Dislocation-state spectrum of plastically deformed *n*-germanium

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The electric conductivity, the Hall effect, and the photoconductivity of the same plastically deformed samples of *n*-germanium with anisotropic structure of 60-degree dislocations were investigated in the temperature interval 80–250 K and in the spectral range 0.4–0.7 eV. The Hall constant depends on the orientation of the magnetic field and of the current relative to the direction of the dislocations. The temperature dependence of the electron density is used to estimate the position of the dislocation states, which turns out to be located in the lower half of the forbidden band. The photoconductivity spectra of the deformed samples have singularities attributed to the excitation of electrons from the same dislocation states into the conduction band.

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INTRODUCTION

The determination of the position of dislocation states (*D* states) in the forbidden band of semiconductors from electric measurements (electric conductivity and the Hall effect) are based on the Shockley-Read ideas of dangling bonds and include an experimental determination of the filling factor *f* and a correct allowance for the energy of the Coulomb interaction of the electrons on the dislocations, which depends on the temperature of the filling coefficient and on the screening mechanism.[2,3] The results of numerous experimental investigations of the electric properties of plastically deformed *n*-germanium,[4-11] reduced within the framework of these concepts, turn out to be quantitatively contradictory: Energy states in both the upper[4,6,7,9] and lower[5,8,10,11] halves of the forbidden band of germanium are associated with dangling bonds of dislocations. An analysis of Refs. 4–11 shows that this uncertainty is due principally to the difference between the absolute values of the experimentally determined filling coefficient *f*. It is therefore necessary to determine the cause of this discrepancy.

Another important source of information on the energy spectrum of the *D* states in germanium may be the photoconductivity (PC) of plastically deformed samples. However, the PC spectra obtained by various authors[12-18] are such that their detailed interpretation is quite difficult. The PC spectra have two broad bands at $h\nu \approx 0.1-0.35$ eV and $h\nu > 0.40$ eV, and in both bands there are sharp maxima as well as such singularities as thresholds, steps, small maxima, which according to data by different authors turn out to be at different energies. This may be due to a number of factors, in particular:

1) The PC spectra connected with the dislocations may be quite complicated because the energy spectrum of the dislocation states has a complicated structure itself.

2) All the investigations of the PC were made on strongly deformed crystals with a disordered dislocation structure (*D* structure), containing various types of dislocations, and this can complicate the PC spectrum even more.

3) The PC spectra can be influenced by surface states.

4) Many investigations were made on crystals produced under various conditions with different filling of the dislocation with electrons, but in no study were the PC and the Hall effect investigated jointly.

Furthermore the PC spectra cannot as a rule show in which half of the forbidden band the investigated states are located. This information can be obtained from reliable electric measurements.

We have therefore deemed it useful to carry out joint investigations of the electric conductivity, of the Hall effect, and of the PC of crystals with ordered structure of 60-degree dislocations under conditions that reduce the influence of the surface states on the PC spectra.

In the present paper we analyze the proposed sources of error in the determination of *f* and consider the possibilities of their elimination. The results of the reduction of the electric measurements are compared with the PC spectra obtained for the same samples.

1. ANALYSIS OF THE CAUSES OF THE SCATTER OF EXPERIMENTAL VALUES OF *f*

Since the dislocations are surrounded by space-charge regions that cannot be penetrated by the free carriers, a plastically deformed crystal constitutes an inhomogeneous system consisting of a conducting isotropic medium and of dielectric pores oriented in a definite manner. The electric conductivity σ and the Hall constant *R* in such a system depend on the angles between the directions of the electric current (J), the magnetic field (H), and the cylindrical pores (D). There are known[5,19] formulas that determine R and the electric conductivities $\sigma_\parallel$ and $\sigma_\perp$ along and across the pores for some variance of relative orientations of J, H, and D.

Orientation I, $(\mathrm{J} \perp \mathrm{D}; \mathrm{D} \perp \mathrm{H})$:

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$$R_1 = R_0/(1-\varepsilon), \tag{1}$$

$$\sigma_1 = \sigma_\perp = \sigma_0(1-\varepsilon)g(\varepsilon). \tag{2}$$

Orientation II, (J ⊥ D;D ∥ H):

$$R_2 = R_0, \tag{3}$$

$$\sigma_2 = \sigma_1. \tag{4}$$

Orientation III, (J ∥ D;D ⊥ H):

$$R_3 = R_1, \tag{5}$$

$$\sigma_3 = \sigma_\parallel = \sigma_0(1-\varepsilon). \tag{6}$$

Here σ_0 and R_0 are the electric conductivity and the Hall constant in the undeformed materials; ε is the fraction of the volume occupied by the cylindrical pores; $g(\varepsilon)$ is a certain function that takes into account the bending of the trajectories of the free carriers around the pores.[19]

In the preceding experimental studies,[4-11] R_0 was measured in a control sample, R_1 was measured in a deformed sample at orientation I, and formula (1) was used to calculate the value of ε, which is connected with the filling coefficient f in the following manner:

$$\varepsilon = N_D f / N_d a. \tag{7}$$

Here N_D is the dislocation density, N_d is the concentration of the donors in the undeformed crystal and determines R_0, and a is the distance between the dangling bonds. It was assumed here with certainty that as a result of the deformation the concentration of the donors between the dislocation cylinders remains unchanged. However, differences between the conditions under which the deformed samples were prepared, particularly differences in the deformation temperatures (300-850 °C, undoubtedly could produce in these studies[4-11] an uncontrollable decrease of the net dislocation contribution to the experimental values of f against the background of the redistribution of the impurities during the time of the plastic deformation, and consequently also an appreciable scatter of these values. Therefore the experimental proof that the donor concentration remains unchanged makes it possible to separate the pure dislocation contribution to the filling coefficient.

