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ISOTOPE SPLITTING OF THE ZERO-PHONON LINE OF Fe^{2+} IN CUBIC III-V SEMICONDUCTORS

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A theoretical study of the isotopic-mass dependence of the internal transitions of Fe^{2+} at a cation site in a cubic zinc-blende semiconductor is presented. The model used is based on crystal-field theory and includes the spin-orbit interaction and a weak dynamic Jahn-Teller coupling between the $^5\Gamma_5$ excited manifold of Fe^{2+} and a local vibrational mode (LVM) of Γ_5 symmetry. The mass dependence of the LVM frequency is described, in the harmonic approximation, within two different limits: the rigid-cage model and a molecular model. In the rigid-cage model, the Fe^{2+} ion undergoes a displacement but the rest of the lattice is fixed. In this case, a simple $M^{-1/2}$ dependence of the frequency is obtained and the Jahn-Teller energy, E_{JT} is independent of the mass. In the molecular model, the four nearest neighbors of the magnetic ion are allowed to move and the LVM then behaves as the Γ_5 mode of a MX_4 tetrahedral molecule leading to a more complicated dependence of the frequency on the isotopic mass and to a mass-dependence of E_{JT}. The theoretical results obtained with these two models are compared with the observed isotopic shifts of the zero-phonon lines in InP:Fe and GaP:Fe corresponding to an optical transition between the vibronic Γ_1 ground state and the lowest Γ_5 state originating from the $^5\Gamma_5$ excited orbital multiplet. A prediction of the isotopic shifts of the zero-phonon line in GaAs:Fe is also presented.

1. INTRODUCTION

The manifestations of the isotopic constitution of solids have received much attention beginning with studies of the atomic volumes of quantum crystals [1] and the discovery of the isotopic mass dependence of the transition temperature of superconductors [2]. Work on the effects of isotopic composition includes the discovery of the enhancement of the thermal conductivity of isotopically enriched Ge relative to that of natural Ge [3], the measurement of isotopic effects on the lattice parameter of Ge [4] and diamond [5] and the dependence of the frequency of the zone center F_{2g} (Γ_{25}^+) optical mode on the inverse square-root of the mass observed in the Raman spectrum of monoisotopic Ge [6,7] and diamond [8]. More recently, the effects of the anharmonicity of the lattice vibrations and of the zero-point motion of the atoms have been observed and analyzed in natural and ^{13}C-enriched diamond [9, 10]. Reviews of some aspects of these topics have been given by Ramdas [11] and Haller [12].

The availability of high purity II-VI and III-V semiconductors with controlled concentrations of impurities and the development of high resolution Fourier transform infrared (FTIR) spectrometers have allowed the experimental determination of isotope effects in these crystals. We mention, for example, the determination of the frequencies of the local vibrational modes (LVM) of light impurities substituting for either the group II or VI host atom in a II-VI semiconductor and their dependence on isotopic composition [13, 14]. The LVM of transition metal ions of the iron group substituting for the cations at random sites in II-VI semiconductors having the zinc-blende structure have also been observed by Mayur *et al.* [15] in infrared absorption with as many lines as there are isotopes of the impurity and with intensities proportional to their natural abundances. Among other such investigations, we also mention the observation of isotope-dependent LVM's of Ni and Cu in CdS and ZnS [16,17].

In this paper we carry out a theoretical study of the absorption spectra of transition-metal ions at cation sites in III-V semiconductors [18]. Prior to 1985 [19], no isotopic effect had been observed in the near infrared absorption spectra of iron-doped InP, GaAs or GaP. Present FTIR spectroscopy has permitted the observation of fine structures in InP:Fe [20,21], GaP:Fe [22], and GaAs:Fe [23] which are attributed to the zero-phonon lines of the four stable isotopes of iron present in the sample in their natural abundances [^{54}Fe (5.82%), ^{56}Fe (91.18%), ^{57}Fe (2.1%), and ^{58}Fe (0.28%) [24]] and have intensities in similar proportions. The lines appear in order of increasing isotopic mass, the transition for ^{54}Fe being the lowest in energy. This is in contradiction with the order expected from the self-energy correction and, therefore, a different mechanism has to be invoked to explain the observed transitions.

We account for this phenomenon in terms of a weak dynamic Jahn-Teller coupling between the $^5\Gamma_5(T_d)$ orbital multiplet of Fe^{2+} and a LVM of symmetry $\Gamma_5(T_d)$. The mass dependence of the LVM frequency is taken in the harmonic approximation assuming either that the nearest neighbors are fixed (rigid cage) or allowing these neighbors to move as in a MX_4 tetrahedral molecule. This analysis is given in Sec. II while Sec. III contains applications to Fe^{2+} in InP, GaP, and GaAs and a comparison with experimental work.

