

# Kinetics of transmutation doping as a method of deep-center spectroscopy in germanium

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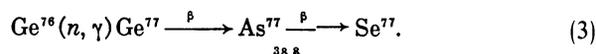
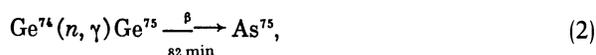
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Doping of germanium by irradiation with thermal neutrons is investigated. The relative concentrations of the elements produced as a result of the irradiation, the degree of compensation, and the energy position of the selenium in the germanium are determined experimentally. It is shown that selenium in germanium is a singly charged center with a level separated by 0.28 eV from the bottom of the conduction band.

## INTRODUCTION

The method of neutron doping of germanium was first specially investigated by Cleland, Lark-Horovitz, and Pigg in 1950.<sup>1</sup> At that time it was known that irradiation in a reactor produces acceptor centers in a Ge samples. These centers can appear for two reasons. First, acceptor properties can be had by various crystal defects produced in a crystal lattice by neutron irradiation. Second, when certain Ge isotopes capture neutrons they become radioactive and when they decay they can be transformed into chemical elements that produce acceptor or donor action in Ge. The occurrence of the second process is due to the fact that prolonged high-temperature annealing does not eliminate all the acceptor centers produced by neutron irradiation. From the data available in 1950 on the cross sections for the capture of thermal neutrons by various germanium isotopes it followed that radioactive transformations should lead to predominant onset of donor (rather than acceptor, as followed from experiment) centers. Lark-Horovitz decided therefore to perform new measurements of the cross sections for capture of various germanium isotopes.<sup>1</sup> The cross sections cited in Ref. 1 for the isotopes Ge<sup>70</sup>, Ge<sup>72</sup>, Ge<sup>73</sup>, Ge<sup>74</sup>, and Ge<sup>76</sup> are respectively 3.25, 0.94, 13.69, 0.60, and 0.35 b. The percentages of these isotopes in natural Ge are respectively 21.2, 27.3, 7.9, 37.6, and 6.1%. The cross sections for Ge-isotope capture were subsequently measured by others. At present there is a large spread in the published data on the capture cross sections of Ge<sup>74</sup> and Ge<sup>76</sup> (Ref. 2). We have no further interest in the isotopes Ge<sup>73</sup> and Ge<sup>74</sup> from the point of view of neutron doping, since they are transformed, when they capture thermal neutrons, into the stable isotopes Ge<sup>73</sup> and Ge<sup>74</sup>. It follows from the cited numbers<sup>1</sup> that the isotope Ge<sup>70</sup> captures 30.4% of all the absorbed thermal neutrons, while Ge<sup>74</sup> and Ge<sup>76</sup> capture 9.8 and 1.2%, respectively. The nuclear reactions into which these isotopes enter after neutron capture can be schematically represented as



Equation (1) describes the transformation of the isotope Ge<sup>70</sup> into the acceptor Ga<sup>71</sup>. The isotope Ge<sup>70</sup> captures a neutron (this capture is accompanied by  $\gamma$  radiation) and is transformed into the unstable isotope Ge<sup>71</sup>, which subsequently is transformed (as a result of K capture), with a half-life 12 days, into the acceptor Ga<sup>71</sup>. The donor-impurity formation processes are described by Eqs. (2) and (3). It follows from (2) that arsenic As<sup>75</sup> is formed from the unstable isotope Ge<sup>75</sup> via  $\beta$  decay, with a half-life 82 min. Besides the shallow acceptor and donors of groups III and IV, there appears in the crystal Se, which is assumed in Ref. 3 to produce in Ge two deep donor levels at depths 0.14 and 0.28 eV from the conduction band. The appearance of Se is described by Eq. (3). When Ge<sup>76</sup> captures a neutron it is transformed into the unstable isotope Ge<sup>77</sup>, which is transformed by  $\beta$  decay, with a half-life 12 h, into the unstable isotope As<sup>77</sup>. The latter is transformed into Se<sup>77</sup> with a half-life 38.8 h. When a sufficiently long time has elapsed after the irradiation, and all the decays described by Eqs. (1)–(3) have already taken place, the final densities of the centers Ga<sup>71</sup>, As<sup>75</sup>, and Se<sup>77</sup> set in; we shall designate them  $N_{\text{Ga}}$ ,  $N_{\text{As}}$ , and  $N_{\text{Se}}$ . Obviously these quantities are equal respectively to the densities of the isotopes Ge<sup>70</sup>, Ge<sup>74</sup>, and Ge<sup>76</sup> that have captured thermal neutrons. According to the data of Ref. 1:

$$N_{\text{Ga}} : N_{\text{As}} : N_{\text{Se}} = 30.4 : 9.8 : 1.2 = 1 : 0.32 : 0.04. \quad (4)$$

