

## Chalcogens in germanium

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The chalcogens S, Se, and Te have been introduced by diffusion into single-crystal germanium. Both thermal- and optical-junction space-charge techniques have been performed in parallel with photoconductivity studies using a Fourier-transform spectrometer. Electronic levels within the energy gap have been monitored from both valence and conduction bands using various techniques. The suggested double-donor states are found to be at  $E_C - 0.28$  and  $E_C - 0.59$  eV for sulfur,  $E_C - 0.268$  and  $E_C - 0.512$  eV for selenium, and  $E_C - 0.093$  and  $E_C - 0.33$  eV for tellurium. Evidence is found for excited states of S, Se, and Te. The neutral center of Se exhibits line spectra and corresponding Fano resonances due to a  $\Gamma_0$  intravalley phonon. The binding energy of the neutral  $2s(A_1)$  state of 7.4 meV is reported. A fitting of the spectra of deeper Se levels is in agreement with a singly ionized center. Electron thermal-emission rates and capture cross sections are reported for the  $E_C - 0.268$ ,  $E_C - 0.28$ , and  $E_C - 0.33$  levels. The capture cross section of the latter shows a  $T^{-3.1}$  temperature dependence. Furthermore, an unidentified double donor exhibiting excited states is found in several samples, having a binding energy of 207 meV. It is suggested to be oxygen related. Finally a comparison is made with data obtained from chalcogen-doped silicon.

### I. INTRODUCTION

Shallow impurities, in particular acceptor states, are well understood in germanium,<sup>1</sup> whereas deep impurities, surprisingly enough, are not as well studied in germanium as in silicon.<sup>1</sup> This is particularly true for deep donor states. Whereas in silicon, for example, the chalcogen double donors have been investigated in detail,<sup>2</sup> similar comprehensive data are still lacking for germanium.

Germanium has four equivalent conduction-band minima in the  $\langle 111 \rangle$  direction,<sup>3</sup> which implies that the  $ns$  states of donors are fourfold degenerate (excluding spin). The degeneracy is partly lifted by the valley-orbit interaction which is largest for the  $1s$  state. In tetrahedral ( $T_d$ ) symmetry, the  $s$  states are split into a singlet  $ns(A_1)$  ground state and a threefold degenerate  $ns(T_2)$  state where  $A_1$  and  $T_2$  are irreducible representations of the  $T_d$  point group.<sup>4</sup> Transitions from the  $1s(A_1)$  ground state to  $p$  states are both dipole- and symmetry-allowed according to effective-mass theory<sup>5</sup> (EMT) and group theory. They can therefore be studied in absorption and photoconductivity measurements. Transitions from the ground state to  $ns(T_2)$  states are dipole-forbidden but symmetry-allowed. Although such transitions are expected to be observed for double donors in germanium as they have been seen in silicon for the chalcogens S, Se, and Te (Ref. 2), no systematic studies of such transitions in germanium have hitherto been reported.

Very pronounced chemical shifts of the ground-state energy have been observed for group-VI donors in silicon.<sup>2</sup> Small, but nevertheless clearly observable, chemical shifts of the  $1s(A_1)$  ground state have been seen for group-V impurities in germanium.<sup>6</sup> In agreement with already published data<sup>7-10</sup> it is therefore reasonable to assume that the binding energies of substitutional double donors (sulfur, selenium, and tellurium) in germanium are

much larger than predicted by EMT. Indeed the first spectroscopic data of selenium-doped germanium published recently<sup>10</sup> have shown that the binding energy for the  $1s(A_1)$  ground state of a neutral selenium-related center in germanium is 268.2 meV, which is only about 13% smaller than the corresponding binding energy in silicon. Considering that the band gap of germanium is 38% smaller than in silicon this implies that the relative binding energies of the charged double donors in germanium are expected to be much larger than in silicon, and it is therefore not unreasonable to assume that the charged state of certain double donors in germanium may be found in the lower half of the band gap. However, chalcogen related centers in the lower half of the band gap have not been observed so far.

The first studies of chalcogen-doped germanium were reported by Tyler.<sup>7</sup> From Hall-effect and optical measurements he observed levels for tellurium in approximately equal concentrations at  $E_C - 0.11$  eV and  $E_C - 0.30$  eV, and for selenium and sulfur at  $E_C - 0.14$  eV and  $E_C - 0.18$  eV, respectively. He also found some evidence for other deep donor levels associated with both of these elements. Since in the case of selenium the concentration of these centers (one at  $E_C - 0.28$  eV, the other with unknown binding energy) was several times larger than the one at  $E_C - 0.14$  eV, Tyler argued whether in the case of selenium and sulfur all levels observed indeed belonged to the same center. Later deep-level transient spectroscopy (DLTS) measurements were reported<sup>8</sup> for selenium- and tellurium-doped germanium. Two levels were observed in both cases with energy positions at  $E_C - 0.11$  eV and  $E_C - 0.30$  eV for selenium and  $E_C - 0.19$  and  $E_C - 0.31$  for tellurium. Similar results were obtained in a study of hydrogen passivation of deep chalcogen-related donor centers in germanium.<sup>9</sup> In addition to the selenium and tellurium results the authors re-

port on two sulfur levels at  $E_C - 0.21$  eV and  $E_C - 0.25$  eV. Whereas the  $E_C - 0.31$ -eV tellurium level was effectively neutralized when exposed to the hydrogen plasma, none of the other chalcogen-related centers were affected by hydrogen.

Substitutional chalcogens form double donors in silicon with three different charge states, and a similar behavior has been suggested for chalcogens in germanium.<sup>11</sup> However, none of the previous electrical measurements gave any information on the charge states of these centers and it was therefore not clear whether or not the levels studied in germanium were different charge states of the same center or whether they belonged to different centers. In a recent study<sup>10</sup> we were able to show that the selenium level at  $E_C - 0.268$  eV is neutral and that the previously reported selenium level at about  $E_C - 0.14$  eV therefore could not be a different charge state of the  $E_C - 0.268$ -eV level. The value of 0.268 eV for the binding energy of the neutral selenium center differs from the value obtained by Pearton<sup>8</sup> but is in reasonable agreement with the data reported by Tyler.<sup>7</sup> Since Tyler found different concentrations for the  $E_C - 0.14$ -eV and  $E_C - 0.28$ -eV levels, his data support our interpretation that these two levels cannot belong to the same center.

If the  $E_C - 0.268$ -eV level is the neutral version of a selenium-related double donor then one would expect the charged center to lie in the lower half of the band gap. The purpose of this study was therefore to investigate whether there are chalcogen-related centers in the lower half of the band gap and, if such centers exist, to study their electronic properties, together with similar investigations of their neutral versions. In particular we attempted to establish the energy position and charge state of the chalcogen-related centers by optical measurements and to compare the optical results with those obtained from electrical measurements.

## II. EXPERIMENTAL DETAILS

Different types of samples were used for our investigations. Photoconductivity studies were performed on Czochralski-grown germanium either with a net donor concentration of less than  $10^{12}$  cm<sup>-3</sup> or with an electron concentration of  $10^{13}$  cm<sup>-3</sup>. The samples were sulfur, selenium, or tellurium diffused at temperatures between 770 and 925°C for 1–24 h. All samples were slowly cooled to room temperature and, after a cleaning procedure, alloyed with Au:Sb contacts. Some experiments were performed on *p*-type horizontally grown germanium with a free-hole concentration of about  $10^{13}$  cm<sup>-3</sup> and Czochralski-grown germanium with a free-hole concentration of about  $10^{14}$  cm<sup>-3</sup>. For these materials a diffusion temperature of 815°C was used for all doping and Au:B was employed for the alloyed contacts.

Junction space charge measurements were performed on Schottky structures and  $n^+p$  diodes. The Schottky diodes were fabricated on horizontally grown 2–3.5 or 0.26–0.4 Ω cm antimony-doped germanium. Before diffusion or ion implantation the samples were polished and etched. The diodes were sulfur-diffused at 730°C for 50 min, selenium-diffused at 765°C (800°C) for 30 min (1

h) and tellurium-diffused at 750°C for nearly 6 h. In order to reduce mass transport during diffusion the doping material was mixed with germanium powder. In the case of selenium some samples were prepared using ion implantation at 100 keV ( $1 \times 10^{14}$  cm<sup>-2</sup>) and successive annealing at 800°C for 1 h. Schottky contacts were obtained by evaporation of gold and Ohmic contacts were prepared by using a GaAl eutecticum.

