Jahn-Teller effect in the $^2T_2$ state of Cu^{2+} in ZnS

B. Clerjaud and A. Gelineau
Laboratoire de Luminescence II, Université de Paris VI, 75230 Paris Cedex 05, France
Equipe de Recherche Associeé au Centre National de la Recherche Scientifique, Paris, France
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The narrow lines at 6927 and 6913 cm^{-1} in emission spectra of Cu^{2+} in cubic ZnS are attributed to the $^2E \rightarrow \Gamma_7$ ($^2T_2$) and $^2E \rightarrow \Gamma_8$($^2T_2$) transitions. The splitting of the $^2T_2$ level and the $g(\Gamma_7)$ gyromagnetic factor are interpreted as being due to a dynamic Jahn-Teller effect in the ground state $^2T_2$. The coupling occurs with E optical phonons with $S_E = E_{JT}/\hbar\omega \simeq 3$. It is essential to consider the effect of ^2E excited state to explain simultaneously the $^2T_2$ splitting and $g(\Gamma_7)$. The ratio between the emission-lines intensities is in agreement with this model.

I. INTRODUCTION

Experimental data about Cu^{2+} in cubic ZnS (zinc blende) such as near-infrared optical spectra[1,2] or Zeeman-effect experiments in the near-infrared absorption spectrum[3,4] have been reported; however, the electron-paramagnetic-resonance spectrum of a Cu^{2+} center with cubic symmetry has not been observed[5] in spite of research in this field.

The Cu^{2+} free ion is a ^2D state. In a crystal field of tetrahedral symmetry, this state is split in a $^2T_2$ ground state and a ^2E excited state. Emission and absorption spectra between these two states are observed in the near-infrared range around 7000 cm^{-1}.[1,2] The spin-orbit coupling further splits the $^2T_2$ state into Γ_7 (lowest) and Γ_8 states. At low temperatures (< 10 K) the emission spectrum exhibits two narrow lines separated by 14 cm^{-1}; in absorption the high-energy line only is observed at 6927 cm^{-1}.[2] Zeeman-effect experiments have been performed on this line leading to a gyromagnetic factor of 0.71 in the ground state Γ_7.[3,4]

Up to now, no theoretical treatment allows the understanding of all these experimental results; this led several authors[6,7] to the hypothesis that these results were not due to copper centers but to cation vacancies. The validity of this hypothesis seems unlikely because their results do not fit the Zeeman experiments: as noted in Ref. 7, the observation of Zeeman splitting rules out the existence of model (*a*) in Ref. 6; on the other hand, in model (*b*) in Ref. 6, six Zeeman components are predicted which is inconsistent with the four components experimentally observed[3,4]; moreover, the ground state of the vacancy should not exhibit the thermalization effects observed.[3,4]

The possibility of the influence of a Jahn-Teller effect in Cu^{2+} in ZnS has been first considered by Broser and Maier[2]; these authors interpret the emission spectrum considering a static Jahn-Teller effect in the ^2E excited state leading to a 14-cm^{-1} splitting in this state. This hypothesis seems improbable because thermalization should occur in the excited state leading to a single line in emission; on the other hand, two lines should be observed in absorption. It seems more reasonable to admit that this splitting occurs in the ground state. Then Bates and Chandler[8,9] have considered a dynamic Jahn-Teller effect in the ground state, but they failed in the explanation of the experimental data. Recently, Yamaguchi and Kamimura[10] have also considered a dynamic Jahn-Teller effect in the ground state; but they attempt to interpret experiments in centers having axial symmetry (ZnO: Cu^{2+}, CdS: Cu^{2+}, and "hexagonal" ZnS: Cu^{2+}).

The investigation of a Jahn-Teller effect in a T_2 level is a complicated problem, because in a site of tetrahedral symmetry, an orbital triplet state can be coupled, apart from the A_1 total symmetrical mode, to one E and to two T_2 vibrational modes,[11] but fortunately recent uniaxial stress experiments performed by Maier[12] have shown that the $^2T_2$ level is coupled predominantly with E modes of vibration: the T_2 ground state is strongly affected by $\langle 001 \rangle$ stress and less affected by $\langle 111 \rangle$ stress. This last result led us to reinvestigate the problem taking into account the coupling of the $^2T_2$ state to only E modes of vibration.

