A microscopic determination of the Jahn–Teller interaction energy in a ZnS–Co crystal

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We investigate the piezospectroscopic effect for the $^4A_2 \to {}^4T_2$ transition in the ZnS–Co crystal. the deformation potentials of the $^4T_2$ term of the Co^{2+} ion are determined. The potentials are calculated for a certain model of the crystal field (exchange-charge model), and the part connected with the nearest neighbors of the impurity ion (ligands) is separated. The dynamics of ZnS crystals are calculated and the projections of the density of the vibrational states in the ligand displacement space are determined. The energy of electron–vibrational interaction between an impurity ion and non-fully-symmetrical vibrations, which are active in the Jahn–Teller effect, is found.

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INTRODUCTION

A lattice defect alters the vibration spectrum of a crystal because of the associated changes in the mass and the force constants. The presence of weakly bound electrons in the defects (the electronic-transition frequencies are of the order of the oscillation frequencies)[1] offers another possibility of perturbing the vibration spectrum on account of the electron-vibrational interaction components that are linear in the displacements of the nuclei. The oscillations mix effectively the closely lying levels; this gives rise to states that are superpositions of electronic and vibrational states, and whose energies differ from the energies of the bare states. These new states can be called local or resonant, depending on the degree of localization near the defect, a degree determined by manner in which the states decay.[2] The effect has a resonant character.

In the case of a truly degenerate (and not quasi-degenerate) electron level, interaction with non-fully-symmetrical vibrations that are active in the Jahn–Teller (JT) effect) gives rise to a shift of the equilibrium positions of the nuclei that neighbor on the defect, along directions determined by the symmetry Γ_k of the electronic level and by the vibrations that interact with it. The symmetry of the latter depends on the irreducible representations (other than the fully-symmetrical one) are contained in the symmetrized product $\{\Gamma_k \times \Gamma_k\}$. Each of the oscillation modes determined by this condition corresponds to several equivalent distorted nuclear configurations, between which migration takes place. Then, just as in the quasi-degeneracy case, localized states are produced having only a genetic connection with the electronic and the vibrational states from which they stem, and frequencies are produced that are shifted relative to the frequencies of these states. Electronic resonance of the degenerate levels plays here the same role as resonance of electronic and vibrational levels in quasi-degeneracy.

In a number of papers[2–7] (including our own,[4] henceforth designated I), the resonant and local states of such type were determined for a number of systems from an analysis of the electron-vibrational spectra corresponding to transitions to orbitally degenerate levels of impurity ions of transition metals. In these studies, the real crystal vibration spectrum was approximated by a large number (from 1 to 4) of effective oscillators of definite symmetry, the infinite set of electron-vibrational states was cut off at terms with sufficiently small values of n (vibrational quantum number), and the matrices of the spin-orbit interaction and the electron-vibrational interaction were diagonalized; a constant (or constants) regarded as a variable parameter and the matrix operator determined by the symmetry of the vibrations and of the electronic level, are separated in the Hamiltonian of the electron-vibrational interaction. The electron-vibrational interaction energies (E_{JT}, see below) obtained from the best fit to the experimental data are equal to ~ 100 cm^{-1}, i.e., they are of the order of the spin-orbit splitting and of the frequencies of the actual vibrations, so that the electron-vibrational interaction in these systems can be regarded as intermediate.

In contrast to this phenomenological treatment, we attempt in this paper to develop a microscopic picture of the electron-vibrational interaction for the $^4T_2$ term of the Co^{2+} ion in a ZnS crystal. To this end we investigate the piezospectroscopic effect in the $^4A_2 \to {}^4T_2$ transition (Sec. 1), determine the deformation potentials, i.e., the constants characterizing the action of various symmetrical components of the strain tensor on the $^4T_2$ term, determine the electron-vibrational interaction constants for the same term within the framework of the model of the complex (Sec. 2), and take into account the dispersion of the vibrations in the crystal (Sec. 3).

1. EXPERIMENTAL RESULTS

The $^4T_2$ term of the tetrahedrally coordinated Co^{2+} ion is split by the spin-orbit interaction into four levels: Γ_8^φ (lower), Γ_6, Γ_8^ψ, and Γ_7 (see Fig. 1 of I). The structures of the absorption and luminescence spectra connected with the $^4A_2 \to {}^4T_2$ transition have been considered earlier in I (see also[5]). In the present study we investigate the action of uniaxial compression on the leading line of the absorption band (the transition $\Gamma_8(^4A_2) \to \Gamma_8^\varphi(^4T_2)$).

The ZnS–Co crystals ($c_{Co} - 0.1$ at.%) constituted a sphalerite microtwin with a concentration of stacking faults (i.e., layers stacked in accordance with the hexagonal packing law) of $\approx 10\%$. The pressure P was applied along the twinning axis [111] and in the plane {111} perpendicular to it, in which the directions for the two twins

TABLE I. Characteristics of the piezospectroscopic effect at the level $\Gamma_8^\varphi(^4T_2)$ (in units of $cm^{-1}/100$ kgf cm^{-2}).

	Experiment		Calculation	
	Cubic centers	Trigonal centers	$Z=0$	$Z=1$
Δ_{001}	1.42	1.12	1.02	1.09
Δ_{111}	0.029	0.031	0.063	0.055
Δ_0	−0.032	−0.026	−0.044	−0.044

were equivalent. We shall henceforth indicate only one of the two equivalent directions. Samples cut in the form of parallelepipeds with edges along the directions $[\bar{1}10]$, $[\bar{1}12]$, [111] and with typical dimensions 2×2×4 mm were placed in a helium cryostat equipped with a device to apply the pressure. The spectra were recorded with an SDL-1 spectrometer.

The piezospectroscopic effect was investigated on the 3524 cm^{-1} line of the cubic centers and on the 3403 line of the trigonal centers (Co^{2+} ions in stacking faults). The results obtained for both lines are shown in Fig. 1.

