

Piezospectroscopic effect in local and resonant oscillations connected with a degenerate electronic state of an impurity center in a crystal

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We investigate the piezospectroscopic effect on a number of lines of the electron-vibrational band ${}^4A_2 \rightarrow {}^4T_1[{}^6F]$ in a ZnS-Co crystal. We show that the resonant and gap oscillations that appear in the spectrum are due to linear interaction of an orbitally degenerate 4T_1 term with degenerate oscillations.

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The interaction of impurity-center electrons with the crystal oscillations is one of the causes of the change in the oscillation spectrum of the crystal. If the electronic levels of the center are not degenerate, and the distance between them is large in comparison with the oscillation frequencies ($\Delta E \gg \hbar\omega$), then this change is due to the quadratic terms in the expansion of the potential energy of the electrons in the displacements of the nuclei (or the symmetrized displacements—the normal coordinates). If the center has closely-lying levels ($\Delta E \sim \hbar\omega$), then the oscillation-frequency shift is due to the linear terms of the electron-vibrational (EV) interaction. The symmetry of the corresponding oscillations Γ_γ is de-

termined by the requirement that the matrix element of the EV interaction, which mixes two levels of symmetry Γ_i and Γ_k , be invariant to the symmetry operations of the point group of the center (the direct product $\Gamma_i \times \Gamma_\gamma \times \Gamma_k$ should contain the fully-symmetrical representation Γ_1). For a degenerate level ($\Delta E = 0$) of symmetry Γ_k , a frequency shift (in the linear approximation) is experienced by the non-fully-symmetrical oscillations Γ_γ that are active in the Jahn-Teller effect (the representation Γ_γ should be contained in the symmetrized direct product $\{\Gamma_k \times \Gamma_k\}$). In^[1-4] this latter mechanism was assumed to cause the local and resonant oscillations that appear in the absorption and luminescent spectra of certain crys-

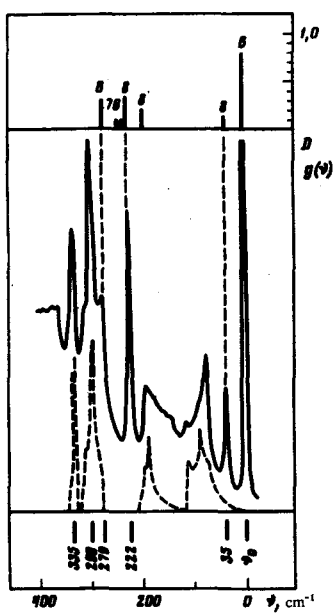


FIG. 1. Low-frequency part of the absorption band, connected with the ${}^4A_2 \rightarrow {}^4T_1[{}^4F]$ transition in a ZnS-Co crystal (D , solid line) at $T=4.2^\circ\text{K}$ and oscillation spectrum of the ZnS crystal ($g(\nu)$, dashed line). $\nu_0 = 5935\text{ cm}^{-1}$. Top—corresponding part of the level scheme of the ${}^4T_1[{}^4F]$ term, calculated with allowance for the EV and spin-orbit interaction. The numbers 6, 7, and 8 label levels with symmetry Γ_6 , Γ_7 , and Γ_8 .

tal activated by transition-metal ions in those cases when the final level of the transition is orbitally degenerate. However, these oscillations can be produced also by other mechanisms, for example by the quadratic terms of the EV interaction, the change of which in the electronic transition cannot be regarded a priori as negligibly small.

In the present study, using a ZnS-Co crystal as an example, we have obtained for the first time experimental proof that in these systems oscillations of the indicated type are indeed due to a linear interaction between non-fully-symmetrical oscillations that are active in the Jahn-Teller effect and degenerate electronic states. We have investigated the piezospectroscopic effect on the sharpest EV lines of the absorption band that is connected with the transition to the orbital triplet 4T_1 of the Co^{2+} ion in the ZnS crystal (the transition ${}^4A_2 \rightarrow {}^4T_1[{}^4F]$). The term closest to it, 4T_2 , is located 2500 cm^{-1} away, a distance much larger than the maximum frequency of the crystal oscillations ($\hbar\omega_{\text{max}} = 350\text{ cm}^{-1}$), so that the frequency shift due to the shift of the electronic states under the influence of the oscillations can be disregarded. The term 4T_1 is split by spin-orbit interaction into four symmetry levels Γ_6 (lowest), Γ_8 , Γ_7 , and Γ_8 . Calculation using the spin-orbit interaction constants determined from the ZnS-Co crystal EPR spectrum,^[5] i. e., typical of precisely this system, shows that the nearest Γ_8 level is located 352 cm^{-1} away from the Γ_6 level. The corresponding section of the absorption band is shown in Fig. 1a. For comparison, the figure shows the spectral density of the oscillations $g(\nu)$ of the ZnS crystal.^[6] We see that in the EV band, besides sections that reflect the form of the $g(\nu)$, there appear also