The use of formula (1) to calculate ε presupposes that all the dislocations are perpendicular to the magnetic field. Since the degree of anisotropy of the dislocation structure was not investigated in practically any of these studies, and the dislocation density was frequently determined from the bending radius,[4-7] this may also be one of the sources of the scatter in the experimental values of f.

Finally, a consistent analysis[5] shows that the measured R_1 can depend in an indeterminate manner on the nature of the contacts and (or) the length of the dislocation cylinders.[5] Therefore, this formula should, strictly speaking, not be used without an experimental verification of the validity of formula (1).

Recognizing that the range of decrease of ε is limited to the experimentally registered values ~10–100%, the arguments presented above are quite sufficient to account for the scatter, reported in Refs. 4–11, of the positions of the dislocation states in germanium. It is clear also that to obtain from Hall measurements reliable information on the dislocation contribution to f it is necessary to produce samples with a really anisotropic and known dislocation structure. The measurements of R_2 in orientation II made on a deformed sample can then yield information on the changes of the impurity situation around the dislocations. The validity of Eq. (1) must be verified on samples in which there are no such changes. To this end it is necessary to determine ε by another method; for example by measuring σ_0 and $\sigma_\parallel$ we can calculate ε from Eq. (6) under the assumption that the mobility of the electrons along the dislocations remains the same as in the control samples.

2. EXPERIMENTAL PROCEDURE

To produce a definite D structure we have used the method of four-point low-temperature flexure around the [011] axis with an artificially produced source of stresses, namely a scratch. The dislocations generated for 3–10 hours by a scratch made on the (100) surface along the sample under the influence of a load on the order of several kg/mm^2 at $T = 460$°C in a vacuum of 10^{-4} Torr. After removing the load, the sample was cooled with the furnace. This method makes it possible[20] to obtain crystals with straight-line 60° dislocations of density 10^5–10^7 cm^{-2}, as determined by selective chemical etching. In the investigated samples we had $N_D = (1-6) \times 10^6$ cm^{-2}. After the deformation, the samples were coated with gold and annealed at $T = 680-700$°C for 10 minutes in an atmosphere of ultrapure argon to eliminate the influence of strain-induced point defects.[21] The cooling rate did not exceed 5° per minute.

The real anisotropy of the dislocation structure in our samples was as follows: the number of etch pits on the $(0\bar{1}1)$ phase exceeds their number on the (100) and $(01\bar{1})$ phases by at least four times. Since the accuracy of the determination of the position of the dislocation states from the electric measurements depends on the accuracy of determining f, we have attempted to decrease as much as possible the experimental errors. Particular attention was paid to the choice of samples with homogeneous distribution of the dislocations over the volume. In different parts of the samples prepared for the measurement, the mean square deviation of the dislocation density from the average value did not exceed ±5%. The maximum errors were ±3% in the determination of the sample dimensions, ±1% in the measurement of the current voltage, and ±1.5% in the magnetic field intensity. To measure the Hall effect, samples were cut with dimensions 1×2×10 mm, and the preferred direction of the dislocations was always perpendicular to the long faces (D ⊥ J) and perpendicular (D ⊥ H) or parallel (D ∥ H) to the magnetic field. These samples were then cut into two or three plates, for which $\sigma_\parallel$ was determined from the measurement of the voltage drop on the current contacts at a known current (J ∥ D). Probe measurements of the distribution of the voltage in the control and deformed samples have shown that in the temperature interval 300–80 K the resistance of the regions next to the contacts is not more than 1–2% of the resistance of the entire sample. This made it possible to determine ε, and consequently also f for the same samples by two independent methods and to check on the validity of Eq. (1). Careful investigations of the homogeneity of the ingots have shown that the scatter of the donor concentration of the cross section and over the length of the ingot, in that part from which the control and deformed samples were cut, did not exceed ±2%. Therefore the maximum resultant error in the determination of f was ±10%.

To measure the PC, a direct current $J = 10^{-5}-10^{-2}$ A (depending on the sample resistance) was made to flow through the sample, and the change of the voltage ΔU on the sample following the illumination was measured. The dark conductance σ_0 and the specific PC σ_{PC} were independent of J. The sample was uniformly illuminated over its entire length, but the contacts themselves were not illuminated. The voltage ΔU was picked off the current leads or lateral contacts. In either case, the value of σ_{PC} was the same, thus indicating that the regions next to the contacts have little influence on PC. In our experiments, the condition $\Delta U \ll U_0$, was satisfied, where U_0 is the voltage on the sample in darkness. According to Ref. 22, in this case $\sigma_{PC}/\sigma_0 \ll 1$ and $\sigma_{PC}/\sigma_0 = \Delta U/U_0$. The accuracy with which PC was measured was 2% at $\sigma_{PC}/\sigma_0 = 10^{-4}$ and 10% at $\sigma_{PC}/\sigma_0 = 10^{-6}$.

