Detection of tunneling annihilation of the donor exciton in CdS:Ni

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(Submitted 26 December 1985)
Pis'ma Zh. Eksp. Teor. Fiz. **43**, No. 4, 187–190 (25 February 1986)

The activation nature of the temperature dependence of the line width of the donor exciton $[d^7e]$ in CdS:Ni has been observed for the first time.

The impurities of $3d$ transition metals in A^2B^6 compounds are isoelectronic impurities which can combine donor and acceptor excitons.[1] In CdS:Ni an exciton bound to Ni was observed for the first time at $T = 4.2$ K by Permogorov *et al.*[2] On the basis of the results of a study of electroabsorption of CdS:Ni at $T = 4.2$ K Sokolov *et al.*[3] have recently concluded that there is a donor exciton in this material at the edge of the Ni photoionization band, according to the scheme $d^8(^3T_1) + \hbar\omega_d \rightarrow [d^7(^4A_2)e]$; $^3T_1$ is the ground state of a d^8 configuration, $^4A_2$ is the ground state of a d^7 configuration, and the square brackets represent the Coulomb interaction between the electron e and the center with d^7 configuration, which is positively charged with respect to the lattice. It was noted in Ref. 2 that the absorption line of a bound exciton broadens and becomes unobservable in 30 K. A strong temperature dependence was observed for an acceptor exciton $[d^{10}h]$ in ZnO:Cu in Ref. 4, for a donor exciton $[d^7e]$ in ZnSe:Ni in Refs. 1 and 5, and for an acceptor exciton $[d^9h]$ and a donor exciton $[d^7e]$ in ZnO:Ni in Ref. 3. The strong temperature dependence could not be explained, since the binding energies of hydrogen-like carriers are approximately equal to 30 meV for CdS:Ni and ZnSe:Ni and 400 meV for ZnO:Cu.

In this letter we report the results of an experimental study of the effect of temperature on the donor exciton line $[d^7e]$ in CdS:Ni in the temperature range 4.2–77 K, using the electroabsorption method. The measurements of electroabsorption were carried out in a manner similar to that in Refs. 3 and 5. Figure 1 shows the spectrum of the amplitude of the second harmonic of electroabsorption, α_2, for three temperatures. This spectrum consists of the leading line at $\hbar\omega_d = 2.191$ eV and weak repetitions with

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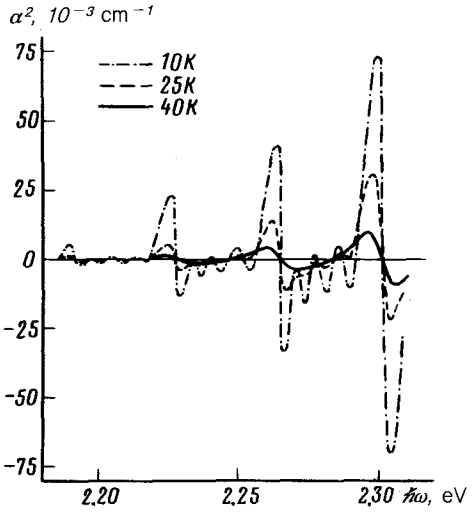

FIG. 1. Spectral dependence of the electroabsorption peaks α_2 at different temperatures. The amplitude of the alternating electric field, $F = F_M \cos \Omega t$, is 20 kV/cm in all cases.

energies of acoustic phonons and strong repetitions with energies of *LO* phonons.

With increasing temperature, the electroabsorption peaks broaden, but we see from the shape of the electroabsorption spectrum that the principal mechanism of the electric field is the shift of the absorption lines toward lower energies (the Stark effect). The absorption line can be approximated by the Lorentz shape

$$\alpha(\hbar\omega) \sim \frac{\gamma}{(\hbar\omega - \hbar\omega_0)^2 + \gamma^2/4},$$

where $\hbar\omega_0$ is the position of the line center, and γ is the line half-width which is inversely proportional to the lifetime τ of the excited state. Assuming that there is only a line shift in the electric field, we find the change in the absorption coefficient $\Delta\alpha \sim 1/\gamma^2$. Since the amplitude peaks of the second harmonic of the electroabsorption $\alpha_2 \sim \Delta\alpha$, we have $\gamma \sim 1/\sqrt{\alpha_2}$. Figure 2 is a plot of $1/\sqrt{\alpha_2}$ as a function of the inverse temperature. We see that at low temperatures the line width varies only slightly with