The  $n^+p$  diodes were fabricated on Czochralski-grown *p*-type germanium with a free-hole concentration of  $2.3 \times 10^{14}$  cm<sup>-3</sup>. The samples were first polished and then diffused with sulfur, selenium, or tellurium at 815°C for 24 h. After cutting the samples in two halves, the surfaces which had the highest concentration of chalcogens were ion implanted with phosphorus at 200 keV ( $10^{13}$  cm<sup>-2</sup>). By etching part of the  $n^+$  layer a well-defined  $n^+p$  diode was obtained. After cleaning the diodes were mounted on an isolated transistor header.

The experimental techniques used for electrical measurements were various forms of junction space-charge techniques,<sup>12</sup> such as dark-capacitance transients<sup>13</sup> and deep-level transient spectroscopy (DLTS).<sup>14</sup> Using these techniques the temperature dependence of thermal emission rates and capture cross sections was studied. When performing these measurements, care was taken to avoid the nonuniform capture rate at the edge of the depletion region. To extend the range of temperatures available for the study of emission and capture rates, single-shot measurements were used in conjunction with DLTS measurements.

The thermal emission rates of holes for energy levels in the lower half of the band gap in *n*-type Schottky structures were studied by first illuminating the diode with near-band-gap light, resulting in a decrease in the electron occupancy of these levels, and then monitoring the capacitance transient due to the thermal filling of the centers with electrons from the valence band after the light source had been removed. The measurements were performed at sufficiently low temperatures to avoid thermal ionization of the neutral centers in the upper half of the band gap.

Isothermal photocapacitance measurements were carried out at constant reverse bias. The spectral sensitivity of this method could greatly be increased for sulfur-doped samples by using the initial-slope technique described in a previous paper.<sup>15</sup> All spectra of optical emission rates were corrected for variations in the photon flux  $\Phi$ .

The low-temperature infrared photoconductivity spectra were recorded at different temperatures and voltages on a Nicolet 8000 HV Fourier transform spectrometer using various sets of filters for the appropriate excitation energies.

## III. RESULTS

### A. Ge:S

Figure 1 shows the results of a typical DLTS run on an *n*-type Schottky diode. Between 15 K and room temperature two peaks were observed, indicating that only two deep levels are present in the upper half of the band gap.

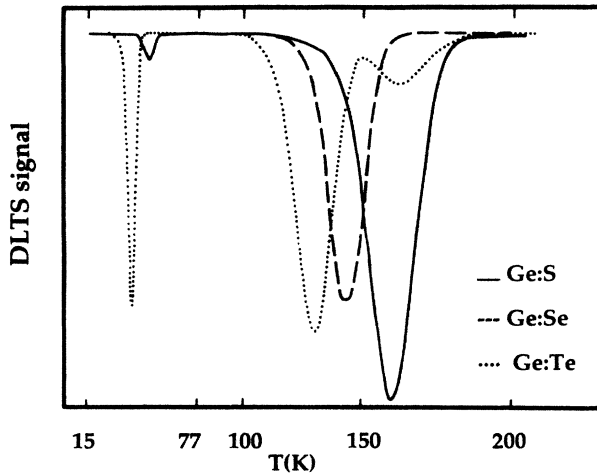


FIG. 1. DLTS spectra of  $n$ -type Schottky diodes in sulfur-, selenium-, and tellurium-doped germanium.

The peak at lower temperatures showed a “thermal activation” energy of about 104 meV. Since the concentration of this level was much lower than the one generating the high-temperature peak, no further measurements were performed on this center. Using single-shot transient measurements it could be shown that the capacitance transients of the peak at higher temperatures were exponential. We also studied the electron-capture process into this level at different temperatures (Fig. 2). Though the measurements could only be performed in a rather limited temperature range the results nevertheless indicate a small temperature dependence, implying a slight increase in the capture cross section  $\sigma_n^t$  with decreasing temperature. These results are in agreement with our optical data which suggest that the sulfur level may have excited states, and therefore a decrease in the capture cross section with increasing temperature due to a cascade process would not be unreasonable. An Arrhenius plot of the thermal emission rate for electrons  $e_n^t$  taking into account the temperature dependence of the electron-capture cross section is shown in Fig. 3. In order to increase the temperature range the data were ob-

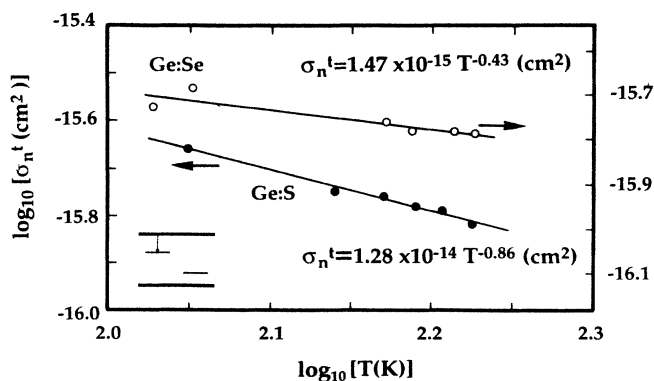


FIG. 2. Temperature dependence of the electron-capture cross section for the  $E_C-0.28$ -eV and  $E_C-0.268$ -eV centers in sulfur- and selenium-doped germanium.

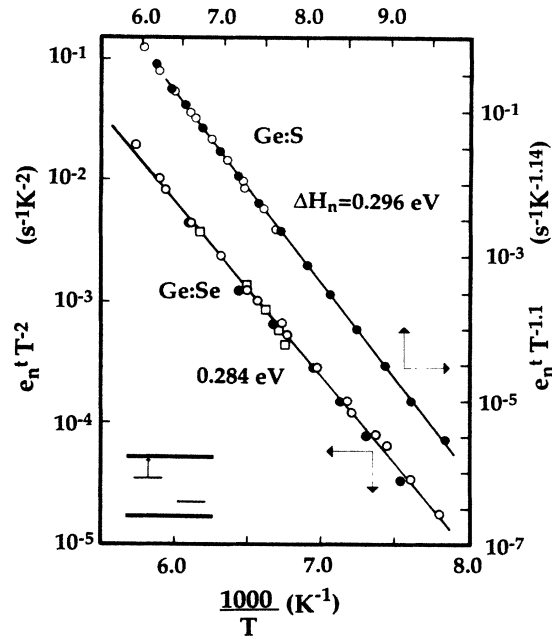


FIG. 3. Electron thermal emission rate vs inverse temperature for the  $E_C-0.28$ -eV center in sulfur-doped germanium, taking into account the temperature dependence of the electron-capture cross section ( $\circ$ , DLTS;  $\bullet$ , single-shot measurements) and for the  $E_C-0.268$ -eV center in selenium-doped germanium assuming a temperature-independent capture cross section ( $\bullet$ , implanted diodes;  $\circ$ , diffused diodes;  $\square$ , from Ref. 8).

tained using both DLTS and single-shot measurements. From the slope of the straight line in Fig. 3, a value of 296 meV was calculated for the enthalpy,  $\Delta H_n$ , of this sulfur-related center. Neglecting the temperature dependence of  $\sigma_n^t$  would have given a slightly smaller value of 288 meV for the enthalpy. Several parameters describing the electronic properties of the  $E_C-0.29$ -eV level, including the capture cross section and calculated Gibb's free energies  $\Delta G_n$  are summarized in Table I. Although  $\Delta G_n$  is close to  $\Delta H_n$  there is a slight decrease with temperature corresponding to an entropy change  $\Delta S_n$  of about  $3k$ . This value should, however, not be too heavily relied upon since the measurements of the capture cross section were difficult to perform and a small error in  $\sigma_n^t$  would result in a considerable change in  $\Delta S_n$ .

The measurements of thermal emission rates of electrons were performed on  $n$ -type Schottky diodes. Although such diodes are not ideal for investigating levels in the lower half of the band gap they can nevertheless be used to study such energy levels when the sample is illuminated with photons of an energy close to the band gap which gives rise to free electron-hole pairs. After removing the light source, a capacitance decrease was observed at lower temperatures which indicated thermal excitation of holes from a center in the lower half of the band gap into the valence band. Figure 4(a) shows that the time dependence of the capacitance decrease was exponential. Since we have been unable to measure the thermal capture cross section of holes,  $\sigma_p^t$ , for this center,

TABLE I. Thermal average velocity  $v_{th}$ , electron capture rate  $c_n^t$  and capture cross section  $\sigma_n^t$ , thermal emission rate of electrons  $e_n^t$ , effective density of states  $N_C$ , Gibb's free energy  $\Delta G_n$ , and calculated energy position  $\Delta G_n^0$  (assuming a degeneracy  $g=2$ ) of the  $E_C-0.29$ -eV center in sulfur-doped germanium at different temperatures  $T$ .