The splitting of the lines in the case of uniaxial compression of the crystal is a reflection of the splitting of the upper level of the transition $\Gamma_8^\varphi(^4T_2)$, since the ground state $^4A_2$ of the Co^{2+} ion, being an orbital singlet, is not split (in first-order perturbation theory). An analysis of the experimental data by means of Kaplyanskiĭ's formulas[8] has made it possible to determine the values of the shift[3)] Δ_0 and the splittings of the level $\Gamma_8^\varphi(^4T_2)$ if P is applied along [111] (Δ_{111}) and along [001] (Δ_{001}). These splittings are proportional to the deformation potentials of this level (Table I). In the calculations we used the following values of the parameters:

$$D_q=385\,\mathrm{cm}^{-1},\quad \overline{r^2}=1.3449\ a_0^2,\quad \overline{r^4}=4.7348\ a_0^4,$$
$$G(Z=0)=4.90,\quad G(Z=1)=4.37.\quad S_s=0.0608,$$
$$S_\sigma=0.0746,\quad S_\pi=0.0499,\quad S_S'=-0.0420\ a_0^{-1},$$
$$S_\sigma'=-0.0294\ a_0^{-1},\quad S_\pi'=-0.0406\ a_0^{-1}.$$

A characteristic feature of the piezospectroscopic effect on the considered level is the strong anisotropy of the deformation potentials.

2. ANALYSIS OF THE DEFORMATION POTENTIALS AND ELECTRON VIBRATIONAL INTERACTION CONSTANTS OF THE Co^{2+} ION IN THE $^4T_2$ STATE

In the representation of the fictitious angular momentum $\tilde{S}=\frac{3}{2}$, the wave functions of the spin-orbit quadruplet $\Gamma_8^\varphi(^4T_2)$ investigated in the piezospectroscopic experiments described above, are equal to

$$|\pm\tilde{^3/_2}\rangle=\mp\frac{1}{\sqrt{30}}(\sqrt{3}|\pm\tilde{1},\pm{}^1/_2\rangle+\sqrt{2}|\tilde{0},\pm{}^3/_2\rangle+5|\mp\tilde{1},\mp{}^3/_2\rangle),$$
$$|\pm\tilde{^1/_2}\rangle=\pm\frac{1}{\sqrt{30}}(3|\pm\tilde{1},\mp{}^1/_2\rangle+3\sqrt{2}|\tilde{0},\pm{}^1/_2\rangle+\sqrt{3}|\mp\tilde{1},\pm{}^3/_2\rangle), \tag{1}$$

where $|\tilde{l}_z, S_z\rangle$ is the wave function of the term $^4T_2$ ($S=\frac{3}{2}$) in the representation of the fictitious angular momentum $\tilde{l}=1$.

Under uniaxial deformation, the shift and splitting of the level Γ_8^φ are determined by the parameters of the effective Hamiltonian acting in the space of the functions (1)

$$\mathscr{H}(\Gamma_8^\varphi)=Ae(\Gamma_1)+B\sum_{\lambda=1,2}\hat{Q}_\lambda(\Gamma_3)e_\lambda(\Gamma_3)+C\sum_{\lambda=1,2,3}\hat{Q}_\lambda(\Gamma_5)e_\lambda(\Gamma_5), \tag{2}$$

where $e_\lambda(\Gamma)$ are linear combinations of the components of the homogeneous strain tensor e_{ij}, which transform in accord with row λ of the irreducible representation Γ of the group T_d

$$e(\Gamma_1)=\frac{e_0}{\sqrt{3}}=\frac{1}{\sqrt{3}}(e_{xx}+e_{yy}+e_{zz}),$$
$$e_1(\Gamma_3)=\frac{1}{2\sqrt{3}}(3e_{zz}-e_0),\quad e_2(\Gamma_3)=\frac{1}{2}(e_{xx}-e_{yy}),$$
$$e_i(\Gamma_5)=e_{jk},\quad (i\neq j\neq k),$$
$$\hat{Q}_1(\Gamma_3)=3\hat{\tilde{S}}_z^2-\tilde{S}(\tilde{S}+1),\quad \hat{Q}_2(\Gamma_3)=\sqrt{3}(\hat{\tilde{S}}_x^2-\hat{\tilde{S}}_y^2),$$
$$\hat{Q}_i(\Gamma_5)=\frac{1}{2}(\hat{\tilde{S}}_j\hat{\tilde{S}}_k+\hat{\tilde{S}}_k\hat{\tilde{S}}_j),\quad (i\neq j\neq k),$$

A, B, and C are the potentials of the hydrostatic, tetragonal and trigonal deformation, respectively.

Expressing the components of the strain tensor in terms of the external pressure P and the elastic constants C_{ij} of the sphalerite lattice, and diagonalizing the Hamiltonian (2), we obtain the isotropic shift

$$A_0=-\frac{AP}{\sqrt{3}(C_{11}+2C_{12})} \tag{3}$$

and the splittings of the level Γ_8^φ at P along [001] and P along [111]

$$\Delta_{001}=\frac{2\sqrt{3}BP}{C_{11}-C_{12}},\quad \Delta_{111}=\frac{CP}{2C_{44}}. \tag{4}$$

The deformation potentials are linear functions of the parameters b_n^m, determined in preceding paper,[9] of the Hamiltonian of the $3d$ electron localized on a cation site of a homogeneously deformed sphalerite lattice

$$A=\frac{2}{5}b_4(\Gamma_1),\quad B=-\frac{28}{75}b_4^0,\quad C=\frac{1}{30}\left(b_2^1+\frac{4}{5}b_4^1\right). \tag{5}$$