It can be seen that the density of the acceptor centers is approximately three times that of the donor centers. Of course, we have in mind only the centers that result from radioactive transformations. The centers present in the crystal prior to irradiation and the centers due to damage to the crystal lattice are not considered at present. Knowing the contents of the different isotopes in the natural Ge and their capture cross sections we can calculate, given the irradiation dose, the densities of the produced donors and acceptors and compared the calculated and experimental results. This was done in Ref. 1. The samples were stored for a long time after the irradiation, to let all the decays take place, and were annealed to eliminate radiation damage. Sufficiently good agreement ( $\sim 30\%$ ) was obtained between the calculated final number of uncomensated centers ( $N_{\text{Ga}} - N_{\text{As}} - 2N_{\text{Se}}$ ) and that determined by experiment. The measurements of Ref. 1, however, do not permit a direct verification of Eq. (4).

We consider now the time variation of the densities of

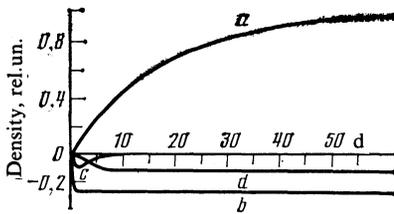


FIG. 1. Calculated time dependences of the densities of the electrically active centers that result from irradiation by thermal neutrons:  $a - \text{Ga}^{71}$ ;  $b - \text{As}^{75}$ ;  $c - \text{As}^{77}$ ;  $d - \text{Se}^{77}$ . The final (asymptotic)  $\text{Ga}^{71}$  density is taken to be unity. The scales of the  $\text{As}^{77}$  and  $\text{Se}^{77}$  plots are magnified 10 times.

the different isotopes after the irradiation. It follows from (1) that the density of the acceptors  $\text{Ga}^{71}$  varies as

$$n_{\text{Ga}}(t) = N_{\text{Ga}} \left\{ 1 - \exp\left(-\frac{\ln 2}{\tau} t\right) \right\}, \quad (5)$$

where  $\tau$  is the half-life of the  $\text{Ge}^{71}$  isotope ( $\approx 12 d$ ) and  $t$  is the time from the instant of irradiation. In the derivation of (5) we have assumed that the irradiation duration is short compared with the time  $t$  of interest to us. The function (5) is plotted in Fig. 1 (curve a). The kinetics of the appearance of the donors  $\text{As}^{75}$  is described by a similar formula, but  $N_{\text{Ga}}$  must be replaced by  $N_{\text{As}}$  and  $\tau$  by the half-life of the  $\text{Ge}^{75}$  isotope (Fig. 1, curve b). The equation that describes the appearance of  $\text{Se}^{77}$  has a more complicated form than the analogous equations for  $\text{Ga}^{71}$  and  $\text{As}^{75}$ . The reason is that the density of the isotope  $\text{As}^{77}$  (from which  $\text{Se}^{77}$  "is obtained") is itself a function of time. We confine ourselves here only to a graphic representation of the time dependences of the densities of the isotopes  $\text{As}^{77}$  and  $\text{Se}^{77}$ , since we shall not need hereafter the corresponding analytic relations. These relations (multiplied for clarity by 10) are shown in Fig. 1 (curves c and d). All the plots of Fig. 1 are normalized to  $N_{\text{Ge}}$ , i.e., the final density of  $\text{Ga}^{71}$ , which sets in after prolonged storage, is taken to be unity. This is done to gain an idea of the relations between the densities of the produced donors and acceptors. Curves b, c, and d of Fig. 1 were plotted using not Eq. (4), but a more accurate one obtained in the present paper:

$$N_{\text{Ga}} : N_{\text{As}} : N_{\text{Se}} = 1 : 0.26 : 0.012. \quad (6)$$

In addition, the half-life of  $\text{Ge}^{71}$  was assumed to be 12.3 d (this value is obtained in the present paper), and the half-lives of the isotopes  $\text{Ge}^{75}$  (82 min),  $\text{Ge}^{77}$  (12 h), and  $\text{As}^{77}$  (38.8 d) were taken from Ref. 1.