$T$ (K)	$10^{-7}v_{th}$ (cm s $^{-1}$ )	$10^9c_n^t$ (cm $^3$ s $^{-1}$ )	$10^{16}\sigma_n^t$ (cm $^2$ )	$e_n^t$ (s $^{-1}$ )	$10^{-18}N_C$ (cm $^{-3}$ )	$\Delta G_n$ (meV)	$\Delta G_n^0(g=2)$ (meV)
135	1.05	1.94	1.86	1.67	3.16	257	265
145	1.09	1.89	1.75	10.5	3.52	253	262
155	1.12	1.85	1.65	52.4	3.89	250	260
165	1.29	2.01	1.56	214	4.27	249	259

a temperature-independent cross section has been assumed when plotting the logarithm of the thermal hole emission  $e_p^t$  versus  $1/T$  [Fig. 4(b)]. From the slope of the Arrhenius plot an unspecified "activation energy" of 149 meV is obtained corresponding to an energy position of about  $E_C-0.6$  eV if it is assumed that the center is pinned to the conduction band.

From the data presented in Fig. 3 we may expect that at about 100 K the neutral sulfur-related center is thermally ionized. If the temperature is chosen somewhat lower, implying that the thermal ionization of the  $E_C-0.29$ -eV level is considerably reduced while the  $E_C-0.6$ -eV level is still thermally ionized, the photoionization threshold of holes of the  $E_C-0.29$ -eV level can be studied by illuminating the sample with photon energies greater than about  $E_g-0.29$  eV (i.e., 0.44 eV), which should result in a capacitance decrease. Such a change, due to a decrease in the diode capacitance, was indeed observed, showing that the change in capacitance was

caused by the excitation of electrons from the valence band into a localized state. The spectral distribution of the capacitance change is presented in Fig. 5 indicating a threshold energy very close to 440 meV. At higher photon energies the measurements were disturbed by the  $E_C-0.6$ -eV level, and hence the spectrum shown in Fig. 5 may deviate somewhat from the spectrum expected for the photoionization cross section of holes for the  $E_C-0.29$ -eV level.

Direct evidence for the interference of the  $E_C-0.6$ -eV level with these measurements was obtained by studying the diode capacitance after removing the light source. For photon energies larger than about 600 meV the capacitance decreased when, after reaching steady state, the illumination was turned off. A decrease in the capacitance implies that electrons were excited thermally from the valence band into a center. Since photons of energy greater than about 600 meV are capable of exciting elec-

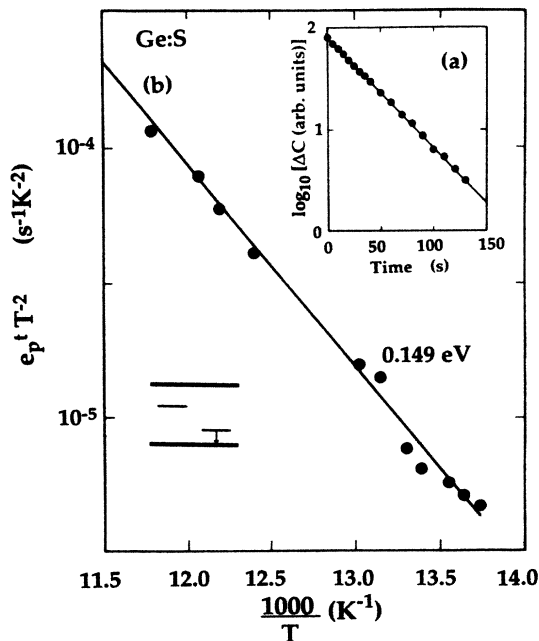


FIG. 4. (a) Capacitance decrease due to the thermal filling of the  $E_C-0.6$ -eV center in sulfur-doped germanium at 116.5 K. (b) Hole thermal emission rate vs inverse temperature for the  $E_C-0.6$ -eV center in sulfur-doped germanium assuming a temperature-independent hole-capture cross section.

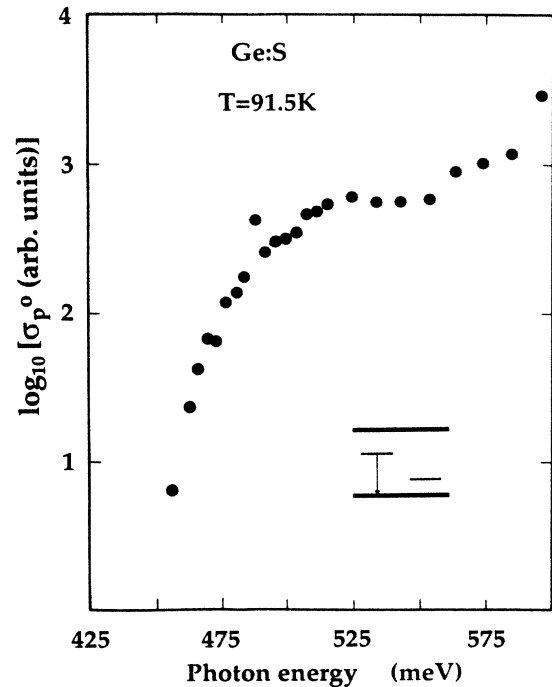


FIG. 5. Spectral distribution of the photoionization cross section for the excitation of holes from the  $E_C-0.28$ -eV center of sulfur-doped germanium into the valence band at 91.5 K.

trons from the  $E_C - 0.6$ -eV level to the conduction band and the amount of the capacitance change  $\Delta C$  after removing the light source was dependent on the photon energy, it is believed that the change in capacitance  $\Delta C$  is caused by the thermal filling of the  $E_C - 0.6$ -eV level with electrons. The spectral dependence of  $\log_{10}(\Delta C)$  at 107 K is shown in Fig. 6, clearly indicating a threshold energy of about 0.6 eV.

Additional optical measurements were performed by studying the photoconductivity properties of sulfur-doped germanium. Using infrared Fourier spectroscopy a spectrum was obtained at 11 K from our  $n$ -type samples showing a threshold energy close to 0.29 eV (Fig. 7) suggesting that the spectrum may be generated by the  $E_C - 0.29$ -eV level. Since the spectrum only shows one line no information could be obtained on whether the energy level is neutral or charged. If it is assumed that the line is caused by transitions from the neutral ground state to the  $2p_0$  state, a binding energy of 280.6 meV is obtained, in reasonable agreement with the calculated energy position (and enthalpy) obtained from our thermal measurements (see also Table I). When the sample was simultaneously illuminated with near-band-gap light a second absorption level with a threshold energy at about 150 meV was observed. It is believed that the absorption edge is caused by the  $E_C - 0.6$ -eV center.

Further analysis of the different threshold energies obtained for the  $E_C - 0.28$ -eV and  $E_C - 0.6$ -eV levels shows that at about 100 K the threshold energies for the  $E_C - 0.6$ -eV level add up to a value of about 749 meV. A similar analysis for the  $E_C - 0.28$ -eV level at about 90 K gives a value of about 720 meV. Both values are close to

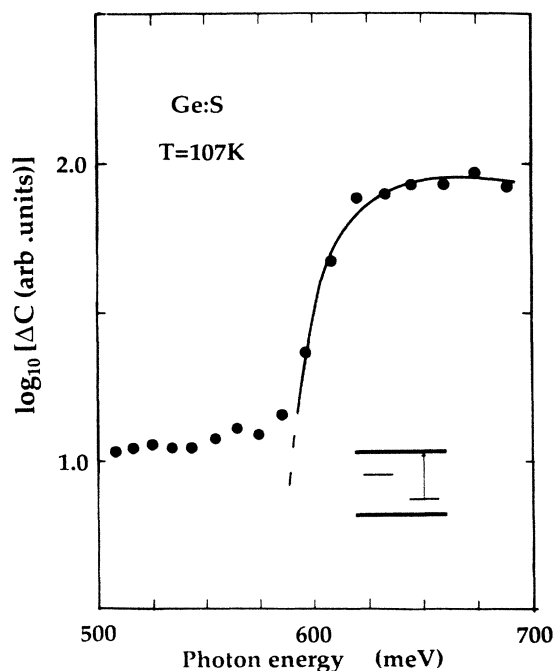


FIG. 6. Spectral distribution for the excitation of electrons from the  $E_C - 0.6$ -eV center into the conduction band at 107 K in sulfur-doped germanium. The line is a guide to the eye.

