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INTERACTION OF EXCITONS BOUND TO 3*d* TRANSITION METAL IONS WITH LATTICE VIBRATIONS IN II–VI SEMICONDUCTORS

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The analysis of an interaction of bound excitons with lattice vibrations for ZnO:Ni and ZnO:Cu is given on the basis of symmetry consideration.

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A large body of experimental information on the interaction of lattice vibration with donor and acceptor excitons (DE and AE) bound to isoelectronic impurities has recently been accumulated. This interaction is very strong. Apart from this, the observed peak position often does not correspond to the phonons from the centre of the Brillouin zone [1]. The analysis of experimental results is based on the fact that DE and AE substantially distort ionic oscillations near the impurity, owing to strong localization of the carrier captured by a non-Coulomb potential. This results in a phonon spectrum exhibiting normal modes of a cluster that consists of an impurity and some lattice ions surrounding it [2]. Excitons localized on an impurity interact with normal oscillations of a given claster.

When an impurity is introduced into the lattice, the motion of the ions that surround the impurity acquires the point symmetry of the impurity site, e.g. T_d for crystals with zincblende structure. Combinations of atomic displacements near the impurity (normal modes) are described by irreducible representations A_1 (breathing mode), E and $2T_2$ of T_d group. These are expressed in terms of irreducible representations of phonons of a perfect crystal. The contribution to normal modes originates from phonons from different Brillouin zone points, and the total number of phonons, that is, the projected density of phonon states, is calculated by a computer. Results of such computations for normal modes A_1(ZnS), E and T_2 (in ZnS, ZnSe, ZnTe) are given in [2]. When the difference in force constants and/or ion masses is large, local or quasilocal lattice vibrations may appear.

If the symmetry of the localized-carrier wavefunction is described by irreducible representations Γ_α, the carrier will interact with the normal modes contained in symmetrized product $[\Gamma_\alpha^2]$. For T_d -structure crystals the wavefunction of an electron captured onto a simple isoelectronic impurity has a symmetry Γ_1, that of a hole the symmetry Γ_{15} (disregarding spin). Consequently, the electron (and the AE) will interact with the normal mode A_1, and the hole (and DE) with the normal modes A_1, E_1, T_2 [3]. When the exciton is localized on the $3d$ impurity, one carrier contributes to the d shell (changing the configuration $d^n \rightarrow d^{n+1}$) and becomes indistinguishable from the other d electrons. Therefore one has to consider the interaction with lattice vibrations of the configurations d^{n-1} and d^{n+1} in the ground state for DE and AE. For example, for $Ni^{2+}(d^8$ configuration) in the case of DE $[d^7e]$ capture, the ground state of the d^7 configuration is $^4A_2$, in the case of AE $[d^9h]$ capture, the ground state of the d^9 configuration is $^2T_2$. With the neglect of spin, the DE will interact with the normal mode A_1 ($[A_2^2] \rightarrow A_1$), and the AE with A_1, E and T_2 ($[T_2^2] \rightarrow A_1 + E + T_2$). The table from [4] furnishes normal cluster oscillation modes with which DE and AE bound on $3d$ impurities interact.

According to [2] the A_1 mode has only one peak in the region of optical vibrations (branch LO) but E and T_2 modes have two peaks (LO and TO branches). This makes possible to distinquish DE and AE bound to V, Cr, Ni and Cu. The predicted character of interaction of bound excitons with lattice vibrations is supported by examples of DE and AE, observed for ZnSe:Ni, ZnS:Ni and ZnTe:O [3, 4].

In the present paper we shall discuss experimental results concerning an interaction of excitons bound to Ni and Cu in ZnO. The phonon spectrum consists of some optical branches Γ_1, $2\Gamma_4$, Γ_5 and $2\Gamma_6$ (another symbols A_1, $2B_1$, E_1 and $2E_2$). On projecting these branches onto the local vibration we see that the Γ_1 and Γ_4 phonons make a contribution to local A_1 mode, and the Γ_5 phonons contribute to the local mode E. Figure 1 shows the spectral dependence of electroabsorption harmonic α_2 for ZnO:Ni and the spectra of luminescence and excitation of luminescence for ZnO:Cu [5]. It should be noted some simularity in these two cases: the peaks 1, 2 and 3 of α_2 spectrum and the peaks β and γ of the excitation luminescence spectrum, broad structures 4 and 5 of the α_2 spectrum and the broad peaks for the luminescence spectrum. Both the more strong peak 6 for the α_2 spectrum and the corresponding peak for the luminescence spectrum are determined by optical phonons $\Gamma_6(A_{1L})$. The wide peaks 4 and 5 for the α_2 spectrum are interpreted as $\Gamma_4(B_1)$ replicas. Γ_4 phonons are forbidden by symmetry for an observation in optical absorption and Raman scattering spectra. In our case these phonons make a contribution to the local mode $A_1([\Gamma_4^2] \rightarrow A_1)$ and therefore they are observed in electroabsorption and luminescence spectra.

It is important to note that TO phonons Γ_5 (E_1) in the spectrum of ZnO:Ni and in the luminescence and excitation luminescence spectra of ZnO:Cu are not displayed as a very strong peak. This can be understood for AE $[d^{10}h]$, because of its interaction with A_1 mode only. The resemblance of the vibrational replicas structure of ZPL for ZnO:Cu and ZnO:Ni allows to make a conclusion that in the case of ZnO:Ni DE $[d^7e]$ is observed, which interacts only with A_1 mode. For

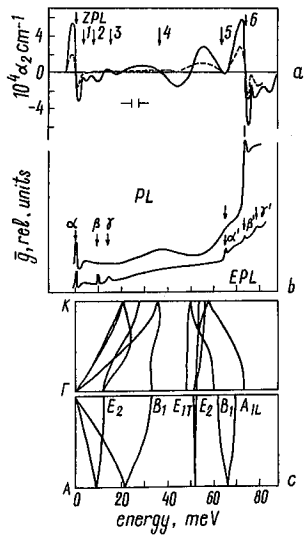

Fig.1. Spectral dependence of the EA second-Harmonic amplitude α_2 for ZnO:Ni (a), the photoluminescence (PL) and excitation photoluminescence (EPL) for ZnO:Cu (b) [5], and dispersion curves of normal lattice vibration modes in ZnO (c) [6]. The position of ZPL at the 2.152 eV for DE in ZnO:Ni and 2.864 eV for AE in ZnO:Cu are given as zero at energy scales for a, b.

a quantitative discussion it is necessery to perfom a calculation of the projected density-of-states for ZnO:Cu and ZnO:Ni.

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