Influence of the dynamic Jahn-Teller effect on the structure of quartet terms of the tetrahedrally coordinated ion Co²⁺ (ZnS — Co)

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The influence of a weak dynamic Jahn-Teller effect on the spectrum of a transition-metal impurity ion in a crystal is considered for the particular case of quartet terms of the tetrahedrally coordinated ion Co^{2+}. It is demonstrated that interaction between a degenerate electron level and limiting optical phonons leads to the appearance of narrow vibronic bands in the spectrum and violates mirror symmetry of the absorption and luminescence spectra. The structure of the configuration quartet terms is calculated in the approximation of weak Jahn-Teller interaction with doubly and triply degenerate oscillations.

When considering the Jahn-Teller (JT) effect due to the interaction of the degenerate electronic states of an impurity center in a crystal with the degenerate vibrations, it is customary to distinguish the cases of the strong electron-vibrational interaction, which leads to a smearing of the detailed vibronic structure of the spectrum, from the moderate or weak interaction, which does not prevent the observation of such a structure. In the latter case, when analyzing the schemes of the electronic and electron-vibrational (vibronic) energy levels connected with the triply degenerate state, one usually starts from the following two approximations:

1) The energy of the JT interaction is much stronger than the energy of the spin-orbit interaction. In this case operators having definite transformation properties, particularly the angular-momentum operator, are suppressed. This suppression leads, for example, to contraction of the picture of the spin-orbit splitting (in first-order perturbation theory), and also to a splitting under the influence of uniaxial compression[1]. Much attention has recently been paid to effects of this type, and they have been investigated in many systems (see, for example,[2]).

2) The JT-interaction energy is much smaller than the spin-orbit interaction energy. In this case the JT interaction plays the role of a weak perturbation that leads to a shift and splitting of the vibronic levels[3]. The concrete analysis of the spectrum is in this case quite complicated, since a small deformation of the spectrum can be produced, in principle, by a number of causes (the influence of covalence, the occurrence of local or quasilocal vibrations connected with an impurity, etc.). Nonetheless, in some cases such an analysis is possible[4].

In the present paper, using the example of the quartet terms of the tetrahedrally coordinated Co^{2+} ion, we consider the influence of the weak dynamic JT effect on the spectrum of a transition-metal impurity ion.

1. SPIN ORBIT SPLITTING OF QUARTET TERMS OF THE Co²⁺ ION

The ground state ^4F of the free Co^{2+} ion (configuration $3d^7$) is split in a crystal field of symmetry T_d into the terms $^4A_2$ (ground state) and $^4T_2$ and $^4T_1$, which are located respectively 10Dq and 18Dq away from the $^4A_2$ term (10Dq is the parameter of the tetrahedral component of the crystal field, i.e., the difference between the energies of the t_2 and e orbitals) (see Fig. 1).

The closest state ^4P of the free Co^{2+} ion is separated from the state ^4F by an interval of 15 000 cm⁻¹. In view of the smallness of the Dq for the case of tetrahedral coordination (Dq = 375 cm⁻¹ for the ion Co^{2+} in ZnS), we have confined ourselves to the weak-field approximation in the consideration of the spin-orbit structure of the terms $^4T_2$ and $^4T_1$, i.e., we have neglected the mixing of the terms that come from the ^4F term of the free ion, as well as the higher terms (the quartet $^4T_1$ (^4P) terms and the doublet terms). Comparison with the results of a calculation made with allowance for the mixing[5] shows that this allowance changes negligibly the relative dispositions of the spin-orbit components of the terms $^4T_2$ and $^4T_1$.

