Observation of new states of an exciton bound to Ni^{2+} in ZnSe

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New absorption lines corresponding to an exciton bound to Ni^{2+} have been observed in the energy interval 2.640–2.750 eV in ZnSe:Ni in a strong alternating electric field. These lines, together with a line reported previously at 1.816 eV, constitute the first experimental proof of the complex spectrum of the exciton bound to Ni^{2+} in ZnSe:Ni. A group-theoretical analysis is carried out for the states of the exciton bound to Ni^{2+}.

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Isoelectronic impurities, i.e., impurities which give up the same number of valence electrons as an atom of the host lattice, would in forming bonds in a crystal, effectively bind excitons. The isoelectronic impurity, which has received the most study,[1] is *N* in GaP. From this case has emerged a clear picture of a bound exciton as a system in which one carrier remains fixed at the impurity while the second carrier is revolving in the Coulomb field of the first. The energy spectrum of an exciton of this type in a cubic crystal consists of only two lines (*A* and *B* in the Thomas—Hopfield terminology[1]). Impurities of the 3*d* elements in II—VI compounds, which substitute for group-II atoms and give up two electrons each in forming ionic—covalent bonds, behave as isoelectronic impurities and are capable, in principle, of binding excitons.

There have been previous reports of the observation of one line (aside from phonon replicas) of an exciton bound to Ni^{2+} in ZnSe:Ni; this line has been observed in the absorption spectrum[2] and in the photoluminescence-excitation spectrum[3] at an energy of 1.816 eV, at the edge of the charge-transfer band. Kazanskiĭ and Ryskin[2] have commented that an exciton bound to Ni^{2+} may have several energy states.

In this letter we report the observation of new absorption lines of an exciton bound to Ni^{2+} in the energy range 2.640–2.750 eV in ZnSe:Ni in a strong alternating electric field ("electroabsorption"). The observation of these lines, along with the line reported previously at 1.816 eV, is the first experimental confirmation of the complex spectrum of the exciton bound to Ni^{2+}. A group-theoretical analysis of the spectrum of an exciton bound to Ni^{2+} predicts several states and furnishes a qualitative interpretation of the continuous spectrum observed experimentally for the bound exciton.

In the experiments we measured the absorption in the energy range 2.560–2.780 eV of ZnSe:Ni in an electric field at temperatures of 77 and 4.2 K. The nickel concentration ranged from 5.4×10^{16} cm^{-3} to 2.7×10^{18} cm^{-3}. We also observed absorption in the region of intracenter transitions, which implies that the nickel is present as Ni^{2+} ions in the ZnSe lattice.

Figure 1 shows the amplitude spectrum of the second harmonic of the absorption, α_2, for ZnSe:Ni; this spectrum has a large number of peaks and valleys. These features

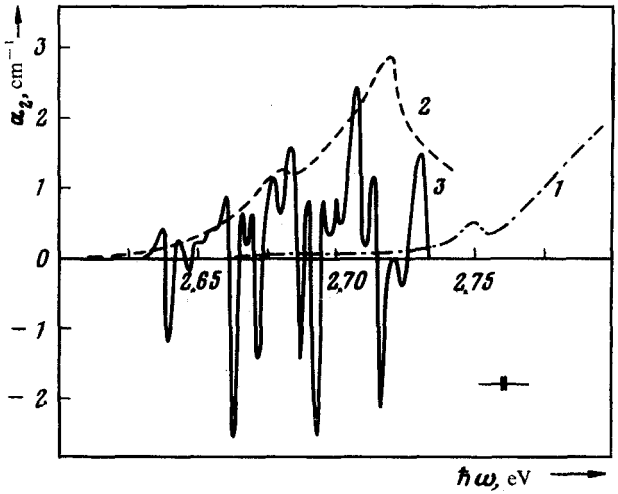

FIG. 1. Amplitude spectrum of the second harmonic of the absorption in a strong electric field, α_2, for ZnSe:Ni samples with two nickel concentrations: 1) 5.4×10^{16} cm^{-3}; 2,3) 5.4×10^{17} cm^{-3}. 1,3) $T=4.2$K; 2) $T=77$ K. The amplitude of the alternating electric field $F=F_N\cos\Omega t$ is 20 kV/cm in all cases.

