Structure of zero-phonon line of Jahn-Teller system for weak vibronic coupling with pseudolocal oscillations

Yu. P. Gnatenko and A. Kh. Rozhko

Physics Institute, Ukrainian Academy of Sciences
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The structure of the zero-phonon line (ZPL) has been observed for the first time for an impurity center in a crystal in the case of an $A_1 \rightarrow T_2$ transition, which can be interpreted as being due to the Jahn-Teller effect in the presence of vibronic coupling with pseudoscalar oscillations.

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As reported in[1], in the case of optical transitions of electrons between singlet and degenerate states, one should expect in weakly linear electron vibrational (EV) interactions the impurity centers in a crystal to have a zero-phonon line (ZPL), of equidistant structure the onset of which is due to splitting of the multiply degenerate levels of the local oscillations active in the Jahn-Teller effect.

We have observed in experiment, for the first time, a ZPL structure for a transition between singlet and triplet electronic states. Our analysis indicates that its appearance is due to the Jahn-Teller effect. The investigated object was a CdS crystal containing Ni^{2+} ions, the introduction of which leads to the formation of deep impurity centers.[2] We investigated the absorption spectrum for the transition between the Stark components $^3T_1$ and $^3A_2$ of the ground F state

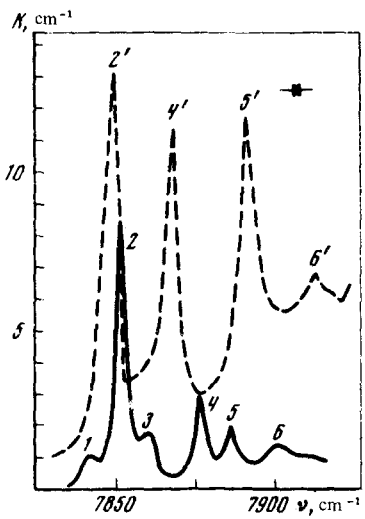

FIG. 1. Absorption spectrum of a CdS: Ni crystal at 4.2 °K. The solid and dashed curves are for the polarizations of the light $\mathbf{E} \parallel C$ and $\mathbf{E} \perp C$, respectively.

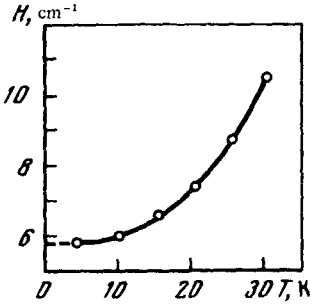

FIG. 2. Temperature dependence of the half-width of the line $J(2)$.

of the Ni^{2+} ion. The $^3T_1$ term is split by the spin-orbit interaction into several levels, the lowest of which has symmetry A_1.[3] When the spin-orbit interaction is taken into account, the excited term $^3A_2$ goes over into the triplet state T_2, for which a weak vibronic coupling with the trigonal oscillations is possible, i.e., the dynamic Jahn-Teller effect is observed. The possibility of the appearance of this effect for the $^3A_2$ term of the Ni^{2+} ion, which is singlet in the orbital momentum but degenerate in the spin, was indicated in[4]. The energy of the Jahn-Teller interaction can amount in this case to several cm^{-1}.[4]

Figure 1 shows the results of measurements of the absorption spectrum for the investigated optical transition. The longest-wavelength intense lines $J(2)$ and $J(2')$ are ZPL lines (the numbers in the parentheses correspond to the line markings in Fig. 1). With rising temperature, the lines broaden and the integrated intensity is noticeably decreased. An analysis of the temperature dependence of the half-width of the $J(2)$ line (see Fig. 2) shows that the one-mode model can be used in this case. This has made it possible[5] to determine the effective energy $\hbar\omega$ of the oscillations responsible for the broadening of the ZPL in the given temperature interval, namely 22 cm^{-1}. The appearance of such low-frequency oscillations may be due to the possible weakening of the force constants in the impurity—crystal system, since the ionic radius of Ni^{2+} (0.69 Å) is much smaller than that of Cd^{2+} (0.94 Å). Regions with perturbed phonon spectra are produced in the lattice near the impurity atoms, and this gives rise to pseudolocal or resonant oscillations, which can be regarded approximately as optical-type local atom motions.[6] Since the impurity ion and its nearest neighbors form almost a regular tetrahedron, oscillations of α, ϵ, and τ_2 symmetry are present.