The lower term $^4A_2$ corresponds to the hole configuration $|t_2^3\rangle$ of the strong field, while the term $^4T_2$ corresponds to the configuration $|t_2^2e\rangle$. In the weak-field approximation, the wave function ψ of the term $^4T_1$ (^4F) is expressed in the following manner in terms of the wave functions of the configurations $|t_2^2e\rangle$ and $|t_2e^2\rangle$ of the strong field:

$$\psi = (|t_2^2e\rangle - 2|t_2e^2\rangle)/\sqrt{5}.$$

Using these functions as the orbital basis, we obtained (by the tensor-operator method) the matrix elements of the spin-orbit interaction. These elements for the doubly (Γ_6, Γ_7) and quadruply (Γ_8) degenerate states into which the terms $^4A_2$, $^4T_2$, and $^4T_1$(^4F) are split with allowance for the spin-orbit interaction are listed in Table I. In this table, ζ and ζ' are the one-electron constants of the spin-orbit interaction:

$$\zeta = -\frac{i}{3}\langle t_2\|\mathcal{H}_{so}\|t_2\rangle, \quad \zeta' = \frac{i}{3\sqrt{2}}\langle t_2\|\mathcal{H}_{so}\|e\rangle.$$

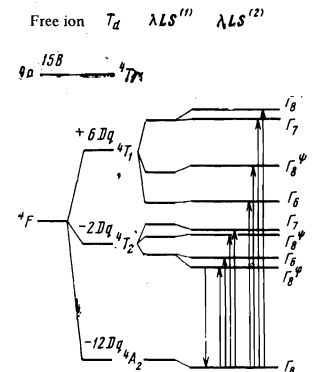If the wave functions are "pure" d-functions, then $\zeta = \zeta'$. The covalent bonds between the transition-metal

FIG. 1. Stark and spin-orbit splitting of the quartet terms of the Co^{2+} ion.

TABLE I. Matrix elements of the spin-orbital interaction of the lower quartet terms of the d^7 configuration.

Γ_8

$$\langle {}^4A_2 | \mathscr{H}_{so} | {}^4T_2 (\Gamma_8^\psi)\rangle = - \frac{\sqrt{5}}{\sqrt{3}} \zeta$$

$$\langle {}^4T_2 (\Gamma_8^\psi) | \mathscr{H}_{so} | {}^4T_2 (\Gamma_8^\psi)\rangle = \tfrac{1}{4} \zeta$$

$$\langle {}^4T_2 (\Gamma_8^\psi) | \mathscr{H}_{so} | {}^4T_1 (\Gamma_8^\psi)\rangle = - \frac{1}{5\sqrt{5}} (\zeta + 4\zeta')$$

$$\langle {}^4T_2 (\Gamma_8^\psi) | \mathscr{H}_{so} | {}^4T_1 (\Gamma_8^\varphi)\rangle = \frac{2}{5\sqrt{5}} (\zeta + 4\zeta')$$

$$\langle {}^4T_2 (\Gamma_8^\varphi) | \mathscr{H}_{so} | {}^4T_2 (\Gamma_8^\varphi)\rangle = - \tfrac{1}{4}\zeta$$

$$\langle {}^4T_2 (\Gamma_8^\varphi) | \mathscr{H}_{so} | {}^4T_1 (\Gamma_8^\psi)\rangle = \frac{2}{5\sqrt{5}} (\zeta + 4\zeta')$$

$$\langle {}^4T_2 (\Gamma_8^\varphi) | \mathscr{H}_{so} | {}^4T_1 (\Gamma_8^\varphi)\rangle = \frac{9}{20\sqrt{5}} (\zeta + 4\zeta')$$

$$\langle {}^4T_1 (\Gamma_8^\psi) | \mathscr{H}_{so} | {}^4T_1 (\Gamma_8^\psi)\rangle = - \tfrac{1}{30} (7\zeta + 8\zeta')$$

$$\langle {}^4T_1 (\Gamma_8^\varphi) | \mathscr{H}_{so} | {}^4T_1 (\Gamma_8^\varphi)\rangle = \tfrac{1}{20} (7\zeta + 8\zeta')$$