We will now try to interpret the 14-cm^{-1} splitting as being due to the spin-orbit interaction, within the ground state, strongly reduced by the Jahn-Teller effect (without the Jahn-Teller effect, this splitting should be of about 1000 cm^{-1}).

II. JAHN-TELLER EFFECT WITHIN $^2T_2$ GROUND STATE: HAM'S TREATMENT

A. Spin-orbit interaction

In order to obtain the magnitude of the Jahn-Teller effect, it is convenient to use a simple approach to the problem considering the spin orbit interaction as a perturbation to the Jahn-Teller problem.[13,14] In this section, we will neglect the effect of the ^2E excited state that we will consider later.

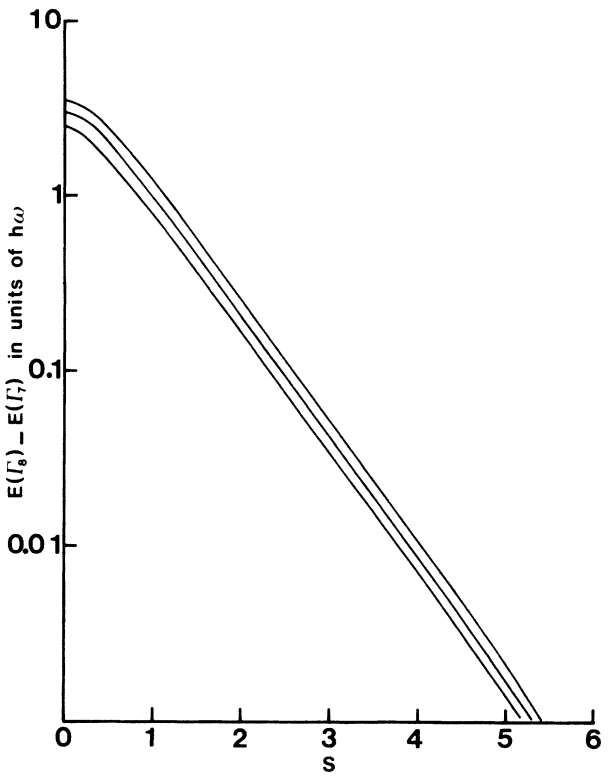

FIG. 1. Splitting of the $^2T_2$ level following Ham's treatment for various values of λ: $\lambda = -\frac{7}{3}\hbar\omega$ (upper curve), $\lambda = -2\hbar\omega$ (middle curve), and $\lambda = -\frac{5}{3}\hbar\omega$ (lower curve).

Ham[13,14] has shown that the spin-orbit interaction can be expressed within the vibronic ground state by the second-order equivalent operator

$$\mathcal{H}_{so} = \lambda' \vec{\mathfrak{L}} \cdot \vec{S} - \frac{\lambda'^2}{\hbar\omega} G(\tfrac{3}{2} S_E)(\vec{\mathfrak{L}} \cdot \vec{S})^2 - \frac{\lambda'^2}{\hbar\omega} \times [G(3S_E) - G(\tfrac{3}{2} S_E)](\mathfrak{L}_x^2 S_x^2 + \mathfrak{L}_y^2 S_y^2 + \mathfrak{L}_z^2 S_z^2) \quad ,$$

where $\vec{\mathfrak{L}}$ is the effective angular momentum within $^2T_2$, $S_E = E_{JT}/\hbar\omega$ represents the Jahn-Teller energy in units of E phonons of frequency ω, $\lambda' = -\lambda e^{-3S_E/2}$ is the reduced spin-orbit constant (λ being the true spin-orbit constant), and

$$G(x) = \sum_{n=1}^{\infty} \frac{x^n}{n \cdot n!} \quad .$$

The spin-orbit interaction splits the $^2T_2$ state into Γ_7 and Γ_8 states whose energies are given by

$$E(\Gamma_7) = -\lambda' - (\lambda'^2/2\hbar\omega)\,[G(3S_E) + G(\tfrac{3}{2} S_E)] \, ,$$

$$E(\Gamma_8) = +\tfrac{1}{2}\lambda' - (\lambda'^2/2\hbar\omega)[G(3S_E) - \tfrac{1}{2} G(\tfrac{3}{2} S_E)] \quad ;$$

it is to be noted that λ is negative for Cu^{2+}; consequently, λ' is positive. The splitting is

$$E(\Gamma_8) - E(\Gamma_7) = +\tfrac{3}{2}\lambda' + \tfrac{3}{4}(\lambda'^2/\hbar\omega) G(\tfrac{3}{2} S_E) \quad .$$

This splitting is plotted in Fig. 1 for different values of λ. For the free ion, λ is equal to -830 cm^{-1}, but taking into account covalency, it is usual to reduce λ by 20–40%.

