

Dynamic Jahn-Teller interaction with Γ_5 phonons in the ground state of Cu^{2+} in cubic II-VI semiconductors

D. Colignon, E. Mailleux, and E. Kartheuser
Institut de Physique, Université de Liège, Liège, Belgium

Murielle Villeret
Department of Mathematics, City University, London EC1V 0HB, United Kingdom
(Received 16 September 1997)

Optical absorption and emission measurements of Cu^{2+} as a substitutional impurity in cubic ZnS and ZnTe are analyzed by means of an electron-phonon coupling model. The 2D term of Cu^{2+} is split by a crystal field of tetrahedral symmetry into a $^2\Gamma_5$ orbital triplet and a $^2\Gamma_3$ orbital doublet. Optical transitions have been observed between these two multiplets in $\text{ZnS}:\text{Cu}^{2+}$ and within the $^2\Gamma_5$ ground state in $\text{ZnTe}:\text{Cu}^{2+}$. The theoretical model is based on crystal-field theory and includes the spin-orbit interaction and a dynamic Jahn-Teller interaction between the electronic $^2\Gamma_5$ states and a transverse acoustic phonon of Γ_5 symmetry. Starting from the ten spin-orbit wave functions appropriate to the orbital triplet and doublet manifolds, the symmetry-adapted vibronic basis is constructed and used to diagonalize the Hamiltonian matrix. Phonon overtones up to $n=14$ are included to ensure convergence of the energy eigenvalues. The measured positions and relative intensities of the spectral lines are described with good accuracy by the theoretical model, including covalency effects. In ZnS, comparison between theory and experiment yields the following values of the physical parameters: the crystal-field splitting $\Delta=5990.6\text{ cm}^{-1}$, the spin-orbit coupling constants $\lambda_1=-667\text{ cm}^{-1}$ and $\lambda_2=-830\text{ cm}^{-1}$, the phonon energy $\hbar\omega=73.5\text{ cm}^{-1}$, and the Jahn-Teller stabilization energy $E_{\text{JT}}=474.5\text{ cm}^{-1}$. The corresponding parameters in ZnTe are $\Delta=6000\text{ cm}^{-1}$, $\lambda_1=-888\text{ cm}^{-1}$, $\lambda_2=-830\text{ cm}^{-1}$, $\hbar\omega=38.8\text{ cm}^{-1}$, and $E_{\text{JT}}=468.5\text{ cm}^{-1}$. [S0163-1829(98)03020-3]

I. INTRODUCTION

The optical and magnetic properties of iron group impurities in semiconductors have been of interest for more than 30 years. The first optical experiments in the 1960s were restricted by relatively low resolution (by modern standards) and most data were explained by simple crystal-field models. Advances in instrumentation and progress in crystal growth technology have improved the resolution by two orders of magnitude leading to the observation of additional fine structures in the absorption and emission spectra of these crystals. This has necessitated the development of more refined theoretical models. One major theoretical improvement consists of the inclusion of a dynamical Jahn-Teller (JT) interaction between the electronic states of the magnetic impurity and either its local vibrational modes or the phonons of the host crystal. This requires the simultaneous diagonalization of the lattice and electronic problems. In the extreme limits of weak or strong coupling this can be done using perturbation theory.¹ However, an exact treatment in the intermediate coupling regime is only possible numerically and has only become feasible due to the recent advances in computer technology.

In this paper, we investigate the optical properties of Cu^{2+} in cubic II-VI semiconductors and provide an in-depth investigation of the optical properties of cubic $\text{ZnS}:\text{Cu}^{2+}$ and $\text{ZnTe}:\text{Cu}^{2+}$. Divalent copper has a single hole in its $3d$ shell and has the simplest electronic structure of all the iron group ions. Therefore, it appears to be an ideal impurity to investigate theoretically. Interest in Cu^{2+} has also been rekindled due to the important role it plays for d -wave super-

conductivity in cuprates.² In a tetrahedrally coordinated material, the lowest term of the $(3d)^9$ configuration of Cu^{2+} , namely, 2D , is split by the crystal field of symmetry T_d into a $^2\Gamma_5$ orbital triplet and a $^2\Gamma_3$ orbital doublet,³ the energy of the former lying below that of the latter (see, for example, Ref. 4). The spin-orbit interaction further splits the $^2\Gamma_5$ level into a Γ_7 doublet and a Γ_8 quadruplet. The $^2\Gamma_3$ level becomes a Γ_8 state, which we label Γ_8' to distinguish it from that arising from $^2\Gamma_5$.

The near-infrared absorption and emission spectra of Cu^{2+} in ZnS were first measured by Broser, Maier, and Schulz⁵ in 1965 with a resolution of 17 cm^{-1} . A year later, Broser and Maier⁶ repeated the experiment with improved resolution. Their absorption spectrum consisted, as before, of a narrow line at 6927 cm^{-1} corresponding to a zero-phonon transition between the Γ_7 ground state and the Γ_8' excited state and a sequence of phonon-assisted transitions. The same line was also observed in the emission spectrum but an additional line at 6913 cm^{-1} could now be resolved. Broser and Maier speculated that this second line was the signature of a JT interaction in the ground state of the magnetic impurity. Shortly after these measurements, de Wit⁷ investigated the Zeeman effect in copper-doped ZnS and determined the g factors of the ground state [$g(\Gamma_7)=0.71\pm 0.02$] and the highest excited state [$g(\Gamma_8')=1.71\pm 0.02$]. The g factor of the ground state is much smaller than the value of 2 expected from a simple crystal-field theory.⁴ Even when the effects of hybridization of the d electrons of the impurity with the sp states of the ligands are included^{8,9} the calculated g factor remains far too large (≈ 1.7). This discrepancy was again tentatively attributed to the effect of a JT interaction.