Γ_6

$$\langle {}^4T_2 | \mathscr{H}_{so} | {}^4T_2\rangle = - \tfrac{1}{4}\zeta$$

$$\langle {}^4T_2 | \mathscr{H}_{so} | {}^4T_1\rangle = \frac{1}{4\sqrt{5}} (\zeta + 4\zeta')$$

$$\langle {}^4T_1 | \mathscr{H}_{so} | {}^4T_1\rangle = - \tfrac{1}{12} (7\zeta + 8\zeta')$$

Γ_7

$$\langle {}^4T_2 | \mathscr{H}_{so} | {}^4T_2\rangle = \tfrac{5}{12} \zeta$$

$$\langle {}^4T_2 | \mathscr{H}_{so} | {}^4T_1\rangle = - \frac{1}{4\sqrt{5}} (\zeta + 4\zeta')$$

$$\langle {}^4T_1 | \mathscr{H}_{so} | {}^4T_1\rangle = \tfrac{1}{20}(7\zeta + 8\zeta')$$

TABLE II. Energies of the spin-orbit components of the terms ${}^4A_2$, ${}^4T_2$, and ${}^4T_1$ (${}^4F$) of the d^7 configuration. (It is assumed that $\zeta = \zeta' = -3\lambda$.)

	Γ	Energy
${}^4A_2$	Γ_8	$-12Dq - \dfrac{3}{2}\dfrac{\lambda^2}{Dq}$
${}^4T_2$	Γ_8^φ	$-2Dq - \dfrac{3}{4}\lambda - \dfrac{261}{128}\dfrac{\lambda^2}{Dq}$
	Γ_6	$-2Dq - \dfrac{3}{4}\lambda - \dfrac{45}{128}\dfrac{\lambda^2}{Dq}$
	Γ_8^ψ	$-2Dq + \dfrac{1}{2}\lambda + \dfrac{3}{8}\dfrac{\lambda^2}{Dq}$
	Γ_7	$-2Dq + \dfrac{5}{4}\lambda - \dfrac{45}{128}\dfrac{\lambda^2}{Dq}$
${}^4T_1$	Γ_6	$6Dq - \dfrac{15}{4}\lambda + \dfrac{45}{128}\dfrac{\lambda^2}{Dq}$
	Γ_8^ψ	$6Dq - \dfrac{3}{2}\lambda + \dfrac{9}{8}\dfrac{\lambda^2}{Dq}$
	Γ_7	$6Dq + \dfrac{9}{4}\lambda + \dfrac{45}{128}\dfrac{\lambda^2}{Dq}$
	Γ_8^φ	$6Dq + \dfrac{9}{4}\lambda + \dfrac{261}{128}\dfrac{\lambda^2}{Dq}$

ion and its ligands influence ζ and ζ'. Calculation of these constants for the tetrahedral complex by the MO LCAO method, in which the molecular orbital of the complex is represented in the form of a linear combination of orbitals of the atoms contained in it, yields the following values[6]:

$$\zeta = a_d^2 \zeta_{3d} - ({}^1\!/_2 a_\pi^2 + 2^{1/2} a_\pi a_\sigma) \zeta_{Lp},$$
$$\zeta' = a_d b_d \zeta_{3d},$$

where a_d, b_d, and a_π, a_σ are coefficients characterizing the contributions of the wave functions of the central ion and of its ligands to the antibonding molecular orbitals of the type $t_2(a_i, i = d, \sigma, \pi)$ and $e(b_d)$, ζ_{3d}, and ζ_{Lp} are one-electron spin-orbit interaction constants for the 3d orbital of the central ion and the Lp orbitals of the ligands. The main influence on the change of ζ is exerted by the term with ζ_{Lp}.[1] For the ZnS-Co system we have $\zeta_{3d} = 534$ cm^{-1} and $\zeta_{Lp} \approx 388$ cm^{-1}. As will be shown below, the values of the parameters a_σ and a_π for this system are apparently quite small and we can put $\zeta = \zeta' = \zeta$ (of the free ion).