We suppose that the coupling occurs with optical phonons whose frequency is about 300 cm^{-1} for ZnS.[15] The spin-orbit splitting of 14 cm^{-1} corresponds to a value of S_E close to 3 (see Fig. 1).

It is to be noted that this value of S_E is almost independent of the choice of the phonon frequency.

B. Gyromagnetic factor

As for the spin-orbit splitting, we use first- and second-order equivalent operators given by Ham[13,14]:

$$\mathcal{H}_H^{(1)} = \mu_B \, (-e^{-3S_E/2}\, \vec{\mathfrak{L}} \cdot \vec{H} + 2\vec{S} \cdot \vec{H}) \quad ,$$

$$\mathcal{H}_H^{(2)} = -\frac{\lambda \mu_B}{\hbar\omega} e^{-3S_E} \times \{[(\vec{\mathfrak{L}} \cdot \vec{S})(\vec{\mathfrak{L}} \cdot \vec{H}) + (\vec{\mathfrak{L}} \cdot \vec{H})(\vec{\mathfrak{L}} \cdot \vec{S})]\, G(\tfrac{3}{2} S_E) + 2(\mathfrak{L}_x^2 S_x H_x + \mathfrak{L}_y^2 S_y H_y + \mathfrak{L}_z^2 S_z H_z) \times [G(3S_E) - G(\tfrac{3}{2} S_E)]\} \quad ,$$

where $\vec{H}$ is the magnetic field. The ground-state gyromagnetic factor is found to be

$$g(\Gamma_7) = -\tfrac{2}{3}\{1 + 2e^{-3S_E/2} - (2\lambda e^{-3S_E}/\hbar\omega) \times [G(3S_E) + G(\tfrac{3}{2} S_E)]\} \quad .$$

$|g(\Gamma_7)|$ is plotted in Fig. 2. For $S_E = 3$, one finds that $|g|$ is very close to 1; on the other hand, to fit the 0.71 experimental value it is necessary to take an unreasonable value of S_E greater than 20. It appears that this perturbation treatment cannot explain simultaneously the available experimental results.

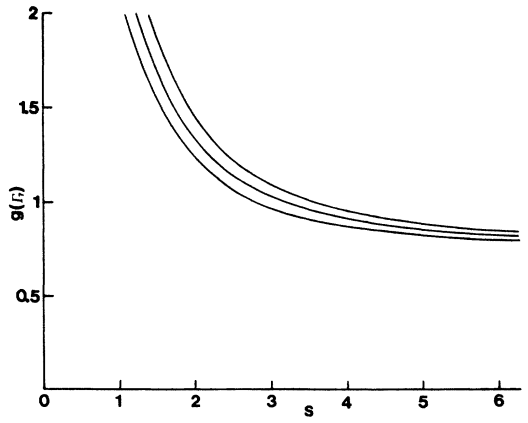

FIG. 2. $|g(\Gamma_7)|$ value following Ham's treatment for various values of λ: $\lambda = -\frac{7}{3}\hbar\omega$ (upper curve), $\lambda = -2\hbar\omega$ (middle curve), and $\lambda = -\frac{5}{3}\hbar\omega$ (lower curve).

It is to be noted, as it has been mentioned by Ham,[13] that this second-order treatment is valid only if the Jahn-Teller energy is much greater than the spin-orbit splitting in the absence of Jahn-Teller coupling. But in our case, the Jahn-Teller energy we have calculated is only 1.5 times the absolute value of the spin-orbit constant λ. It is thus questionable whether higher-order terms have to be taken into account. That is why we have performed an "exact" calculation diagonalizing the Jahn-Teller-plus-spin-orbit Hamiltonian. We will present this calculation in Sec. III.