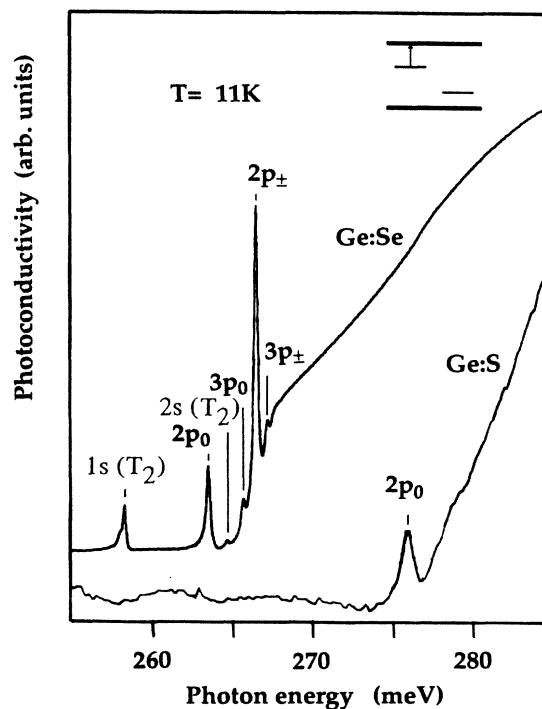


FIG. 7. Photoconductivity spectrum of sulfur- and selenium-doped germanium. The assignment of the lines is made with respect to the final state of the transitions.

the band gap energy suggesting that the assignment of the different threshold energies is reasonable.

### B. Ge:Se

A typical DLTS spectrum of a selenium-doped  $n$ -type implanted Schottky diode is shown in Fig. 1. Only one significant peak was observed in the temperature range between 77 K and room temperature. In some diffused samples an additional peak at lower temperature was observed which will be discussed later.

The capture cross section of electrons for the dominant center was studied as a function of temperature and the results are presented in Fig. 2. As in the case of sulfur, the temperature range available for the DLTS measurements was rather small. Furthermore, using the pulse-train technique<sup>12</sup> small deviations were obtained at low temperatures, due to disturbances from shallower levels. The results nevertheless suggest a weak temperature dependence implying a decrease in the capture cross section with increasing temperature. Single-shot measurements showed that the capture process was exponential as it was in the case of sulfur.

An Arrhenius plot of the thermal emission rate for electrons is shown in Fig. 3 assuming a temperature-independent capture cross section. The results were obtained in both diffused and ion-implanted diodes. For comparison results published previously by Pearton and Tavendale<sup>9</sup> are also shown. From the slope of the Arrhenius plot an activation energy of 0.284 eV is calculated. This value does not change much if the weak tem-

TABLE II. Summary of the thermodynamic parameters of electron capture and emission of the  $E_C - 0.268$ -eV center in selenium-doped germanium.

$T$ (K)	$10^{-7}v_{th}$ ( $\text{cm s}^{-1}$ )	$10^9 c_n^t$ ( $\text{cm}^3 \text{s}^{-1}$ )	$10^{16} \sigma_n^t$ ( $\text{cm}^2$ )	$e_n^t$ ( $\text{s}^{-1}$ )	$10^{-18} N_C$ ( $\text{cm}^{-3}$ )	$\Delta G_n$ (meV)	$\Delta G_n^0(g=2)$ (meV)
135	1.05	1.90	1.82	1.28	3.16	260	268
145	1.09	1.91	1.76	8.03	3.52	257	266
155	1.12	1.92	1.72	39.8	3.89	255	264
165	1.29	2.15	1.67	162	4.27	254	264

perature dependence of the capture cross section is taken into account resulting in an enthalpy of 0.288 eV. Using the absolute values of the capture coefficient  $c_n^t$  the thermal emission rate  $e_n^t$  and the effective density of states  $N_C$  at different Gibbs temperatures the temperature dependence of the Gibbs free energy  $\Delta G_n$  and the change in entropy  $\Delta S_n$  were calculated (Table II). As in the case of sulfur-doped germanium the change in entropy is about  $2k$ . Although none of our measurements has yielded a value for the electronic degeneracy,  $g$ , it is nevertheless interesting to calculate the energy position  $\Delta G_n^0$  of the center using the relation<sup>16</sup>

$$\Delta G_n^0 = \Delta G + kT \ln g.$$

Since our optical data indicate that the center is probably pinned to the conduction band we assumed  $g=2$  (Table II). Considering the uncertainty in thermal measurements it is interesting to note that an almost

temperature-independent value of 265 meV was obtained for  $\Delta G_n^0$ , which is rather close to the optical binding energy of 268.22 meV measured with Fourier-transform spectroscopy.<sup>10</sup>

In order to study energy levels in the lower half of the band gap the  $n$ -type Schottky diodes were illuminated with photons close to the band-gap energy. After removing the light source an exponential dark-capacitance decrease was observed as in the case of sulfur [Fig. 8(a)]. Since the capacitance decreased after removing the light source the change can only be generated by thermal ionization of a center in the lower half of the band gap. We were unable to measure the temperature dependence of the capture cross section for holes, and hence a temperature-independent cross section had to be assumed when plotting the thermal emission rate of holes,  $e_p^t$  [Fig. 8(b)]. From an Arrhenius plot an unspecified activation energy of 0.245 eV was obtained. If the center is the charged version of the  $E_C - 0.268$ -eV center then this value would correspond to an energy position of about  $E_C - 0.5$  eV if it is assumed that the center is pinned to the conduction band. An energy level at about 240 meV above the valence band at 36 K was confirmed by photo-capacitance measurements on  $n^+p$  diodes. After short-circuiting, the capacitance increased in reverse-biased diodes when illuminating the sample with photon energies larger than about 250 meV. Though the spectrum could only be measured over less than one order of magnitude, a threshold energy close to 240 meV could nevertheless clearly be observed. DLTS on these  $n^+p$  diodes revealed a level situated in the lower half of the band gap, having the same hole emission characteristics [Fig. 8(b)] as the  $n$ -Schottky diode above.

Further information on the pinning of the  $E_C - 0.5$ -eV center to the conduction band was obtained from photo-conductivity measurements on  $p$ -type samples. Figure 9 shows such spectra monitored at 180, 105, and 40 K. With decreasing temperature the energy of the sensitivity edge increased from 202 meV at 180 K to about 240 meV at 40 K. Comparing the temperature dependence of the threshold energy with the temperature dependence of the band gap (Fig. 10) a similar variation with temperature is observed in both cases. This result is easily understood if it is assumed that the 202-meV edge at 180 K originates from a center in the lower half of the band gap, the energy position of which with respect to the conduction band is rather temperature independent. If this center is the charged version of the  $E_C - 0.268$ -eV center, which we have been unable to prove, then the hole capture into the  $E_C - 0.5$  eV state should not be governed by a cascade

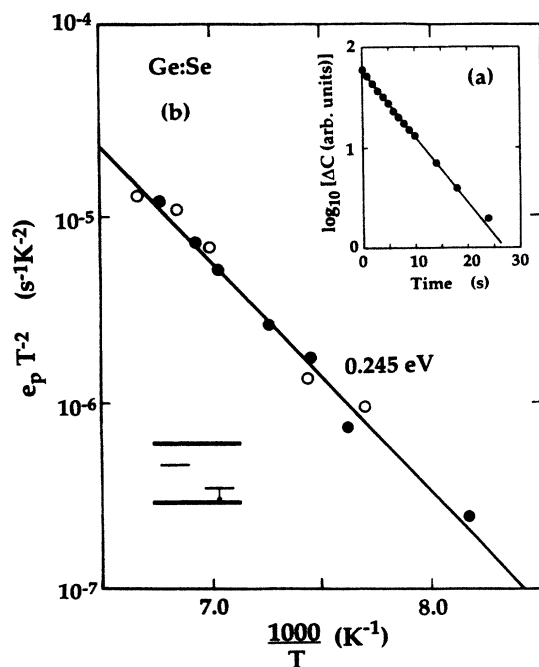


FIG. 8. (a) Capacitance change due to the thermal filling of the  $E_C - 0.51$ -eV center in selenium-doped germanium. (b) Arrhenius plot of the thermal emission rate for holes in selenium-doped germanium assuming a temperature-independent capture cross section ( $\bullet$ ,  $n$ -Schottky diodes;  $\circ$ ,  $n^+p$  diodes).