The potentials of (5) were calculated within the framework of the model of pointlike exchange charges (see[9]), in which explicit account was taken of the Coulomb interaction of the $3d$ electron with all the pointlike ions in the lattice, and the contribution to the energy of the im-

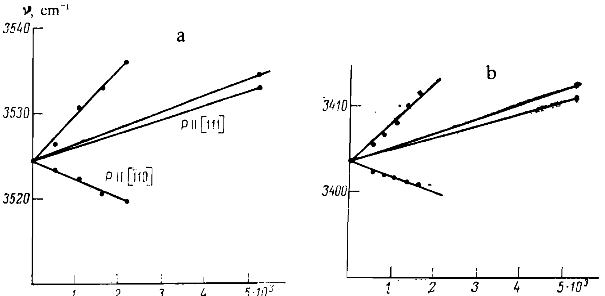

FIG. 1. Piezospectroscopic effect on the lines 3524 cm^{-1} (a) and 3403 cm^{-1} (b) in the ZnS-Co crystal.

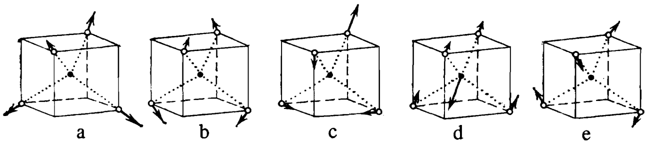

FIG. 2. Symmetrized deformations of the tetrahedral complex, characterized by normal coordinates: a—fully symmetrical deformation Γ_1; b—tetragonal Γ_3, c—trigonal (macroscopic) Γ_5^a, d—trigonal (microscopic) Γ_5^b, e—rotation Γ_4.

purity ion from the overlap of the electron clouds of its valence electrons and the ligands is approximated by a quadratic form of the corresponding overlap integrals with one phenomenological parameter determined from the Stark structure of the $3d$-shell spectrum.

We write down the deformation potentials (5) in explicit form in terms of the parameters of the models, and separate the contributions A_1, B_1, and C_1, which correspond to the energy of the interaction of the $3d$ electrons with the nearest neighbors (four S ions in the vertices of a tetrahedron):

$$A=A_1+\Delta A, \quad B=B_1+\Delta B, \quad C=C_1^{(e)}+C_1^{(W)}W+C_1^{(D)}D+\Delta C, \tag{6}$$

$$A_1=-\frac{16}{45}\frac{e^2G}{r_0}(RS_4'-S_4)+\frac{640}{729}\frac{e^2\overline{r^4}}{r_0^5}Z, \quad \Delta A=-0.076\frac{e^2\overline{r^4}}{r_0^5}Z, \tag{6a}$$

$$B_1=\frac{128}{135}\frac{e^2G}{r_0}S_4+\frac{1024}{2187}\frac{e^2\overline{r^4}}{r_0^5}Z, \quad \Delta B=0.201\frac{e^2\overline{r^4}}{r_0^5}Z, \tag{6b}$$

$$C_1^{(e)}=\frac{16}{945}\frac{e^2G}{R}(14S_4-3S_2'R-4S_4'R)+\frac{16}{315}\frac{e^2\overline{r^2}}{R^3}Z+\frac{80}{567}\frac{e^2\overline{r^4}}{R^5}Z,$$

$$C_1^{(W)}=\frac{8}{945}\frac{e^2G}{R}(9S_2-3S_2'R-16S_4-4S_4'R)+\frac{4}{63}\frac{e^2\overline{r^2}}{R^3}Z, \tag{6c}$$

$$C_1^{(D)}=\frac{4}{63}\frac{e^2\overline{r^2}}{R^3}Z; \quad \Delta C=-\frac{e^2\overline{r^2}}{r_0^3}Z[0.0185+0.0093(W+D)]+0.0528\frac{e^2\overline{r^4}}{r_0^5}Z.$$

Here $2r_0$ is the lattice constant, $R=\sqrt{3}r_0/2$ is the radius of the first coordination sphere, $Z|e|$ is the charge of the Zn ion, $\overline{r^n}$ is the mean value of the n-th degree of the radius of the $3d$ orbital, $S_n=S_s^2+S_\sigma^2+k_nS_\pi^2$, $k_2=1$, $k_4=-\frac{4}{3}$; S_s, S_σ, S_π are the overlap integrals of the $3d$ function with the $3s$, $3p\sigma$, and $3p\pi$ functions of sulfur, $S_n'=dS_n/dR$; G is a parameter of the model and can be found at a fixed value of Z from the difference between the energies of the e and t_2 states of the $3d$ electron in the static crystal field of sphalerite[9]

$$10Dq=\frac{8}{3}\frac{e^2G}{R}S_4+1.389\frac{e^2\overline{r^4}}{r_0^5}Z. \tag{7}$$

We have separated in the trigonal deformation potential (see (6c)) the terms due to the displacement ($C_1^{(W)}$) and polarization ($C_1^{(D)}$) of the sublattice of the sulfur ions relative to the sublattice of the zinc ions (see Fig. 2). The internal microscopic deformation that produces the piezoelectric effect in the sphalerite lattice is characterized by dimensionless parameters W and D,[9] the values of which were obtained in the shell model by using the parameters of model II of the dynamics of the sphalerite lattice[10]: $W=-1.48$, $D=2\cdot10^{-4}/Z$; these values were used in the calculation of the potential of the trigonal deformation C. The mean values $\overline{r^n}$, the overlap integrals, and their derivatives were calculated with the atomic wave functions of Co and S.[11] Since the effective charge on the ions Zn in ZnS is close to 0.7,[12] the values of the parameter G were obtained from (7) at $Z=0$ and $Z=1$, and were cited above.