An electron-phonon interaction with the d states of the impurity is indeed possible and to investigate this interaction it is best to classify the vibrational modes of the crystal according to the site symmetry of the magnetic ion rather than according to the space group of the host. From symmetry considerations, it then follows that the matrix elements of the electron-phonon interaction between states in the ${}^2\Gamma_3$ multiplet vanish for a phonon mode of symmetry Γ_5 while matrix elements in the ${}^2\Gamma_5$ multiplet need not vanish for phonons of symmetries Γ_3 and Γ_5 . The first theoretical (but unsuccessful) attempt to explain the experimental data by introducing a dynamic JT coupling was provided by Bates and Chandler¹⁰ who used a phenomenological approach to introduce a coupling with either a Γ_3 or Γ_5 phonon in the lowest multiplet of Cu^{2+} . Subsequently, Yamaguchi and Kamimura¹¹ investigated the JT interaction with a local vibrational mode of Cu^{2+} but only examined the optical spectra and g factors of centers with axial symmetry. Further information on the absorption and emission spectra was provided by Maier and Scherz,¹² who were able to better resolve the phonon sidebands of $\text{ZnS}:\text{Cu}^{2+}$ and who investigated the JT interaction of the Cu states with a phonon of Γ_3 symmetry. Neither model could account for all the experimental data. An attempt was also made¹³ to investigate the coupling with a Γ_5 phonon but this was also unsuccessful for reasons that will be discussed later. Finally, Clerjoud and Gelineau¹⁴ tried to explain the additional line at 6910 cm^{-1} as being due to the spin-orbit interaction within the ground state, strongly reduced by the JT effect.

In 1984, Weinert and Scherz¹⁵ calculated the JT coupling forces for $\text{ZnS}:\text{Cu}^{2+}$ using a self-consistent LCAO calculation of a cluster of 17 atoms with the impurity in the center. They found that there is only a weak coupling to the optical and localized modes but that a strong coupling is possible with the acoustic modes. More recently, high-resolution spectroscopy and Zeeman measurements¹⁶⁻¹⁸ were performed on polytypic copper-doped ZnS and, in contradiction to the conclusions of Ref. 15, an interpretation in terms of a JT coupling to a local vibrational mode of Γ_3 symmetry was attempted. Finally, Volz *et al.*¹⁹ have measured the infrared absorption spectrum of $\text{ZnTe}:\text{Cu}^{2+}$ between 800 cm^{-1} and 2000 cm^{-1} . They interpreted their data in terms of a JT interaction with a Γ_3 phonon in the ${}^2\Gamma_3$ multiplet.

There does not seem to be a consensus on the interpretation of the optical data in $\text{ZnS}:\text{Cu}^{2+}$ and $\text{ZnTe}:\text{Cu}^{2+}$. First, it is not at all clear which phonon mode (Γ_3 or Γ_5) contributes the most to the JT interaction in the orbital ground state of

Cu^{2+} . Second, the existing theories are somewhat incomplete as they try to explain at most three lines in the spectrum together with the g factor of the ground state.

In this paper, we attempt to clarify the situation. We show that a JT interaction with a phonon of Γ_5 symmetry leads to a consistent interpretation of a large number of electric-dipole transitions associated with the Cu impurity in cubic ZnS and ZnTe. The model used is similar to the one we successfully employed to explain the positions and intensities of the infrared absorption and emission lines of Fe^{2+} in CdTe (Ref. 20) and several other II-VI semiconductors.²¹ The plan of the paper is as follows. In Sec. II we describe the theoretical model used to treat the JT interaction of the Cu^{2+} impurity with a phonon of Γ_5 symmetry. In Sec. III, we calculate the energies and intensities of the allowed transitions for cubic $\text{ZnS}:\text{Cu}^{2+}$ and $\text{ZnTe}:\text{Cu}^{2+}$ and compare our results with the experimental data. We also give a critical discussion of the various existing theories. Finally, our conclusions are given in Sec. IV.

II. THEORETICAL FORMALISM

We consider a dynamic Jahn-Teller coupling between the ${}^2\Gamma_5$ multiplet of Cu^{2+} and a phonon of Γ_5 symmetry. The effective Hamiltonian describing the problem is

$$H = H_0 + V_c(T_d) + \lambda \mathbf{L} \cdot \mathbf{S} + H_{\text{JT}}, \quad (1)$$

where H_0 is the Hamiltonian of the free ion omitting the spin-orbit interaction $\lambda \mathbf{L} \cdot \mathbf{S}$ and H_{JT} is the JT interaction. The tetrahedral crystal potential $V_c(T_d)$ gives the separation Δ between the ${}^2\Gamma_3$ and ${}^2\Gamma_5$ multiplets.

Symmetry arguments show that there are, in principle, two different effective spin-orbit coupling constants: λ_1 corresponding to matrix elements within the ${}^2\Gamma_5$ orbital ground state of the impurity and λ_2 for elements mixing the ${}^2\Gamma_5$ and ${}^2\Gamma_3$ orbital states. In practice, these two constants are taken as phenomenological parameters whose values are to be extracted from the experimental data. Physically, they reflect the fact that the bonds between the impurity and the anions are partially covalent. This is because the d electrons of the Cu^{2+} impurity are not completely localized and spend part of their time in the vicinity of the anions. There results a hybridization between the Cu electrons and the sp orbitals of the anions which delocalizes the d electrons.

