

independent of T in this interval, that the electron gas is degenerate.

Measurement of the Hall effect at room temperature has shown that the electron density in the CuS film is of the order of 10^{20} cm⁻³ at thicknesses 200 and 500 Å.

In the case of films of these thicknesses, the values of the maximum measurement error referred to the values of the amplitude is on the average 0.4 and 0.3, respectively.

Thus, the observed temperature oscillations are beyond the measurement error and the maximum value of the amplitude corresponds to a temperature ~150°K.

The periods of the oscillation change insignificantly with decreasing thickness (by approximately 1°K).

It is also seen from the figure that the smaller the film thickness the stronger the oscillatory dependence of ρ on T and the ratio of the two succeeding periods for a given thickness increases with increasing temperature like

$$\frac{\Delta T_n}{\Delta T_{n+1}} \approx \frac{T_n^{1/2}}{T_{n+1}^{1/2}} .$$

The authors believe that the observed temperature oscillation of the resistivity of the CuS films is due to the non-equidistant arrangement of the subbands in the high-temperature quantum size effect, in accord with the theory of S.S. Nedorezov [7].

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SINGLET AND TRIPLET EXCITON-IMPURITY STATES IN SEMICONDUCTORS

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The approximations on the basis of which exciton-impurity complexes in crystals are considered usually do not take into account exchange, spin-orbit,