The results of the calculation of the deformation potentials are given in Table II, while the experimental characteristics of the piezospectroscopic effect on the transition $\Gamma_8(^4A_2)\to\Gamma_8^\varphi(^4T_2)$ and those calculated from Eqs. (3) and (4) are compared in Table I.[4)]

The agreement between experiment and a theory that uses no fit parameters whatever can be regarded as satisfactory, and this gives grounds for using the exchange-charge model for the separation of the contributions made to the trigonal deformation potential by two types of trigonal deformation. The strong anisotropy of the effect is due, first, to the peculiarity of the wave functions of the T_2 state produced as a result of the Stark splitting of the F state of the free ion, and second, to the partial cancellations of the contributions to the combined potential of the trigonal deformation C from the macroscopic ($C_1^{(e)}$) and microscopic ($WC_1^{(W)}$) deformations.[5)] In the case $Z=0$, for example, the contribution to the specific splitting Δ_{111} from the macroscopic deformation (at $W=D=0$) is $\Delta_{111}^{(e)}=0.147$ cm^{-1}/100 kgf/cm^2, while the contribution of the microscopic deformation is $\Delta_{111}^{(W,D)}=-0.084$ cm^{-1}/100 kgf/cm^2.

As seen from Tables I and II, a change of the effective charge, within reasonable limits, exerts no essential influence on the results of the calculation, i.e., the contribution of the ion charges to the deformation potentials is relatively small, and the greater part of this contribution is connected with the ligands, (i.e., $A_1\gg\Delta A$, $B_1\gg\Delta B$, $C_1\gg\Delta C$). Consequently, when considering the electron-vibrational interaction we can confine ourselves to allowance for the interaction of the impurity ion only with the vibrations of the nearest neighbors. An arbitrary deformation (static or dynamic) of the tetrahedral complex CoS$_4$ can be resolved in the symmetrical coordinates $Q_\lambda(\Gamma)$ that form the bases of the irreducible representations Γ_1, Γ_3, Γ_5^a, Γ_5^b, Γ_4 of the group T_d—Fig. 2. The Hamiltonian of the lattice with isolated impurity ion in the state $^4T_2$ will be expressed in the form

$$\mathscr{H}=\Big\{\mathscr{E}_0+\sum_{qj}\hbar\omega_j(q)\Big[a_{qj}^+a_{qj}+\frac{1}{2}\Big]\Big\}I+\frac{1}{2}\lambda(\mathit{l}S)+\sum_{\lambda,i}\hat{V}_\lambda(\Gamma_i)Q_\lambda(\Gamma_i),$$

$$(\lambda,\ i=1,3,4,5^a,5^b), \tag{8}$$

TABLE II. Deformation potentials of the level $\Gamma_8^\varphi(^4T_1)$ and of the electron-vibrational interactions constants of the $^4T_2$ term (in cm^{-1}).

Z	A	B	C	$A_1=r_0V(\Gamma_1)$	$B_1=\frac{2\sqrt{2}r_0V(\Gamma_3)}{15}$	$C_1^{(e)}=-\frac{2\sqrt{2}r_0V(\Gamma_5^a)}{15}$	$C_1^{(W)}=-\frac{2r_0V(\Gamma_5^b)}{15}$
0	1799	1185	579	1799	1185	1380	541
1	1844	1257	520	1867	1197	1549	699

where $\mathscr{E}_0$ is the energy of the $^4T_2$ level, I is a unit matrix, λ is the spin-orbit interaction constant,[6] a_{qj}^+ and a_{qj} are the creation and annihilation operators of phonons with wave vector q and frequency $\omega_j(\mathbf{q})$ from the branch j.

The parameters of the electron-vibrational interaction in the electronic operators, $\hat{V}_\lambda(\Gamma_i)$, can be connected with the deformation potentials of the spin-orbit state, $\Gamma_8^\varphi(^4T_2)$, by expressing the symmetrical coordinates of the CoS_4 complex, which are induced by the long-wave lattice vibration, in terms of the component of the dynamic deformation constant

$$Q_\lambda(\Gamma_1)=r_0e(\Gamma_1),\quad Q_\lambda(\Gamma_3)=\sqrt{2}r_0e_\lambda(\Gamma_3),\quad Q_\lambda(\Gamma_5{}^a)=\sqrt{2}r_0e_\lambda(\Gamma_5),$$
$$Q_\lambda(\Gamma_5{}^b)=r_0We_\lambda(\Gamma_5),\quad Q_\lambda(\Gamma_4)=\sqrt{2r_0}\theta_\lambda, \tag{9}$$

where θ_i are the components of the axial vector of the rotations. Taking the spin-orbit interaction into account, the effective Hamiltonian of the electron-rotational interaction in the basis $|\tilde{l}_z, S_z\rangle$ of the term $^4T_2$ is equal to

$$\mathscr{H}^{(\theta)}=-(\lambda\theta/4)\,[\hat{S}\hat{l}]=-(\lambda/4\sqrt{2r_0})\,Q(\Gamma_4)\,[\hat{S}\hat{l}].$$

The corresponding coupling constant λ/r_0 is smaller by two orders of magnitude than the coupling constants with the vibrations of symmetry Γ_1, Γ_3, Γ_5 (see below) and will henceforth be assumed equal to zero.

The representations Γ_1 and Γ_3 are encountered in the expansion of the deformation of the complex one time each, and the corresponding deformation potentials A and B of the level Γ_8^φ characterize directly the electron-vibrational interaction of the term $^4T_2$ with the vibrations of the same symmetry. However, the trigonal deformation potential C by itself yields no information on the interaction with the trigonal vibrations Γ_5^a and Γ_5^b. The two types of trigonal deformation arise simultaneously under uniaxial compression, and the piezospectroscopic experiments yield the result of their joint action. Their contributions can be separated only within the framework of some crystal-field model; this is why we have used the exchange-charge model in the present paper.

