components of $\tilde{\Gamma}_5$. This is a manifestation of a weak JTE. In order to approach this observation from a quantitative point of view, we propose that any other possible ZPL is at least one order of magnitude less than the ZPL already characterized. This allows us to define an upper limit for the effect. Let us just recall that, in the case of iron in II-VI compounds, the first two or three ZPL have comparable magnitude.[5,6,25]

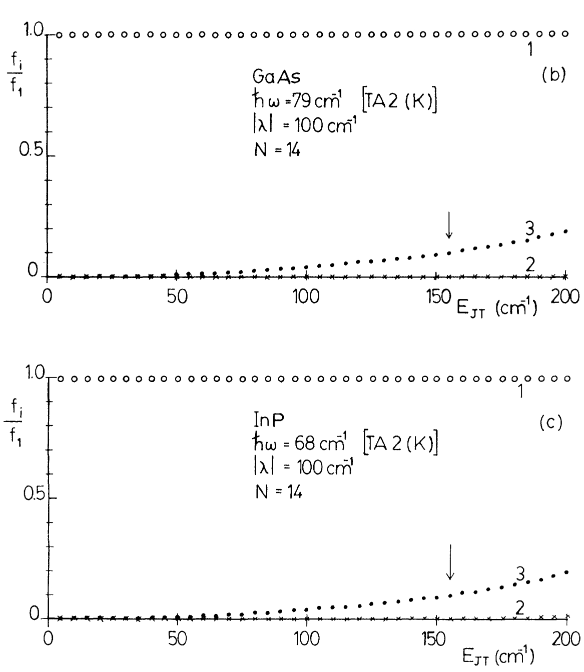

FIG. 6. Relative intensities corresponding to the three leading absorptions $|\tilde{\gamma}_i(\gamma_j,N),s\rangle \Longrightarrow |\tilde{\Gamma}_5(\Gamma_{5a},N),k\rangle$ in sequential order as energy increases. Three different systems are considered: (a) for GaP:Fe^{2+}, (b) for GaAs:Fe^{2+}, and (c) for InP:Fe^{2+}. In all of these systems there would be just one dominant zero-phonon line if $E_{JT} < 150$ cm^{-1}.

The diagonalization of the Hamiltonian is then performed fixing $10|Dq|$ and λ in the way described above, fixing the $\hbar\omega$ values in accordance with Table I and varying just one parameter: E_{JT}. Thus the upper limit on the JT energy is directly obtained.

Figure 6 gives the relative intensity of the three leading relative intensities f_i/f_1 [where $i=1,2,3$ runs over the first three levels originated from $|\tilde{\Gamma}_5(\Gamma_j,N),k\rangle$] which have a zero-phonon component due precisely to the admixture introduced by the JT Hamiltonian. The case of GaP:Fe^{2+} is presented in Fig. 6(a), while GaAs:Fe^{2+} is presented in Fig. 6(b), and InP:Fe^{2+} is presented in Fig. 6(c). For E_{JT} over 150 cm^{-1}, a second ZPL would begin to appear. Since this fact has not been observed in the experiments for any of the different systems considered in the present analysis, we must conclude that $E_{JT} < 150$ cm^{-1} for the vibronic coupling to the upper multiplet of Fe^{2+} in III-V semiconductors.

In any case we expect that the value of E_{JT} would be larger for the upper multiplet than for the lower one. This was the result for the II-VI compounds and should hold true for the III-V compounds as well. The reason for this is related to the different electronic wave functions involved in these two couplings. It is possible that the excited $^5T_2$ multiplet would be described by external orbitals while the lower energy ^5E multiplet would be described by internal orbitals which are less sensitive to the vibrations of the environment.

V. CONCLUDING REMARKS

The Jahn-Teller coupling acts on the electronic levels of magnetic impurities in binary semiconductors. For the case of Fe^{2+} in III-V compounds, the calculations based on a linear JT Hamiltonian give results that agree with the spectroscopy experiments. However, we have found that the coupling to electronic functions of different multiplets is indeed different both with respect to the active phonon and magnitude of the coupling.

The unequal difference among luminescence lines of Fe^{2+} in zinc-blende semiconductors is a clear manifestation of a weak Jahn-Teller effect. A single-phonon and linear JT Hamiltonian leads to a good quantitative explanation of both the energy and the relative intensities of the observed lines. Generally speaking, we can say that the representative phonon has an energy close to the phonons corresponding to the points TA(L) of the corresponding lattice dynamics. On the other hand, the value of E_{JT} does not vary significantly when going from one compound to another: About 8 cm^{-1} is an acceptable common value.

We also performed calculations using the value $E_{JT}=0.0024\ cm^{-1}$ reported by West *et al.* for InP.[7] However, we did not find any noticeable effect for the phonon energies used in previous analysis for the different systems under consideration.

The exercise of extending these calculations to those semiconductors for which there is no luminescence data indicates that the spectrum of InSb would be extremely attractive for testing these calculations in a more sensitive way. Such a system is quite similar to CdTe:Fe^{2+} where there are more than just four ZPL in the spectra. However, it would be worthwhile to investigate the possibility of performing far-infrared-absorption experiments in the cases of GaSb:Fe^{2+}, InAs:Fe^{2+}, and InSb:Fe^{2+} in the case the narrow energy gap allows it. Such an experiment proved to be a very sensitive test for the JTE in the case of CdTe:Fe^{2+}.[4,24,31]

The JTE does not manifest itself in an appreciable way for the upper $^5T_2$ multiplet in III-V semiconductors with iron as a substitutional impurity. This is not to say that the effect does not exist. The clear manifestation of this effect for Fe^{2+} in II-VI semiconductors, with both zinc-blende and wurtzite structures,[32] indicates that the smaller ionicity of III-V compounds is associated to a less important vibronic coupling. In the present paper we have calculated upper limits for E_{JT} such that the resulting lines would not be clearly observable in absorption experiments. For GaSb:Fe^{2+}, InAs:Fe^{2+}, and InSb:Fe^{2+} a common value of $150\ cm^{-1}$ could be taken as an upper limit for the coupling to the upper multiplet.

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