# Absorption spectra in electron transitions between excited states of impurities in germanium

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The absorption spectra of slow donors, for electron transitions between excited states, were measured in the 2–0.5 mm band by the method of double modulation of the magnetic field.

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A study of the spectra of photoconductivity of shallow impurities in photothermal ionization of the ground state[1] turned out to be a valuable method for the investigation of semiconductors (e.g., [2,3]). The use of this method in the submillimeter band, where the optical transitions are realized only between excited states, has yielded many new data on the energy structure of shallow impurity centers.[4]

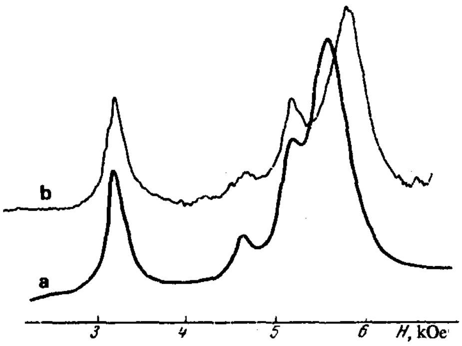

FIG. 1. Spectra of absorption (a) and photoconductivity (b) in Ge : Sb, $T = 14$ K, $\lambda = 740\ \mu$.

Inasmuch as the photothermal ionization of the excited states is a complicated process connected with the absorption of the photon following a transition of an electron between the excited states and its subsequent thermal ejection into the band, the information obtained from the absorption spectra would add significantly to the results on the photoconductivity, for example, it would facilitate the identification of the transition, and would make it possible to determine the lifetimes at the excited states of the impurity and the probabilities of the transitions between different states.

An experimental investigation of the absorption spectra, especially for the excited states, where the population is smaller by several orders of magnitude than in the ground state, encounters considerable difficulties because of the impossibility of modulating the absorption effect. Therefore the investigations have so far been confined to absorption spectra in electron transitions from the ground state in doped Ge ($N_D \approx 10^{15}$ cm$^{-3}$).[5]

We have investigated the absorption spectra due to electron transitions between excited states of shallow donors under the conditions of the Zeeman effect in pure Ge ($N_D + N_A < 10^{14}$ cm$^{-3}$) in the submillimeter band (2–0.5 mm), at temperatures $T \approx 8$–25 °K. The measurements were performed with a high-sensitivity spectrometer with backward-wave tubes, using the method of double modulation of the magnetic field employed in EPR spectroscopy. High-frequency modulation with depth $\lesssim 200$ Oe was carried out at a frequency 75 Hz, as well as a sawtooth sweep of the magnetic field within the limits of the recorded spectrum (0.3–5 kOe), with a period of several minutes. The shape of the spectrum was reconstructed from the derivative signal by means of an integrator with a time constant 1.5 hr. The measurements were performed by transillumination; the detector was $n$-InSb. Contacts were placed on the investigated sample, so that both the absorption spectra and the photoconductivity spectra could be recorded under the conditions of one experiment. The sample was 10 mm thick and was so oriented that the magnetic field was parallel to the [111] crystallographic axis. The sensitivity of the apparatus made it possible to register transitions with intensity corresponding to an absorption coefficient $\alpha = 10^{-4}$ cm$^{-1}$. Altogether, more than 10 transitions were recorded in the absorption spectra.

By way of example, Fig. 1 shows the absorption and photoconductivity spectra obtained at $T = 14$ °K for a Ge : Sb sample. We see that the ratio of the intensities of the transitions are different for the two spectrograms, and the positions of the lines, as well as for other investigated lines, coincides, with the exception of the lines with energy $\epsilon_0 = 1.87$ meV in a zero magnetic field. Figure 2 shows the temperature dependences of the intensities of several absorption lines for the same sample with $\epsilon_0 = 1.31$, 1.11, and 1.87 meV. At low $T$, an exponential section of $\alpha(1/T)$ is observed for each line, and from this section it is possible to determine the energy gap $\Delta\epsilon_H$ between the ground states and the initial state of the corresponding transition. Thus, for example, for the lines $2s \rightarrow 2p_{\pm1}$(1.87 meV) and $3p_0 \rightarrow 3d_{\pm1}$(1.31 meV), which were identified in[4], $\Delta\epsilon_H$ amounts to $7.3 \pm 0.3$ and $8.25 \pm 0.3$ meV, respectively. The difference between the initial states of these transitions, which is equal to the difference of the energies of the levels $2s$ and $3p_0$, is 0.96 meV, which agrees well with the 0.96 meV calculated in[6], and the energy of the ground state of the Sb impurity in Ge, with allowance for the data of[6], is $10.9 \pm 0.4$ meV. For the unidentified transition with $\epsilon_0 = 1.11$ meV the value of $\Delta\epsilon_H$ is $9 \pm 0.3$ meV, so that its initial state can be assumed to be the level $3p_0$ or $3s$.[6] With increasing $T$, a weakening of the temperature dependence is observed and even an absolute decrease of the absorption; these can be attributed to equalization of the populations of the levels that participate in the transitions, and to depletion of the ground state of the impurities.