The investigations were performed in the temperature interval 80–260°K and at an incident-light energy $h\nu = 0.4-0.7$ eV, when the light is weakly absorbed by the volume so that the concentration of the nonequilibrium carriers is practically constant over the volume. We note that the spectral dependence of the intensity of the incident light had no singularities and was smooth, and that the coefficient of light reflection from the samples was constant in the entire investigated range. To decrease the fraction of the scattered light with $h\nu > E_g$ (the width of the forbidden band) we used germanium filters up to 10 mm thick at room temperature.

Since the photoconductivity in the initial and in the deformed samples decreased slowly after the light was turned on (the fall-off time at nitrogen temperature was of the order of minutes), we used mainly unmodulated illumination. But to improve the sensitivity at $T > 160$ K, when the PC fall-off time became less than 0.1 sec, we used also modulated illumination of frequency 20 Hz. In view of the strong nonlinear dependence of σ_{PC} on the sample illumination intensity I, we shall present hereafter the σ_{PC}/σ_0 spectral dependence rather than that of $\sigma_{PC}/I\sigma_0$.

The investigations were made on n-geranium single crystals cut from five different ingots grown by the Czochralski method. The concentration of the shallow donors N_d in ingots No. 1–5 was respectively 1.1, 1.6, 2.4, 2.8×10^{13} and 1.1×10^{14} cm^{-3}, while the density of the growth dislocations did not exceed 10 cm^{-2}. The carrier lifetime at room temperature was 100–200 sec. No presence of oxygen was observed in the infrared absorption spectra.

3. EXPERIMENTAL RESULTS

We note first that the principal changes in the electric properties of deformed samples, connected with the filling of the dislocation states by electrons, occur in the temperature range 260–80°K. They are reflected in the temperature dependence of the Hall constant and the electric conductivity for the control (1) and deformed (2–5) samples from ingot No. 3, which are shown in Figs. 1 and 2.

The constancy of the Hall constant R in the control sample (curve 1 of Fig. 1a) at $80 \leqslant T \leqslant 240$ K indicates that there are no deep electrically active impurities. In the deformed sample (curve 2) there is a clearly pronounced difference, observed by us for the first time ever, between the absolute values of the Hall constants R_1 and R_2. It is important that in all the investigated deformed samples we have $R_1 > R_2$, but in different ingots $R_1 > R_2$, vary in different manners relative to R_0. Thus for ingots No. 1 and No. 3 we always have $R_1 > R_0$, and the difference between R_1 and R_0 noticeably exceeds the experimental error and increases with increasing N_D. In the same samples, R_2 increases somewhat compared with R_0, but when account is taken of the anisotropy of the D structure and of the error in the measurement of R, it can be assumed that this change is due to a contribution of dislocations that are not parallel to H when R_0 is measured. For example, assuming that in the deformed sample (curve 2) from ingot No. 3 (Fig. 1a) the difference between R_0 and R_1 or R_2 is due only to dislocations perpendicular to the magnetic field in the respective orientations I and II, the values of R_1 and R_2 at 80°K correspond [in accordance with formula (1)] to $\varepsilon_1 = 0.38$ and $\varepsilon_2 = 0.09$—which are the fractions of the volumes occupied by the corresponding dislocations. The difference between ε_1 and ε_2 corresponds to a 4:1 anisotropy of the D structure, in good agreement with the real anisotropy (5;1) in sample 2 and with the experimental error in the determination of the absolute

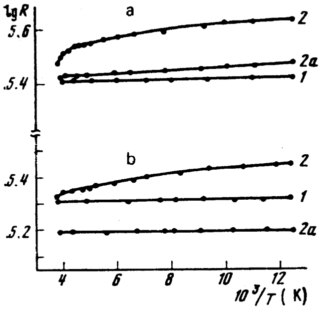

FIG. 1. Temperature dependence of the Hall constant in control (curve 1) and deformed (curve 2) samples from ingots No. 3 with $N_d = 2.4 \cdot 10^{13}$ cm^{-3}, $N_D = 2.6 \cdot 10^6$ cm^{-2} (a) and No. 4 with $N_d = 2.8 \cdot 10^{13}$ cm^{-3} and $N_D = 5.3 \cdot 10^6$ cm^{-2} (b). Curves 2 pertain to the orientation I (D⊥H), and curves 2a to the orientation II (D∥H).

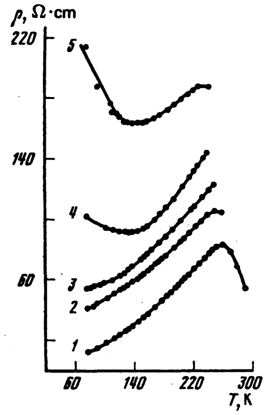

FIG. 2. Temperature dependence of the resistivity of the control (curve 1) and deformed (curves 2–5) samples with N_D equal, respectively, to 3, 3.8, 5.2, and 6×10^6 cm^{-3} from ingot No. 3. The electric field is directed along the predominant dislocation direction.

value of R, i.e., it can be assumed that the impurity makeup around the dislocations has remained unchanged.