Neutron doping of germanium has been quite extensively used for research purposes, particularly to study hopping conduction.<sup>4</sup> The main advantage of the method is the homogeneity of the doping over the volume of the sample. In the sample studied until recently in all these applications, the density of the doping centers no longer varied with time, i.e., the measurement was preceded by prolonged aging of the sample. In our opinion, however, the neutron-doping method can find wider applications if the kinetics of the radioactive decay is used. In fact, if the measurements are made at a sufficiently short time after the irradiation and annealing, we gain a unique opportunity of investigating the process of interest to us in a sample in which the degree of doping varies continuously, and the Fermi level runs through

practically the entire band gap. In particular, this procedure allows us (as will be demonstrated below) to determine the levels of the electrically active centers in Ge. So far, only two reports were published<sup>5,6</sup> of investigations of the kinetics of neutron doping of Ge. Zabrodskii<sup>5</sup> determined the exact degree of compensation, i.e., the density ratio of the acceptors and donors produced by neutron doping. In Ref. 6 we investigated the dependence of the dislocation microwave conductivity of Ge on the position of the Fermi level. The results of these studies have shown that the variation of the density of shallow doping centers with time is sufficiently well described by Eqs. (1) and (2). There exists, however, a time interval in which the electric properties of the sample should be determined by deep centers [whose appearance is described by Eq. (3)], even though their density is substantially lower than those of the shallow  $\text{Ga}^{71}$  and  $\text{As}^{75}$  centers. Obviously, such a situation arises when the shallow donors and acceptors cancel one another; this occurs in the sixth day after the instant of irradiation.

In the present investigation we used the Hall effect to study the kinetics of neutron doping of Ge, with particular attention to an assessment of the role of deep  $\text{Ge}^{77}$  centers (this was not done in Refs. 5 and 6). Besides, we want to demonstrate, with  $\text{Se}^{77}$  as an example, that neutron-doping kinetics can be used to determine the level positions and the deep-center densities, i.e., it can serve as a method of electron spectroscopy of germanium.

## EXPERIMENTAL TECHNIQUE

The samples for the measurements were cut from an ingot of ultrapure Ge (donor density  $\sim 2 \cdot 10^{11} \text{ cm}^{-3}$ ). The samples were coated with a protective tin layer and irradiated in the channel of the reactor of the Institute of Theoretical and Experimental Physics (with a thermal-to-fast neutron ratio 300:1). The irradiation time ( $\approx 10$  min) was chosen such that the final density of the introduced acceptors was  $\sim 3 \cdot 10^{14} \text{ cm}^{-3}$ . After the irradiation the samples were annealed for 12 h at 450 °C (first sample) and 500 °C (second sample), followed by cooling at a rate 1 deg/min. This is the usual annealing procedure in neutron doping; it is assumed to be sufficient to eliminate radiation damage. After anneal-

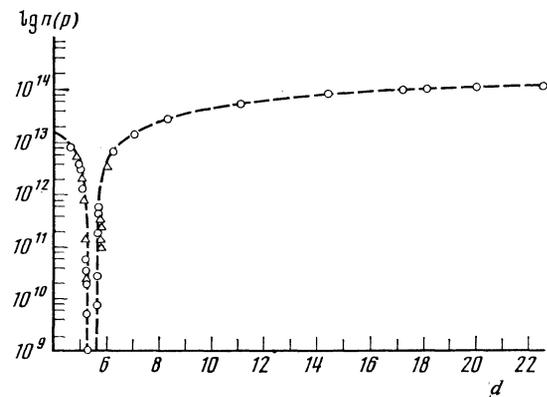


FIG. 2. Electron (hole) density in band vs. time after irradiation.  $\circ$ —1st sample,  $\triangle$ —2nd sample, dashed line—calculated curve; left- and right-hand branches—electron and hole densities, respectively.

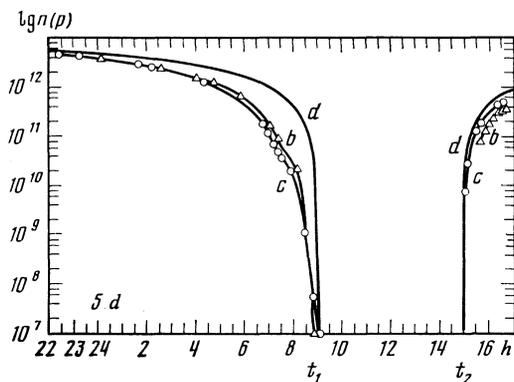


FIG. 3. Time dependence of the electron (hole) density in the band near the conversion instant, *c*, *b*—experimental curves for 1st and 2nd samples, respectively, *d*—calculated curve. Left- and right-hand branches—electron and hole densities, respectively.

ing, the tin layer was ground off and the samples were etched in CP-4a. The samples were parallelepipeds measuring  $1 \times 3 \times 6$  mm. Indium current contacts were attached to the  $3 \times 1$  face, and Hall and potential contacts to the  $6 \times 1$  face. The setup used permitted Hall measurements to be made in the temperature interval 4.2–600 K with the temperature stabilized to within  $0.1^\circ$  (at  $T < 77$  K) and  $1^\circ$  (at  $T > 77$  K). The magnetic field (7800 G) was perpendicular to a broad ( $3 \times 6$ ) face of the sample. The carrier density in the band was calculated from the measured Hall constant under the assumption that the Hall and drift mobilities are equal. The measurements were made as uninterruptedly as possible at various temperatures. The minimum time interval between successive measurements was determined by the rate of establishment of the required temperature in our setup.