Table II shows the values obtained for the energies of the spin-orbit components of the terms ${}^4A_2$, ${}^4T_2$, and ${}^4T_1$(${}^4F$) by diagonalizing the spin-orbit interaction matrices in second-order perturbation theory.

The spin-orbit splitting of the term ${}^4T_2$ (accurate to second-order terms) can be described by the effective Hamiltonian

$$\mathscr{H}_{so}({}^4T_2) = \xi(LS) + \mu(LS)^2 + \sigma S^2 + \rho (L_x^2 S_x^2 + L_y^2 S_y^2 + L_z^2 S_z^2), \quad (1)$$

where

$$\xi = \frac{1}{2}\lambda - \frac{4}{5}\frac{\lambda^2}{Dq}, \quad \mu = \frac{11}{40}\frac{\lambda^2}{Dq}, \quad \sigma = \frac{2}{5}\frac{\lambda^2}{Dq}, \quad \rho = -\frac{15}{4}\frac{\lambda^2}{Dq};$$

$L = (L_x, L_y, L_z)$ is a vector operator corresponding to the orbital angular momentum $L = 1$, and $S = {}^3\!/_2$. The first two terms of (1), which depend only on the values of the total angular momentum $J^2 = L^2 + S^2 + 2L \cdot S$, split the ${}^4T_2$ term into levels corresponding to values of J equal to $({}^7\!/_2)(\Gamma_8^\varphi, \Gamma_6)$, $({}^5\!/_2)(\Gamma_8^\psi)$, and $({}^3\!/_2)(\Gamma_7)$, while the last term splits the level $J = {}^7\!/_2$ into two and

mixes the levels Γ_8^φ and Γ_8^ψ. Neglecting this last effect (the corresponding off-diagonal matrix element is quite small), we obtain the energy values listed in Table II in the basis of the 12 functions corresponding to the indicated L and S. The effective Hamiltonian of the term ${}^4T_1({}^4F)$ is given in[8].

2. THE DYNAMIC JAHN-TELLER EFFECT ON THE ${}^4T_2$ TERM

The total Hamiltonian of the system should take into account, besides (1), also the elastic and kinetic energies of the lattice ($\mathscr{H}_{vib}$) and the interaction of the impurity-ion electrons with the crystal vibrations. The latter leads to the appearance in the spectrum of vibronic transitions that accompany the purely electronic transitions. The mechanism of excitation of the vibronic transitions reduces to a change in the equilibrium position of the nuclei in the electronic transition and to a mixing of the electronic states in nuclear vibrations. For the sphalerite structure, the selection rules allow vibronic transitions for all points of high symmetry of the Brillouin zone, and these transitions account for the curve of the vibrational-state density of the crystal, although they do not coincide with it in all details.

The interaction of the degenerate electronic states with tetrahedral-complex vibrations having symmetry E and T_2 disturbs this picture of electronic transitions repeating with frequencies typical of the crystal. If this interaction is small in comparison with the spin-orbit interaction, then it is advantageous to regard it as a perturbation with respect to the Hamiltonian $\mathscr{H} = \mathscr{H}_{so} + \mathscr{H}_{vib}$.[3] To simplify the problem, one usually considers the interaction of the electronic state with the normal vibrations of a certain effective frequency (or two frequencies). Under this assumption, $\mathscr{H}_{vib}$ and the perturbation term $\mathscr{H}_{JT}$ can be written in the form

$$\mathscr{H}_{vib} = {}^1\!/_2\mu^{-1}[P_\vartheta^2 + P_\varepsilon^2 + \mu^2\omega^2(Q_\vartheta^2 + Q_\varepsilon^2) + P_\xi^2 + P_\eta^2 + P_\zeta^2 + \mu^2\omega^2(Q_\xi^2 + Q_\eta^2 + Q_\zeta^2)], \quad (2)$$

$$\mathscr{H}_{JT} = V_E(Q_\vartheta \mathscr{S}_\vartheta + Q_\varepsilon \mathscr{S}_\varepsilon) + V_T(Q_\xi \mathscr{T}_\xi + Q_\eta \mathscr{T}_\eta + Q_\zeta \mathscr{T}_\zeta), \quad (3)$$

where μ is the reduced mass, Q_i $(i = \vartheta, \epsilon)$, Q_j $(j = \xi, \eta, \zeta)$, and P_i, P_j are the normal coordinates and conjugate momenta of the E and T_2 vibrations, while

$\mathscr{E}_i$ and $\mathscr{T}_j$ are electronic operators that can be expressed in terms of L_x, L_y, and L_z[3].