gap oscillations (lines $\nu_0 + 222\text{ cm}^{-1}$ and resonance oscillations (lines $\nu_0 + 279$ and $\nu_0 + 35\text{ cm}^{-1}$). The corresponding states were attributed in^[3,4] to interaction of the term ${}^4T_1[{}^4F]$ with the non-fully-symmetrical oscillations. The system of the EV levels of this term was calculated with allowance for the spin-orbit and linear EV interaction. The calculation scheme is described in^[3,4]. The spectrum of the crystal oscillations was approximated by two effective oscillators with $\hbar\omega_1 = 90$ and $\hbar\omega_2 = 300\text{ cm}^{-1}$. Of the two types of non-fully-symmetrical oscillations interacting with the term T_1 , namely Γ_3 (tetragonal) and Γ_5 (trigonal), only the Γ_3 oscillations were taken into account. We included states corresponding to excitation of oscillators to the first two vibrational levels including simultaneous excitation of two oscillators to the first level. Those singularities of the spectrum which are not connected with $g(\nu)$ are best approximated by calculation at Jahn-Teller interaction energy values (in terms of which the coupling constants in the Hamiltonian of the EV interaction can be expressed) $E_{JT}^1 = 170\text{ cm}^{-1}$ and $E_{JT}^2 = 350\text{ cm}^{-1}$. We see that a sufficiently weak EV interaction ($E_{JT} \sim \hbar\omega$) leads to the appearance of resonance and gap oscillations, which can be regarded as hybrid, i. e., partly oscillator (lattice) and partly electronic states. The intensities of the corresponding lines are proportional to the contributions of the electronic states.

The piezospectroscopic effect was investigated on ZnS-Co crystals with sphalerite microtwin structure (stacking-fault concentration^[1] 10%). The pressure was applied along the twinning axis [111] and in the {111} plane, the directions in which are equivalent for both members of the twin.^[6]

When the crystal is uniaxially compressed, the ν_0 line ($\Gamma_8[{}^4A_2] \rightarrow \Gamma_6[{}^4T_1]$ transition) experiences only a shift in accordance with the symmetry of the level^[2] Γ_6 . A similar behavior is exhibited also by those spectral regions which reflect $g(\nu)$, particularly the lines $\nu_0 + 299\text{ cm}^{-1}$ and $\nu_0 + 335\text{ cm}^{-1}$; they shift together with the line ν_0 . The line $\nu_0 + 35\text{ cm}^{-1}$ splits at arbitrary pressure directions into two components. This shows that its symmetry is Γ_8 (and not Γ_6) and that a noticeable con-

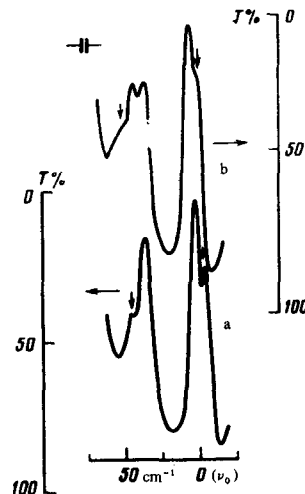


FIG. 2. Piezospectroscopic effect on the lines ν_0 and $\nu_0 + 35\text{ cm}^{-1}$; $P \parallel [\bar{1}12]$; a) $P=0$, b) $P=1440\text{ kgf/cm}^2$.

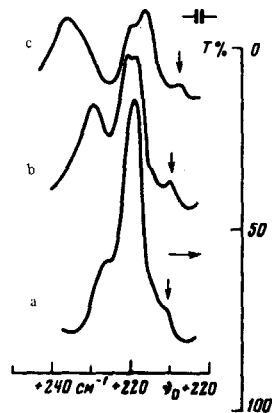


FIG. 3. Piezospectroscopic effect on the line $\nu_0 + 222 \text{ cm}^{-1}$: $P \parallel [112]$; a) $P=0$, b) $P=1000 \text{ kgf/cm}^2$.

tribution is made to the corresponding state by two electronic states Γ_8 of the 4T_1 term. The line $\nu_0 + 222 \text{ cm}^{-1}$ behaves in a peculiar manner, namely, when pressure is applied, a short-wave shoulder is split from it and builds up. At large pressures, the initially more intense line splits into two components. Thus, two closely located states Γ_8 and Γ_6 or Γ_7 , between which intensity transfer is effected under the influence of pressure, are connected with the line. The behavior of the most typical lines of the low-frequency part of the band, under uniaxial compression, is therefore, in qualitative agreement with the level scheme constructed on the basis of the shape of the band.

The model used in the calculation is the simplest one. A more elaborate model (using a larger number of effective oscillators), allowing for the Γ_5 oscillations and for inclusion of higher vibrational states), would provide a better description of the spectrum. However, the very fact that gap and resonance oscillations appear in this system as a result of a linear EV interaction with non-fully-symmetrical oscillations which are active in the Jahn-Teller effect seems beyond any doubt to us.

¹In addition to the cubic centers, other centers also manifest themselves in the spectra^[7,8]. The corresponding lines (Figs. 2, 3) are indicated by the arrows.

²The (4A_2) ground state is an orbital singlet that does not split under uniaxial compression (in first-order perturbation theory).

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