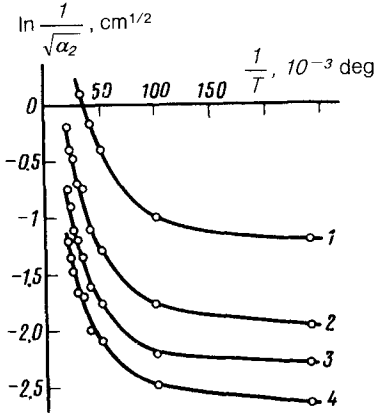

FIG. 2. Peak height $1/\sqrt{\alpha_2}$ versus the inverse temperature.

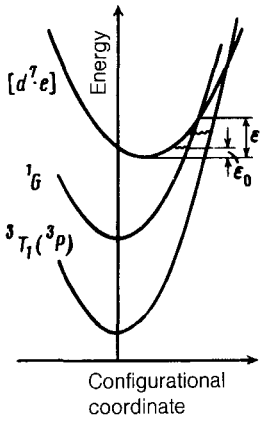

FIG. 3. Diagram of the energy states of the donor exciton $[d^7e]$ and of the excited $(d^8)^*$ configurations, which illustrates the possible manifestations of the tunneling annihilation of the donor exciton $[d^7e] \rightarrow (d^8)^*$.

the temperature and at temperatures of 20–50 K the experimental points can be approximated by the activation function $\gamma \sim \exp(-T_0/T)$, where T_0 is 35–40 K. The value of γ is defined as the difference in energies of the positive and negative peaks,[6] α_2. The value of γ determined in this manner as a function of the inverse temperature also has an activation nature at temperatures 20–50 K, and T_0 is also $\sim$40K.

Such a strong temperature dependence of γ cannot be attributed to the ionization of the donor exciton, but it can be qualitatively understood in terms of the theory of radiationless capture of an electron by a deep impurity center, which has recently been developed by Abakumov *et al.*[7] The capture by a deep impurity center is usually described in terms of the configurational curves. The point at which the ground-state curve crosses the excited-state curve is removed a distance ϵ from the equilibrium position of the excited state (Fig. 3). The value of ϵ is comparable to the distance between the terms in the equilibrium positions. At high temperatures, unattainable for all practical purposes, the capture should have an activation nature with an activation energy ϵ. Abakumov *et al.*[7] have shown that at the actual temperatures the capture has the complicated nature of a thermally stimulated tunneling and that it occurs at a "saddle-point" energy ϵ_0 which is considerably lower than ϵ.

In the case of radiationless annihilation of a bound exciton, the tunneling may occur to different excited states of a d^8 configuration. The existence of such transitions is confirmed by the fact that the spectrum of the luminescence excitation inside the center exhibits peaks which coincide with the absorption lines of the donor exciton $[d^7e]$ in CdS:Ni (Ref. 8) and the acceptor exciton $[d^9h]$ in ZnSe:Ni (Ref. 9). Figure 3 shows the terms $^3T_1(^3P)$ and ^1G for illustration. The second term splits into the $^1A_1$, ^1E, $^1T_1$, and $^1T_2$ states in the crystal field. The tunneling efficiency depends not only on the barrier width and the temperature but also possibly on the symmetry and spin multiplicity of the final state. Because of the coexistence of the parallel tunneling-annihilation channels, this process is efficient and more probable than radiative recombination, which has not been observed in the case of excitons bound to Ni in the A^2B^6 compounds.

The low value of the saddle-point activation energy obtained by us, $\epsilon_0 = kT_0 \approx 3.5$ meV, qualitatively explains well the very strong temperature dependence in the tem-

perature interval 20–50 K of the line width of the donor exciton which is bound to Ni in CdS. In principle, this mechanism can be used to explain the temperature dependence of the exciton lines which are bound to $3d$ impurities in other A^2B^6 compounds. The tunneling annihilation of the donor or acceptor excitons cannot, however, be understood more clearly or described quantitatively without constructing a theory of this phenomenon.

We wish to thank I. A. Merkulov and K. A. Kikoin for a useful discussion of the experimental results.

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Translated by S. J. Amoretty