The action of the perturbation (3) should be regarded in the basis of the zeroth-approximation functions, which represent the product of 12 electronic wave functions (the eigenfunctions of $\mathscr{H}_{SO}$) by the eigenfunctions of the harmonic oscillator corresponding to the E or T_2 vibration. The perturbation mixes the vibronic levels belonging to the same as well as to different electronic states (within the limits of a given term). In accordance with the selection rules for the harmonic oscillator, the vibration quantum numbers n_i and n_j can change by ± 1.[2] When terms with $n_i = 1$ are taken into account, the perturbation matrix for the E vibration has a rank corresponding to the sum $(\Gamma_6 + \Gamma_7 + 2\Gamma_8) + (\Gamma_6 + \Gamma_7 + 2\Gamma_8) \times \Gamma_3 = 3\Gamma_6 + 3\Gamma_7 + 6\Gamma_8$, and breaks up into a sixth-rank matrix (Γ_8) and two third-rank matrices (Γ_6 and Γ_7). When terms with $n_i = 2, 3$, etc. are taken into account, it is necessary to use in place of Γ_3 the symmetrized products $\Gamma_3 \times \Gamma_3$, $\Gamma_3 \times \Gamma_3 \times \Gamma_3$, etc.

For the E vibration we constructed the perturbation matrices for $n_i = 1, 2$, and 3. Solution of the corresponding secular equations with a BESM-4 computer has shown that if we are interested only in the lower energy levels that include the excitation of the zero and one quanta of the E vibrations, then inclusion of the terms $n_i = 3$ changes only insignificantly the level position obtained with allowance for the terms $n_i = 2$. We have therefore confined ourselves to $n_j = 2$ for the T_2 vibration. Since the second-order correction for the level Γ_8^{φ} (Table II) has a value $\sim\lambda$, we used for the initial values of the levels $n_i = 0$ and $n_j = 0$ the exact values obtained by diagonalizing the spin-orbit interaction matrices with the computer. The resultant values of the energy (they are shown at the top in Figs. 3b and 4) differed negligibly from the values obtained in second-order perturbation theory, with the exception of the levels Γ_8^{φ}, for which the correction reached 20 cm^{-1}.[3]

Figure 2 shows the positions of the energy levels corresponding to the zeroth and first vibronic levels in the frequency range 0—30 cm^{-1}, obtained with allowance for the interaction of the term $^4T_2$ with the E and T_2 vibrations (n_i, $n_j = 2$) with frequency $\hbar\omega = 300$ cm^{-1}.[4] The designations of the vibronic levels point to their

origin. For example, Γ_8: $\Gamma_8^{\varphi} + \hbar\omega$ in Fig. 2a denotes a level having a symmetry Γ_8 and connected with the transition of the Co^{2+} ion to the state $\Gamma_8^{\varphi}(^4T_2)$ and excitation of one E-vibration quantum. The abscissas represent the energy of the JT interaction, which characterizes the depth of the potential energy minimum and is connected with the coefficients V_E and V_T by the relations

$$E_{JT} = V_E^2 / 2\mu\omega^2, \quad E_{JT} = 2V_T^2 / 3\mu\omega^2.$$

As seen from Fig. 2, the JT interaction leads to a shift and mixing of different vibronic levels. The latter is indicated on the right in the form of the coefficients representing the contribution made to the vibronic functions by the corresponding electronic states (for $E_{JT} = 150$ cm^{-1}). The mixing of the electronic states into the terms n_i, $n_j \neq 0$ leads (for the case of weak or moderate electron-vibrational interaction) to a transfer of the intensities from the purely electronic lines into the vibronic ones, i.e., to excitation of vibronic lines.

