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RADIATIVE CAPTURE OF ELECTRONS BY NEUTRAL AND SINGLY-CHARGED ZINC IONS IN GERMANIUM

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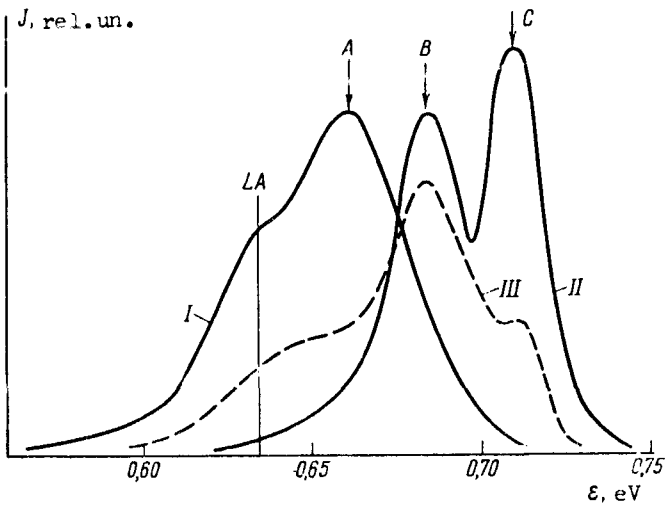
In radiative transitions of carriers to neutral impurity centers in semiconductors such as Ge and Si (minimum of the conduction band located at the center of the Brillouin zone), the probabilities of phononless and phonon transitions vary with the type of impurity. Pokrovskii and Svistunova [1] have shown that this is connected with the depths of the corresponding levels in the forbidden band. The extent to which the transition-probability ratio depends on the chemical nature of the impurity atoms or its charge state is still unclear, however. Thus, for example, in optical transitions in which As and Sb atoms take part, this ratio changes appreciably [2], in spite of the small difference in the energy levels (E_{Sb} = 0.0096 eV and E_{As} = 0.0127 eV). This is due apparently to the different sizes of the Sb and As atoms, and consequently to the different form of the Coulomb fields of these atoms in the lattice.

Special interest attaches to radiative recombination at deep multiply-charged impurities, all the more since there is still no adequate theory of deep impurities [3,4].

We have investigated the emission corresponding to electron transitions to the energy levels of zinc atoms in the charge states Zn^0 and Zn^-. Zinc produces in germanium two acceptor levels with energies 0.03 and 0.09 eV over the top of the valence band. The Zn concentration in our experiments ranged from 1×10^{15} to 4×10^{17} cm^{-3}. Nonequilibrium carriers were produced in the sample by injecting holes through a p-n junction or by illumination. All samples had n-type conductivity, so that under equilibrium conditions all the Zn atoms were in the $Zn^=$ state. The measurements were made in the temperature interval 20 - 150°K.

At temperatures from 60 to 150°K the recombination-radiation spectrum included lines corresponding to electron transitions to the Zn^- level (0.09 eV) and to the valence band. At low injection levels the spectrum contained only an emission line corresponding to an electron transition to the Zn^- level (Fig. 1, curve I). The maximum with quantum energy

0.661 eV (A) corresponds to a phononless transition to the 0.09 eV level. As seen from the figure, the radiation was accompanied by emission of a longitudinal acoustic (LA) phonon with



Recombination-radiation spectra of germanium doped with zinc and antimomy. I - N_{Sb} = 4 a x10^{15} cm^{-3}, N_{Zn} = 1 x 10^{15} cm^{-3}, T = 78°K; II - N_{Zn} = 3 x 10^{16} cm^{-3}, N_{Sb} = 5 x 10^{17} cm^{-3}, T = 32°K, i = 90 mA; III - N_{Zn} = 3 x 10^{16} cm^{-3}, N_{Sb} = 5 x 10^{17} cm^{-3}, T = 30°K, i = 30 mA. A - line corresponding to phononless transition to Zn^- ion; B - line corresponding to electron transition with emission of LA phonon (E_{LA} = 0.0274 eV) to Zn^0 ion; C - line corresponding to electron transition to the valence band with emission of LA phonon (E_{LA} = 0.0274 eV).

energy E_{LA} = 0.0274 eV. It is obvious that the total line width ($\Delta E \sim 0.060$ eV) is determined by both the phononless and the phonon transition contributions, the intensities of the two being commensurate. The presence of an intense phononless transition can be attributed to the fact that the electron is captured by a deep negatively-charged center. In such a capture, the selection rules for band-band transitions or for transitions from a band to a hydrogen-like level, resulting from the symmetry of the points L(1, 1, 1) and Γ(0, 0, 0) [5] are relaxed to a considerable degree, and this leads to the appearance of the phononless transition.

The presence of a Coulomb barrier for the electron captured by a negative zinc ion explains the difference between the energy of the optical transition from the conduction band (0.075 eV) and the thermal ionization energy (0.09 eV) [6]. Thus, the Coulomb barrier in capture by a negatively charged center is 0.015 eV.

The presence of a long-wave "tail" with weakly pronounced structure is due to scatter of the impurity centers, resulting from the Coulomb interaction between the donors and acceptors, which at the given concentration (N_{Zn} = 1 x 10^{15} cm^{-3} and N_{Sb} = 4 x 10^{15} cm^{-3}) amounts to only 2 - 3 MeV. In addition, an increase in the impurity concentration to 5 x 10^{17} cm^{-3} gives rise only to a slight change in the line width. It can apparently be assumed that the existence of a long-wave "tail" of the emission line is connected with emission of phonons of a different type.

When the temperature was lowered to 30°K, we observed radiation with a quantum energy 0.683, following capture of electrons by a shallow (0.03 eV) level of Zn^0 (Fig. 1, curve II). From a comparison of spectra I and II we see that when the electrons are captured by a shallow level the emission spectrum is a straight line corresponding to radiative transition of an electron with emission of phonons of one type (LA), corresponding to the usual conditions for recombination by a shallow acceptor level in Ge. There are no phonon emissions of any other type.

In the case of low injection levels at the same temperatures (30°), the relative role of the radiation connected with electron capture by Zn^- increases, and the intensity of the emission produced when the electrons go over into the valence band decreases (curve III). Thus, apparently no phononless transitions of electrons to Zn^0 take place.

The activation energy determined from the position of the emission line for Zn^0 turns out to be 0.03 eV, in good agreement with the data obtained by other methods [6]. It is obvious that the absence of a barrier in the capture of an electron by Zn^0 eliminates the difference between the thermal and optical ionization energies.

It is interesting to note that optical transitions of electrons to different charge states of Zn in Ge appear in sequence, depending on the temperature interval, in investigations of one and the same sample. At low temperatures, when the zinc atoms are in the $Zn^=$ charge state, we obviously have a consecutive capture of two holes, so that the zinc atom goes over into the Zn^0 state ($Zn^= + p + p \rightarrow Zn^0$). This is followed by radiative capture of an electron by the Zn^0 ion. At higher temperatures, owing to the thermal ejection of holes from the 0.03 eV level, transitions predominantly to the 0.09 eV level appear.

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IONIZATION OF Ar ATOMS IN THE Ar^+ EXCITED STATE

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Recent publications point to an important role played by electron-atom collision processes in which the states of two atomic electrons are changed. An example of such a double process is the ionization of an Ar atom with simultaneous excitation of Ar^+ [1,2]:

$$Ar(3p^6) + e \rightarrow Ar^+(3p^4 L_i S_i 4p) + e + e. \qquad (1)$$

When the atom is described by orthogonal single-electron wave functions, the cross section of this process in the first Born approximation is equal to zero. The sudden-perturbation ap-