### EXPERIMENTAL RESULTS

Figure 2 shows the experimental time dependence of the carrier density in the band for samples 1 and 2 at 77 K. It shows also the corresponding calculated dependence (we shall discuss it below). Figure 3 shows the same dependences

as in Fig. 2, but near the region of conversion from *n*- to *p*-type. In this region the shallow donors ( $\text{As}^{75}$ ) and acceptors ( $\text{Ga}^{71}$ ) turn out to be compensated, and at sufficiently high temperatures the electric properties of the sample should be determined by the deep Se centers. Figure 4 shows the temperature dependences of the electron density in the conduction band, obtained during the time of the “dip” in Figs. 2 and 3. The number at each point on Fig. 4 makes it possible, by using Table I, to determine the corresponding measurements time. (The table lists the times of measurement of the experimental points of Fig. 4, reckoned from the start of the sixth day.) The time interval between succeeding points ( $\sim 5$  min) was short enough to be able to neglect the changes that occur in the sample during the time necessary for 5–6 measurements. The points in Fig. 4, obtained as a result of successive measurements, were joined by solid lines. The slopes of these lines enabled us to estimate the energy position of the level that supplies the electrons to the conduction band. In the calculation of the activation energy account was taken, of course, of the temperature dependence of the effective density of states of the conduction band.

### DISCUSSION OF RESULTS

The experimental plots in Figs. 2 and 3 have exactly the form expected on the basis of reaction (1)–(3). Very soon after the irradiation, the  $\text{As}^{75}$  donor density in the sample reaches its final value  $N_{\text{As}}$ . The density  $N_{\text{Ga}}(t)$  of the acceptors, on the other hand, increases relatively slowly (see Fig. 1). The sample therefore becomes *n*-type after a certain time, but the density of the uncompensated donors decreases continuously. At  $T = 77$  K the electron density in the band is equal to the density of the uncompensated shallow  $\text{As}^{75}$  donors, therefore the left-hand branches of the curves in Figs. 2 and 3 are simply the differences between the densities of the  $\text{As}^{75}$  donors and  $\text{Ga}^{71}$  acceptors:

$$n(t) = N_{\text{As}} - n_{\text{Ga}}(t). \quad (7)$$

For a certain time, shallow  $\text{As}^{77}$  donors exist in the samples (Fig. 1c), but their density is low ( $\leq 0.01N_{\text{Ga}}$ ), and we shall

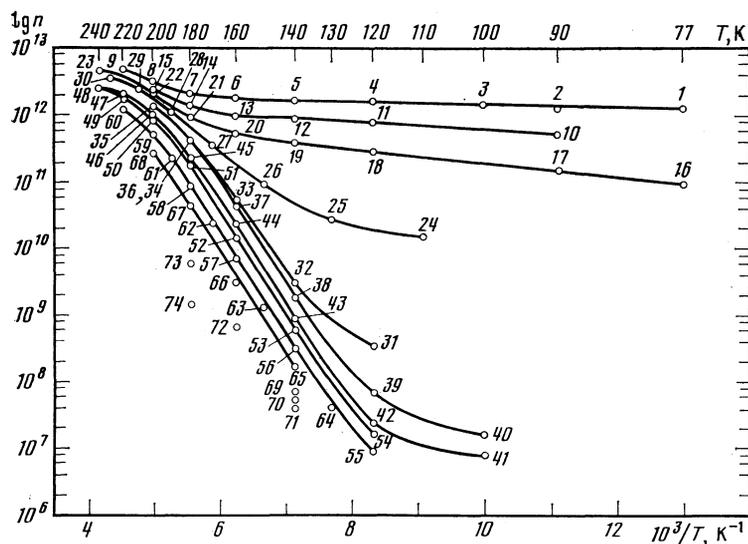


FIG. 4. Temperature dependences of the electron density in the conduction band for the second sample. The dependences were plotted in a time interval ( $\sim 9$  h) near the conversion.

