Biexciton-impurity complexes in uniaxially compressed germanium with simple bands

V. D. Kulakovskiĭ and I. V. Kukushkin
Institute of Solid State Physics, Academy of Sciences of the USSR

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It is found that in germanium it is possible for two excitons to be found on a neutral donor even in strongly compressed crystals with complete removal of the degeneracy of electron and hole bands.

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The possibility of the formation of a bound state of a neutral donor and exciton or an exciton-impurity complex (EIC) in semiconductors follows from their analogy with hydrogen atoms.[1] From this analogy, one would expect that attachment of a second exciton to the EIC on a neutral donor (acceptor) in semiconductors with nondegenerate bands, just as the attachment of a third atom to a hydrogen molecule, will turn out to be unfavorable due to repulsive forces between electrons (holes) with identical spins. The existence of bound multiexciton–impurity complexes has heretofore been established reliably only in semiconductors with degenerate bands, in which more than two electrons (holes) can be found in the 1*s* shell due to the additional orbital degeneracy of the bands.[2] On the other hand, it was found in investigations of recombination radiation of complexes in strongly compressed Ge crystals doped with antimony, carried out in the present work that in Ge bound biexciton–impurity complexes on neutral donors remained stable even with complete removal of the degeneracy of electron and hole bands.

We studied Ge(Sb) crystals with $N_{\text{Sb}} = 5 \times 10^{14}$ cm^{-3}. The technique of uniaxial homogeneous compression of crystals with dimensions 3 × 3 × 10 mm was described previously.[3] Optical excitation was carried out with the help of an LT-2 laser ($\lambda = 1.06$ μm) with a power of 4 W. The spectral instrument consisted of a double monochromator with gratings with 600 lines/mm and a dispersion of 8 Å/mm. The radiation was detected by a cooled Ge(Cu) photoresistance in the synchronous detection mode. Measurements in magnetic fields $H \lesssim 5$ T were used to identify the electronic structure of the complexes.

The lowest stability of the electron-hole fluid and, therefore, the greatest density of excitons in Ge, is attained in crystals that are strongly compressed along an axis close to ⟨100⟩, when the degeneracy of the conduction and valence bands is removed and the anisotropy of the valence bands is minimum.[3,4] In order for it to be possible to neglect the degeneracy of the conduction band, in studying multiexciton-impurity complexes (MEIC) on neutral donors, the energy gap up to the nearest, relative to the principal, valley ΔE_c must be much greater than both the binding energy of the MEIC and the magnitude of the orbital-valley splitting $(\Gamma_1 - \Gamma_5)$ of the donors. For this reason, we chose Ge for the studies with very fine donor Sb, for which the $\Gamma_1 - \Gamma_5$ splitting is only 0.3 meV.[5] The E_2 binding energy in Ge(Sb), compressed along the ⟨100⟩ axis, with a degenerate conduction band, as follows from our measurements, is $\Delta_2 \lesssim 1.5$ meV. Taking this into account, we concentrated on the deformation of Ge(Sb) crystals along the ⟨1.1.16⟩ axis, when for $P \gtrsim 500$ MPa the quantity ΔE_c reaches 6–7 meV. We obtained similar results in Ge(Sb) for $\mathbf{P} \parallel \langle 116 \rangle$ with $\Delta E_c \approx 15$ meV as well. However, the fraction of E_2IC in this case was lower due to the lower density of the exciton gas phase.

Figure 1 shows the emission spectra of Ge(Sb) crystals, strongly compressed along the ⟨1.1.16⟩ axis, at different temperatures and excitation densities W. For $W < 0.5$ W/cm^2, both in the phonon-free and in the LA component of the emission spectrum, only a single line α, corresponding to EIC emission, was observed. For high excitation densities $W \sim 20$ W/cm^2, three more lines appear in the LA components, α_2, β_2, and FE, and only one of these, α_2, appears in the phonon-free region. The intensities of the α_2 and β_2 lines decrease with increasing temperature, but the ratio of their intensities does not depend either on the excitation density or on the temperature. We can therefore conclude that they correspond to transitions out of a single state. The intensity of the emission lines of free excitons, FE, increases with increasing temperature due to the dissociation of bound states (Fig. 1).