We use the following symmetry-adapted wave functions to describe the electronic states.

$$\begin{aligned} \Gamma_7: \quad \chi_{-1/2} &= \frac{1}{\sqrt{3}}(-i|\epsilon_1; \tfrac{1}{2}\rangle - |\epsilon_2; \tfrac{1}{2}\rangle + i|\epsilon_3; -\tfrac{1}{2}\rangle), & \chi_{+1/2} &= \frac{1}{\sqrt{3}}(-i|\epsilon_1; -\tfrac{1}{2}\rangle + |\epsilon_2; -\tfrac{1}{2}\rangle - i|\epsilon_3; \tfrac{1}{2}\rangle). \\ \Gamma_8: \quad \phi_{-3/2} &= \frac{1}{\sqrt{6}}(-i|\epsilon_1; -\tfrac{1}{2}\rangle + |\epsilon_2; \tfrac{1}{2}\rangle + 2i|\epsilon_3; \tfrac{1}{2}\rangle), & \phi_{-1/2} &= \frac{1}{\sqrt{2}}(i|\epsilon_1; \tfrac{1}{2}\rangle - |\epsilon_2; \tfrac{1}{2}\rangle), \\ \phi_{+1/2} &= \frac{1}{\sqrt{2}}(-i|\epsilon_1; -\tfrac{1}{2}\rangle - |\epsilon_2; -\tfrac{1}{2}\rangle), & \phi_{+3/2} &= \frac{1}{\sqrt{6}}(i|\epsilon_1; \tfrac{1}{2}\rangle + |\epsilon_2; \tfrac{1}{2}\rangle + 2i|\epsilon_3; -\tfrac{1}{2}\rangle). \\ \Gamma'_8: \quad \phi'_{-3/2} &= |\gamma_2; \tfrac{1}{2}\rangle, & \phi'_{-1/2} &= -|\gamma_1; -\tfrac{1}{2}\rangle, & \phi'_{+1/2} &= |\gamma_1; \tfrac{1}{2}\rangle, & \phi'_{+3/2} &= -|\gamma_2; -\tfrac{1}{2}\rangle, \end{aligned} \quad (2)$$

where $|\pm\frac{1}{2}\rangle$ are the spin states. The Γ_5 orbital state vectors ϵ_1 , ϵ_2 , and ϵ_3 transform as yz , zx , and xy , respectively, under the operations of T_d and are given in terms of the orbital wave functions of the free ion $|M_L\rangle$ ($M_L=2,1,0,-1,-2$) by $\epsilon_1=i2^{-1/2}(|1\rangle+|-1\rangle)$, $\epsilon_2=2^{-1/2}(|1\rangle+|-1\rangle)$, $\epsilon_3=i2^{-1/2}(|2\rangle+|-2\rangle)$. The state vectors $\gamma_1=|0\rangle$ and $\gamma_2=2^{-1/2}(|2\rangle+|-2\rangle)$ belong to Γ_3 and behave as $2z^2-x^2-y^2$ and $\sqrt{3}(x^2-y^2)$, respectively. Diagonalizing the Hamiltonian $H-H_{JT}$ in the electronic basis (2) yields analytic expressions for the energies of the Γ_7 , Γ_8 , and Γ'_8 states in the absence of JT interaction (see also Ref. 22):

$$E(\Gamma_7)=\lambda_1,$$

$$E(\Gamma_8)=\frac{\Delta}{2}\left[1-\frac{\sigma_1}{2}-\sqrt{\left(1+\frac{\sigma_1}{2}\right)^2+6\sigma_2^2}\right], \quad (3)$$

$$E(\Gamma'_8)=\frac{\Delta}{2}\left[1-\frac{\sigma_1}{2}+\sqrt{\left(1+\frac{\sigma_1}{2}\right)^2+6\sigma_2^2}\right],$$

where $\sigma_{1,2}=\lambda_{1,2}/\Delta$.

The theoretical formalism used to treat the JT interaction is similar to that described in detail in Ref. 20, where a study was made of the vibronic states of Fe^{2+} in a tetrahedral environment taking into account a weak JT coupling of the ground orbital doublet with a phonon of Γ_3 symmetry and a strong interaction of the excited orbital triplet with a Γ_5 phonon. It will be shown in Sec. III that, to explain the experimental data, it is sufficient to consider an interaction with a Γ_5 phonon in the orbital ground state of Cu^{2+} . Therefore, we neglect the weak coupling with a phonon of Γ_3 symmetry. For a triply degenerate mode of symmetry Γ_5 , the JT Hamiltonian takes the form

$$H_{JT}=\sum_{i=1}^3\left[\frac{P_i^2}{2M}+\frac{1}{2}M\omega^2Q_i^2\right]+V_0\sum_{i=1}^3Q_iM_i \quad (4)$$

$$=\sum_{i=1}^3\hbar\omega\left(a_i^\dagger a_i+\frac{1}{2}\right)+K\sum_{i=1}^3(a_i^\dagger+a_i)M_i. \quad (5)$$

Here Q_i is the normal coordinate of the vibrational mode of mass M and frequency ω , P_i is the momentum variable canonically conjugated with Q_i , V_0 is the electron-phonon coupling constant, and $a_i(a_i^\dagger)$ is a destruction (creation) operator for a phonon mode belonging to the i th row of Γ_5 . The matrices M_1 , M_2 , and M_3 are given in Eqs. (19) of Savona, Bassani, and Rodriguez²³ and the parameter K equals $V_0(\hbar/2M\omega)^{1/2}$. In \mathbf{Q} space, the potential energy reaches an absolute minimum along the directions $[\bar{1}\bar{1}1]$, $[1\bar{1}\bar{1}]$, $[11\bar{1}]$, and $[\bar{1}\bar{1}\bar{1}]$ and the quantity $(V_0^2/3M\omega^2)=(2K^2/3\hbar\omega)=E_{JT}$ is called the Jahn-Teller stabilization energy.