In the deformed samples made of ingots Nos. 2, 4, and 5, on the contrary, R_2 decreases by 20–40% compared with R_1, patently in excess of the experimental error. In some samples $R_1 > R_0$ (Fig. 1b) and in others $R_1 < R_0$. We assume that the noticeable decrease of R_2 in these ingots is the consequence of uncontrollable processes of redistribution of the impurities during the time of introduction of the dislocations and the annealing of the point defects, and is evidence of the change of the impurity makeup around the dislocations. These ingots can therefore not be used for quantitative investigations of the influence of dislocations on the energy spectrum of the crystal.

Inasmuch as in ingots Nos. 1 and 3 the impurity environment around the dislocations remained unchanged, the decrease of R_1 in the deformed samples made of these ingots, compared with R_0, is the consequence of the filling of the states inside the D cylinders by electrons. Therefore all the investigations were made on samples made of ingots Nos. 1 and 3, and the results obtained for these two ingots agreed within the limits of experimental error.

A consequence of the acceptor action of the dislocations is also the decrease of the electric conductivity $\sigma_{\parallel}$ of the deformed samples 2–5 from ingot No. 3 compared with the conductivity σ_0 of the control (1) sample (Fig. 2). As expected, the conductivity of the deformed samples decreases with increasing N_D. The investigation of the trapping of electrons by dislocations was carried out by us at $T < 240$ K, since at higher temperatures the intrinsic electrons and holes make a substantial contribution to the electric conductivity (Fig. 2, curve 1).

The experimental data on the temperature dependence of R and σ in the control and deformed samples were used by us to calculate the fraction of the volume ε occupied by the dislocations by means of formulas (1) and (6), and the obtained values of ε were used to calculate the filling factor f with the aid of formula (7). The temperature dependences of the values of ε obtained in this manner for samples 2–5 and of the values of f averaged over several samples are shown in Figs. 3 and 4. We note first that the values of f obtained by

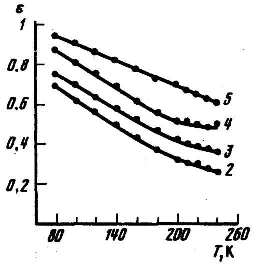

FIG. 3. Temperature dependence of the fraction of the volume occupied by dislocation cylinders, calculated from formula (4) for samples 2–5 from ingot No. 3.

the two methods agree within the limits of experimental error. Some differences between f obtained by these methods and observed at low temperatures can be attributed to the influence of the scattering by dislocations perpendicular to the current in the course of the measurement of $\sigma_{\parallel}$, which leads to a decrease of the electron mobility, i.e., to an apparent increase of ε and accordingly of f. The importance of this result must be emphasized, since it demonstrates that Eq. (1) is valid and that its use in the investigation of semiconductors with sufficiently well ordered D structure is justified. It follows from Fig. 4 that at $T < 200$ K the filling coefficient increases linearly with decreasing temperature, reaching a value 0.15 ± 0.01 at 80° K. Measurement of the Hall effect of several samples down to 4.2 K have shown that the increase of f at $T < 80$ K amounts to ~10%, i.e., the change of the filling of the D states occurs mainly at $T > 80$ °K.

The photoelectric investigations were initiated with a study of the nature of the impurities PC observed in the initial and control samples of germanium, and with a search for the conditions under which the influence of the PC can be reduced to a minimum. The following singularities were revealed: 1) a smooth spectral dependence at $h\nu > 0.3$ eV (Fig. 5, curves 1); 2) a sublinear dependence of the PC on the intensity of the incident light; 3) the presence of long (up to 10^3 sec) fall-off times of this PC at 80 °K; 4) a decrease of the value of σ_{PC} with increasing temperature and a practically complete vanishing of this quantity in the initial samples at 140–160 K.

The aggregate of these data is typical of barrier recombination mechanisms and cannot be attributed to the participation of pointlike noninteracting impurity centers in the PC. The large potential barriers can result from the bending of the bands near the surface as well as around clusters and dislocations. In dislocation-free sufficiently pure germanium with concentration of electrically active impurities ~10^{13} cm^{-3}

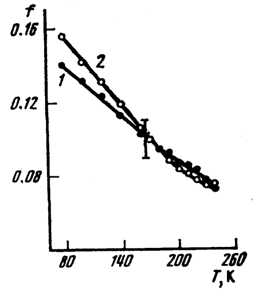

FIG. 4. Temperature dependence of the filling coefficient calculated from formula (7) using the results of the measurements of the electric conductivity (○) and of the Hall constant (●), averaged over several samples.

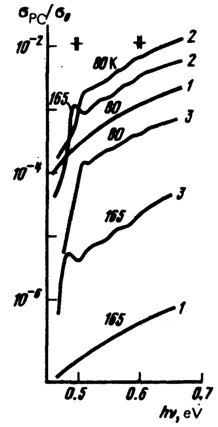

FIG. 5. Spectral dependence of PC in a control sample 1 and in deformed samples 2 ($N_D = 2.6 \cdot 10^6$ cm^{-2}) and 3 ($N_D = 5.9 \cdot 10^6$ cm^{-2}) from ingot No. 3 (donor density $N_d = 2.4 \times 10^{13}$ cm^{-3}) at various temperatures.