The properties of the emission spectrum of Ge(Sb) described above have a natural explanation if we assume that the lines α_2 and β_2 correspond to recombination of electrons and holes in E_2IC (Fig. 2). As in the case of MEIC in the presence of degenerate valleys

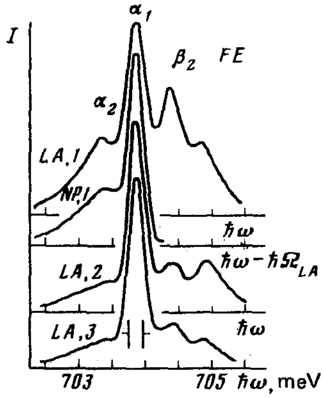

FIG. 1. Emission spectra of Ge(Sb) compressed along the ⟨1.1.16⟩ axis at $P = 500$ MPa. *LA* and *NP* components 1 were recorded at $T = 1.6$ K, $W = 20$ W/cm^2; the *LA* components 2 and 3 correspond, respectively, to $T = 2$ K, $W = 20$ W/cm^2 and $T = 1.6$ K, $W = 6$ W/cm^2. For convenience in making comparisons, the *Np* spectrum is displaced by the magnitude of the *LA* phonon energy.

in the conduction band,[2,6] transitions to the ground state (β_2 line), corresponding to recombination of a weakly bound electron, are visible only in the phonon component, while transitions to an excited state (α_2 line), when an electron from an inner shell recombines, occur with a transfer of Brillouin momentum both to the phonon and to the impurity center. It is evident from a comparison of the splitting of the α_2 and β_2 lines (=0.95 ± 0.03 meV) and the binding energy of EIC, determined according to the position of the α_1 and FE lines (0.94 ± 0.04 meV) that the excited state of EIC (EIC*) is unstable. For this reason, the large half-width of the line α_2 is not surprising. In Ge(Sb) crystals compressed along the ⟨100⟩ axis, only EIC* are stable due to the degeneracy of the conduction bands, and the α_2 line narrows. The binding energy of the second exciton in E_2IC, is equal to the splitting of the β_2 and FE lines for $P > 400$ MPa both with **P** ∥ ⟨1.1.16⟩ and with **P** ∥ ⟨116⟩, is 0.35 ± 0.05 meV.

The stability of E_2IC in the absence of band degeneracy, if we start from the analogy with hydrogen molecules, is unexpected. For this reason, it is very important to study the splitting of the emission lines in a magnetic field, based on which it is possible to draw conclusions about the structure of the complexes. Figures 2 and 3 show the results of such measurements. It is evident from Fig. 3 that transitions occur out of the lowest spin sublevel of EIC to both spin sublevels of the neutral donor (the α_1^π and α_1^σ lines, whose in-

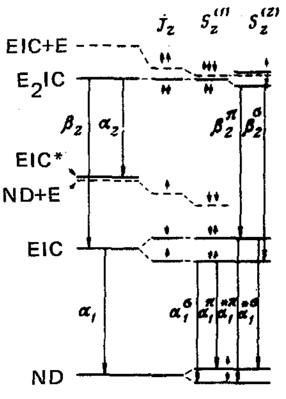

FIG. 2. Diagram of the splitting of the energy levels of complexes and allowed transitions in a magnetic field.