In a real basis made up of eigenfunctions of the fictitious angular momentum $\tilde{l}$, viz., ψ_X, ψ_Y, and ψ_Z (see[13], p. 284 of the Russian translation), the effective interaction of the Hamiltonian of the ion Co^{2+} in the state $^4T_2$ with degenerate oscillations takes the form

$$\mathscr{H}_{JT}=V(\Gamma_3)\,[\hat{\mathscr{E}}_\theta Q_1(\Gamma_3)+\hat{\mathscr{E}}_\varepsilon Q_2(\Gamma_3)]$$
$$+\sum_{i=XYZ}[V(\Gamma_5{}^a)Q_i(\Gamma_5{}^a)+V(\Gamma_5{}^b)Q_i(\Gamma_5{}^b)]\,\hat{T}_{2i},$$

where the operators $\hat{\mathscr{E}}_\vartheta$, $\hat{\mathscr{E}}_\varepsilon$, $\hat{T}_{2i}$ are given in the book of Abragam and Bleaney (p. 285 of the Russian translation), while the coupling constants, with (2) and (9) taken into account, are equal to (the constant of the coupling with fully-symmetrical vibrations is equal to $V(\Gamma_1)=A_1/r_0$)

$$V(\Gamma_3)=\frac{15B_1}{2\sqrt{2}\,r_0},\qquad V(\Gamma_5{}^a)=-\frac{15C_1^{(e)}}{2\sqrt{2}\,r_0},\qquad V(\Gamma_5{}^b)=-\frac{15C_1^{(W)}}{2r_0} \tag{10}$$

(we neglect the polarization of the sulfur ions in the course of the vibrations).

As seen from Table II, the constants of the coupling with the tetragonal and trigonal vibrations are of the same order of magnitude. The change produced in the energy of the $^4T_2$ term by the electron-vibrational interaction can be approximately estimated within the framework of the one-mode model; in particular, if we neglect the interaction with the trigonal vibrations and put $\lambda=0$, then

$$E_{JT}=V^2(\Gamma_3)/2\mu\omega_{eff}^2, \tag{11}$$

where μ is the mass of the sulfur atom and ω_{eff} is the frequency of the vibrations of symmetry Γ_3.[7] Putting $\omega_{eff}=300\ cm^{-1}$ (see below), we obtain from (10) and (11) (at $Z=0$) $E_{JT}=32\ cm^{-1}$,[8] i.e., E_{JT} is comparable in magnitude with the $^4T_2$-term splitting due to the spin-orbit interaction. This circumstance demonstrates the need for simultaneously taking into account, in the calculation of the JT effect, both the interactions with the Γ_3 and Γ_5 vibrations and the spin-orbit interaction.

3. ELECTRON VIBRATIONAL INTERACTION WITH CONTINUOUS VIBRATION SPECTRUM

The value of E_{JT} in the case $\lambda=0$, $V(\Gamma_5^a)=V(\Gamma_5^b)=0$ can be calculated also with account taken of the dispersion of the lattice vibrations. Expanding the symmetrical coordinates $Q_\lambda(\Gamma_3)$ in the normal coordinate of the impurity lattice

$$Q_\lambda(\Gamma)=\sum_f Q_\lambda(\Gamma,f)\,(a_f+a_f{}^+)\,(\hbar/2\omega_f)^{1/2} \tag{12}$$

($f=(\mathbf{q},j)$ in the regular lattice), after substituting (12) in (8) and eliminating the terms linear in a_f and a_f^+, we obtain a system energy shift by an amount

$$E_{JT}(\Gamma_3)=\frac{V^2(\Gamma_3)}{2}\sum_f\frac{|Q_\lambda(\Gamma_3,f)|^2}{\omega_f{}^2}. \tag{13}$$

Introducing the Green's function of the impurity lattice in the space of the symmetrical coordinates

$$G_D(\Gamma,\Gamma',\omega^2)=\sum_f\frac{Q_\lambda(\Gamma,f)Q_\lambda{}^*(\Gamma',f)}{\omega^2-\omega_f{}^2-i\varepsilon},$$

we obtain from (13)

$$E_{JT}(\Gamma_3)=\frac{V^2(\Gamma_3)}{\pi}\int_0^{\omega_0}\operatorname{Im}G_D(\Gamma_3,\Gamma_3,\omega^2)\frac{d\omega}{\omega}, \tag{14}$$

where ω_0 is the end-point frequency of the vibrational spectrum of the lattice. In the case of a "strong" JT effect, due to interaction with trigonal vibrations,

$$E_{JT}(\Gamma_5)=\frac{4}{3\pi}\int_0^{\omega_0}\frac{d\omega}{\omega}[V^2(\Gamma_5{}^a)\operatorname{Im}G_D(\Gamma_5{}^a,\Gamma_5{}^a,\omega^2)+2V(\Gamma_5{}^a)V(\Gamma_5{}^b)$$
$$\times\operatorname{Im}G_D(\Gamma_5{}^a,\Gamma_5{}^b,\omega^2)+V^2(\Gamma_5{}^b)\operatorname{Im}G_D(\Gamma_5{}^b,\Gamma_5{}^b,\omega^2)]. \tag{15}$$

The Green's function of the impurity lattice is connected with the Green's function of the regular lattice G by the relation

$$G_D=G(1+\Delta\Phi\cdot G)^{-1}, \tag{16}$$

where $\Delta\Phi$ is the lattice-perturbation matrix and includes the change of the mass in the substituted site and the change of the strength constants. Assume that the matrix $\Delta\Phi$ has nonzero elements only in the space of the displacements of the CoS_4 complex. In this case the vibrations of the complex can be characterized by two force constants: central (along the direction of the bond) and tangential (perpendicular to it). The former, $\Phi(\Gamma_1)$, characterizes the fully-symmetrical vibration, and the latter $\Phi(\Gamma_3)$ the tetragonal. The trigonal vibrations are characterized by combinations of these constants.