TABLE I

| <i>N</i> | 1                | 2                | 3                | 4                | 5                | 6                | 7                | 8                | 9                | 10               |
|----------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|
| <i>t</i> | 4 <sup>45</sup>  | 4 <sup>51</sup>  | 4 <sup>54</sup>  | 5                | 5 <sup>07</sup>  | 5 <sup>15</sup>  | 5 <sup>25</sup>  | 5 <sup>33</sup>  | 5 <sup>40</sup>  | 6 <sup>30</sup>  |
| <i>N</i> | 11               | 12               | 13               | 14               | 15               | 16               | 17               | 18               | 19               | 20               |
| <i>t</i> | 6 <sup>32</sup>  | 6 <sup>37</sup>  | 6 <sup>42</sup>  | 6 <sup>45</sup>  | 6 <sup>55</sup>  | 7 <sup>20</sup>  | 7 <sup>25</sup>  | 7 <sup>30</sup>  | 7 <sup>33</sup>  | 7 <sup>36</sup>  |
| <i>N</i> | 21               | 22               | 23               | 24               | 25               | 26               | 27               | 28               | 29               | 30               |
| <i>t</i> | 7 <sup>40</sup>  | 7 <sup>48</sup>  | 7 <sup>55</sup>  | 8 <sup>15</sup>  | 8 <sup>20</sup>  | 8 <sup>25</sup>  | 8 <sup>30</sup>  | 8 <sup>35</sup>  | 8 <sup>40</sup>  | 8 <sup>45</sup>  |
| <i>N</i> | 31               | 32               | 33               | 34               | 35               | 36               | 37               | 38               | 39               | 40               |
| <i>t</i> | 9 <sup>10</sup>  | 9 <sup>15</sup>  | 9 <sup>20</sup>  | 9 <sup>25</sup>  | 9 <sup>30</sup>  | 9 <sup>35</sup>  | 9 <sup>40</sup>  | 9 <sup>43</sup>  | 9 <sup>46</sup>  | 9 <sup>50</sup>  |
| <i>N</i> | 41               | 42               | 43               | 44               | 45               | 46               | 47               | 48               | 49               | 50               |
| <i>t</i> | 9 <sup>55</sup>  | 10 <sup>10</sup> | 10 <sup>17</sup> | 10 <sup>20</sup> | 10 <sup>25</sup> | 10 <sup>30</sup> | 10 <sup>35</sup> | 10 <sup>50</sup> | 11               | 11 <sup>04</sup> |
| <i>N</i> | 51               | 52               | 53               | 54               | 55               | 56               | 57               | 58               | 59               | 60               |
| <i>t</i> | 11 <sup>07</sup> | 11 <sup>13</sup> | 11 <sup>20</sup> | 11 <sup>24</sup> | 11 <sup>45</sup> | 11 <sup>55</sup> | 12               | 12 <sup>05</sup> | 12 <sup>10</sup> | 12 <sup>15</sup> |
| <i>N</i> | 61               | 62               | 63               | 64               | 65               | 66               | 67               | 68               | 69               | 70               |
| <i>t</i> | 11 <sup>21</sup> | 11 <sup>28</sup> | 11 <sup>34</sup> | 11 <sup>37</sup> | 12               | 12 <sup>06</sup> | 12 <sup>13</sup> | 12 <sup>21</sup> | 12 <sup>50</sup> | 13               |
| <i>N</i> | 71               | 72               | 73               | 74               | —                | —                | —                | —                | —                | —                |
| <i>t</i> | 13 <sup>20</sup> | 13 <sup>30</sup> | 13 <sup>40</sup> | 14               | —                | —                | —                | —                | —                | —                |

not consider them. The deep Se<sup>77</sup> donors do not influence the form of the left-hand branches of the curves of Figs. 2 and 3, so that at 77 K they supply no electrons to the conduction band. At the instant  $t_1 = 5.375$  d (Fig. 3), the shallow donors and acceptors are mutually compensated:

$$n_{Ga}(t_1) = N_{As}. \tag{8}$$

We consider now the time interval from  $t_1$  to  $t_2$ , when

$$N_{As} \leq n_{Ga}(t) \leq N_{As} + \alpha n_{Se}(t).$$

The coefficient  $\alpha$  is equal to 1 or 2, depending on whether Se is a singly or double charged donor in Ge. In this interval there are practically no carriers in the bands at 77 K, since the produced shallow Ga<sup>71</sup> acceptors are compensated by the electrons from the Se<sup>77</sup> donors, and the excitation of the electrons from the deep Se level can be neglected. At the instant  $t_2 = 5.625$  d we have

$$n_{Ga}(t_2) = N_{As} + \alpha n_{Se}(t_2). \tag{9}$$

At  $t > t_2$  there appear in the crystal uncompensated shallow Ga<sup>71</sup> acceptors and the type of conductivity changes from  $n$  to  $p$ . Thus, the right-hand branches of the curves of Figs. 2 and 3 are described by the formula

$$p(t) = n_{Ga}(t) - (N_{As} + \alpha n_{Se}(t)), \tag{10}$$

where  $p(t)$  is the hole density in the valence band. At sufficiently long times (after reactions (2) and (3) have already taken place) Eq. (10) can be rewritten in the form

$$p(t) = N_{Ga} \left[ 1 - \exp\left(-\frac{\ln 2}{\tau} t\right) \right] - N_D, \tag{11}$$

where  $N_D = N_{As} + \alpha N_{Se}$ .