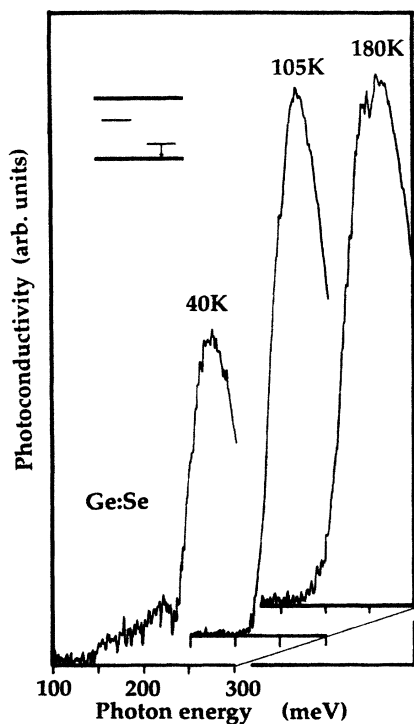


FIG. 9. Photoconductivity spectra at different temperatures in  $p$ -type germanium samples doped with selenium.

process. This is in agreement with the spectra presented in Fig. 9 not showing any line spectra. Hence, anticipating a positive temperature dependence of  $\sigma_p^t$ , the enthalpy for the hole emission is expected to be somewhat smaller than the unspecified activation energy of about 0.245 eV mentioned earlier.

Transitions from the  $E_C - 0.5$ -eV center into the conduction band should start at photon energies of about 500 meV and if the center is the ionized version of the  $E_C - 0.268$ -eV center then the spectrum is expected to reflect the presence of excited states. Using a modified Fourier photoadmittance spectroscopy (FPAS) technique<sup>17</sup> a spectrum with a threshold energy of about 505

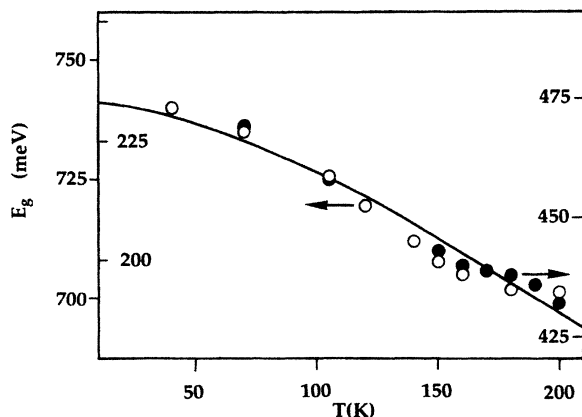


FIG. 10. Temperature dependence of the hole photoconductivity edge for the  $E_C - 0.51$ -eV ( $\circ$ ) and  $E_C - 0.268$ -eV centers ( $\bullet$ ) in selenium-doped germanium. For comparison the temperature dependence of the band gap (—) is also shown (outer scale).

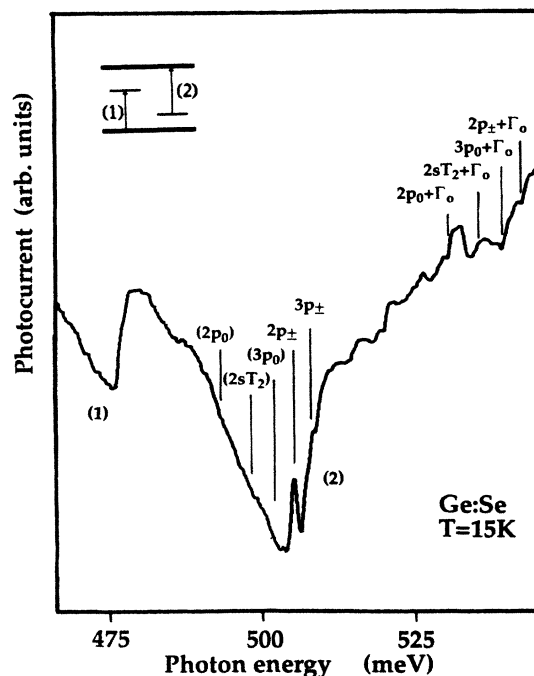


FIG. 11. Photocurrent spectrum of selenium-doped germanium at 15 K showing the line spectrum and Fano resonances of the  $E_C - 0.51$ -eV center and the sensitivity edge for the hole excitation of the  $E_C - 0.268$ -eV center (see text).

meV was indeed observed (Fig. 11). Since the spectrum shows only two clearly resolved lines their assignment might have caused some difficulties if the spectrum had not contained a structure at higher energies in the continuum which was highly reproducible in detail. It is therefore very probable that the structure in the continuum originates from Fano resonances.<sup>18</sup> Since, in the case of the neutral center the phonon involved in the Fano resonances was the intravalley  $\Gamma_0$  (37.7 meV, see Ref. 19) phonon (see below), it is obvious that the same phonon should be involved in the Fano resonances of the  $E_C - 0.5$ -eV center. Comparing the Fano resonances with the spectrum obtained by direct optical excitation the assignment of the total spectrum is fairly straightforward. The best fit which was obtained is shown in Fig. 11. The positions of the arrows in the continuum part of the spectrum were obtained by adding the  $\Gamma_0$  phonon energy to the transition energies from the  $1s(A_1)$  ground state to corresponding excited states. Transition energies, calculated binding energies and EMT values for the ground state and excited states are summarized in Table III.<sup>20,21</sup> If our assignment of the peaks in the spectrum is correct then there is no doubt that the  $E_C - 0.5$ -eV center is singly ionized supporting our previous assumption that it might be the charged state of the  $E_C - 0.268$ -eV center. Adding the binding energy of the  $2p_{\pm}$  excited state (6.92 meV) to the transition energy from the ground state to the  $2p_{\pm}$  state, a binding energy of 512.4 meV is obtained in reasonable agreement with our thermal data. The spectrum is temperature independent in the temperature range studied, which gives further support to our as-

TABLE III. Comparison of measured energy levels in selenium-doped germanium with experimental (Ref. 20) and calculated (Ref. 21) results for shallow impurity levels in germanium. All energies are in meV.

	EMT	$P$	$Se^0$	$Se^+$
$3p_{\pm}$	1.03	1.05	1.04	$3.9/4=0.98$
$2p_{\pm}$	1.73	1.73	1.73	$6.92/4=1.73$
$3p_0$	2.56	2.56	2.57	$10.4/4=2.55$ (Fano)
$2s$	3.52			
$2s(T_2)$			3.58	
$2p_0$	4.74	4.74	4.75	$19.2/4=4.80$ (Fano)
$2s(A_1)$			7.4 (Fano)	
$1s$	9.81			
$1s(T_2)$		9.93	9.95	
$1s(A_1)$		12.76	268.2	512.4

sumption that the  $E_C-0.512$ -eV level is pinned to the conduction band.

The energy position of the center was further confirmed by photocapacitance measurements in  $n^+p$  diodes at about 80 K. For photon energies larger than about 0.5 eV the diode capacitance decreased, confirming that electrons from the thermally filled  $E_C-0.512$ -eV level were excited into the conduction band with a threshold energy of about 0.5 eV.

Further inspection of Fig. 11 reveals that the spectral distribution of the modified FPAS spectrum at 15 K contains a second sensitivity edge at about 475 meV. We studied this part of the spectrum at different temperatures and, as shown in Fig. 12, there is no doubt that the threshold energy moves to a lower energy with increasing temperature. Plotting the threshold energy as a function of temperature (Fig. 10) it is readily seen that the temperature dependence of the threshold energy is close to that for the band-gap energy and that the signal therefore obviously originates from the excitation of electrons from the valence band into the  $E_C-0.268$ -eV center. It is interesting to note that at 15 K the threshold energy of this transition together with the binding energy of the  $E_C-0.268$ -eV level adds up to a value of about 743 meV, which is very close to the band-gap energy, suggesting that any lattice relaxation connected with this center is very small.