The phonon states and their overtones are classified according to the irreducible representations of the group T_d and were obtained using the method of Ref. 23. We denote by $A(n)$, $B(n)$, $C_i(n)$, $D_j(n)$, and $E_j(n)$ ($i=1,2;j=1,2,3$) the overtones of order n of a Γ_5 phonon that belong to the Γ_1 , Γ_2 , Γ_3 , Γ_4 , and Γ_5 irreducible representations of T_d .

To find the eigenvalues of the total Hamiltonian operator (1) we start with a set of symmetry-adapted vibronic wave

functions that are linear combinations of products of the electronic [Eq. (2)] and vibrational states with coefficients given by the Clebsch-Gordan coefficients for the group T_d .³ Use of the multiplication table³ for the group T_d shows that all vibronic states belong to the Γ_6 , Γ_7 , or Γ_8 irreducible representations. To save space, we do not display the vibronic states but merely show a few examples. The state $|\chi_{-1/2};A(0)\rangle$ is the lowest vibronic state transforming under the operations of T_d as the first row of Γ_7 . The first excited state belonging also to the first row of Γ_7 is given by

$$\frac{1}{2\sqrt{3}}(-i\sqrt{3}|\phi_{-3/2};E_1(1)\rangle+\sqrt{3}|\phi_{-3/2};E_2(1)\rangle$$

$$+i|\phi_{1/2};E_1(1)\rangle+|\phi_{1/2};E_2(1)\rangle-2i|\phi_{-1/2};E_3(1)\rangle). \quad (6)$$

To fix ideas, we also note that the matrix element of the Jahn-Teller interaction H_{JT} between these states is simply equal to $-K$.

With the set of basis vectors obtained in this fashion we can diagonalize the full Hamiltonian matrix. To obtain convergence on the energy values of the vibronic states involved in the transitions investigated in Sec. III, it was necessary to include overtones up to order $n=14$. The use of symmetry-adapted vibronic wave functions has two advantages. As all vibronic states belong to Γ_6 , Γ_7 , or Γ_8 , the Hamiltonian matrix becomes block diagonal, with submatrices corresponding to these symmetries. In the basis of the symmetry-adapted vibronic states, it is also easy to use selection rules and to evaluate the transition probabilities, thereby greatly simplifying the identification of the absorption and emission lines. Finally, we note that the product $\Gamma_4\otimes\Gamma_8=\Gamma_6\oplus\Gamma_7\oplus 2\Gamma_8$ contains two Γ_8 states that must both be included explicitly in the vibronic basis. The same holds for $\Gamma_5\otimes\Gamma_8=\Gamma_6\oplus\Gamma_7\oplus 2\Gamma_8$. A Jahn-Teller interaction between these two Γ_8 states will occur whenever $\Delta n=\pm 1$. If 14 phonon overtones are included the Γ_6 , Γ_7 , and Γ_8 submatrices have dimensions 565, 565, and 1135, respectively.

III. APPLICATIONS AND DISCUSSION

A. ZnS: Cu^{2+}

As discussed in the introduction, the optical properties of Cu^{2+} in ZnS have been investigated extensively.^{5-7,12,16-18} The most detailed optical data have been provided by Maier and Scherz¹² and we begin our discussion with an in-depth investigation of their spectra. We first recall the main characteristics of the absorption and emission spectra. The absorption spectrum consists of a narrow line at 6924 cm^{-1} corresponding to a zero-phonon transition from the Γ_7 ground state to the excited Γ'_8 multiplet. Several sequences of phonon replicas are also observed. From our point of view, the emission spectrum is much more interesting. In addition to the zero-phonon transition at 6924 cm^{-1} there appears another narrow line at 6910 cm^{-1} and a series of additional transitions that cannot be interpreted as phonon replicas. Several attempts have been made to explain these lines but none of the available theories reproduce the entire

electronic spectrum. We show here that it is possible to explain all the emission lines using the model described in Sec. II.

We base our choice of phonon mode on the model we have developed to investigate the infrared spectrum of Fe^{2+} in various II-VI semiconductors.^{20,21} In Refs. 20 and 21, we had found that the near- and far-infrared spectra could be explained well by considering a strong JT interaction between the $^5\Gamma_5$ orbital multiplet of Fe^{2+} and a TA phonon of average energy corresponding to the various TA modes and a weak coupling of the $^5\Gamma_3$ orbital ground state with a Γ_3 TA(L) phonon. In this paper we extend this model to the case of Cu^{2+} . Since the orbital ground state is now the Γ_5 triplet, we introduce a strong JT coupling between this state and a TA(L) phonon of Γ_5 symmetry. The weak interaction with a Γ_3 phonon is neglected because the optical measurements on copper-based II-VI semiconductors do not clearly reveal the coupling with those modes, contrary to the more complete data for iron-based compounds. Our choice of coupling to a TA(L) phonon is in agreement with the results of Weinert and Scherz.¹⁵ Also the TA(L) phonon, observed in the ZnS host at an energy $\hbar\omega = 70 \text{ cm}^{-1}$ Refs. 12 and 24, appears to be the only transverse acoustic mode not involved in phonon-assisted transitions.