Equation (11) contains three parameters,  $N_{Ga}$ ,  $\tau$ , and  $N_D$ . These parameters can be determined from the experimental plot of Fig. 2. A convenient procedure for this purpose was proposed by Zabrodskii.<sup>5</sup> It consists of rewriting (11) in the form

$$\ln[N_{Ga} - N_D - p(t)] = \ln N_{Ga} - \frac{\ln 2}{\tau} t \tag{12}$$

and, using the connection between the hole density in the band and the Hall constant  $R(t)$ ,

$$p(t) = \frac{r}{qR(t)}, \tag{13}$$

where  $r$  is the Hall factor and  $q$  the electron charge, to obtain from (12)

$$\ln\{q^{-1}[R^{-1} - R^{-1}(t)]\} = \ln \frac{N_{Ga}}{r} - \lambda t. \tag{14}$$

The quantity  $R$  in (14) determines the final difference between the center densities:

$$R = R(\infty) \quad \text{or} \quad N_{Ga} - N_D = \frac{r}{qR}. \tag{15}$$

The quantity  $R$  is connected with the degree  $k = N_D/N_{Ga}$  of the compensation of the sample in the case of neutron doping. From (15) we have

$$R = \frac{r}{qN_{Ga}(1-k)}. \tag{16}$$

Equation (14) is that of a straight line. Drawing a straight line through the experimental data we can determine  $\tau$  and  $N_{Ga}/r$  and then use (16) to determine  $k$ . The straight line obtained in this manner is shown in Fig. 5. Zabrodskii's method is convenient because  $k$  can be determined without knowing the Hall factor  $r$ . Using (14) we obtained  $\tau = 12.3 \pm 0.3$  d. (The inaccuracy of  $\tau$  is due to the scatter of the experimental points.) The value of  $k$  obtained from (16) lies in the interval 22–30%. With the aid of the times  $t_1$  and  $t_2$  and the obtained value of  $\tau$  we can independently determine the final densities of the shallow (As<sup>75</sup>) and deep (Se<sup>77</sup>) centers. Rewriting (8) in the form

$$N_{As} = N_{Ga} \left[ 1 - \exp\left(-\frac{\ln 2}{\tau} t_1\right) \right]$$

and substituting the values  $\tau = 12.3 \pm 3$  d and  $t_1 = 5.375$  d, we get

$$N_{As} = (0.26 \pm 0.005) N_{Ga}. \tag{17}$$

Using relations (8) and (9) we find

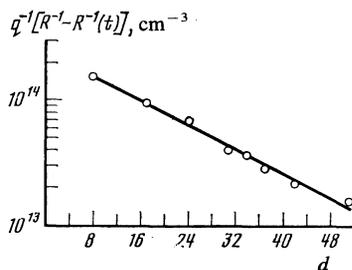


FIG. 5. Experimental points—values of left-hand side of Eq. (14) at various instants of time. The line was drawn by least squares.

$$\alpha n_{\text{Se}}(t_2) = n_{\text{Ga}}(t_2) - n_{\text{Ga}}(t_1) = N_{\text{Ga}} \left[ \exp\left(-\frac{\ln 2}{\tau} t_1\right) - \exp\left(-\frac{\ln 2}{\tau} t_2\right) \right] = 0,01 N_{\text{Ga}}. \quad (18)$$

From an analysis of reaction (3) (Fig. 1) it follows that

$$N_{\text{Se}}(t_2) = 0,88 N_{\text{Se}}, \text{ therefore } \alpha N_{\text{Se}} = 0,012 N_{\text{Ga}}. \quad (19)$$