2. THEORETICAL FORMALISM

The zero-phonon line observed in Refs. [20-23] is attributed to a transition within the ground term of doubly ionized iron substituting group III elements at random sites of symmetry T*d*. In the framework of crystal-field theory, the ground term ^5D of the free ion splits into doublet ($^5\Gamma_3$) and triplet ($^5\Gamma_5$) orbital multiplets, separated by energy Δ, the former lying below the latter. The spin-orbit interaction further splits the tenfold-degenerate $^5\Gamma_3$ multiplet into five levels of symmetries Γ_1, Γ_4, Γ_3, Γ_5, and Γ_2, listed in order of increasing energy. The excited $^5\Gamma_5$ multiplet separates [25] into levels of increasing energy Γ_5', Γ_4', Γ_3', Γ_5'', Γ_4'', and Γ_1'. The zero-phonon line corresponds to a transition between the Γ_1 ground state and the Γ_5' excited state. In order to explain the observed isotopic dependence of this spectral line it is necessary to introduce a Jahn-Teller interaction with a LVM. The vibrational modes of a tetrahedral molecule (MX_4) are classified [26] according to the irreducible representations of T_d as $\Gamma_1 + \Gamma_3 + 2\Gamma_5$ using standard notation [27]. As we shall see, only the Γ_5 modes can give rise to a mass dependence of the zero-phonon line.

The energy levels of the Fe^{2+} ion are obtained di-agonalizing the Hamiltonian matrix

$$H = H_0 + V_c(T_d) + \lambda L \cdot S + H_{JT} \qquad (1)$$

where H_0 is the Hamiltonian of the free ion omitting the spin-orbit interaction, $\lambda L \cdot S$; $V_c(T_d)$ is the crystal potential and H_{JT} the Jahn-Teller interaction. The spin-orbit coupling is taken into account not only within the $^5\Gamma_3$ and $^5\Gamma_5$ multiplets but also explicitly in terms mixing the two orbital multiplets. The theoretical formalism used to treat the Jahn-Teller interaction is similar to that described in detail in Ref. [28] where a study was made of the vibronic states of Fe^{2+} in a tetrahedral environment taking into account a weak Jahn-Teller coupling of the orbital ground state multiplet with a phonon of symmetry Γ_3 and a strong interaction of the excited orbital triplet $^5\Gamma_5$ with a phonon of symmetry Γ_5. The model was successfully applied to explain with high accuracy the positions and intensities of the absorption and emission lines of CdTe:Fe^{2+} in the near and far infrared. This formalism is presently used to describe the interaction between the $^5\Gamma$s orbital electronic state of Fe^{2+} and a LVM of symmetry Γ_5. For a triply degenerate mode of symmetry Γ_5, the Jahn-Teller Hamiltonian takes the form

$$\begin{aligned} H_{JT} &= \sum_{i=1}^{3}\left[\frac{P_i^2}{2M} + \frac{1}{2}M\omega^2 Q_i^2\right] + V_0\sum_{i=1}^{3} Q_i M_i \\ &= \sum_{i=1}^{3}\hbar\omega(a_i^\dagger a_i + \frac{1}{2}) + K\sum_{i=1}^{3}(a_i^\dagger + a_i)M_i. \qquad (2) \end{aligned}$$

Here Q_i, is the normal coordinate of the vibrational mode of mass M and frequency ω, P_i the momentum variable canonically conjugated with Q_i, V_0 the electron-phonon coupling constant, and $a_i(a_i^\dagger)$ a destruction (creation) operator for a vibrational mode belonging to the ith row of Γ_5. The matrices M_1,M_2, and M_3 are those used by Savona *et al.* [29] to describe the electron-phonon interaction and the parameter K equals $V_0(\hbar/2M\omega)^{1/2}$. The quantity $(V_0^2/3M\omega^2) = (2K^2/3\hbar\omega) = E_{JT}$ is called the Jahn-Teller energy. To describe the isotope shift of the zero-phonon line we need to determine the mass-dependence of the frequency of the LVM for which we use a valence force model of the MX_4 molecule in the harmonic approximation. The energy required to stretch (or contract) a bond by Δr_i is taken equal to $\frac{1}{2}k_r(\Delta r_i)^2$ while that required to alter a bond angle is $\frac{1}{2}k_\theta(R\Delta\theta_{ij})^2$, where k_r and k_θ are the force constants and R is the bond length.