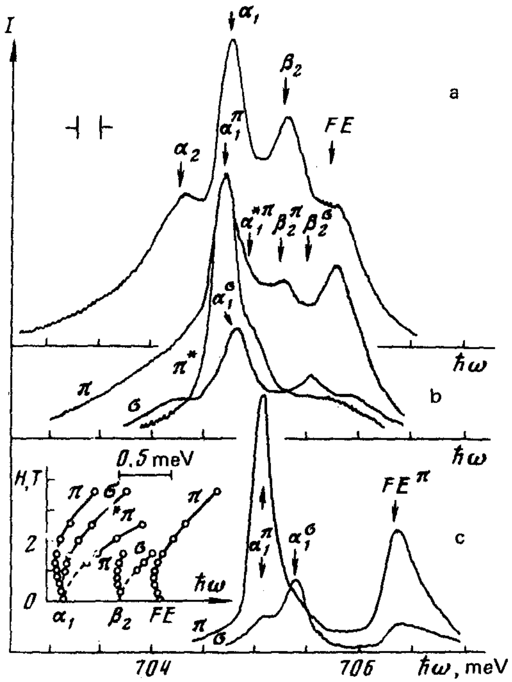

FIG. 3. *LA* emission spectra (π and σ components) of Ge(Sb) in a magnetic field $\mathbf{H} \parallel \mathbf{P} \parallel \langle 1.1.16 \rangle$, recorded in a Voigt geometry ($\mathbf{H} \perp \mathbf{k}$) at $P=429$ MPa, $T=1.6$ K, and $W=25$ W/cm² with a constant amplification factor: a) $H=0$; b) $H=0.8$ T; c) $H=3.6$ T. The spectrum marked with an asterisk at $H=0.8$ T was recorded at $W=5$ W/cm² (×4). The dependences of the positions of the lines on the magnetic field are shown in the inset.

tensity ratio ($I_\pi : I_\sigma = 3:1$) is determined by the ratio of the matrix elements from the π and σ transitions and does not depend on the magnitude of the splitting). Therefore, two electrons in EIC form a spin singlet. In the phonon-free spectrum, where the α_1 line has the shortest wavelength, it is possible to observe also the π component (more intense than σ) of the radiation from the excited spin state of EIC, $\alpha_1^{*\pi}$. The ratio $I(\alpha_1^{*\pi})/I(\alpha_1^{\pi})$ decreases exponentially with increasing magnetic field due to the thermal depopulation of the excited state. The $\alpha_1^\pi - \alpha_1^\sigma$ splitting corresponds to an electronic g factor on the neutral donor g_e (ND) = 1.5 ± 0.1, while the $\alpha_1^\sigma - \alpha_1^{*\pi}$ splitting corresponds to the g factor of a hole in EIC g_h (EIC) = −3.2 ± 0.1.

Two components β_2^π and β_2^σ are also observed in the β_2 line (Figs. 2 and 3), corresponding to transitions from the low spin state of E$_2$IC, whose splitting, as expected, corresponds to the splitting of the EIC ground state ($g_h = -3.2$). Therefore, in E$_2$IC: 1) two holes form a spin singlet and 2) there is only one electron in the outer shell. Because of the presence of Zeeman splitting of free excitons and the absence of such splitting of electrons in EIC and electrons in the ground shell and holes in E$_2$IC, the EIC binding energies and, especially, E$_2$IC decrease when a magnetic field is switched on (Fig. 2). This is indicated by the approach of the α_1 and β_2 lines, corresponding, respectively, to transitions between the ground state of EIC and ND and E$_2$IC and EIC, to the emission line of excitons (Fig. 3). A strong decrease in the intensity of the α_2 and β_2 lines, which for $H > 2.5$ T disappear from the spectrum even at $T = 1.6$ K and with the highest (≈ 100 W/cm^2) excitation densities, is observed at the same time.

Thus, in studies of emission from uniaxially compressed Ge(Sb) crystals with nondegenerate bands, we discovered biexciton–impurity complexes, whose stability does not follow from the direct analogy to hydrogen. The reasons for the stability of such complexes could be a strong anisotropy of the conduction band or electron-phonon interaction, absent in the case of hydrogen. The electron-phonon interaction in Ge, a covalent crystal, although it is small, could turn out to be important due to the very small binding energy ($\Delta_2 \sim 0.3$ meV).

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