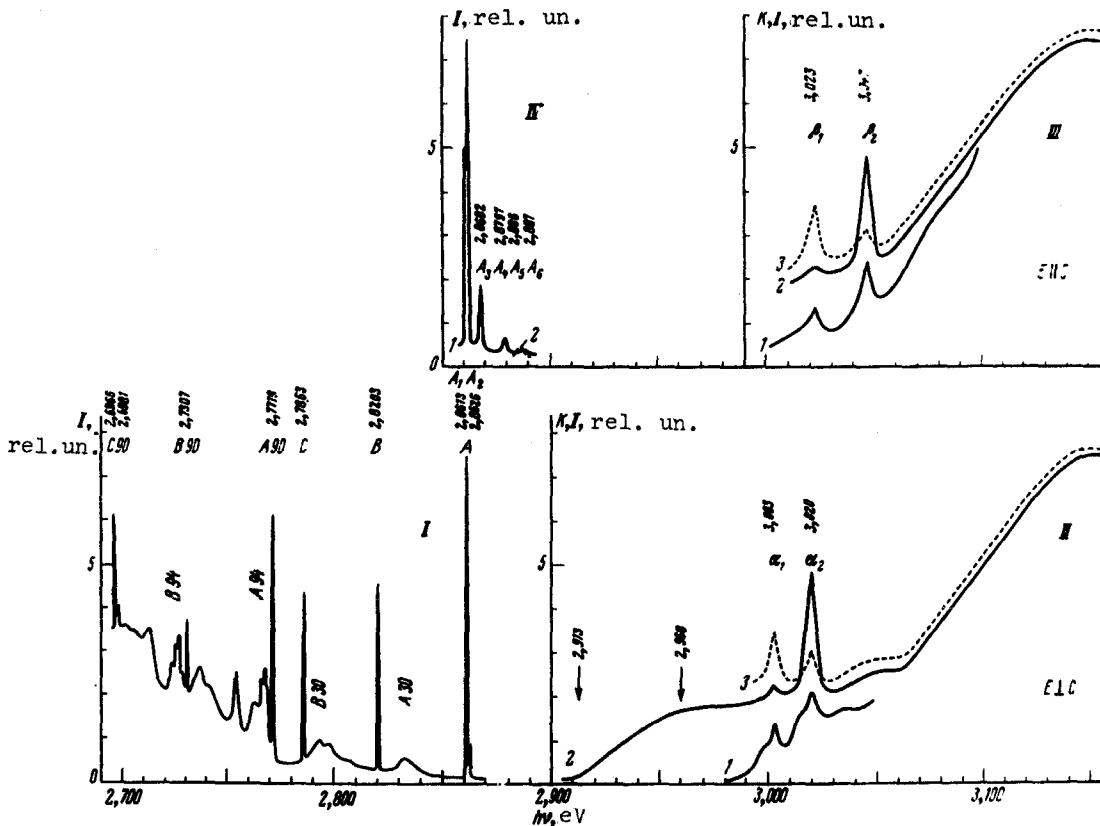


Fig. 1. Photoluminescence spectra [I ($T = 4.2^\circ\text{K}$, $\vec{E} \perp \vec{C}$), IV ($T = 77^\circ\text{K}$: 1 - $\vec{E} \perp \vec{C}$, 2 - $\vec{E} \parallel \vec{C}$)], absorption spectra ($T = 77^\circ\text{K}$: II - 1 - $\vec{E} \perp \vec{C}$, III - 1 - $\vec{E} \parallel \vec{C}$), and excitation functions for the A complexes ($T = 77^\circ\text{K}$: II - 2 - $\vec{E} \perp \vec{C}$, III - 2 - $\vec{E} \parallel \vec{C}$) and for the B complexes ($T = 77^\circ\text{K}$: II - 3 - $\vec{E} \perp \vec{C}$, III - 3 - $\vec{E} \parallel \vec{C}$) of the single crystals $\alpha\text{-SiC}$ (6H). K, I - absorption coefficient and luminescence intensity in relative units.

and other interactions of the momenta [1]. This is justified for complexes with sufficiently large radius. It was found experimentally [2, 3] that in some cases the energy spectrum of the exciton-impurity complexes has a structure due to the j-j interaction of the electron and hole. This interaction is important in crystals with sufficiently large spin-orbit splitting of the valence band. In the opposite case, other types of interaction are also possible. It is to be expected that an important role will be played in exciton-impurity complexes of sufficiently small radius by the exchange interaction, similar to that considered for free excitons [4, 5].

The purpose of the present work was to establish the very existence of the interactions indicated above and to determine the relation between them for three-particle exciton-impurity complexes in semiconductors.

A suitable object for this purpose is silicon carbide. In one of its polytypes $\alpha\text{-SiC}$ (6H) the absorption edge is due to indirect transitions, the spin-orbit splitting of the valence band is about 0.005 eV, and the crystal splitting exceeds 0.030 eV [6, 7]. Nitrogen produces donor states and can occupy three non-equivalent positions in the $\alpha\text{-SiC}$ (6H) lattice. For each of these, the nearest surrounding is tetrahedral, but the distances from the tetrahedra to the nearest sites in the direction of the optical axis differ

appreciably. Therefore each atom of the substitution impurity is in a field of symmetry C_{3v} . The unit cell possesses the same symmetry.

On each of the non-equivalent donors there are produced three-particle exciton-impurity complexes which give at low temperatures the luminescence spectrum represented by curve I of Fig. 1. The lines A, B, and C correspond to phononless transitions of the excitons localized on the non-equivalent donors of type A, B, and C respectively. Each line together with the phonon replica bands (some of them are marked in the figure) forms a spectral series. Each series contains the lines A-90, B-90, and C-90, which correspond to transitions with excitation of local oscillations of impurity centers (nitrogen) [7].

Curves II-1 and III-1 of Fig. 1 represent the absorption spectra of the same crystals for $\vec{E} \perp \vec{C}$ and $\vec{E} \parallel \vec{C}$. Such spectra were observed by the authors earlier [8]. It is important that in the investigated crystals in the region of the luminescent series (A, B, C) no absorption lines were observed. Curves II-2 and III-2 represent the excitation functions of line A, measured at two polarizations. Analogous excitation functions are obtained also for the lines A-90. Curves II-3 and III-3 are also excitation functions, but pertain to the line B or B-90. Attempts to measure the excitation functions for the line C turned out to be less successful, since this line is weak and lies against a rather intense background of phonon replicas of the preceding series. On occasions we were successful in observing a singularity for $\vec{E} \perp \vec{C}$ at 2.960 eV.