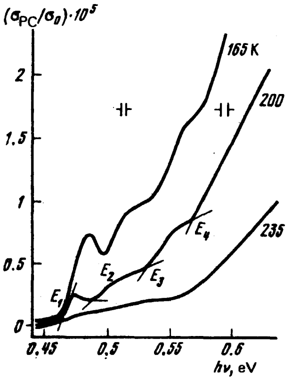

FIG. 6. Spectral dependence of PC in deformed sample 3 at various temperatures.

one can hardly expect a large number of electrically active clusters. We have nevertheless annealed the initial samples at $T \approx 850\,^\circ$C, followed by quenching and slow cooling, processes capable of changing the concentration and state of the clusters. However, after the annealing the investigated photoelectric and optical characteristics of these samples remained unchanged. At the same time, the size of the potential barrier due to the surface states can be controlled by means of an electric field. In fact, by varying the polarity of the voltage applied to the lateral non-illuminated faces, we observed an increase or a decrease of σ_{PC} by 20–30%. The described singularities of the PC spectra of undeformed germanium are typical of all the investigated ingots of n- and p-type germanium, i.e., they are not connected with the character of the impurities. All this can indicate that in dislocation-free undeformed germanium the PC at $h\nu < 7$ eV is due to the presence of surface states. The smooth dependence of σ_{PC} on $h\nu$ also agrees with the presence of a continuous spectrum of surface states in the forbidden band of the germanium.[23]

One of the methods of decreasing the influence of the surface on the experimentally observed PC was proposed in Ref. 18 in connection with the use of samples with large dimensions. We, to the contrary, paid attention to the fact that the impurity PC in undeformed crystals decreases with increasing temperature and that is almost unobservable at $T > 165$ K. At the same time, according to the Hall data the filling coefficient f is still large enough ($f \approx 0.08$) even at 200 K (Fig. 4). Consequently, the Coulomb barrier around the dislocations at these temperatures should also be quite appreciable. In this connection one could expect in the deformed crystals an increase in the lifetime of the electrons compared with control samples, and a significant excess of the PC connect with dislocations over the PC connected with surface states. Experiment has confirmed this assumption.

As follows from Fig. 5, the PC in control sample 1 is much less than the PC in deformed samples 2 and 3 already at 165 K, and at $T > 165$ K it is completely unobservable, although PC of deformed samples is observed also at $T = 235$ K (Fig. 6). When the temperature is lowered from 165 K the difference between the values of PC in control and deformed samples decreases. Thus, at 80 K and $h\nu > 0.45$ eV in deformed sample 2 the PC is still higher by one order of magnitude than the PC of the control sample (Fig. 5, curves 1 and 2) while in the deformed sample 3 the PC is even less than in the control sample (Fig. 5, curves 1 and 3). An approximately similar ratio of the quantities PC in the control and deformed samples is preserved at 80 °K and in the longer-wavelength region of the spectrum ($h\nu < 0.45$ eV), and this makes the analysis of these experimental data difficult. Recognizing that at $h\nu > 0.65$ eV interband absorption of light it is initiated in the control and deformed samples, we have confined ourselves to the interval $0.45 \leq h\nu \leq 0.65$ eV.

A distinguishing feature of the PC spectra of deformed crystals is the clearly pronounced threshold at $h\nu < 0.5$ eV, which was previously observed[16-18] in this region of the spectrum, and the three steps at $h\nu \gtrsim 0.5$ eV, two of which (E_2 and E_3, see Fig. 6) were observed by us for the first time. These steps are more clearly seen on the spectral plot of σ_{PC} of the deformed sample 3, which is shown in Fig. 6 in a linear scale for several temperatures. The same figure shows how the values of the threshold energy E_1 and of the steps E_2–E_4 in the deformed samples were determined. It turned out that the values of E_1–E_4 depend on the temperature (Fig. 7), and this, together with the absence of such singularities as in all the control samples investigated by us (more than 30) from different ingots, as well as in the spectral dependences of the reflection coefficient and of the intensity of the incident light, excludes the possibility of attributing the threshold of E_1 and of the steps to apparatus factors. The values of E_1–E_4 at a given temperature depend little on the donor concentration and on the dislocation density in the samples. We note finally that we observed no notice-

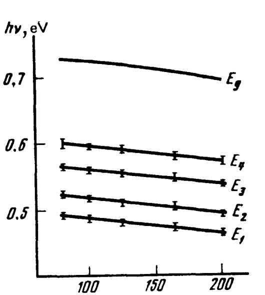

FIG. 7. Temperature dependence of the position of the threshold E_1 and of the steps E_2–E_4, averaged over six samples with different N_D and N_d; E_g is the width of the forbidden band of germanium in accordance with the data of Ref. 26.

able polarization dependence of the PC in either the control or the deformed samples.

4. DISCUSSION OF RESULTS

The acceptor action of the dislocations and the dependence of the Hall constant on the orientation of the predominant direction of the dislocations relative to the magnetic-field direction demonstrate convincingly that the dislocations in n-germanium are indeed surrounded by cylindrical regions in which there are no free carriers. According to Ref. 24, this situation is possible if the screening of the dislocations is produced mainly by ionized impurities. To this end it is necessary to satisfy the condition of strong filling of the dislocations with electrons:

$$\alpha = e^2 f / \varkappa a k T \gg 1, \tag{8}$$

where e, $\varkappa$, and k are respectively the electron charge, the dielectric constant, and the Boltzmann constant. This case was first considered by Read[2] and these cylindrical regions around the dislocations are called Read cylinders. In our case $\alpha = 5$ at 80 °K and $\alpha = 1.3$ at 200 °K. This means that the main contribution to the screening of the dislocations is indeed made by ionized impurities. The free electrons, however, can penetrate into the D cylinders, and this can lead to some smearing of their boundaries. The dimension of the smeared layer in our case is $0.25 r_0$ at 80 K and $0.47 r_0$ at 200 K, where r_0 is the average radius of the Read cylinder, defined as in Ref. 24. These values were obtained from the formulas of Ref. 24 under the condition that the concentrations of the free electrons on the boundaries of these layers are 30 and 7% of their concentration far from the dislocations. Such a smearing of the boundaries of the Read cylinders can decrease the accuracy with which f is determined, especially at high temperatures.