The dynamical behavior of an MX_4 molecule has been described in the literature [30]. The frequencies of the vibrational modes are given by $\omega(\Gamma_1) = (k_r/M\text{-})^{1/2}$, $\omega(\Gamma_3) = (3k_\theta/M\text{-})^{1/2}$ and

$$\begin{aligned}\omega_{\pm}^{2}(\Gamma_5) = {} & \frac{k_r}{2M_-}\left(1+\frac{4M_-}{3M}\right)+\frac{k_\theta}{M_-}\left(1+\frac{8M_-}{3M}\right)\\ & \pm\left[\left(\frac{k_r}{2M_-}\left(1+\frac{4M_-}{3M}\right)+\frac{k_\theta}{M_-}\left(1+\frac{8M_-}{3M}\right)\right)^2\right.\\ & \left.-2\frac{k_r k_\theta}{M_-^2}\left(1+\frac{4M_-}{M}\right)\right]^{1/2} \qquad (3)\end{aligned}$$

where M is the mass of the central atom, e.g. Fe, M-the mass of the X atom and $\omega \pm (\Gamma_5)$ refers to the angular frequencies of the two Γ_5 modes. We note that, in the Γ_1 and Γ_3 modes, the central atom remains stationary while this is not the case for the Γ_5 modes whose frequencies depend on M. In many compound semiconductors [14], k_r is one to two orders of magnitude greater than k_θ and, in a first approximation, the contribution proportional to k_θ can be disregarded. If bond bending is neglected, ω-$(\Gamma_5) = 0$ and

$$\omega_+(\Gamma_5) = \left[\frac{k_r}{M_-}\left(1+\frac{4M_-}{3M}\right)\right]^{1/2}. \qquad (4)$$

It is this mass dependence of the LVM angular frequency that we employ in Sec. III. We assume that k_r and k_θ are independent of M since they depend entirely on the electronic nature of the bonds. The only ingredient that we require is the ratio of the angular frequencies $\omega_+(\Gamma_5)$ associated with two different isotopes of the central atom with masses M_1 and M_2. The actual vibrational frequency for the most abundant isotope of the central atom will be selected to agree with experiment as discussed in Sec. III. Once M_1 / M_2 is known, the ratio of the coupling constants K_1/K_2 is also fixed as it is equal to $(M_2\omega_2)^{1/2}/(M_1\omega_1)^{1/2}$. Note that the Jahn-Teller energy as defined above (i.e., in terms of the isotopic mass, M, and not a reduced mass taking into account the effect of the nearest neighbors) also varies with M.

In order to estimate the reliability of the MX_4 molecular model we also consider the extreme limit in which the nearest neighbors are so rigidly attached to the host crystal that they can be viewed as forming a rigid cage around the central atom. In this limit, M- $\rightarrow \infty$ and equation (3) reduces to ω- $(\Gamma_5) = 0$ and

$$\omega_+(\Gamma_5) = \left[\frac{4(k_r+4k_\theta)}{3M}\right]^{1/2}, \qquad (5)$$

so that $\omega_1/\omega_2 = (M_1/M_2)^{1/2}$, where we assume that the force constants, k_r and k_θ, are independent of the mass. In this model, the JT energy, E_{JT}, is independent of the mass but the coupling constant varies as $M^{1/4}$.

3. APPLICATIONS AND DISCUSSION

3.1. Isotopic shifts in InP:Fe

The vibronic energy levels are obtained diagonaliz-ing the total Hamiltonian matrix (1). The physical parameters used in the calculation are: the crystal-field-splitting Δ, the spin-orbit coupling parameter λ, the vibrational mode frequency ω, the Jahn-Teller energy E_{JT}, and the coupling constant K. We take λ to be equal to the free ion value (-100 cm^{-1} for Fe^{2+}) but the other parameters are determined from a fit to the experimental data using the following procedure. An approximate value of Δ is obtained by fitting the observed energy of the zero-phonon line of ^{56}Fe in the absence of the Jahn-Teller interaction. In a second step, a Jahn-Teller coupling is introduced with the Fe gap mode that gives the most prominent feature in the absorption spectrum as a phonon side band with a shift of $\omega(^{56}\mathrm{Fe}) = 295$ cm^{-1} [20,21]. The frequencies of the other isotopes of Fe^{2+} are obtained from $\omega(^{56}\mathrm{Fe})$ together with equation (4) or (5). The Jahn-Teller energy is chosen to reproduce simultaneously the transition energies of the zero-phonon lines of ^{56}Fe and ^{54}Fe. This requires a slight readjustment of the value of Δ. With the values of the parameters so obtained, the Hamiltonian matrix is diagonalized once again to determine all the energy levels. Six overtones of the gap mode are included in the calculation but the convergence has been checked by including up to 12 gap mode overtones.