The parameters needed in our calculation have been adjusted self-consistently as follows. An approximate value of the crystal-field splitting, Δ , is obtained by fitting the energy of the zero-phonon line corresponding to the $\Gamma_8' \rightarrow \Gamma_7$ transition at an energy of 6924 cm^{-1} . In accord with energies of the states Γ_7 and Γ_8 in the absence of JT interaction, the spin-orbit coupling constant λ_1 within the $^2\Gamma_5$ multiplet is chosen, in a first approximation, to reproduce the $\Gamma_8' \rightarrow \Gamma_8$ transition observed at 6114 cm^{-1} . Finally, the JT energy E_{JT} is taken so as to explain the second narrow line observed in the emission spectrum at 6910 cm^{-1} . The introduction of the JT interaction of course requires a slight readjustment of the values of Δ and λ_1 . The phonon energy $\hbar\omega$ is taken close to 70 cm^{-1} and adjusted to reproduce the emission line at 6881 cm^{-1} . The spin-orbit coupling constant λ_2 between the $^2\Gamma_5$ and $^2\Gamma_3$ multiplets was kept equal to the free Cu^{2+} ion value, $\lambda_{\text{fi}} = -830 \text{ cm}^{-1}$,²⁵ as the experimental information is not sufficient to allow for a finer determination of its value. The final set of parameters, after convergence of the self-consistent fitting procedure, is $\Delta = 5990.6 \text{ cm}^{-1}$, $\lambda_1 = -667.4 \text{ cm}^{-1}$, $E_{\text{JT}} = 474.5 \text{ cm}^{-1}$, $\hbar\omega = 73.5 \text{ cm}^{-1}$. These parameters correspond to a Huang-Rhys factor $S = E_{\text{JT}}/\hbar\omega = 6.5$. Before proceeding further, it is important to comment on the value of λ_1 obtained from our fit. The ratio $\lambda_1/\lambda_{\text{fi}}$ is a measure of the degree of covalency in the Cu-S bonds. Our fit leads to a ratio $\lambda_1/\lambda_{\text{fi}} = 0.83$, close to the ratio 0.79 obtained experimentally by Dietz *et al.*²⁶ for $\text{ZnO}:\text{Cu}^{2+}$. It is also not very different from the values 0.70 given by Yamaguchi and Kamimura¹¹ and Maier and Scherz¹² and 0.71 obtained by Broser *et al.*⁵ Following the theory of Vallin and Watkins,²⁷ the ratio 0.83 means that the d electrons of the Cu ion spend 83% of their time in the vicinity of the magnetic impurity and only 17% of the time in the vicinity of the sulfur atoms.

The diagonalization of the Hamiltonian H with the parameters given above leads to the transition energies listed in

TABLE I. Comparison between the calculated and experimental energies (referred to the energy, 6924 cm^{-1} of the lowest $\Gamma_8' \rightarrow \Gamma_7$ zero-phonon line) in $\text{ZnS}:\text{Cu}^{2+}$. The last column gives the calculated relative intensities, taking as unity the intensity of the reference line at 6924 cm^{-1} . Parameters: $\Delta = 5990.6 \text{ cm}^{-1}$, $\lambda_1 = -667.4 \text{ cm}^{-1}$, $\lambda_2 = -830 \text{ cm}^{-1}$, $\hbar\omega = 73.5 \text{ cm}^{-1}$, $E_{\text{JT}} = 474.5 \text{ cm}^{-1}$.

Experimental energy (cm^{-1})	Relative experimental energy (cm^{-1})	Calculated relative energy (cm^{-1})	Relative intensity
6924	0	0	1
6910	14	14	0.27
6881	43	43	0.7
		52.1	0.16
6846	78	77.3	0.15
6824	100	93.8	0.24
		128.5	0.06
6761	163	154.4	0.06
6715	209	211.7	0.01
6114	810	810	14.75
6024	900	886.8	5.03
		971	1.67
5804	1120	1133	1.24

column 3 of Table I. For simplicity, the energies are referred to the energy (6924 cm^{-1}) of the lowest $\Gamma_8' \rightarrow \Gamma_7$ zero-phonon line. For comparison, we give the corresponding experimental energies in column 2 of Table I. Column 1 gives the raw experimental data (emission lines). For information we display in Fig. 1 the behavior of the lowest-energy levels (referred to the energy of the lowest Γ_7 vibronic state) as a function of the JT energy and indicate by a vertical line the value of E_{JT} for which agreement with the experimental data is obtained. In addition, we have evaluated the g factor of the lowest Γ_7 state and found $g = 1.48$. This is smaller than the value obtained from Eqs. (7–51) of Ref. 8, which takes into account the modification of the g factor due to covalency effects. Indeed, an orbital reduction factor $k = 0.83$ taken

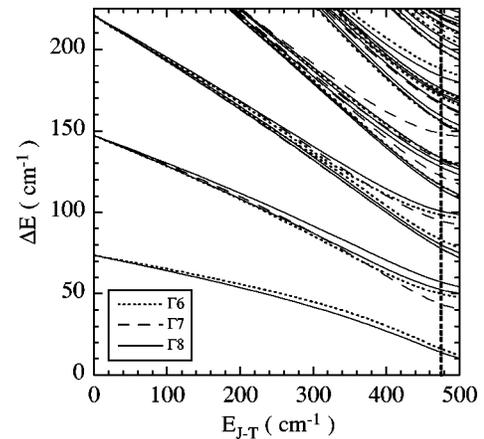


FIG. 1. Dependence of the lowest-energy levels on the Jahn-Teller energy. All energies have been referred to the energy of the lowest Γ_7 vibronic state. The vertical line indicates the value of E_{JT} for which agreement to the experimental data is obtained.