The presented estimates show that in the deformed samples investigated by us the dislocations are indeed surrounded by Read cylinders, although without sharp boundaries, and this is why we observe different R_1 and R_2. This difference offers more direct proof of the existence of cylinders than the anisotropy of the carrier mobility, since the latter can be due to the anisotropy of the point defects that become redistributed in the course of the plastic deformation.[25]

The fact that within the limits of experimental error R_0 and R_2 are equal in deformed samples from ingots Nos. 1 and 3 enables us to separate the pure dislocation contribution to f. This is confirmed by the agreement between the values of f determined by two methods, and by the small scatter (within the limits of errors) of f from sample to sample for ingots Nos. 1 and 3. At the same time, in the samples from ingots 2, 4, and 5, at the same dislocation densities, the filling coefficient calculated in the usual manner from the Hall data differs by several times (from 0.03 to 0.12 at 80 K). On the other hand if we use for the calculation R_1 and R_2, then in some cases f increases to 0.2. The non-reproducibility of the filling coefficient in ingots Nos. 2, 4, 5 enables us to regard as one of the principal causes of the scatter of the Hall-measurement results in Refs. 4–11 to be the local change, after the deformation and annealing, of the impurity environment around the dislocations, a factor heretofore not taken into account in the calculation of f from R_0 and R_1.

On the basis of the foregoing we assume that the experimental values of f shown in Fig. 4 and obtained for ingots Nos. 1 and 3 are due to the filling of only dislocation states. We shall use these values of f for a quantitative estimate of the position, in the forbidden band, of the level ε_1 connected with these D states. We obtain the estimate by the traditional method[2] in the minimum-energy approximation, which is valid at $\alpha \gg 1$. In this case

$$\mathscr{E}_F = \mathscr{E}_1 + \mathscr{E}^*. \tag{9}$$

Here $\mathscr{E}^*$ is the potential electron sitting on the dislocation, in the field of other electrons and positive ions:

$$\mathscr{E}^* = \frac{e^2 f}{\varkappa a}\left[3 \ln\left(\frac{f}{f_c}\right) - 0.232\right], \tag{10}$$

where $f_c = a(\pi N_d)^{1/3}$ ($a = 4.5 \times 10^{-8}$ cm) for 60° dislocations in germanium), $\mathscr{E}_F$ is the Fermi level in the deformed sample. Since the concentrations of the electrons in the control sample and in the deformed sample outside the D cylinders are equal ($R_0 \approx R_2$), it follows that $\mathscr{E}_F$ coincides with the value of the Fermi energy in the control sample, a fact which we indeed employed to calculate $\mathscr{E}_1$. The positions of the levels $\mathscr{E}_F$ and $\mathscr{E}_1$ in (9) are reckoned from the top of the valence band. Using the data of Ref. 26 on the temperature dependence of the width of the forbidden band E_g of germanium to calculate $\mathscr{E}_F$ we obtained the value $\mathscr{E}_1 = 0.25 \pm 0.05$ eV for all the deformed samples obtained by us from ingots Nos. 1 and 3. Within the limits of experimental error, the value of $\mathscr{E}_1$ is independent of temperature.

Thus, within the limits of applicability of the Read formula (10) for $\mathscr{E}^*$, the D level, which determines the change of the Hall constant at $T < 240$ °K, lies in the lower half of the forbidden band of germanium. Taking into account the limited validity of the formula for $\mathscr{E}^*$, the smearing of the Read cylinder, and the experimental error (±0.05 eV) connected with the accuracy of the determination of $\mathscr{E}^*$, we see that the value of $\mathscr{E}_1$ obtained from the Hall measurements must be verified by another method. We use for this purpose the spectral dependences we obtained for the PC, since the influence of the surface states on the singularities of these spectra can be neglected. In fact, from the electric measurements it follows that in weakly deformed samples, (for example sample 2 of Fig. 1a) the Fermi level at a given temperature remains the same as in the initial sample. Therefore the parameters of recombination via surface centers should not change noticeably as a result of the deformation. Consequently, in such deformed crystals the PC connected with the surface states should not differ excessively from that in the control samples. Inasmuch as in the control samples $\sigma_{PC}/\sigma_0 < 10^{-6}$ at $T > 165$ K, and the change of the dark electric properties of the deformed crystals indicates that the state inside the D cylinders are filled with electrons, it can be assumed that in weakly deformed samples, at the same temperatures, we observe PC connected only with dislocations. And since at all the investigated temperatures the singularities of the PC spectra are the same in all the deformed samples and are absent from the control samples (Fig. 5), it appears that these singularities of the PC are connected with D states. We propose therefore that we have succeeded in observing PC due to excitation of these states under conditions when the influence of the surface is negligibly small and we propose to study the singularities of this PC even when an appreciable impurity PC is observed in the control samples.