The imaginary parts of the lattice Green's functions

$$\mathrm{Im}\,G(\Gamma,\Gamma',\omega^2)=\pi\sum_{\mathbf{q},j}Q_\lambda(\Gamma,j\mathbf{q})Q_\lambda^*(\Gamma',j\mathbf{q})\,\delta(\omega^2-\omega_j^2(\mathbf{q})) \tag{17}$$

were calculated with the characteristics of the sphalerite vibrational spectrum, determined within the framework of the shell model with the set of parameters II (see[10]). The calculation and the diagonalization of the dynamic matrix were carried out with the BÉSM-6 computer. The calculations were made for wave-vector values that are uniformly distributed in the irreducible part of the Brillouin zone $\mathbf{q}=\pi(q_1, q_2, q_3)/r_0$, where $q_i=n_i/n$, and n_i are integers so chosen that $\mathbf{q}$ does not go outside the limits of the irreducible part. At $n=48$, a total of $N=442\,368$ points is taken into account in the complete Brillouin zone. For each value of the wave vector $\mathbf{q}$, the diagonalization of the dynamic matrix yields six values of the square of the frequency ω_j^2, belonging to three acoustic and three optical branches, and accordingly six polarization vectors each for the cores and shells of the ions located in the lattice sites. Having at our disposal this information for the entire Brillouin zone, we calculate the density of the distribution of the vibrations in the squares of the frequency

$$f(\omega^2)=\sum_{\mathbf{q}j}\delta(\omega^2-\omega_j^2(\mathbf{q}))/6N$$

and the functions (17). The explicit form of $Q_\lambda(\Gamma, j\mathbf{q})$ can be obtained by expressing $Q_\lambda(\Gamma)$ in terms of the displacements of the atoms of the complex CoS_4 and expanding the latter in the normal vibrations of the lattice.

To change over from distributions in the squared frequencies to distributions in the frequencies, the corresponding functions must be multiplied by 2ω, namely, $F(\omega)=2\omega f(\omega^2)$. A plot of $F(\omega)$ is shown in Fig. 3, which contains also the so-called projected state densities of the regular crystal

$$H_{\Gamma_i}(\omega)=(2\omega/\pi)\,\mathrm{Im}\,G(\Gamma_i,\Gamma_i,\omega^2),\quad H_{\Gamma_5}'(\omega)=(2\omega/\pi)\,\mathrm{Im}\,G(\Gamma_5^a,\Gamma_5^b,\omega^2). \tag{18}$$

It is seen that the vibrations Γ_1, Γ_3, and Γ_5^a are represented mainly in the optical branches and can be described with a certain accuracy by one effective oscillator each ($\omega_{\mathrm{eff}}\approx 300$ cm^{-1}). The Γ_5^b vibrations are distributed over the entire vibration spectrum.

The central ion of the complex does not take part in the vibrations Γ_1 and Γ_3, and therefore $\Delta\Phi(\Gamma_1)$ and $\Delta\Phi(\Gamma_3)$ in (16) are diagonal matrices of rank 1 and 2, respectively, the nonzero elements of which are equal to the changes of the force constants $\Phi(\Gamma_1)$ and $\Phi(\Gamma_3)$. Information on the change of the central force constant can be obtained from an analysis of the spectrum of the Raman scattering of the light in the ZnS-Co crystal.[14] A comparison of the scattering spectrum connected with excitation of fully-symmetrical vibrations with the corresponded projected density at different values of $\Delta\Phi(\Gamma_1)$ (calculated from (18) with allowance for (16)) shows that agreement is reached at $\Delta\Phi(\Gamma_1)/\Phi(\Gamma_1)=-0.20$, i.e., when the central force constant is decreased by 20%.[14] It is natural to assume that the change of the tangential force constant does not exceed this value. An indirect confirmation of this estimate obtained from an analysis of the electron-vibrational structure of the luminescence spectrum, particularly its part connected with excitation of optical vibrations. The constants of the electron-vibrational interaction of the level $\Gamma_8^\varphi(^4T_2)$ with the vibrations Γ_3, Γ_5^a, and Γ_5^b are all of equal order, which is also the order of the difference between the electron-vibrational interaction constants of the levels $\Gamma_8^\varphi(^4T_2)$ and $\Gamma_8(^4A_2)$ with the Γ_1 vibrations are of the same order (we recall that this difference is equal to $-5V(\Gamma_1)$). Therefore the electron-vibrational structure of the luminescence spectrum (see Fig. 3a in I) is a reflection of the density of all the vibrations indicated above (although the separation of the contributions of each of them is difficult) and should duplicate with some accuracy the combined density of these vibrations. As follows from (14), a decrease of $\Phi(\Gamma_1)$ leads to a redistribution of the in-

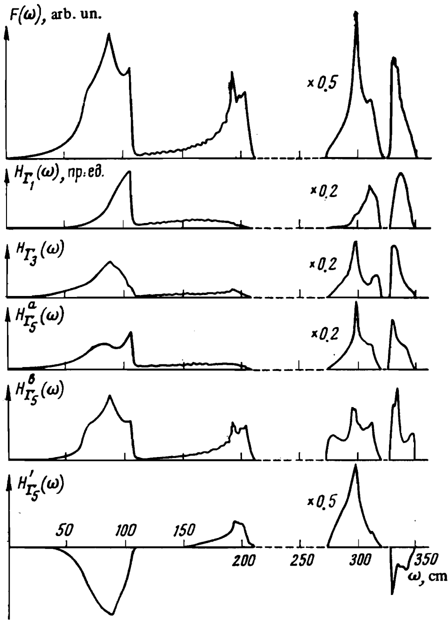

FIG. 3. Total density and projected densities of the vibrations in the ZnS crystal.

tensities among the LO and TO maxima of the H_{Γ_1} curve in favor of the second of them; the same takes place also for the Γ_3 vibration. Thus, for example, at $\Delta\Phi/\Phi = -0.2$, the ratio of the areas of the LO and TO maxima decreases (in comparison with the regular crystal) by 49% for the Γ_1 vibrations and by 33% for the Γ_3 vibrations. Thus, the indicated ratio is a sensitive criterion of the change of the force constants.9) In the luminescence spectrum this ratio is equal to 0.38, i.e., only 24% smaller than its value for the total density of the oscillations $F(\omega)$, for which it is equal 0.5 in accord with the degeneracy multiplicity of the corresponding vibrations. This estimate shows that the decrease of the tangential force function is small enough, and the value given above (−0.2) is apparently indeed the upper bound of $\Delta\Phi(\Gamma_3)/\Phi(\Gamma_3)$.