Similar arguments are valid for the  $E_C-0.512$ -eV level. In this case the two energies add up to a value of about 750 meV at 15 K, which again is close to the band-gap energy.

The photoconductivity spectrum originating from the excitation of electrons from the  $E_C-0.268$ -eV level into the conduction band has been published previously.<sup>10</sup> Excited states up to  $3p_{\pm}$  could be studied, including the valley-orbit split states  $1s(T_2)$  and  $2s(T_2)$ , revealing that the center has  $T_d$  symmetry and, hence, is probably the isolated selenium double donor in germanium. These investigations have been continued and in Fig. 13 (inset) the photoconductivity spectrum of  $Se^0$  is presented for photon energies of between 250 and 350 meV. A closer inspection of the continuum part reveals a structure which is believed to originate from the interaction between a continuum state in the conduction band and a

semidiscrete electron-phonon state (Fano resonance). The resonance, occurring at the smallest energy, differs from the  $1s(T_2)$  line by exactly the  $\Gamma_0$  phonon energy. In Fig. 13 the part of the  $Se^0$  spectrum corresponding to excitations from  $1s(A_1)$  into the conduction band has therefore been shifted by 37.7 meV to smaller energies and plotted together with the extrinsic part of the spectrum on an enlarged scale. Since phonon interaction is involved in the occurrence of Fano resonances, forbidden bound-to-bound transitions can be investigated when studying Fano resonances. Hence, comparing the two spectra in Fig. 13 it is quite obvious that, for example, the resonance observed at about  $261 \text{ meV} + \Gamma_0$  originates from the  $2s(A_1)$  state. The energies of the observed

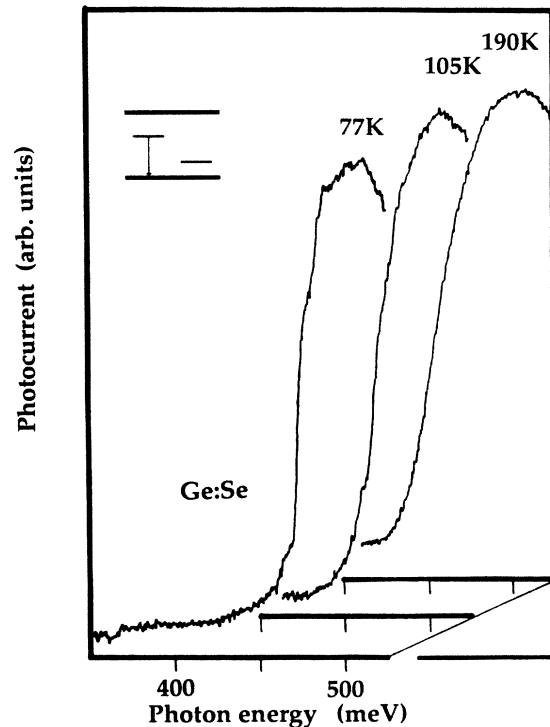


FIG. 12. Sensitivity edge of the hole excitation for the  $E_C-0.268$ -eV center in selenium-doped germanium at different temperatures.



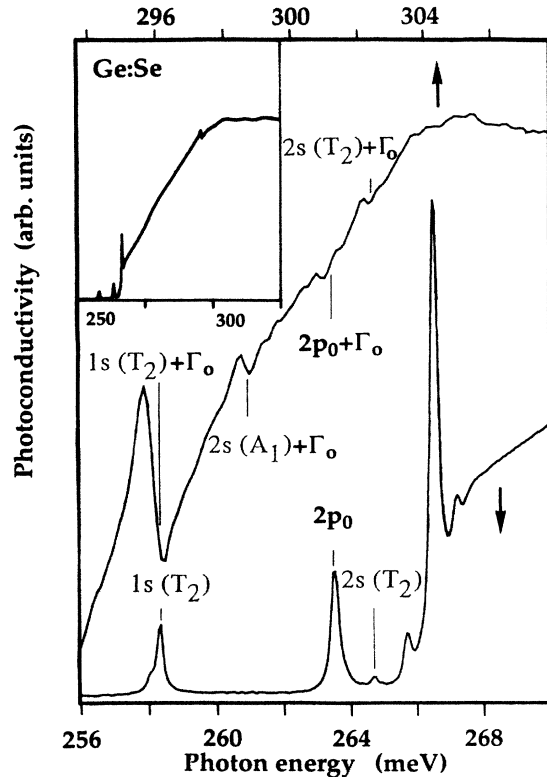


FIG. 13. Photoconductivity spectrum of selenium-doped germanium showing the line spectrum and Fano resonances of the  $E_C - 0.268$ -eV center. For comparison the upper spectrum has been shifted to a 37.7 meV ( $\Gamma_0$  phonon energy) lower energy. The total spectrum is shown in the inset.

transitions between the ground state and various excited states of  $\text{Se}^0$  are presented in Table IV. The calculated ground-state energy, the resulting binding energies and the calculated binding energies using effective mass theory (EMT) are also given.

### C. Ge:Te

Tellurium is, in comparison with sulfur and selenium, a slow diffuser in germanium.<sup>7,8,22</sup> This means that the highest concentrations were obtained in a thin surface layer which may be contaminated by other impurities such as oxygen. Figure 1 shows the results of a typical DLTS run on  $n$ -type Schottky diodes.

The peak at about 135 K has an enthalpy of 0.22 eV and is present in all our tellurium-doped samples. Since

the peak is also observed in some of our selenium-doped samples it is not necessarily related to tellurium. However, since Pearton's<sup>8,9</sup> results indicate a tellurium-related level at  $E_C - 0.19$ -eV, and our data of the capture cross section for the  $E_C - 0.22$ -eV level deviate from the values obtained for the similar level in Se-doped samples the possibility that tellurium may be involved in the  $E_C - 0.22$ -eV level cannot be disregarded. Comparisons of several photoconductivity spectra have indicated the existence of two singly charged centers with slightly different binding energies,  $E_C - 0.19$  and  $E_C - 0.207$  eV. The weak  $E_C - 0.19$  level was not detected in sulfur- and selenium-doped samples, whereas the  $E_C - 0.207$ -eV level was observed in sulfur-, selenium-, and tellurium-doped samples and will be discussed later.

We were not able to measure the temperature dependence of the electron-capture cross section for the center causing the DLTS peak at about 25 K, and hence only an unspecified activation energy of 92 meV from a  $\log_{10}(e_n^i T^{-2})$  versus  $1/T$  plot can be presented (Fig. 14) for this center. We observed a similar low-temperature peak in some of our Se-doped samples, but we were not able to conclude whether or not this peak was identical to the peak in Te-doped samples.

In order to obtain more accurate information on the binding energy of the  $E_C - 0.09$ -eV center we studied the photoconductivity response of  $n$ -type tellurium-doped samples. Figure 15 shows a spectrum obtained between 60 and 100 meV at 12.5 K. Though the structure is not very pronounced there is nevertheless a slight indication of a line spectrum close to the sensitivity edge. A tentative assignment of the spectrum is presented in Fig. 15 resulting in a binding energy of 91.5 meV for the  $1s(A_1)$  ground state of a neutral center, which is close to the energy value obtained from thermal measurements and in reasonable agreement with previous data.<sup>7,23</sup> The energies of the observed transitions between the ground state and different excited states are summarized in Table V together with calculated EMT binding energies.

Measurements of the electron-capture cross section  $\sigma_n^i$  for the center causing the DLTS peak at about 165 K in Fig. 1 could only be performed in a rather limited temperature range [Fig. 16(a)]. Although we believe that  $\sigma_n^i$  decreases with increasing temperature, the temperature dependence of  $T^{-3.1}$  should not be completely relied upon. Taking into account the temperature dependence of  $\sigma_n^i$  a value of 332 meV is obtained for the enthalpy from an Arrhenius plot of the thermal emission rate  $e_n^i$  [Fig. 16(b)]. These results are in reasonable agreement

TABLE IV. Summary of thermodynamic parameters for electron capture and emission of the  $E_C - 0.33$ -eV center in tellurium-doped germanium.