To ascertain the extent to which the resultant picture is sensitive to the exact position of the electronic energy levels, the position of these levels was varied in a range 20—30 cm^{-1}. It turned out that these vibrations have little effect on the relative positions of the vibronic levels.

3. EXPERIMENTAL RESULTS AND THEIR DISCUSSION

We investigated the absorption and luminescence spectra of ZnS:Co crystals obtained by hydrothermal synthesis and from the melt under pressure. The former had the structure of sphalerite, while the latter contained an appreciable ($\approx 10\%$) concentration of stacking faults, layers arranged in accordance with a hexagonal stacking that is not in equilibrium at room temperature. To decrease the stacking-fault concentration, the crystals were roasted for 10—12 hours at T = 800°, and this decreased the indicated concentration by one half. The Co content in the crystals was 0.01—0.2 wt%. The absorption spectra were recorded with Spectromaster and Perkin-Elmer Model 225 spectrophotometers, and the luminescence spectra were recorded with the SDL-1 apparatus. The crystals were cooled to T = 4.2°K.

The spectra of the crystals with the stacking faults were made complicated by the peculiar presence of optical centers of many types in these crystals, owing to the intrusion of the activator into close-packing layers that differed in structure. This phenomenon has been investigated in detail in our earlier studies[9,10] and will not be considered here. Figures 3b and 4 show the ZnS:Co crystal absorption bands at 2.2—2.9 μ (transition $^4A_2 \to ^4T_2$) and 1.2—1.7 μ ($^4A_2 \to ^4T_1$ transition). The lines α(3398 cm^{-1}) and β(3500 cm^{-1}) in Fig. 3b are connected with the Co^{2+} ions in the stacking faults. The luminescence spectrum of the crystal is shown in Fig. 3a. The line frequencies (reckoned from the "frontal" lines of the transitions) are given in Table III. As seen from Figs. 3b and 4, the total width of the bands (after subtracting the phonon "tail") agrees in general with the picture of the spin-orbit splitting of the $^4T_2$ and $^4T_1$ terms, calculated under the assumption that $\zeta = \zeta' = \zeta$ (of the free ion), and thus the spin-orbit interaction is not suppressed either by covalence or as a consequence of the JT effect. However, the picture itself, i.e., the number of components (after subtracting
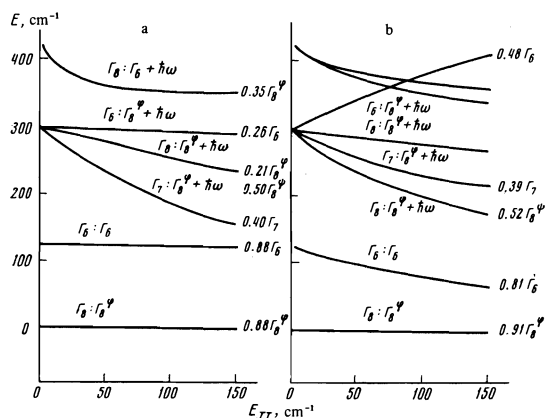