The weak EV interaction of the excited state T_2 with oscillations of τ_2 symmetry leads to the onset of the ZPL structure described in[1]. Consequently,

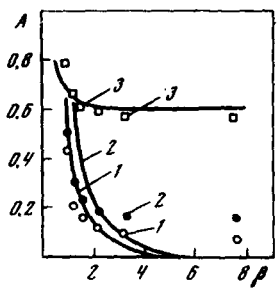

FIG. 3. Dependence of the ratios $J(1)/J(2)$, $J(3)/J(2)$, and $J(1)/J(3)$ of the intensities of the lines 1, 2, and 3, respectively, on $\beta=\hbar\omega/kT$. Points—experimental values, solid curves—calculated.

attention is called to two lines in the absorption spectrum, $J(1)$ and $J(3)$ symmetrically located 10 cm^{-1} away from the intense line $J(2)$. With rising temperature the relative position of the lines, i.e., the equidistance, remains unchanged. At the same time, an increase is observed in the intensities of the lines $J(1)$ and $J(3)$ and, as noted above, that of $J(2)$ decreases (see plots 1 and 2 of Fig. 3). This temperature dependence of the lines agrees qualitatively with the prediction of[1], if the lines $J(1)$, $J(2)$, and $J(3)$ are regarded as the K_0', K_0, and K_+ components of ZPL. It appears that the frequency effect is extremely weak in this case and leads only to a broadening of the ZPL components. Figure 3 shows also theoretical plots 1 and 2. The deviation of the experimental points from the calculated curves in the region of large $\beta = \hbar\omega/kT$ may be due to the fact that when the intensities of the ZPL components were calculated in the theory of[1], no account was taken of their decrease as a result of the presence of optical transitions that lead to the appearance of the vibronic structure of the spectrum. This circumstance should have in practice little effect on the ratio of the intensities by lines $J(1)$ and $J(3)$. Indeed, in this case (see Fig. 3, plot 3), a rather good agreement, not only qualitative but also quantitative, is observed between the experimental values and those calculated over the entire range of variation of β. The discrete ZPL spacing $\Delta = B^2/\hbar\omega = 10$ cm^{-1} determines directly the energy of the Jahn-Teller interaction, $E_{JT} = 4\Delta/3 = 13$ cm^{-1}. Since $E_{JT} < \hbar\omega$, a weak Jahn-Teller interaction is realized in this case, as expected.

The manifestation of the polarization in the absorption spectrum is possibly due not only to the presence of a small trigonal crystal field for the wurtzite crystal CdS, but also to the fact that the Jahn-Teller interaction is somewhat larger for the polarization $\mathbf{E} \perp C$ (C is the crystal optical axis) than in the case $\mathbf{E} \parallel C$. This is also the reason why at $\mathbf{E} \perp C$ the absorption spectrum does not contain the lines $J(1')$ and $J(3')$, since they become smeared and masked by more intense lines. Favoring this assumption is the fact that the $J(2')$ line wider than the $J(2)$ line, this being due to the larger amplitude of the τ_2 oscillations for the $\mathbf{E} \perp C$ polarization.[6] Moreover, when account is taken of only the trigonal crystal field, the $J(2')$ line should have a shorter wavelength than the $J(2)$ line.

In addition to the ZPL line, Fig. 1 shows also other lines of vibronic nature.[7] Thus, lines $J(4)$ and $J(4')$ can be ascribed to transitions to a vibronic level of T_2 symmetry with $n = 1$, while $J(5)$ and $J(5')$ to a level with the same symmetry but with $n = 2$. The energy positions of the vibronic bands with $n = 1$ and $n = 2$ relative to the ZPL line agree with the value of $\hbar\omega$ determined above. The indicated lines, can be interpreted in other terms as bound states of an electron localized on a deep impurity center and situated in a degenerate excited state, with pseudoscalar oscillations, i.e., as dielectric local vibrational modes.[8,9]

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