As will be shown below, it follows from independent considerations that  $\alpha = 1$ . We thus obtain from (17) and (19) the equation (6) used to plot the curves of Fig. 1. It follows from it, in particular, that the degree of compensation is  $q = 0.272 \pm 0.005$ . Equation (6) is obviously valid for any irradiation dose if all the reactions (1)–(3) are due to capture of thermal neutrons. However, there always exists a certain number of captures of nonthermal resonant neutrons,<sup>2</sup> and this can make (6) dependent on the type of reactor used for the irradiation.<sup>1)</sup> Since we used a heavy-water reactor with a large cadmium ratio, it can be assumed that in our case the contribution from captures of nonthermal neutrons was small enough. In our experiments  $N_{\text{Ga}} - N_{\text{As}} - N_{\text{Se}} = 1.85 \cdot 10^{14} \text{ cm}^{-3}$  and from (6) it follows that  $N_{\text{Ga}} = 2.54 \cdot 10^{14} \text{ cm}^{-3}$ ,  $N_{\text{As}} = 0.66 \cdot 10^{14} \text{ cm}^{-3}$ , and  $N_{\text{Se}} = 3.0 \cdot 10^{12} \text{ cm}^{-3}$ . Using these values, the curves of Fig. 1, and Eqs. (7) and (10) we calculated the curves of Figs. 2 and 3. They agree with the experimental ones at the instants  $t_1$  and  $t_2$  because we used the values of  $t_1$  and  $t_2$  to determine relation (6). It can be seen that reactions (1)–(3) describe well the kinetics of the neutron doping. Attention must be called to the rate of decrease of the electron density in the conduction band. At our irradiation dose, the density of the  $\text{Ga}^{71}$  acceptors increased in six days at  $4.4 \times 10^{11}$  per hour. The electron density in the conduction band should decrease at the same rate, provided that all the electrons are supplied to the band from centers shallow enough to become fully ionized at 77 K. As seen from Fig. 4, however, starting with 7 h (here and below the time begins six days after the irradiation) the electron density in the band decreases much more slowly. This is evidence, in our opinion, that in the time interval from 7 to 9 h an appreciable fraction of the electrons is supplied to the band by deep centers that are only partly ionized at 77 K. We shall return to a discussion of this question. We consider now the temperature dependences shown in Fig. 4. It can be seen that from 7 to 9 h the slope of the solid lines increases continuously, so that the electron density in the band cannot be associated with a definite level. (To decrease the clutter in Fig. 4, we left out several curves pertaining to this time.) We assume in this connection that there exist in the sample electrically active centers (connected possibly with non-annealed defects), whose levels are distributed in a certain energy interval in the upper half of the forbidden band. It is just these levels that slow down the decrease of the density in Fig. 3. It follows from Fig. 4 that within two hours (from 7 to 9 h) the electrons are captured from these centers by the produced  $\text{Ga}^{71}$  acceptors. Since  $\sim 10^{12}$  acceptors per  $\text{cm}^3$  are produced in the two hours, we can conclude that the center density is also  $\sim 10^{12} \text{ cm}^{-3}$ . Starting with 9 h, the experimental points lie on straight lines whose slope corresponds to the level  $0.285 \pm 0.005 \text{ eV}$  (from the bottom of the conduction band). It appears that these levels are connected

with  $\text{Se}^{77}$ . This result does not agree with the prevailing notions concerning the energy levels of Se in Ge, according to which not one but two levels are attributed to Se, 0.14 and 0.28 eV. If in our experiments Se in Ge were a doubly charged donor, we would observe in the first half of the “dip” the 0.14 eV level. The  $\text{Ga}^{71}$  acceptors produced during that time would gradually deplete the upper 0.14-eV level, and in the second half of the “dip” we could observe the 0.28 eV level. (From these considerations it follows, in particular, that neutron doping is a powerful method of spectroscopy of centers with deep levels in Ge.) We have found in the literature only fragmentary data on Se in Ge.<sup>2,7</sup> All these data stem from an unpublished paper by Taylor. According to this paper, when Se is introduced into Ge (either by diffusion or by growth from the melt), 0.14 and 0.28 eV levels are produced, with the density of the centers with 0.28 eV levels several times larger than the density of those with 0.14 eV levels. This is explained in Ref. 3 and 7 by the possibility that Se can penetrate both to sites and to interstices and form thereby electrically active centers. It is possible that the discrepancy between our results and the universally accepted level scheme of Se in Ge is that the Se produced by neutron doping is located only at the lattice sites, and corresponds in this position to only one energy level, 0.28 eV.

We have already determined the Se density with the aid of Eq. (18). Actually (18) states that the duration of the “dip” (6 h) of Fig. 3 is the time during which there appear in the sample as there are deep centers with 0.28 eV levels. From this we obtain directly  $n_{\text{Se}}(t_2) = 6 \times 4 \cdot 10^{11} \text{ cm}^{-3} = 2.64 \cdot 10^{12} \text{ cm}^{-3}$ . On the other hand, the carrier density in the band, measured using the Hall effect, is equal to the density of the deep center with  $E = 0.28 \text{ eV}$ , provided that the temperature is high enough for all the centers to become ionized.