FIG. 2. Relative energies of the spin-orbit levels Γ_8^{φ}, Γ_6, and their vibrational replicas with excitation of one phonon E(a) and T_2 vibrations (6) as a function of the JT-interaction energy. $\hbar\omega = 300$ cm^{-1}, $\zeta = \zeta' = \zeta$ (of the free ion). The energies are given relative to the energy of the level Γ_8^{φ}. On the right are indicated the contributions of the electronic (phononless) wave functions to the wave functions of the corresponding vibronic states at the value $E_{JT} = 150$ cm^{-1}.
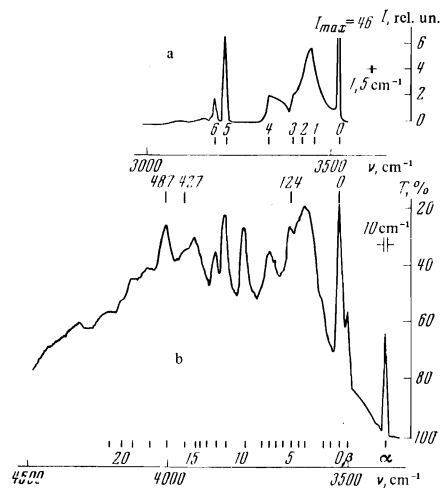
FIG. 3. Absorption (b) and luminescence (a) bands corresponding to the $^4A_2 \rightleftharpoons {}^4T_2$ transition. The lines connected with the transition $\Gamma_8(^4A_2) \rightarrow \Gamma_8^\varphi(^4T_2)$ are made congruent. The frequencies of the other lines (singular points) are given in Table III.
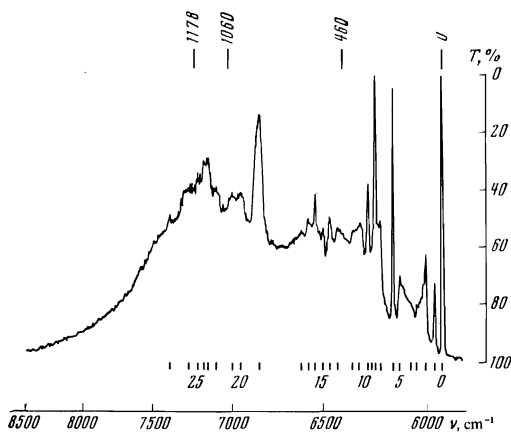

FIG. 4. Absorption band corresponding to the $^4A_2 \rightarrow {}^4T_1$ (^4F) transition. The line frequencies are given in Table III.

TABLE III. Structure of luminescence bands and absorption bands of the Co^{2+} ion in a AnS:Co crystal.

Transition $^4T_2 \rightarrow {}^4A_2$ 0(3518 cm^{-1})		Transition $^4A_2 \rightarrow {}^4T_2$ 0(3518 cm^{-1})			Transition $^4A_2 \rightarrow {}^4T_1$ 0(5935 cm^{-1})			
Line No.	v, cm^{-1}	Line No.	v, cm^{-1}	Line No.	v, cm^{-1}	Line No.	v, cm^{-1}	Line No.	v, cm^{-1}
0	0	α	--120	10	250	0	0	14	555
1	70	β	--18	11	303	1	35	15	529
2	95	0	0	12	331	2	72	16	597
3	120	1	24	13	362	3	111	17	631
4	189	2	43	14	380	4	133	18	669
5	305	3	88	15	394	5	186	19	898
6	336	4	103	16	425	6	222	20	1000
		5	125	17	484	7	279	21	1053
		6	146	18	539	8	299	22	1152
		7	165	19	598	9	315	23	1198
		8	181	20	636	10	335	24	1223
		9	206	21	677	11	374	25	1244
						12	410	26	1327
						13	484	27	1438

their replicas with limiting lattice-vibration frequencies) and their relative disposition do not agree with the theory of spin-orbit interaction. The luminescence spectrum connected with the transition to the orbital singlet makes it possible to reconstruct the form of the vibronic spectrum accompanying the $^4T_2 \rightarrow {}^4A_2$ transition[11]. In this spectrum, in particular, there clearly appears a gap between the acoustic and optical modes (205–276 cm^{-1}).