III. NUMERICAL DIAGONALIZATION OF JAHN-TELLER-PLUS-SPIN-ORBIT HAMILTONIAN WITHIN THE VIBRATIONAL STATES OF $^2T_2$

We consider the following Hamiltonian:

$$\mathcal{H}=\mathcal{H}_0\mathcal{J}+\frac{1}{2\mu}\left[P_\theta^2+P_\epsilon^2+\mu^2\omega^2\,(Q_\theta^2+Q_\epsilon^2)\right]\mathcal{J}$$

$$+V_E\left[Q_\theta\epsilon_\theta+Q_\epsilon\epsilon_\epsilon\right]+\lambda\,\vec{L}\cdot\vec{S}\quad,$$

where $\mathcal{H}_0$ is the cubic crystal-field Hamiltonian, P_θ and P_ϵ are the momenta conjugate to the reduced coordinates Q_θ and Q_ϵ, μ is the effective mass of the mode, and V_E is the Jahn-Teller coupling coefficient. It is to be noted that the matrices ϵ_θ, ϵ_ϵ, and $\lambda\vec{L}\cdot\vec{S}$ cannot be simultaneously brought to diagonal form; consequently, computer calculation has been used for various values of λ and S_E. This calculation has been performed on a C.I.I. 10070 computer. This diagonalization should be performed on an infinite number of vibrational states. In fact for $S_E \leq 5$ the convergence limit is reached for 10 phonons ($n_\theta+n_\epsilon=10$).

The energy-level diagram is given in Fig. 3 for $\lambda=-\frac{7}{3}\hbar\omega$. This value of λ has been chosen to avoid accidental degeneracies ($\frac{3}{2}\mid\lambda\mid\neq p\hbar\omega$ with p integer) in order to clarify the figure. In Fig. 4 we have plotted the splitting between the two lowest levels for three values of λ. The $g(\Gamma_7)$ value is issued from first-order perturbation of $\mu_B(\vec{L}+2\vec{S})\vec{H}$ within the computer wave functions. $\mid g(\Gamma_7)\mid$ is plotted in Fig. 5.

We note that the 14-cm^{-1} splitting between the two lowest levels is explainable with $S_E\simeq 3.25$; the corresponding value of $\mid g\mid$ is about 1.1. These results are very close to those obtained with Ham's treatment. It seems that Ham's treatment gives results close to the diagonalization as soon as $E_{JT} > \mid\lambda\mid$.

The $\mid g\mid$ value calculated is thus too large. Taking into account a reduction in the orbital part of the Zeeman interaction due to covalency should diminish $\mid g\mid$ of about 0.1 and lead to a still too large $\mid g\mid$ value. The relative disagreement between the experimental and calculated g value led us to investigate the effect of the ^2E excited state.

IV. INFLUENCE OF THE ^2E EXCITED STATE

We have seen previously that a perturbation treatment gives results close to an "exact" calculation for the vibrational levels of $^2T_2$; therefore, we will use a perturbation calculation again for the ^2E, seeing that the lowest vibrational level of the ^2E state lies at about 23 phonons above the ground state $^2T_2$.

We take the simplest hypothesis admitting that there is no Jahn-Teller effect in the excited state ^2E (this hypothesis has been verified for other E states in ZnS: ^5E ground state of Fe^{2+},[15,16] ^5E excited state of Cr^{2+},[17] and ^4E excited state of Mn^{2+}[18] but unsatisfied in the ^2E ground state of Sc^{2+}[19]).

A. Spin-orbit interaction

If we admit the Jahn-Teller energy of the $^2T_2$ state to be small compared with the splitting Δ ($\Delta>0$) between the ^2E and the $^2T_2$ states, a simple approach to the problem is to investigate first the corrections to the spin-orbit coupling in the $^2T_2$ state from a second-order perturbation treatment involving the ^2E state and then to reduce all off-diagonal terms of the equivalent operator obtained by the Jahn-Teller reduction factor $e^{-3S_E/2}$.

This equivalent operator is given by[20]

$$\mathcal{H}_{so}^{2E}=-(2\lambda^2/\Delta)\left[(\vec{\mathfrak{L}}\cdot\vec{S})+(\vec{\mathfrak{L}}\cdot\vec{S})^2\right]\quad.$$

This operator can be written alternatively as

$$\mathcal{H}_{so}^{2E}=-\frac{\lambda^2}{\Delta}(\vec{\mathfrak{L}}\cdot\vec{S})-\frac{2\lambda^2}{\Delta}\left(\mathfrak{L}_x^2S_x^2+\mathfrak{L}_y^2S_y^2+\mathfrak{L}_z^2S_z^2\right)$$

$$-\frac{\lambda^2}{\Delta}\left[(\mathfrak{L}_x\mathfrak{L}_y+\mathfrak{L}_y\mathfrak{L}_x)(S_xS_y+S_yS_x)+\text{cyclic}\right]$$