All the foregoing gives grounds for assuming that the singularities of the PC spectra observed by us in deformed crystals, and primarily the threshold E_1, are due to participation of the D states in the optical-excitation processes. However, from the PC spectra we cannot identify the part of the forbidden band in which these states are located, since the PC can be connected with excitation of electrons from filled D states into the conduction band, or from the valence band into empty D states. In the former case the PC is effected by the free electrons, and in the latter by holes in the valence band. According to the electric measurement data, in the temperature interval 260–80 °K in n-germanium, the dislocations exhibit acceptor action and capture electrons. This causes them to be negatively charged and surrounded by a Coulomb barrier of sufficient magnitude, since the filling coefficient is quite large ($f = 0.08$ at 200 °K and $f = 0.15$ at 80 K). Consequently, the recombination of the nonequilibrium electrons via dislocations should be hindered, and it is this which leads to long decay times σ_{PC} of the PC after the light is turned off. The same barrier should contribute to recombination of the nonequilibrium carriers and to shorten their lifetime, if the PC is due to holes. In our samples the σ_{PC} are high at low temperatures, a fact difficult to attribute to recombination of holes, inasmuch as even at room temperature, when the influence of the barrier is small, we have $T \sim 10^{-6}$ sec at $N_D > 10^c$ cm^{-2} in the case of interband excitation of the light. It can therefore be assumed that the observed PC is due to excitation of electrons in dislocation states into the conduction band. Then the threshold E_1 should correspond to a D level located at a distance $\mathscr{E}_1 = E_g - E_1 = 0.24$ eV from the valence band (the data on the temperature dependence of the width of the forbidden band were taken from Ref. 26), with $\mathscr{E}_1$ having a weak dependence on the temperature (Fig. 7). According to the results of the electric measurements, the upper filled D level lies above the top of the valence band likewise at a distance 0.25 ± 0.05 eV. It can therefore be assumed that the same D level is determined from the measurements of the Hall effect and of the PC.

Thus, combined investigations of the Hall effect and of the PC give grounds for connecting the threshold E_1 with the excitation of the electrons from the level $\mathscr{E}_1 = 0.24$ eV into the conduction band. Another interpretation of the jump of the PC near $h\nu = 0.45$ eV was proposed in Ref. 18, according to which the PC in this part of the spectrum is due to holes in the valence band which appear as a result of excitation of valence electrons from the D states that are located 0.25 eV away from the bottom of the conduction band. An unambiguous answer to this question can be obtained by measuring the photo-Hall effect near helium temperatures.

No one has previously observed the steps E_2 and E_3 in plastically deformed germanium. In analogy with the foregoing, we can suggest that the steps E_2–E_4 are due to excitation of electrons into the conduction band from levels located at distances $\mathscr{E}_2 = 0.21$ eV, $\mathscr{E}_3 = 0.17$ eV, and $\mathscr{E}_4 = 0.14$ eV from the top of the valence band. This number of closely located levels calls for the assumption that the spectrum of the D states in germanium has a rather complicated structure. This assumption agrees with the complicated form of the spectrum of the recombination radiation of plastically deformed germanium,[27,28] which has maxima at energies 0.5, 0.53, 0.56, and 0.59 eV.[27]

We note that we have not observed the PC threshold due to excitation of electrons into the conduction band from the D level $\mathscr{E}_0 \approx 0.1$ eV above the top of the valence band, determined from the electric measurements on deformed p-germanium.[29] The possible reason is that the light energy needed for this transition is close to the energy E_g of the interband transitions.

Since the distances between the threshold E_1 and the step E_2 as well as the distance between the steps E_2 and E_3 or E_3 and E_4, are close to the energy of the optical phonons in germanium[30] and depend little on temperature (Fig. 7) can also be assumed that these steps E_2–E_4 are connected with excitation of electrons into the conduction band from the level $\mathscr{E}_1$ with participation of 1–3 optical phonons, or from the levels $\mathscr{E}_1$ and $\mathscr{E}_2$ with participation of one or two phonons. The influence of the electron-phonon interaction on the PC spectra was observed in GaAs doped with a deep acceptor (copper),[31] and manifested itself in the appearance of two PC steps adjacent to the PC threshold. The experimental curve agreed well in this case with the theory only if account was taken of the electron-phonon interaction. The agreement between the results of the electric and photoelectric measurements on the deformed samples with the ordered D structure is convincing proof of the existence of the $\mathscr{E}_1$ level connected with the D states. A quantitative calculation of the cross section of the photoionizations of this level, with allowance for the electron-phonon interaction, as well as additional experimental investigations, will help explain finally the nature of the steps E_2–E_4.