$T$ (K)	$10^{-7}v_{th}$ ( $\text{cm s}^{-1}$ )	$10^9 c_n^i$ ( $\text{cm}^3 \text{s}^{-1}$ )	$10^{16} \sigma_n^i$ ( $\text{cm}^2$ )	$e_n^i$ ( $\text{s}^{-1}$ )	$10^{-18} N_C$ ( $\text{cm}^{-3}$ )	$\Delta G_n$ (meV)	$\Delta G_n^0(g=2)$ (meV)
135	1.05	1.85	1.67	1.27	3.16	260	268
145	1.08	1.48	1.61	8.22	3.52	255	263
155	1.12	1.20	1.25	41.7	3.89	249	259
165	1.29	0.95	1.02	173	4.27	246	256

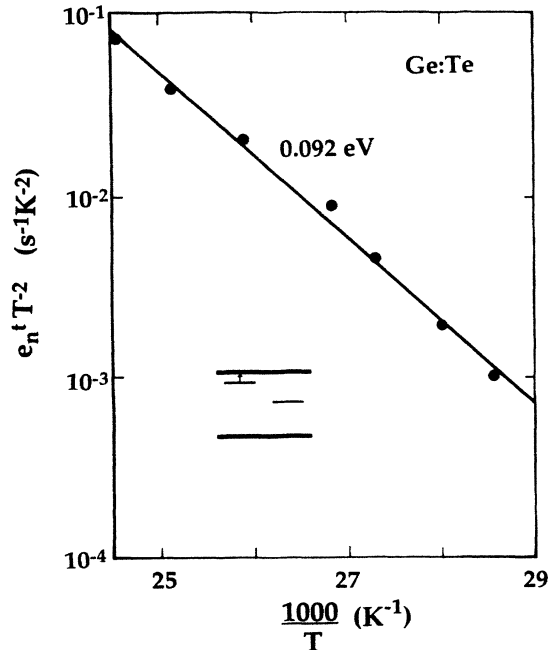


FIG. 14. Arrhenius plot of the thermal emission rate for electrons in tellurium-doped germanium assuming a temperature-independent capture cross section.

with data previously published by Tyler<sup>7</sup> who reported that tellurium causes two centers of equal concentrations at  $E_C - 0.11$  eV and  $E_C - 0.30$  eV. If our  $E_C - 0.33$ -eV level is the  $\text{Te}^+$  center, then one would expect the electron capture to be governed by a cascade process and therefore the capture cross section should decrease with increasing temperature, as was observed [Fig. 16(a)].

Transitions from the valence band into the  $E_C - 0.33$ -eV center were studied by performing steady-state photo-

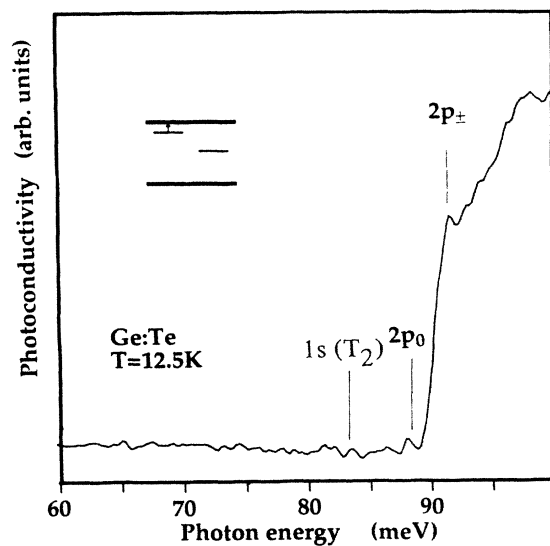


FIG. 15. Photoconductivity spectrum of tellurium-doped germanium at 12.5 K showing the line spectrum of the  $E_C - 0.09$ -eV center. A tentative assignment of the lines is also shown.

TABLE V. Comparison of measured energy levels in tellurium-doped germanium with calculated (Ref. 21) results using EMT. Values in parentheses are less certain. All energies are in meV.

	EMT	$\text{Te}^0$	$\text{O}^+$
$3p_{\pm}$	1.03		
$2p_{\pm}$	1.73	1.73	$6.92/4 = 1.73$
$3p_0$	2.56		$10.27/4 = 2.57$
$2s$	3.52		
$2s(T_2)$			$(13.35/4 = 3.34)$
$2p_0$	4.74	(4.7)	$19.11/4 = 4.78$
$2s(A_1)$			
$1s$	9.81		
$1s(T_2)$			
$1s(A_1)$		93.4	206.6

current measurements (Fig. 17) as a function of temperature. A threshold energy close to 450 meV moving to smaller energies with increasing temperature was observed. A second threshold at about 650 meV was revealed at higher temperatures. Both threshold energies are in agreement with the energy position of the  $E_C - 0.09$ -eV and  $E_C - 0.33$ -eV centers. The increase in the signal for the  $E_C - 0.33$ -eV center with increasing temperature is due to the decreasing electron occupancy of the center due to thermal ionization.

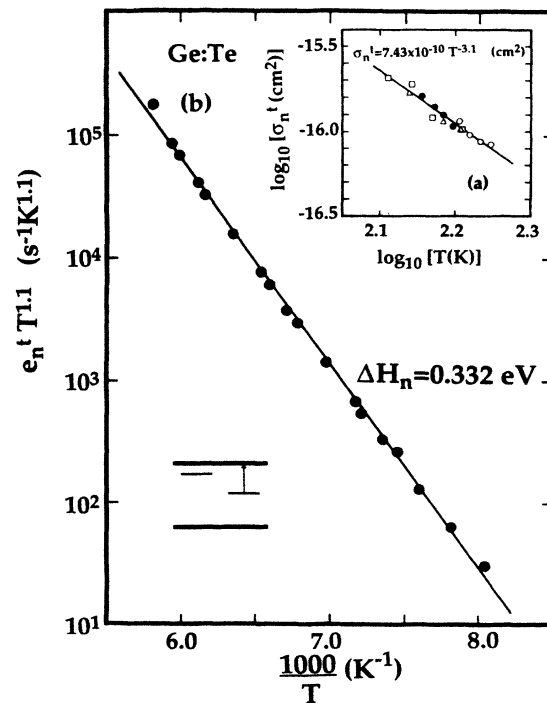


FIG. 16. (a) Temperature dependence of the electron-capture cross section for the  $E_C - 0.33$ -eV center in tellurium-doped germanium [ $\bullet$ ,  $\Delta$  DLTS;  $\circ$ , isothermal DLTS;  $\square$ ,  $\Delta C(t=0)$ ]. (b) Electron thermal emission rate vs inverse temperature for the  $E_C - 0.33$ -eV center in tellurium-doped germanium taking into account the temperature dependence of the electron-capture cross section.

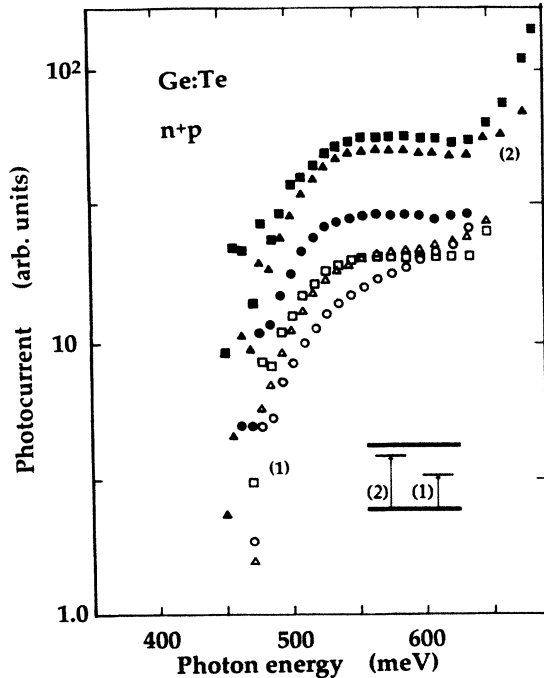


FIG. 17. Spectral distribution of the steady-state photocurrent in tellurium-doped  $n+p$  diodes at different temperatures.  $\circ$ , 79 K;  $\triangle$ , 91 K;  $\square$ , 108 K;  $\bullet$ , 117 K;  $\blacktriangle$ , 125 K,  $\blacksquare$ , 134 K.