The data on the excitation functions offer evidence that unlike the previously advanced assumption [8], the lines α_1 and β_1 are due to the B centers, and α_2 and β_2 to the A centers. They are connected with the excited states of the exciton-impurity complexes at the corresponding centers, since such a large Stokes shift (0.15 - 0.17 eV) of the ordinary type is impossible at the observed narrowness of the luminescence lines (10^{-4} eV). The absorption lines are likewise not wide enough (5×10^{-3} eV). They cannot be due to transitions to the excited states connected with the presence of levels with $n = 2$ at the donor centers, since the probability of such transitions would be smaller than for $n = 1$. This will be justified also when account is taken of the anomalous enhancement of the absorption lines due to their proximity to the exciton band [9], since indirect transitions take place in the investigated crystal.

We believe that the absorption lines are due to dipole-allowed transitions, and the luminescence lines to forbidden ones. If we assume that the two corresponding classes of levels of the complexes are due to exchange interaction

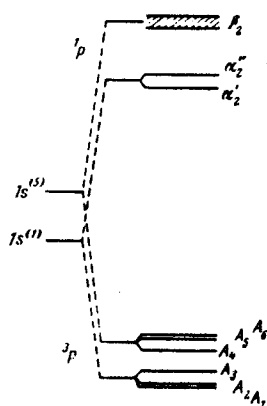


Fig. 2. Scheme of energy states for A complexes in α -SiC (6H).

between the electron and the hole, then when account is taken of the crystal and spin-orbit splittings we obtain the level scheme shown in Fig. 2 for the A complexes. Here the states $1s^{(1)}$ and $1s^{(5)}$ are levels of the isolated donor with account of the intravalley splitting in the tetrahedral field, similar to what takes place in silicon [10], and the minimum distance of the level $1s^{(1)}$ from the valence band, as is seen from the long-wave excitation function, amounts to 2.913 eV. The magnitude of the multi-valley splitting for the A centers is about 25 meV. The exchange interaction leads to the formation of singlets (1P) and triplets (3P) with an energy interval between them 0.15 - 0.16 eV¹⁾. The fine structure of the

¹⁾ It is important here that the electron at the donor is in the s-state, and the wave function of the hole should be of the p-type in accordance with the symmetry of the valence band.

singlets and triplets is the result of splitting in the crystal field (C_{3v}) and spin-orbit interaction. The former is close to 8 meV and the latter is about 1.3 meV.

It is interesting that in the luminescence spectrum of α -SiC (6H) it is possible to observe besides the A line also five lines that increase gradually in intensity with increasing temperature [7]. The form of these lines at 77°K is shown in Fig. 1 (curve IV). In the absorption spectrum, the α lines also have a fine structure. The presence of a fine structure in luminescence and absorption is in good agreement with the scheme of Fig. 2, where the relative position of the levels is shown on the basis of the experimental data.

It must be assumed that the intercombination transitions become partially allowed because of the spin-orbit interaction. The ratio of the oscillator strength of the dipole-allowed transitions to the oscillator strength of the intercombination transitions is equal in order of magnitude to the ratio of the square of the exchange splitting to the square of the spin-orbit splitting. We have measured directly the damping time of the A series upon excitation in the absorption α_2 line. It turned out that $\tau = 8 \times 10^{-5}$ sec. This agrees well with the corresponding values of the splitting, if it is assumed that for dipole-allowed transitions $\tau \sim 10^{-8}$ sec.

Thus, the spectroscopic manifestations of singlet and triplet exciton-impurity states in semiconductors were found for the first time, with α -SiC (6H) crystals as the example. The nature of these states is due to the exchange electron-hole interaction, which turns out to be sufficiently large for small-radius complexes.

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DIRECT OBSERVATION OF FLUCTUATIONS OF DEUTERIUM DISTRIBUTION IN ($Nb_{0.33}Ti_{0.66}$) $D_{0.33}$

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The values of the equilibrium dissociation pressure calculated for hydrides of group-IV metals by the model of statistically distributed hydrogen do not agree with the experimentally obtained values. Libowitz proposed [1] that this disparity is due to the presence of fluctuation inhomogeneities of the hydrogen distribution in these hydrides. Insofar as the authors know, no experimental observation of hydrogen fluctuations in hydrides was ever reported.