From formulas (14) and (15), using $V(\Gamma_i)$ from Table II ($Z=0$), we obtain $E_{JT}(\Gamma_3)=93$ cm^{-1} (regular crystal),10) $E_{JT}(\Gamma_3)=114$ cm^{-1} ($\Delta\Phi=-0.2$), $E_{JT}(\Gamma_5)=100$ cm^{-1} (regular crystal).

To conclude this section we note that in the calculation of the splittings and the shift of the Γ_8^φ (the value of Δ) we have neglected the local change of the elastic constants. In fact, the change of the normal rigidity (with respect to the bond) of $\Delta\Phi(\Gamma_1)$ leads to a change of the local compressibility in the ratio

$$C(\Gamma_1)_{\mathrm{loc}}/C(\Gamma_1)=[1+\Delta\Phi(\Gamma_1)G(\Gamma_1,\Gamma_1,0)]^{-1}=\Phi(\Gamma_1)/[\Phi(\Gamma_1)+\Delta\Phi(\Gamma_1)],$$

from which it is seen that a 20% decrease of the normal rigidity should increase Δ_0 by 25%. The changes in the calculated values of Δ_{001} and Δ_{111} are not larger.

4. CONCLUSION

The values of the electron-vibrational interaction parameters ($E_{JT}(\Gamma_i)$, $i=3, 5$) obtained in this paper for the $^4T_2$ term of the Co^{2+} ion in ZnS show that for the investigated system there actually is produced an intermediate electron-vibrational interaction wherein local and resonant states shifted relative to the frequencies of the bare electronic and vibrational states by an amount on the order of the frequency itself. We note that direct experimental proof of the existence of similar states in the crystal ZnS-Co was obtained earlier.[15]

Since $V(\Gamma_3)$, $V(\Gamma_5^a)$, and $V(\Gamma_5^b)$ are of the same order of magnitude (Table II), the structure of the electron-vibrational levels of the term $^4T_2$ is determined by the electron-vibrational interaction both with the tetragonal and the trigonal vibrations. Even for the tetragonal vibrations, which are connected mainly with the optical branches (Fig. 3), the single-mode model is not a good approximation, since the influence of the acoustic branches is not small. On the other hand, introduction of one more (low-frequency) effective oscillator to take into account the influence of these branches is not justified, since the dispersion for them is of the order of the vibration frequency. The situation is even more complicated when electron-vibrational interactions with tetragonal vibrations is considered. An adequate description of the electron-vibrational structure of the spectrum is possible only by solving rigorously the problem of the interaction with the continuous vibration spectrum, as was done by Polinger and Rozenfel'd[16] for the simplest problem of a doubly degenerate level interacting with tetragonal vibrations.

The values of the constants of the electron-vibrational interaction with vibrations of various symmetry, obtained in this paper, and the spectral densities of these vibrations (with allowance for the possible influence of the impurity ion) make it possible to consider for this system processes in which an essential role is played by the electron vibrational interaction, e.g., determine the times of the spin-orbit and spin-lattice relaxation, and others.

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1) This situation can be regarded as quasi-degeneracy.

2) The terms "bound" and "hybrid" are also used for these states. With respect to large-radius centers, for which the change of the properties can be interpreted within the framework of the macroscopic description, the term "dielectric mode" is used.[1]

3) The shifts of the centers of gravity of the $^4T_2$ term and of its spin-orbit levels (without allowance for the change of the spin-orbit interaction constant is −1/5 of the shift of the center of gravity of the $\Gamma_8(^4A_2)\rightarrow\Gamma_8^\varphi(^4T_2)$ transition.

4) When comparing the experimental and calculated characteristics of the piezospectroscopic effect we do not take into account the fact that the upper level of the transition is vibronic, i.e., it receives, in general, contributions from all the electron-vibrational levels that have a symmetry Γ_8. However, as is clear from I (see Fig. 2), the main contribution to this level is made by the state Γ_8^φ, and neglect of all other levels introduces an error not larger than 10–20% in the calculated value.

5) We note that for the term $^5T_2$ of the Fe^{2+} ion in ZnS, which is the result of the Stark splitting of the ^5D term of the free Fe^{2+} ion, the anisotropy of the deformation potentials (which is much smaller) is due practically entirely to the second of the indicated reasons.[9]

6) In the ZnS–Co crystal we must distinguish between two spin-orbit interaction constants, diagonal and off-diagonal, but their values are close to the values of λ of the free Co^{2+} ion (−178 cm^{-1}), and this value can be used to estimate the electron-rotational interaction constant (see below).

7) The quantity E_{JT} is frequently used as a parameter that characterizes the electron-vibrational interaction with definite non-fully-symmetrical vibrations (in the case, with the tetragonal ones), and if the interaction with other non-fully-symmetrical vibrations (trigonal) and the spin-orbit interaction are not negligibly small.

8) Koidl *et al.*[5] obtained, within the framework of a phenomenological theory in which only interaction with tetragonal vibrations are taken into account, a value $E_{JT}(\Gamma_3)=40$ cm^{-1}, at which the structure of the electron-vibrational band, connected with the transition to the $^4T_2$ term, is described in the best manner.