A comparison of the temperature dependences of the absorption and photoconductivity line intensities shows that the probability $W(T)$ of electron ejection following photothermal ionization of excited states is determined, for certain transitions, say with $\epsilon_0 = 1.87$ meV, only by the final state $\epsilon_k$ and is proportional to $\exp - (\epsilon_k/kT)$ (dependences of this type were observed in[2]), and in a

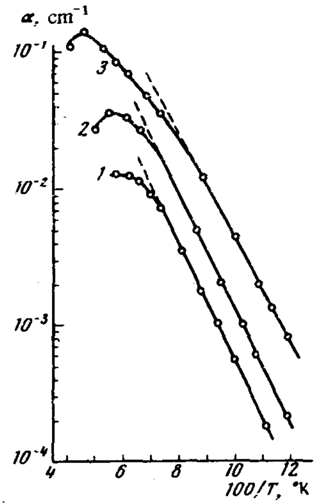

FIG. 2. Temperature dependence of the line intensity $\alpha$ of the absorption lines with $\epsilon_0 = 1.11$ meV and $\lambda = 1044\ \mu$ (1), 1.31 meV and 895 $\mu$ (2), and 1.87 meV and 685 $\mu$ (3); $H = 1$ kOe. The plots are given for the lighter components of the spectrum.

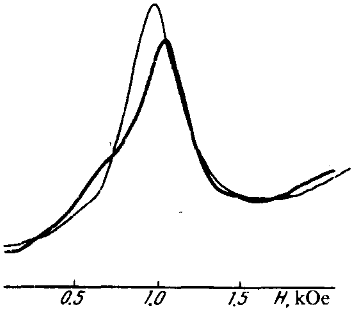

FIG. 3. Absorption line (thin) and photoconductivity line (thick) of Ge : Sb for the lighter components of the transition $2s \to 2p_{\pm1}(\epsilon_0 = 1.87$ meV).

number of cases a large contribution to the photoconductivity signal is made also by ejection from the initial state. Thus, for the 1.31-meV line there is observed a nonmonotonic $W(T)$ dependence with a maximum at $T \sim 8$ °K.

Interesting singularities were revealed for the $(2s \to 2p_{\pm1})$ transition ($\epsilon_0 = 1.87$ meV). The absence of two transitions connected with the splitting of the 2*s* level from the photoconductivity spectra[4] has given rise to a discussion in the literature.[7] The absorption spectrum for this transition turns out to be represented by two poorly resolved components of different intensity (Fig. 3). The splitting of the 2*s* level, extrapolated to zero magnetic field and obtained from these measurements, amounts to $0.03 \pm 0.01$ meV, in fair agreement with the value 0.07 meV predicted in[7] for Sb.

The absence from the photoconductivity spectrum of a weak line corresponding to a transition from the singlet level, and the relative line shifts corresponding to a transition from the triplet state from the photoconductivity and absorption spectra (see Figs. 1 and 3), show that the photothermal ionization of the excited states of shallow impurities in Ge cannot always be described by two independent processes—optical transition of the electrons between excited states and thermal ejection of the carriers into the band.

Additional experiments carried out on Ge : As, for which one should expect in accordance with[7] a larger splitting of the 2*s* state, have revealed the presence of two lines corresponding to transitions from the singlet and triplet states, both in the absorption and in the photoconductivity spectra. The splitting in a zero magnetic field, amounts to $0.4 \pm 1$ meV.

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