TABLE II. Comparison between the calculated and experimental energies in ZnTe:Cu²⁺. The last column gives the calculated relative intensities, taking as unity the intensity of the lowest line at 1069.9 cm⁻¹. Parameters: $\Delta = 6000$ cm⁻¹, $\lambda_1 = -888.1$ cm⁻¹, $\lambda_2 = -830$ cm⁻¹, $\hbar\omega = 38.8$ cm⁻¹, $E_{JT} = 468.5$ cm⁻¹.

E_{exp} (cm ⁻¹)	E_{th} (cm ⁻¹)	Relative intensity
1069.9	1069.9	1
1101.2	1101.2	0.5
1105.1	1107.5	0.05
1130.9	1118.8	0.05
1145.1	1140.9	0.1
1155.7	1151.8	0.04

from the ratio $\lambda_1/\lambda_{\bar{n}}$ leads to $g = 2/3(2k+1) = 1.77$. Thus, we find that the JT interaction further reduces the value of g by about 20%. This reduction is smaller than that generally predicted using Ham's theory¹ and is not sufficient to obtain agreement with the measured value $g(\Gamma_7) = 0.71$.⁷

To confirm our assignment of the transitions, we also evaluated (Table I) the relative intensities of the transitions.²³ Electric-dipole transitions between the levels originating from the $3d^9$ configuration in the free ion are, of course, forbidden because the states all have even parity. However, the tetrahedral potential lacks inversion symmetry and, hence, mixes odd and even parity states so that electric-dipole transitions become allowed. Group theory shows that the transition probability depends on a single matrix element denoted by $\langle \epsilon_3 | \sum_a z_a | \gamma_1 \rangle$, where the states ϵ_3 and γ_1 are the orbital states defined in Sec. II and z_a is the z component of the position vector \mathbf{r}_a . The sum over a includes all electrons in the ion. For a transition between states belonging to the rows κ_i and κ_j of the irreducible representations Γ_i and Γ_j , respectively, we calculate the matrix element $|\langle \Gamma_j, \kappa_j | \sum_a z_a | \Gamma_i, \kappa_i \rangle|^2$. The constant $\langle \epsilon_3 | \sum_a z_a | \gamma_1 \rangle$ can, in principle, be determined from the ratio of electric-dipole to magnetic-dipole intensities. However, lack of detailed experimental information on these intensities precludes the determination of the constant, and to avoid this difficulty we list, in Table I, the intensities relative to the intensity of the $\Gamma'_8 \rightarrow \Gamma_7$ zero-phonon line. Only transitions with non-negligible intensities are displayed in Table I.

The results of Table I show that our model accounts for all the observed electronic transitions with good accuracy. We remark that there is no JT coupling with a Γ_5 phonon mode in the ${}^2\Gamma_3(\Gamma'_8)$ electronic state (apart from a weak contribution arising from the spin-orbit mixing between ${}^2\Gamma_5$ and ${}^2\Gamma_3$). Therefore, one could expect an evenly spaced progression of absorption lines in the ${}^2\Gamma_5 \rightarrow {}^2\Gamma_3$ spectrum. Our calculations show indeed such a sequence of absorption peaks, separated by approximately 73.5 cm⁻¹. As far as we know, these lines have not been observed experimentally.^{5,12} This is in agreement with our calculated intensities, which are much weaker than that of the zero-phonon line.

It is, at this stage, interesting to compare our results with the different theories that have been proposed in the past. The only previous attempt to treat a JT coupling with a Γ_5 phonon is that of Sauer, Scherz,¹³ and Maier.¹³ They considered a phonon of energy 200 cm⁻¹ representing an average

of phonon energies in ZnS but were unable to explain quantitatively all the observed transitions. A close examination of their results also shows that they neglected the JT coupling between the two Γ_8 states arising from $\Gamma_4 \otimes \Gamma_8$ and $\Gamma_5 \otimes \Gamma_8$. We recall that this interaction is explicitly included in our calculation. Maier and Scherz¹² have investigated the possibility of interaction with one or two phonons of Γ_3 symmetry. First they took a strong JT coupling with a Γ_3 phonon of energy 200 cm⁻¹ chosen to be a representative average of all interacting lattice modes. In a second approach, they then investigated a JT coupling with up to six overtones of two Γ_3 phonons with energies, 100 cm⁻¹ and 300 cm⁻¹, corresponding to the two maxima in the phonon density of states of the ZnS lattice. We have been able to reproduce these results but found that, to achieve convergence on the energy levels, it is necessary to include up to 12 overtones of the Γ_3 phonon. Even so, both models proposed by Maier and Scherz¹² lead to energies that are incompatible with the experimental data. In addition, we have attempted a fit to the emission spectrum using a TA(L) phonon of Γ_3 symmetry ($\hbar\omega \approx 70$ cm⁻¹) but this attempt was unsuccessful. Clerjaud and Gelineau¹⁴ have also considered an interaction with a Γ_3 phonon but, in contrast to other calculations and in contradiction with the subsequent conclusions of Weinert and Scherz,¹⁵ they assumed that the coupling occurs with optical phonons whose frequencies are about 300 cm⁻¹ for ZnS. In their theory the low value of $g(\Gamma_7)$ is well reproduced but difficulties remain in explaining the higher vibronic states. Finally, we mention the interpretation proposed by Telahun *et al.*,¹⁸ who consider a coupling with a local vibrational mode of Γ_3 symmetry and energy $\hbar\omega = 262$ cm⁻¹ to explain the lines at 6924, 6910, and 6114 cm⁻¹. Using their model and the parameters given in their paper we were unable to reproduce their results. We also note that the Huang-Rhys factor $S = 0.81$ used by Telahun *et al.*¹⁸ is much smaller than that obtained in our model (see Table I).

