Formation of electron-neutral donor complexes in indirect optical transitions in germanium crystals

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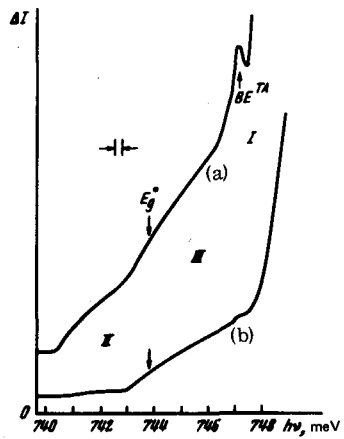
A structure due to indirect optical transitions of electrons from the valence band to levels of complexes comprising an electron and a neutral donor has been observed in the spectral distribution of the photoconductivity of germanium crystals containing shallow donors.

It was suggested in[1] that electron-impurity complexes consisting of neutral donors bound to electrons can exist in semiconducting crystals. The similarity of the electronic structure of such a complex with the structure of the negative hydrogen ion H^0 has made it possible to estimate the binding energy of the electron with the neutral donor. This energy, according to[1], should be about 1/20 of the donor ionization energy. An electron-impurity complex consisting of a neutral donor and an electron will henceforth be called for brevity a D^- complex.

The investigation of D^- complexes is of considerable interest, since there are many data pointing to their important role in the scattering[2] and recombination[3,4] of the carriers at low temperatures, in the impurity conductivity,[5] and in other phenomena.[6]

We have proposed that the absorption and photoconductivity (PC) spectra near the indirect edge of the intrinsic germanium absorption one can observe singularities due to the transition of the electrons from the valence band to the levels of the D^- complexes. Since such transitions produce D^- complexes and free holes, these singularities in the absorption and PC spectra should take the form of "steps" characteristic of level-band transitions. Since the binding energy of a D^- complex with a shallow donor in germanium does not exceed 1.6 meV,[7] and the binding energy of the indirect exci-



Photoconductivity spectrum of germanium crystal containing 2×10^{15} atoms of Sb per cm^3 at temperatures $T=4.2$°K (a) and 1.7°K (b).

ton is 3.8 meV, [8] the absorption spectrum due to the formation of these impurity complexes can be masked by relatively intense indirect exciton absorption. Indeed, an analysis of the absorption spectra obtained in[9] for doped germanium, and also in the present study, has revealed no structure capable of being identified with the mentioned mechanism of D^--complex formation. Since the efficiencies of the mechanisms whereby carriers are produced by exciton decay and inoptical transitions with D^--complex formation can be different, we deemed it of interest to analyze the spectral distribution of the PC near the intrinsic absorption edge.

We investigated the spectral distribution of the PC in germanium crystals doped with Sb, P, and As donors in the phononless region and in the region of transitions with excitations of TA and LA phonons. A typical sample measured $2\times5\times4$ mm^3. The contacts were deposited on the two smaller faces by fusing-in an In-As alloy in vacuum. The PC signal was registered at 600 Hz using a mechanical chopper for the light beam and a synchronous-detection circuit.

The figure shows the PC spectra of a germanium crystal containing 2×10^{15} Sb atoms per cm^3. The spectra show clearly three photocurrent steps due to different absorption and PC mechanisms. Step I is connected with simultaneous excitation of the indirect excitons and TA phonons, which ensure satisfaction of the wave-vector conservation law. Naturally, this step is observed in the absorption and photocurrent spectra of both pure crystals and those doped with various impurities. Step II is due to phononless production of indirect excitons with simultaneous elastic scattering by the impurity atoms. This step is present in the absorption and PC spectra of crystals containing both donor[9,1)] and isoelectronic impurity centers.[10] The energy positions of steps I and II relative to the edge of the forbidden band E_g^0 do not depend on the nature of the impurities, but are determined by the energy of the TA phonon and by the binding energy of the indirect exciton, i.e., by the properties of the germanium crystal lattice.

Step III is observed only in germanium crystals containing donor centers. The small degree of compensation of the samples (less then 10%) used in the present experiments, and also the low field intensity (1 V/cm) at which the PC was investigated, give grounds for assuming that step III is due to the presence of neutral donor centers in the crystal. The fact that the observed singularity takes the form of a step indicates that the transition takes place between a level and a band. The energy position of this step depends on the type of the main impurity. Thus, the start of the step III is shifted relative to E_g^0 to the lower-energy region in germanium crystals doped with antimony, by 1.0 ± 0.2 Mev, by 1.3 ± 0.2 meV if doped with phosphorus, and 1.6 ± 0.2 meV if doped with arsenic.[2)] These shifts are in good agreement with binding energies of the electron with the neutral donors in germanium, as obtained in a study[7] of the PC spectra in the far infrared. This allows us to conclude that the step III observed in the PC spectrum is due to indirect phononless transition of an electron from the valence band to the level of the D^- complex. Analogous indirect transition with excitation of LA phonons were observed by us in PC spectra at higher energies.

The line BE^{TA} located near the start of step I is due to the formation and photoactive decay of electrons bound to neutral antimony donors. The width of this line in the PC spectra shown in the figure was determined by the spectral width of the monochromator slit, 0.3 meV in our case.

A comparison of spectra a and b shown in the figure shows that when the temperature is lowered from 4.2 to 1.7°K the photocurrent due to the formation and photoactive decay of the excitons decreases significantly, whereas the photocurrent in step III (after subtracting the contribution of step II) does not change noticeably. This indicates that the mechanisms whereby carriers are produced following exciton decay and upon absorption of light in step III are different. It is apparently this difference which ensures the possibility of observing the structure in the PC spectrum, a structure that cannot be observed directly in the spectrum of the abosrption coefficient.

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1) Phononless formation of free excitons with scattering by antimony atoms is much less effective than the analogous process with phosphorus or arsenic atoms, [1] and so far as we know it has been observed in the present study for the first time.

2) The PC spectra of germanium doped with antimony or phosphorus reveal, besides steps I, II, and III, also a group of lines in the phononless region, due to the formation and photoactive decay of excitons bound with the neutral donors.

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