Examining the curves of Fig. 4, plotted at the start of the “dip” (when the deep centers with 0.28 level are still insignificantly compensated by the shallow acceptors  $\text{Ga}^{71}$ ), we see that at high temperatures the electron density in the band is  $\sim 3 \cdot 10^{12} \text{ cm}^{-3}$ , i.e., we arrive at one and the same value. Our value of the  $\text{Se}^{77}$  density is substantially lower than the one expected on the basis of the data of Ref. 1. From the capture cross sections and percentage content of the Ge isotopes given in Ref. 1 follows relation (14), whereas our results lead to (6). The discrepancy is possibly due to fact that in Ref. 1 the capture cross sections and the percentage content of the  $\text{Ge}^{76}$  isotope are overestimated.

It should be noted in this connection that the values cited in different papers for the  $\text{Ge}^{76}$  capture cross section differ greatly. Thus the value  $\sigma_{76} = 0.142 \pm 0.03 \text{ b}$  cited in Ref. 8 is 2.5 times smaller than the value of Ref. 1 and agrees much better with our results. The value of  $\sigma_{76}$  can be determined with the aid of our result

$$N_{\text{Ga}} : N_{\text{Se}} = 1 : 0,012. \quad (20)$$

To this end, besides using (20), we must specify the percentage contents of the  $\text{Ge}^{70}$  and  $\text{Ge}^{76}$  isotopes in natural Ge, and the  $\text{Ge}^{70}$  capture cross section. Fortunately, the values given for these quantities in various papers are close enough. We use for the sake of argument the data of Ref. 8. The contents of  $\text{Ge}^{70}$  and  $\text{Ge}^{76}$  are 20.7 and 7.7%, and the  $\text{Ge}^{70}$

capture cross section is 3.43 b. Then

$$N_{\text{Ga}}:N_{\text{Se}} = \frac{20,7 \cdot 3,43}{7,7 \sigma_{\tau_6}}, \text{ a,}$$

and using (20) we get

$$\sigma_{\tau_6} = 0,11 \text{ b.}$$

We have performed similar measurements for a sample annealed 10 min at 700 °C followed by slow (~1 deg/min) cooling to 500 °C and annealing at 500 °C for 12 h. It was found that in such a sample the density of centers having energies distributed in the interval ( $E_c$ ,  $E_c - 0.28$  eV) decreased substantially, the duration of the "dip" and the density of the centers with 0.28 levels remained the same as before, but the 0.14 eV level was not observed.

## CONCLUSIONS

1. It was shown that neutron doping provides a simple direct method of deep-center spectroscopy in Ge.
2. Se in Ge is a singly charged center with a level separated by 0.28 eV from the conduction band.
3. The relation between the densities of the acceptors

produced by neutron doping are:  $N_{\text{Ga}}:N_{\text{As}}:N_{\text{Se}} = 1:0.26:0.012$ ; the degree of compensation is  $k = 0.27$ ; the half life of  $\text{Ge}^{70}$  is  $\tau = 12.3 \pm 0.3$  days, and the cross section for capture of a thermal neutron by the  $\text{Ge}^{76}$  isotope is  $\sigma_{\text{Ge}^{76}} = 0.011$  b.

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<sup>1)</sup>This circumstance was pointed out to us by F. M. Vorobkalo.

<sup>1</sup>J. W. Cleland, K. Lark-Horovitz, and J. C. Pigg, Phys. Rev. **78**, 814 (1950).

<sup>2</sup>A. G. Beda, V. V. Vainberg, F. M. Vorobkalo, and L. I. Zarubin, Fiz. Tekh. Poluprov. **15**, 1546 (1981) [Sov. Phys. Semicond. **15**, 916 (1981)].

<sup>3</sup>A. G. Milnes, Deep Impurities in Semiconductors, Wiley, 1973.

<sup>4</sup>H. Fritsche and M. Cuevas, Phys. Rev. **119**, 128 (1960).

<sup>5</sup>A. G. Zbrodskii, Pis'ma v Zh. Eksp. Teor. Fiz. **33**, 258 (1981) [JETP Lett. **33**, 243 (1981)].

<sup>6</sup>Yu. A. Osip'yan, V. M. Prokopenko, and V. I. Tal'yanskii, *ibid.* **36**, 64 (1982) [**36**, 77 (1982)].

<sup>7</sup>W. W. Tyler, J. Phys. Chem. Solids **8**, 59 (1959).

<sup>8</sup>S. F. Mughabghab and B. I. Garber, Neutron Cross Sections, BNL, **1**, 235 (1973).

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