B. ZnTe:Cu²⁺

To the best of our knowledge, the optical properties of ZnTe:Cu²⁺ have only been investigated by Volz *et al.*,¹⁹ who measured the absorption spectrum of this crystal in the range 800–2000 cm⁻¹. They observe a zero-phonon line at 1069.9 cm⁻¹ accompanied by additional sharp lines between 1100 and 1200 cm⁻¹ as well as several phonon-assisted transitions at lower and higher energies. They attribute the line at 1069.9 cm⁻¹ to a transition between Γ_7 and Γ'_8 and the additional lines to a JT interaction between a Γ_3 phonon and the ${}^2\Gamma_3$ excited orbital state. This leads to values of $\Delta = 1024$ cm⁻¹ and $\lambda_1 = \lambda_2 = -45$ cm⁻¹. This interpretation is in striking contrast with the models used to explain the absorption and emission spectra of ZnS:Cu²⁺. The value of Δ used by Volz *et al.*¹⁹ is typically five to six times smaller than the values of the crystal-field splitting observed for Cu²⁺ in ZnS, CdS, and ZnO. The value of $\lambda_1 = \lambda_2$ is almost 20 times smaller than the free-ion $\lambda_{\bar{n}}$ value leading to a ratio $\lambda_1/\lambda_{\bar{n}} = 0.05$. This is physically unreasonable as this would imply that the d electrons in Cu²⁺ are so delocalized as to spend only 5% of their time in the vicinity of the Cu²⁺ ion. A reexamination of the spectrum therefore appears to be needed.

We propose here to attempt an interpretation of the absorption spectrum of ZnTe:Cu²⁺ based on exactly the same model as that used to interpret the optical data in ZnS:Cu²⁺. Thus, we consider a JT interaction between the ${}^2\Gamma_5$ ground multiplet of the magnetic impurity and a Γ_5 phonon of the ZnTe host. As in the case of ZnS we assume that the phonon participating in the JT coupling is the TA(L) phonon, which, in ZnTe, has energy $\hbar\omega = 42 \text{ cm}^{-1}$. In complete contrast to the work of Volz *et al.*,¹⁹ we attribute the zero-phonon line at 1069.9 cm^{-1} to a $\Gamma_7 \rightarrow \Gamma_8$ transition and the other sharp lines as arising from vibronic states in the lowest multiplet of Cu²⁺. The fitting procedure for the parameters is slightly different in this case as the experimental information available is different. Since we assume that the observed zero-phonon line correspond to a transition from Γ_7 to Γ_8 , we have no information on the Γ_8' state. Thus, we cannot determine Δ from a fit to a transition with this level as the final state. We fix $\Delta = 6000 \text{ cm}^{-1}$ to be of the order of magnitude of the crystal-field splitting of Cu²⁺ in various II-VI compounds. The spin-orbit coupling constant λ_2 , which is known to be much less affected by covalency than λ_1 ,²⁷ is kept equal to the free-ion value as for ZnS. We choose λ_1 to reproduce the energy of the line at 1069.9 cm^{-1} . The JT stabilization energy is fitted to the first excited line at 1101.5 cm^{-1} ; this also requires a slight modification of the energy of the phonon.

The following values of the physical parameters are then obtained: $\lambda_1 = -888.0 \text{ cm}^{-1}$, $E_{JT} = 468.5 \text{ cm}^{-1}$, $\hbar\omega = 38.8 \text{ cm}^{-1}$, $S = 12.1$. The diagonalization of H with these parameters leads to transition energies in reasonable agreement with the experimental data and the results for the calculated transitions and their relative intensities are listed in Table II.

To explain the available experimental data we had to use a value $|\lambda_1|$ larger than the free-ion value. This can, *a priori*, appear surprising. To attempt to explain this value we have looked at calculations of λ_1 that take into account the mixing of the one-electron orbitals of the magnetic ion with the ligand orbitals. Vallin and Watkins²⁷ have carried out such a calculation for Cr²⁺ in II-VI compounds. Taking into account the hybridization with the p orbitals of the ligands only and using a number of approximations to reduce the problem to a one-parameter model, they obtained an expression for λ_1 [see Eq. (51) of Ref. 27] that always leads to a reduction in magnitude of λ_1 for Cr²⁺. The same conclusion would also hold in the case we are considering as Eq. (51) of Ref. 27 can readily be transformed for Cu²⁺ by replacing the factor of (1/4) by (-1) . However, this result is purely a consequence of the approximations used by Vallin and Watkins.

More recently, Viccaro *et al.*²⁸ have also used a molecular-orbital theory similar to that of Vallin and Wat-

kins to derive expressions for λ_1 and λ_2 for Cr²⁺ in GaAs, within the framework of ligand-field theory. In contrast to Vallin and Watkins, they include the hybridization with the s orbitals of the ligands. They also take into account “nonlocal” terms that involve both the wave functions of the central ions and the wave functions of the ligands [see Eq. (13) of Ref. 28]. Again this equation is for Cr²⁺ but can easily be rewritten for Cu²⁺. The nonlocal terms are usually considered to be small (Refs. 28–30), in which case the sign of the correction to the free-ion value depends on the relative signs of the last three terms in Eq. (13) of Ref. 28, i.e., on the signs of the admixture coefficients. An evaluation of these coefficients as well as a detailed investigation of the nonlocal terms for Cu²⁺ in ZnTe and ZnS is under way but is beyond the scope of this paper. Finally, we note that more detailed experimental results would be needed to refine the values of the parameters (including λ_1) determined from a fit to experiment.