cannot be attributed to an effect of the electric field on intracenter transitions in the d^8 configuration, since the energy-level scheme for this case[4] and the crystal-field parameters[5] for ZnSe:Ni rule out the existence of appropriate levels of the d^8 configuration, i.e., levels to which transitions from the ground state could produce lines in the immediate vicinity of the fundamental absorption edge. By analogy with Refs. 6 and 7, we believe that the peaks and valleys in the absorption result from an effect of the field on the absorption lines of a bound exciton. This interpretation is based on the following experimental observations: 1) the strong temperature dependence of the α_2 spectral features; 2) the quadratic dependence of these features in weak fields; 3) the characteristic shape of the longest-wavelength α_2 spectral feature, which corresponds to a broadening of the exciton line in the field; 4) the growth of the α_2 spectral features with increasing nickel concentration; and 5) the small width of these features, which is comparable to the width of the intracenter-absorption lines. [Like intracenter transitions, transitions to bound-exciton states are transitions between highly localized multi-electron states of a system. The width of the narrow lines of the intracenter transition $^3T_1(F)\rightarrow{}^3T_1(P)$ is 2 meV, while the width of the absorption features is a 3 meV; the instrumental resolution is better than 1 meV.]

As Fig. 1 shows, the α_2 peaks and valleys are not arranged in a strictly periodic manner, with separations equal to the energies of optical phonons ($LO=31.4$ meV, $TO=25.6$ meV), although the separations in some cases are approximately equal to LO or TO. Furthermore, the α_2 valleys do not shrink with increasing $\hbar\omega$, as they should if they were phonon replicas. It is difficult to unambiguously identify all the absorption features. Nevertheless, the absence of any structure in the interval 2.560–2.640 eV (i.e., at a distance 2 LO below all the absorption features) is good evidence that the longest-wavelength features observed in the absorption spectrum are no-phonon lines of an exciton bound to a Ni^{2+} ion.

According to Kazanskiĭ and Ryskin[2] and Bishop *et al.*,[3] the line at 1.816 eV corresponds to a bound-exciton state which is observed at the edge of the charge-transfer band in ZnSe (see also Ref. 8). We believe that the absorption features, which

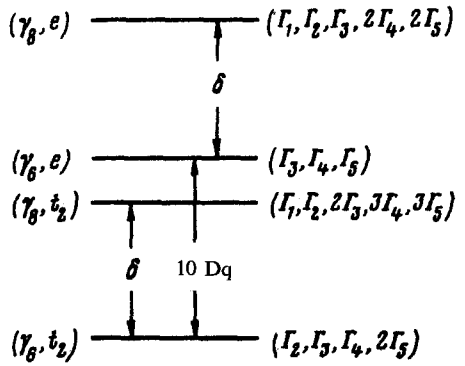

FIG. 2. Bound-exciton states which appear due to the excitation of an electron from the t_1 orbital to the t_2 antibonding orbital. The corresponding hole densities are shown at the left. $10Dq = 0.55$ eV, $\delta = 0.4$ eV.

we observe in the interval 2.640–2.750 eV, represent other states of an exciton bound to Ni^{2+}, which appear as a result of the complex structure of the charge-transfer band.

To interpret the charge-transfer band in ZnSe:Ni, we consider a cluster consisting of an Ni^{2+} ion and four Se^{2-} ions, at the vertices of a tetrahedron. The antibonding e and t_2 molecular orbitals consist primarily of the $3d$ wave functions of Ni^{2+}; the t_1 filled orbital, which is nearest these antibonding orbitals, is made up of p wave functions of Se^{2-}. The strong spin—orbit interactions splits this state into two parts (γ_8, γ_6), which are separated by a distance δ. The lower electronic configuration $(\gamma_8^4, \gamma_6^2 e^4 t_2^4)$ has a $^3T_1$ ground term, which in turn is split by the spin—orbit interaction in the $3d$ states of the Ni^{2+} ion. The ground level of the impurity center is a Γ_1 state. The charge-transfer spectrum is associated with the excitation of an electron from the t_1 orbital of the ligands to the t_2 antibonding orbital. The hole in the t_1 shell interacts with holes in the t_2 or d shells, and this interaction is equivalent to the formation of a bound exciton.

Figure 2 shows the state scheme of the exciton bound to Ni^{2+} in ZnSe:Ni. In the electric dipole approximation the allowed transitions are $\Gamma_1 \rightarrow \Gamma_5$; there are eight such transitions in a 0.95-eV-wide bnad. For an accurate calculation of the bound-exciton structure and for an identification of the observed bound-exciton spectral features with definite states it would be necessary to carry out calculations for the $[NiSe_4]$ cluster and to take into account finer-scale interactions.

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