A comparison of the absorption and luminescence spectra corresponding to the $^4A_2 \rightleftharpoons {}^4T_2$ transition (Fig. 3) reveals those spectral singularities that are connected with the orbital degeneracy of the $^4T_2$ term. These include primarily the rather narrow absorption band 10 in the region of the gap, as well as the bands 8 and 9. These bands cannot be connected with either the spin-orbit components of the $^4T_2$ term (their position is indicated in Fig. 3b) or with the vibronic transitions to these components with limiting frequencies of the lattice vibrations (there are no symmetrical lines in the luminescence spectrum). Nor can these bands be due to quasilocal vibrations, since it is unlikely that the transition in the internal 3d shell would be accompanied by a strong change in the force constants, leading to the appearance of these vibrations. The presence of bands 8–10 in the absorption spectrum points to an interaction between the vibronic states in the sense considered in Sec. 2. As follows from the results of this section, the interaction with both vibration modes leads to the appearance of lines whose frequencies are shifted relative to the vibration frequency and fall in the region of the gap between the acoustic and optical branches. In both cases, the most intense vibronic line falls in the region of the gap at $E_{JT} \approx 100$ cm^{-1} $< \lambda = 178$ cm^{-1} $< \hbar\omega = 300$ cm^{-1}. Thus, the JT effect is indeed weak in this case. The picture shown in Figs. 2a and 2b are in general close to each other; to choose between them, it is necessary to investigate in detail the symmetries of all the singular points of the band by studying the magnetic dichroism, the linear dichroism under uniaxial compression, or the polarization characteristics of the absorption and luminescence spectra.

As follows from Fig. 2, the lower vibronic level of the $^4T_2$ term has in any case the symmetry Γ_8 and its fourfold degeneracy is in the main electronic (rather than vibronic) in nature. As shown by piezospectroscopic experiments, the 3518 cm^{-1} line, at all directions of uniaxial compression, splits into two components; this splitting reaches 16 cm^{-1} at a load of 25 kg/mm^2[10].

Some differences in the absorption and luminescence spectra in the low-frequency region of the spectrum apparently offer evidence of interaction of the considered transition not only with the optical but also with the acoustic phonons.

In the 1.2–1.7 μ absorption band (Fig. 4), attention is called to line 6, which like line 10 in the 2.2–2.9 μ band, cannot be explained without making use of the dynamic JT effect. The narrowness of this line and the character of the piezospectroscopic effect on it offer evidence that it has, in the main, an electronic nature and apparently corresponds to a transition to the Γ_8^ψ level, which is shifted relative to the Γ_6 level as a result of the JT interaction. We note also the lines 1 and 7, which probably have a predominantly vibronic nature.

The present study and[4] show that even a weak JT interaction which does not lead to suppression of the orbital angular momenta or of other electronic operators significantly alters the form of the impurity-ion spectrum and in many cases can be reliably identified. In ZnS crystals activated with transition-metal ions, the JT interaction of the degenerate levels with a narrow band of the extreme TO phonons leads to the appearance of relatively narrow vibronic bands in the spectra. Thus, for these systems the concept of effec-

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tive vibration frequency is not merely a simple mathematical device that makes it possible to avoid considering the interaction of the degenerate term with the entire vibration spectrum of the crystal, but reflects the actual distinguishing features of the electron-vibrational interaction in these systems.

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[1] This term leads even to a reversal of the sign of ζ in the case of the Cr^{2+} ion in ZnTe or CdTe [7].

[2] In the calculation of the vibrational matrix elements we have assumed that the oscillators have one and the same (unshifted) equilibrium position at different minima of the potential energy. This assumption, generally speaking, is incorrect (the dynamic JT effect itself is due to migrations of the system between equivalent minima), but has a justification if the spin-orbit splitting picture is not contracted (see below), since the contraction characterizes the overlap integral between the wave functions of the oscillators at different minima.

[3] The parameters used were $\lambda = 178$ cm^{-1} and $Dq = 375$ cm^{-1}.

[4] This frequency is close to the limiting frequencies of the TO phonons in the sphalerite lattice. As a rule, it becomes manifest in the form of intense maxima in the vibronic spectra of ZnS crystals activated with transition-metal ions.

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