IV. CONCLUSIONS

We have shown that the absorption and emission spectra observed in ZnS:Cu²⁺ and ZnTe:Cu²⁺ can be explained consistently within the framework of crystal-field theory, including hybridization with the orbitals of the ligands of the host crystal and an intermediate dynamic Jahn-Teller interaction between the electronic states of the ${}^2\Gamma_5$ ground multiplet of Cu²⁺ and a TA(L) phonon of Γ_5 symmetry. Further confirmation of our model would be given by absorption measurements within the ${}^2\Gamma_5$ ground multiplet. We have proposed an interpretation of the absorption measurements in ZnTe:Cu²⁺ based on the same theoretical model as that used to explain the experimental data in ZnS:Cu²⁺. However, more complete absorption and emission measurements are needed in order to draw more precise conclusions on an additional Jahn-Teller coupling with phonons of Γ_3 symmetry and covalency effects.

ACKNOWLEDGMENTS

One of us (M.V.) wishes to thank the Nuffield Foundation (U.K.) for financial support. This work was supported by the Fonds National de la Recherche Scientifique (Belgium, Grant No. 9.456.96F), Academic Research Collaboration between Fonds National de la Recherche Scientifique, the Commissariat Général aux Relations Internationales, and the British Council, 1997-98 (BEL-0366-3), and by the North Atlantic Treaty Organization (NATO Research Grant No. 960666). D.C. and E.M. are grateful to the Fonds pour la formation à la Recherche dans l’Industrie et l’Agriculture (FRIA Belgium) for research grants.

¹F. S. Ham, Phys. Rev. **138**, A1727 (1965).

²See, for example, D. M. Newns, C. C. Tsuei, and P. C. Pattnaik, Phys. Rev. B **52**, 13 611 (1995); V. M. Loktev, Low Temp. Phys. **22**, 1 (1996).

³The group-theoretical notation for the point groups and the irreducible representations follows G. F. Koster, J. O. Dimmock, R. G. Wheeler, and H. Statz, *Properties of the Thirty-Two Point*

Groups (MIT Press, Cambridge, MA, 1966).

⁴M. Villeret, S. Rodriguez, and E. Kartheuser, Phys. Rev. B **43**, 14 115 (1991).

⁵I. Broser, H. Maier, and H.-J. Schulz, Phys. Rev. **140**, A2135 (1965).

⁶I. Broser and H. Maier, J. Phys. Soc. Jpn. Suppl. **21**, 254 (1966).

⁷M. de Wit, Phys. Rev. **177**, 441 (1969).

- ⁸C. J. Ballhausen, *Introduction to Ligand field Theory* (McGraw-Hill, New York, 1962).
- ⁹U. Scherz, *J. Phys. Chem. Solids* **31**, 995 (1970).
- ¹⁰C. A. Bates and P. E. Chandler, *J. Phys. C* **4**, 2713 (1971).
- ¹¹T. Yamaguchi and H. Kamimura, *J. Phys. Soc. Jpn.* **33**, 953 (1972).
- ¹²H. Maier and U. Scherz, *Phys. Status Solidi B* **62**, 153 (1974).
- ¹³U. Sauer, U. Scherz, and H. Maier, *Phys. Status Solidi B* **62**, K71 (1974).
- ¹⁴B. Clerjaud and A. Gelineau, *Phys. Rev. B* **9**, 2832 (1974).
- ¹⁵C. M. Weinert and U. Scherz, *Phys. Status Solidi B* **124**, 287 (1984).
- ¹⁶P. Thurian, R. Heitz, T. Jentsch, A. Hoffmann, and I. Broser, *Physica B* **185**, 239 (1993).
- ¹⁷T. Telahun, P. Thurian, A. Hoffmann, I. Broser, and U. Scherz, *Mater. Sci. Forum* **196-201**, 767 (1995).
- ¹⁸T. Telahun, U. Scherz, P. Thurian, R. Heitz, A. Hoffmann, and I. Broser, *Phys. Rev. B* **53**, 1274 (1996).
- ¹⁹M. P. Volz, C.-H. Su, S. L. Lehoczky, and F. R. Szofran, *Phys. Rev. B* **46**, 76 (1992).
- ²⁰D. Colignon, E. Kartheuser, S. Rodriguez, and M. Villeret, *Phys. Rev. B* **51**, 4849 (1995).
- ²¹D. Colignon and E. Kartheuser, *Z. Phys. Chem., Bd.* **201**, 119 (1997).
- ²²U. Scherz, *J. Phys. Chem. Solids* **30**, 2077 (1969).
- ²³V. Savona, F. Bassani, and S. Rodriguez, *Phys. Rev. B* **49**, 2408 (1994).
- ²⁴N. Vagelatos, D. Wehe, and J. King, *J. Chem. Phys.* **60**, 3613 (1974).
- ²⁵A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions* (Clarendon, Oxford, 1970).
- ²⁶R. E. Dietz, H. Kamimura, M. D. Sturge, and A. Yariv, *Phys. Rev.* **132**, 1559 (1963).
- ²⁷J. T. Vallin and G. D. Watkins, *Phys. Rev. B* **9**, 2051 (1966).
- ²⁸M. H. de A. Viccaro, S. Sundaram, and R. R. Sharma, *Phys. Rev. B* **25**, 7731 (1982). Note the missing factor $\zeta_{p,p}$ before the final curly bracket in Eq. (13) of this paper. See also Refs. 29 and 30 of the present paper.
- ²⁹Y.-Y. Zhou and F.-Z. Li, *Phys. Rev. B* **51**, 14 176 (1995).
- ³⁰D.-H. Li, F.-H. Li, and Y.-Y. Zhou, *Solid State Commun.* **105**, 59 (1998).