We note that the value $\mathscr{E}_1 = 0.25$ eV obtained in the present paper differs substantially from the value $\mathscr{E}_0 \approx 0.1$ eV above the top of the valence band, which follows from the electric measurements in strongly deformed p-germanium[29,32,33] and is also connected with the D states. If the level $\mathscr{E}_0$ exists also in weakly n-germanium, then excitation of electrons from this level into the conduction band should occur at higher temperatures than from the level $\mathscr{E}_1$, i.e., against the background of the excitation of intrinsic electrons and holes, and this would make difficult a quantitative reduction of the Hall data in the region of the intrinsic conductivity. Thus, the results of electric measurements in weakly deformed *n*-germanium do not contradict the existence of the level of $\mathscr{E}_0$, i.e., at least two levels in the lower half of the forbidden band are apparently connected with the dislocations in germanium. The relatively large value $f \approx 0.07$ at 240° K and the presence of steps in the spectral dependence of the PC can offer evidence also of a more complicated structure of the *D*-state spectrum in the energy interval 0.1–0.25 eV above the top of the valence band. This question calls for further investigations, and the use of crystals with ordered anisotropic dislocation structure seems quite promising to us in this sense.

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[1] W. Shockley, Phys. Rev. **91**, 228 (1953).
[2] W. T. Read, Phil. Mag. **45**, 775 and 1119 (1954).
[3] W. Schröter and R. Labusch, Phys. Stat. Sol. **36**, 539 (1969).
[4] R. A. Logan, G. L. Pearson, and P. A. Kleinman, J. Appl. Phys. **30**, 885 (1959).
[5] R. M. Broudy, Adv. Phys. **12**, 135 (1963).
[6] L. I. Kolesnik, Candidate's dissertation, Moscow, 1976.
[7] B. Podör, Acta Phys. Acad. Sci. Hungarica 23, 393 (1967).
[8] P. Gondi, S. Mantovani, and F. Schintu, Nuovo Cimento 2, 13 (1971).
[9] Yu. A. Osip'yan and S. A. Shevchenko, Zh. Eksp. Teor. Fiz. **61**, 2330 (1971) [Sov. Phys. JETP **34**, 1248 (1972)].
[10] R. Labusch and R. Schettler, Phys. Stat. Sol. (a) **9**, 455 (1972).
[11] A. Cavallini, P. Gondi, and A. Castaldini, *ibid.* **43**, K205 (1977).
[12] Z. Golaski, T. Figielski, and M. Jastrjebska, Phys. Stat. Sol. **11**, K35 (1965).
[13] Z. Golaski and T. Figielski, *ibid.* **20**, K1 (1967).
[14] H. G. Miles, J. Appl. Phys. **40**, 2720 (1969).
[15] W. Barth and G. Longohr, Phys. Stat. Sol. (a) **3**, K289 (1970).
[16] H. R. Weber, *ibid.* **25**, 445 (1974).
[17] W. Barth, K. Elsasser, W. Guth, and E. Kamienicki, *ibid.* **39**, 249 (1977).
[18] D. Mergel and R. Labusch, *ibid.* **41**, 431 (1977); 42, 165 (1977).
[19] H. F. Matare, Defect Electronics in Semiconductors, Wiley, 1971, Chap. 8.
[20] V. I. Nikitenko and A. I. Polyanski, Proc. All-Union Conf. on Structure Defects in Semiconductors, Part I, Novosibirsk, 1970.
[21] S. A. Shevchenko and A. I. Kolyubakin, Fiz. Tekh. Popluprov. **13**, No. 5 (1979) [Sov. Phys. Semicond. **13**, No. 5 (1979)].
[22] S. M. Ryvkin, Fotoélektricheskie yavleniya v poluprovodnikakh (Photoelectric Phenomena in Semiconductors), Fizmatgiz, 1963.
[23] P. I. Baranskiĭ, V. P. Klochkov, and I. V. Potykevich, Poluprovodnikovaya élektronika (Semiconductor Electronics), Naukova Dumka, 1975.
[24] R. A. Vardanyan, Zh. Eksp. Teor. Fiz. **73**, 2313 (1977) [Sov. Phys. JETP **46**, 1210 (1977)].
[25] V. G. Eremenko, V. I. Nikitenko, and E. B. Yakimov, Pis'ma Zh. Eksp. Teor. Fiz. **26**, 72 (1977) [JETP Lett. **26**, 65 (1977)].
[26] Y. P. Varschni, Physics 34, 149 (1967).
[27] A. A. Gippius and V. S. Vavilov, Fiz. Tverd. Tela (Leningrad) **4**, 2426 (1962), **6**, 2361 (1964) [Sov. Phys. Solid State **4**, 1777 (1963), **6**, 1873 (1965)].
[28] W. Barth, M. Bettini, and U. Osterlag, Phys. Stat. Sol. (a) **3**, K177 (1970).
[29] W. Schröter, Phys. Stat. Sol. **21**, 211 (1967).
[30] Yu. I. Ukhanov, Opticheskie svoĭstva poluprovodnikov (Optical Properties of Semiconductors), Nauka, 1977.
[31] T. K. Ashirov, A. A. Gutkin, S. E. Kumenov, and V. E. Sedykh. Fiz. Tekh. Poluprov. **12**, 1750 (1978) [Sov. Phys. Semicond. **12**, 1036 (1978)].
[32] Yu. A. Osip'yan and S. A. Shevchenko, Zh. Eksp. Teor. Fiz. **65**, 698 (1973) [Sov. Phys. JETP **38**, 345 (1973)].
[33] Yu. A. Osip'yan, V. I. Tal'yanskiĭ, and S. A. Shevchenko, *ibid.* **72**, 1543 (1977) [**45**, 810 (1977)].

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