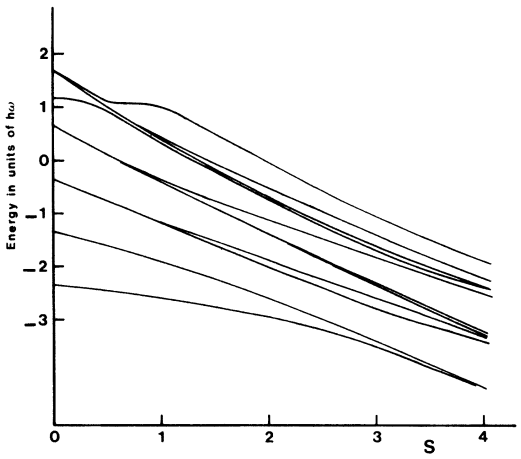

FIG. 3. Vibronic energy levels of the $^2T_2$ electronic state for $\lambda=-\frac{7}{3}\hbar\omega$. For clearness, we have only drawn the levels arising from the zero-phonon Γ_8 state ($E=-\frac{1}{2}\lambda=\frac{7}{6}\hbar\omega$ for $S=0$) and from the Γ_7 level and the four first corresponding vibrational levels ($E=\lambda+n\hbar\omega$, $n=0$ to 4 for $S=0$).

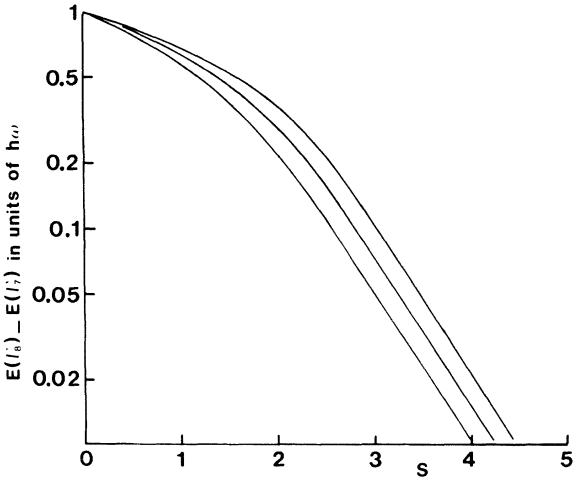

FIG. 4. Splitting between the two lowest levels obtained from computer calculation for $\lambda = -\frac{7}{3}\hbar\omega$ (upper curve), $\lambda = -2\hbar\omega$, and $\lambda = -\frac{5}{3}\hbar\omega$.

in a $S = \frac{1}{2}$ spin manifold, the second term is equal to $-(\lambda^2/\Delta)\mathcal{J}$ ($\mathcal{J}$ is the unit matrix), and the third term is equal to zero, because $(S_x S_y + S_y S_x)$ is proportional to the anticommutator of the Pauli matrices. The energy levels, to order λ^2/Δ, are given by

$$E'(\Gamma_7) = E(\Gamma_7) - \lambda^2/\Delta + (\lambda^2/\Delta)\, e^{-3S_E/2} \quad ,$$

$$E'(\Gamma_8) = E(\Gamma_8) - \lambda^2/\Delta - (\lambda^2/2\Delta)\, e^{-3S_E/2}$$

when $E(\Gamma_7)$ and $E(\Gamma_8)$ are given in Sec. II. Now the splitting is

$$E'(\Gamma_8) - E'(\Gamma_7) = -\tfrac{3}{2}(\lambda + \lambda^2/\Delta)\, e^{-3S_E/2} + \tfrac{3}{4}(\lambda^2/\hbar\omega)\, e^{-3S_E}\, G\,(\tfrac{3}{2}S_E) \quad .$$

The influence of ^2E is very weak ($\sim 1\ \mathrm{cm}^{-1}$) but comparable to the second-order effect within the $^2T_2$ state.