When we examined the rigid-cage model we found agreement between the calculated zero-phonon lines and the experimental results using a Jahn-Teller energy of 50 cm^{-1}. However, with this value of E_{JT}, we obtain far more optical absorption lines than observed experimentally [20, 21] for electric-dipole transitions to higher vibronic states. This seems to indicate that the value of the Jahn-Teller energy that we have used is too large to obtain consistent results with the rest of the absorption spectrum. Thus, within the rigid-cage model, we cannot simultaneously describe the isotopic effect of the zero-phonon line and obtain a good interpretation of the additional absorption peaks. Therefore, we have extended the calculation using the MX_4 model [equation (4)] to describe the mass-dependence of the LVM frequency. The procedure used to extract the parameters in this case is identical to that described above and the parameters and results obtained with this model are displayed in Table I. Again the isotopic shifts are described with high accuracy. However, in contrast to the results obtained in the rigid-cage model, the Jahn-Teller energy needed to reproduce the isotope dependence of the zero-phonon line is much smaller and varies slightly with isotopic mass. This means that, within the MX_4 model, we obtain a better theoretical description of the overall absorption spectrum.

Table 1. *Comparison between the calculated and experimental energies of the four zero-phonon lines of* Fe^{2+} *in InP in the* MX_4 *model with* $\Delta = 3071.4\ cm^{-1}$

	E_{th}(cm^{-1})	**E_{exp} [21] (cm^{-1})**	**$\hbar\omega$ (cm^{-1})**	**K (cm^{-1})**	**E_{JT} (cm^{-1})**
^{54}Fe	2843.54	2843.54	297.3	97.6	21.4
^{56}Fe	2843.85	2843.85	295.0	96.2	20.9
^{57} Fe	2844.00	2843.99	293.9	95.5	20.7
^{58} Fe	2844.15	2844.16	292.8	94.9	20.5

Table 2. *Comparison between the calculated and experimental energies of the four zero-phonon lines of* Fe^{2+} *in GaP in the* MX_4 *model with* $\Delta = 3584.8\ cm^{-1}$

	E_{th}(cm^{-1})	**E_{exp} [22] (cm^{-1})**	**$\hbar\omega$ (cm^{-1})**	**K(cm^{-1})**	**E_{JT} (cm^{-1})**
54$_{Fe}$	3341.9	3341.9	326.0	112.6	25.9
^{56} Fe	3342.3	3342.3	323.5	111.0	25.4
^{57} Fe	3342.5	3342.6	322.3	110.3	25.2
^{58} Fe	3342.7	3342.8	321.1	109.5	24.9

Table 3. *Calculated and experimental energies of the zero-phonon lines of* Fe^{2+} *in GaAs in the* MX_4 *model with* $\Delta = 3238.9\ cm^{-1}$

	E_{th}(cm^{-1})	**E_{exp} [23] (cm^{-1})**	**$\hbar\omega$ (cm^{-1})**	**K (cm^{-1})**	**E_{JT} (cm^{-1})**
^{54}Fe	3001.55	3001.55	278.3	114.8	31.6
^{56}Fe	3001.90	3001.90	275.00	113.4	31.2
^{57} Fe	3002.07		273.5	112.8	31.0
^{58}Fe	3002.24		271.9	112.1	30.8

3.2. GaP.Fe and GaAs.Fe

A similar analysis has been carried out for Fe^{2+} in GaP and GaAs within the framework of the MX_4 model. The results, requiring no further elaboration, are displayed in Table II for GaP. Appropriate predictions for similar behavior in GaAs are given in Table III.

In conclusion, we have shown that the isotopic shifts of the zero-phonon line in iron-doped III-V semiconductors provide useful information about the Jahn-Teller active gap mode or LVM in the excited multiplet of the magnetic impurity. The present work, based on a weak Jahn-Teller interaction between the orbital $^5\Gamma_5$ multiplet of Fe^{2+} and a gap mode (InP:Fe and GaP:Fe) or LVM (GaAs:Fe) of Γ_5 symmetry whose frequencies are described by the MX_4 molecular model, is in reasonable agreement with experiment. In this paper, we have neglected the difference in zero-point energy between the initial and final states of the transition, due to the different electronic charge distributions in those electronic states [33]. A rough estimate of this effect shows that it accounts for less than 10 % of the total isotopic shift. Finally, further absorption and emission measurements are needed in order to refine the theoretical model to account for the overall spectrum. This would also provide important information about the Jahn-Teller interaction with extended phonon modes and the modification of the spin-orbit coupling due to covalency effects [31].

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