9) For the Γ_5^b vibration in which the central ion participates, the matrix $\Delta\Phi$ includes the change of the mass of the impurity ion. This circumstance is not taken into account, since the mass defect is relatively small ($\Delta M/M\approx 0.1$).

10) The difference from the value obtained within the framework of the single-mode model (Sec. 2) is due to the fact that allowance for the acoustic branches greatly increases the value of E_{JT}, owing to the factor $1/\omega^2$ (see (13)).

1. I. B. Levinson and E. I. Rashba, Usp. Fiz. Nauk **111**, 683 (1973) [Sov. Phys. Usp. **16**, 892 (1974)].

2. F. S. Ham, W. M. Schwartz, and M. C. M. O'Brien, Phys. Rev. **185**, 548 (1969).

3. F. S. Ham and G. A. Slack, Phys. Rev. **B4**, 777 (1971).

[4] A. I. Ryskin, A. L. Natadze, and S. A. Kazanskiĭ, Zh. Eksp. Teor. Fiz. **64**, 910 (1973) [Sov. Phys. JETP **37**, 462 (1973)].
[5] P. Koidl, O. F. Schirmir, and U. Kaufmann, Phys. Rev. **B8**, 4926 (1973).
[6] T. Yamaguchi and H. Kamimura, J. Phys. Soc. Jap. **33**, 953 (1973).
[7] S. Wittekoek, R. P. van Stapele, and A. W. Wijma, Phys. Rev. **B7**, 1667 (1973).
[8] A. A. Kaplyanskiĭ, Opt. Spektrosk. **16**, 1031 (1964).
[9] A. V. Vasil'ev, B. Z. Malkin, A. L. Natadze, and A. I. Ryskin, Fiz. Tverd. Tela (Leningrad) 17, 3167 (1975) [Sov. Phys. Solid State 17, 2091 (1976)].
[10] N. Vagelatos, D. Wehe, and J. S. King, J. Chem. Phys. **60**, 3613 (1974).
[11] E. Clementi, IBM J. Res. Dev. **9**, Suppl. (1965).
[12] A. A. Levin, Ya. K. Syrkin, and M. E. Dyatkina, Usp. Khim. **38**, 193 (1965).
[13] A. Abragam and B. Bleaney, Electron Paramagnetic Resonance of Transition Metals, Oxford, 1970, Vol. 2.
[14] A. L. Natadze, I. V. Pevnitskiĭ, A. I. Ryskin, and G. I. Khil'ko, Fiz. Tverd. Tela (Leningrad), in press.
[15] A. V. Vasil'ev, A. L. Natadze, and A. I. Ryskin, Pis'ma Zh. Eksp. Teor. Fiz. **22**, 43 (1975) [JETP Lett. **22**, 19 (1975)].
[16] V. Z. Polinger and Yu. B. Rozenfel'd, Zh. Eksp. Teor. Fiz. **70**, 597 (1976) [Sov. Phys. JETP **43**, 310 (1976)].

Electrical properties of one-dimensional metals

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We construct a method for rigorously evaluating the properties of one-dimensional metals in the field of impurities taking both types of scattering into account, quasi-classical forward scattering of electrons and backward scattering (i.e., from the neighborhood of the momentum p_o to the neighborhood of $-p_o$, where p_o is the Fermi momentum). In contrast to the method proposed by Berezinskiĭ {Zh. Eksp. Teor. Fiz. **65**, 1251 (1974) [Sov. Phys. JETP **38**, 620 (1974)]} the present approach possesses a higher degree of automatism; it enables us to generalize to the case of a quasi-one-dimensional system and to take into account scattering by phonons. We give a detailed account of the method itself in the present paper and demonstrate how it can be applied by calculating as an example the conductivity and permittivity of a one-dimensional metal. We correct a result in Berezinskiĭ's paper.

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1. INTRODUCTION

Recently people have become interested in one-dimensional and quasi-one-dimensional problems. A distinctive feature of these problems is the fact that many approximate methods applicable to three-dimensional systems become unsuitable for one-dimensional ones. The exact solution of various problems for one-dimensional systems is connected with considerable difficulties and even when it is possible to find it the corresponding method makes it impossible to generalize it to the quasi-one-dimensional case (three-dimensional perturbation of a one-dimensional system).

One of those one-dimensional problems is the problem of the electrical resistivity of a one-dimensional metal in which the electrons are scattered by randomly distributed impurities. Berezinskiĭ[1] recently solved this problem. Unfortunately, the very ingenious method applied by him does not permit generalization to the quasi-one-dimensional case. At the same time such a generalization is of considerable interest as real systems are not purely one-dimensional. As an example we may mention the quasi-one-dimensional compounds which are the base of TCNQ, where the electrons have the possibility to make transitions between filaments. Another example is a semi-metal in a strong magnetic field where apart from the one-dimensional motion along the field there is a finite transverse motion described by an oscillator wavefunction.

We have been able to construct a new method for studying the properties of a one-dimensional system of electrons which interact with random impurities; this method enables us to generalize it to the quasi-one-dimensional case. In the present paper, the aim of which is an exposition of the method, we restrict ourselves to the problem of the electrical resistivity of a purely one-dimensional metal which was already solved by Berezinskiĭ.[1] In subsequent papers we shall consider quasi-one-dimensional systems.

§1. THE GREEN FUNCTION

We shall assume that the electrons have an energy spectrum

$$\varepsilon=p^2/2m. \qquad (1)$$

We shall assume $T=0$ (if we neglect phonons, see[2], the temperature affects the results only when $T\sim\varepsilon_F$). In the equilibrium state the electrons are then degenerate and the Fermi momentum is connected with the electron density by the relation

$$n_e=2p_0/2\pi. \qquad (2)$$