B. Gyromagnetic factor

The ^2E contribution to the gyromagnetic factor is given by the second-order terms arising from the combined effect of the orbital part of $\mu_B(\vec{L} + 2\vec{S})\vec{H}$ and the spin-orbit interaction. The correction to the Zeeman interaction in the $^2T_2$ state from coupling to ^2E is given by the equivalent operator[20]

$$\mathcal{H}_H^{2E} = -\frac{8\lambda}{\Delta}\mu_B \vec{S}\cdot\vec{H} - \frac{2\lambda}{\Delta}\mu_B \times[(\vec{\mathcal{L}}\cdot\vec{S})(\vec{\mathcal{L}}\cdot\vec{H}) + (\vec{\mathcal{L}}\cdot\vec{H})(\vec{\mathcal{L}}\cdot\vec{S})] + 12\frac{\lambda}{\Delta}\mu_B[\mathcal{L}_x^2 S_x H_x + \mathcal{L}_y^2 S_y H_y + \mathcal{L}_z^2 S_z H_z] \quad .$$

This operator can be written alternatively as

$$\mathcal{H}_H^{2E} = -\frac{8\lambda}{\Delta}\mu_B \vec{S}\cdot\vec{H} + \frac{8\lambda}{\Delta}\mu_B \times[\mathcal{L}_x^2 S_x H_x + \mathcal{L}_y^2 S_y H_y + \mathcal{L}_z^2 S_z H_z] - \frac{2\lambda}{\Delta}\mu_B[(\mathcal{L}_x\mathcal{L}_y + \mathcal{L}_y\mathcal{L}_x)(S_x H_y + S_y H_x) + \text{cyclic}] \quad ,$$

where the third term is off diagonal and consequently reduced by $e^{-3S_E/2}$. The calculation leads to

$$g'(\Gamma_7) = -\frac{2}{3}\left(1 + 2e^{-3S_E/2} - \frac{2\lambda}{\hbar\omega}\, e^{-3S_E} \times[G\,(3S_E) + G\,(\tfrac{3}{2}S_E)] + \frac{4\lambda}{\Delta}(1 - e^{-3S_E/2})\right) \quad .$$

The important fact is the appearance of the $4\lambda/\Delta$ term which is of the same order of magnitude and of opposite sign to the term $-(2\lambda/\hbar\omega)\, e^{-3S_E} G(3S_E)$. The total effect of the second-order term is thus much lower than the effect of the terms arising from the vibrational terms of $^2T_2$ only. The contribution to $g'(\Gamma_7)$ due to the ^2E level is $+0.23$ for $S_E = 3$, $\Delta = 6900\ \mathrm{cm}^{-1}$, and $\lambda = -2\hbar\omega$. The resulting $g'(\Gamma_7)$ value is thus close to -0.8 (without taking into account the reduction in the orbital part of the Zeeman interaction due to covalency). It is thus essential to consider the ^2E excited state to explain simultaneously the position of the lines and the Zeeman data.

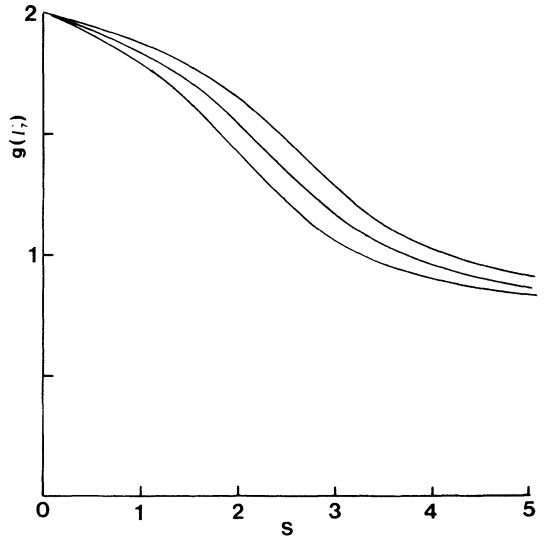

FIG. 5. $|g(\Gamma_7)|$ value obtained from computer calculation for $\lambda = -\frac{7}{3}\hbar\omega$ (upper curve), $\lambda = -2\hbar\omega$, and $\lambda = -\frac{5}{3}\hbar\omega$.

C. Alternative treatment

A more rigorous treatment requires the examination of the influence of the excited vibrational states of ^2E. As a matter of fact, these vibrational states are not orthogonal to those of the $^2T_2$ ground state, and it is questionable whether their cumulative effect is of importance.

The corresponding second-order calculation involves summations that lead to $K(x,y)$ functions[21] which are defined as

$$K(x,y)=\sum_{n=0}^{\infty}\frac{x^n}{(y+n)n!} \quad .$$

$K(x,y)$ represent the overlap between the zero-phonon $^2T_2$ vibrational state and ^2E vibrational states.

We give the results of the calculation

$$E''(\Gamma_7)=E(\Gamma_7)-\frac{\lambda^2}{\hbar\omega}\times e^{-S_E}\left[K\left(S_E,\frac{\Delta}{\hbar\omega}\right)-K\left(-\frac{S_E}{2},\frac{\Delta}{\hbar\omega}\right)\right],$$

$$E''(\Gamma_8)=E(\Gamma_8)-\frac{\lambda^2}{\hbar\omega}\times e^{-S_E}\left[K\left(S_E,\frac{\Delta}{\hbar\omega}\right)+\frac{1}{2}K\left(-\frac{S_E}{2},\frac{\Delta}{\hbar\omega}\right)\right] \quad ,$$

$$g''(\Gamma_7)=g(\Gamma_7)-\frac{8\lambda}{3\hbar\omega}\times e^{-S_E}\left[K\left(S_E,\frac{\Delta}{\hbar\omega}\right)-K\left(-\frac{S_E}{2},\frac{\Delta}{\hbar\omega}\right)\right] \quad .$$

If $y\gg x$, the asymptotic value of $K(x,y)$ is e^x/y. In this limit these expressions are identical to those obtained in Secs. IV A and IV B.

V. TRANSITIONS PROBABILITY

A. Transitions between the ^2E and $^2T_2$ levels

Zeeman effect experiments have shown that the transitions between the ^2E and $^2T_2$ levels have the electric dipole character.[3]

We call, respectively, p_7 and p_8 the transition probabilities in emission between the lowest ^2E state and the spin orbit levels Γ_7 and Γ_8 arising from $^2T_2$. Without Jahn-Teller effect, a straightforward calculation gives $p_7/p_8=\frac{1}{2}$. We have investigated the influence of the Jahn-Teller effect on that ratio.

The use of Ham's treatment leads to a tedious calculation because it is necessary to express the perturbed ground-state functions on the basis of the vibrational states. We preferred for simplicity to use the eigenvectors given by our computer calculation. The ratio p_7/p_8 is given now by

$$p_7/p_8=\tfrac{1}{2}(a/b)^2 \quad ,$$

where a and b are admission coefficients of the lowest vibrational states for Γ_7 and Γ_8. For $S_E=3$ and $\lambda=-2\hbar\omega$, we have $|a/b|=2.65$ leading to $p_7/p_8=3.5$, which is close to the experimental ratio of about 3.2 (obtained from the spectrum published in Ref. 2).

B. Transitions between the Γ_7 and Γ_8 levels

Gerbaux has performed, in the laboratory of Hadni in Nancy, far-infrared absorption experiments on our samples in order to observe directly the absorption between the lowest spin-orbit levels Γ_7 and Γ_8. This experiment has been unsuccessful. This fact is not very surprising because the electric dipole moment transforming as T_2 the square of its matrix elements within $^2T_2$ is reduced by a factor of the order of $e^{-3S_E}\simeq 10^{-4}$. More precisely the use of the eigenvectors furnished by the computer calculation gives the ratio R of the square of the matrix elements with and without Jahn-Teller effect. We have calculated

$$R=4.8\times10^{-4} \text{ for } S_E=3, \quad \lambda=-2\hbar\omega \ .$$

Moreover, the absorption transition probabilities are proportional to the spin-orbit splitting which is reduced by a factor $\simeq e^{-3S_E/2}\simeq 0.01$. We can thus estimate that the Jahn-Teller effect reduces the transition probability by a factor greater than 10^5.

VI. CONCLUSION

The narrow lines characteristic of the absorption and emission near infrared spectra as well as the ground state gyromagnetic factor of cubic ZnS:Cu^{2+} are well explained by assuming a dynamical Jahn-Teller effect in the ground state. A coupling to E modes of vibrations is sufficient to interpret the experiments with a Jahn-Teller energy about $3\hbar\omega=900$ cm^{-1}. It is essential to take into account the effect of the ^2E excited state to explain the gyromagnetic factor, however it is not necessary to consider a Jahn-Teller effect in the excited state.

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