#### D. Ge:O

None of our germanium samples were deliberately doped with oxygen. However, as mentioned earlier, one of the DLTS peaks in tellurium-doped germanium was also observed in some of our selenium-doped samples. The electron-capture cross section of the center connected with this peak in Te-doped samples decreased with increasing temperature as  $T^{-2.08}$  suggesting some type of cascade capture process. Taking into account the temperature dependence of the electron-capture cross section and plotting  $\log_{10} e_n^t \times T^{0.08}$  versus  $1/T$  where  $e_n^t$  is the thermal emission rate of electrons, an enthalpy of 222 meV was obtained (Fig. 18). It has been suggested that one of the thermal oxygen donors in germanium should cause a level at about 0.2 eV.<sup>24-26</sup> Most of the thermal oxygen donors in silicon are known to be double donors. If our center at  $E_C - 0.2$  eV is due to oxygen it is interesting to know whether the center is neutral or charged. A photocurrent spectrum in the range between 170 and 210 meV for a selenium-doped sample exhibiting a DLTS peak at about 125 K is shown in Fig. 19. A straightforward assignment of the line spectrum revealed that the center is charged. Adding the EMT binding energy of 6.92 meV to the measured energy for the transition from the ground state into the  $2p_{\pm}$  excited state a binding energy of 206.6 meV was obtained for the  $1s(A_1)$  ground state. We have been unable to show that the  $E_C - 207$ -meV center is due to oxygen. However, because of the good agreement of our optical and thermal data with results previously published this possibility cannot be excluded.

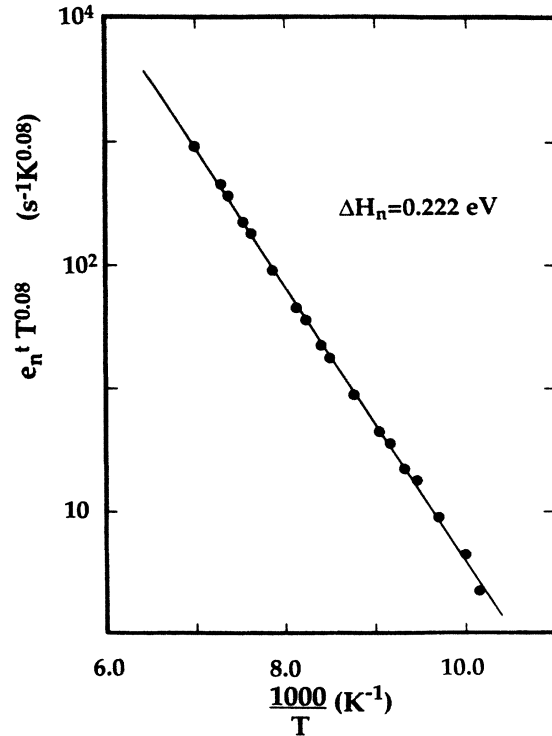


FIG. 18. Thermal emission rate of electrons vs  $1/T$  for the  $E_C - 0.207$ -eV center observed in tellurium-doped germanium taking into account the temperature dependence of the electron-capture cross section.

#### IV. DISCUSSION

Comparing the energy positions of chalcogen-related centers in our samples with those previously published (Fig. 20) it is easily seen that our data differ quite considerably from some of the results obtained from DLTS

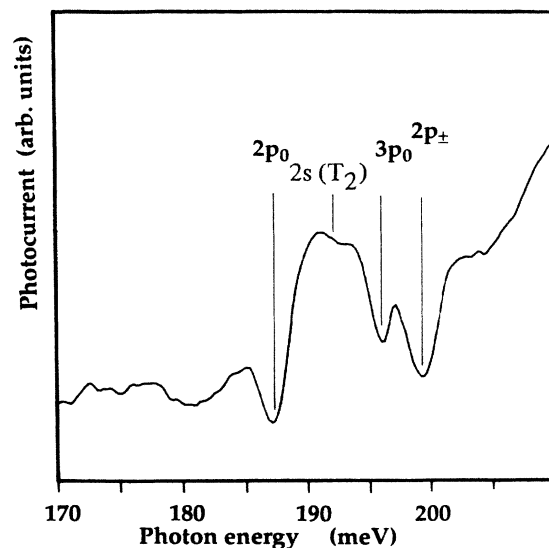


FIG. 19. Photoconductivity spectrum observed in selenium-doped germanium showing the line spectrum of the  $E_C - 0.206$ -eV center. The energy spacing of the lines clearly indicates that the center is charged.

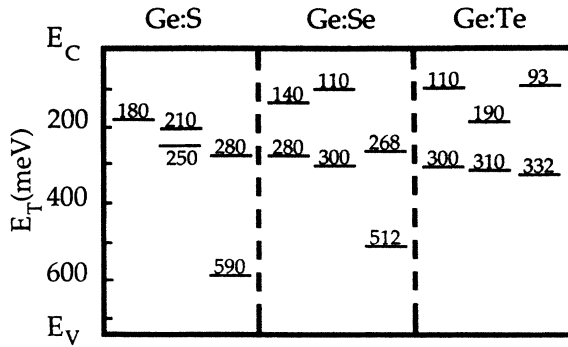


FIG. 20. Survey of published data (Refs. 7, 8, 9, 11, and this work) on the energy position of centers observed in sulfur-, selenium-, and tellurium-doped germanium.  $E_T$  is the binding energy of the centers with respect to the conduction band.

measurements. It is also interesting to note that very poor agreement is obtained for the shallowest states in sulfur- and selenium-doped germanium, suggesting that these states may be more complicated centers or may not be related to chalcogens at all.

Figure 20 also shows that no chalcogen-related centers have previously been observed in the lower half of the band gap. Since for Ge:S and Ge:Se, the energy separation of these centers from the valence band is comparable to the energy distance of the chalcogen-related centers in the upper half of the band gap from the conduction band, the measurements were disturbed by the mutual interference of the neutral and charged centers. We therefore performed our measurements in both  $n$ -type and  $p$ -type samples and great care was taken to establish the relative energy positions of the different centers from capacitance measurements. If the charged centers for sulfur and selenium are situated in the lower half of the band-gap absorption spectra exhibiting excited states are only expected for transitions to the conduction band. However, these transitions are severely disturbed by transitions from the valence band into the neutral centers. This is one of the reasons why the measurements were difficult to perform. Another reason is that the doping properties of chalcogens in germanium are not well understood. It is therefore not surprising that both the tentative neutral and charged centers of tellurium have been observed previously in Hall-effect measurements<sup>7</sup> since in the case of tellurium both centers are situated in the upper half of the band gap. It is also worthwhile to mention that apart from the centers discussed in this paper no other chalcogen-related centers have been observed by us. We would also like to stress the good agreement of our thermal data with optical results supporting the assignment of the centers.

As mentioned earlier the purpose of our investigation was to find out if chalcogens form double donors in germanium, where the charged centers are situated in the band gap and what electronic properties they have. Unambiguous evidence that two centers are coupled is normally difficult to establish<sup>27</sup> and quite often very good diode structures are needed. We had no access to such

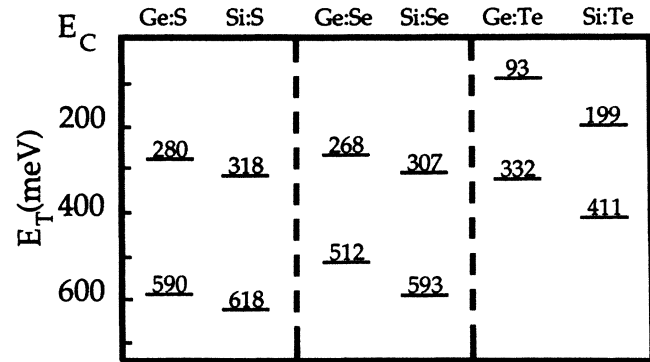


FIG. 21. Comparison of energy positions for isolated chalcogen centers in germanium and silicon.

samples and therefore only indirect arguments can be given.

Comparing the energy positions of chalcogens studied in germanium with those for isolated centers in silicon (Fig. 21) an interesting close resemblance is observed. This resemblance and the fact that the  $E_C - 0.268$  eV center in Ge:Se has  $T_d$  symmetry suggests that the other chalcogen centers in germanium are also isolated centers. The only deviation from this resemblance is observed for tellurium. As for silicon, the binding energies of the deeper states are almost twice as large as for the neutral states, again with the exception of tellurium. This agreement strongly supports our interpretation that the deeper chalcogen states in Fig. 21 are probably the charged versions of isolated double donors. This interpretation is further supported by the temperature dependence of the electron-capture cross section and the fact that line spectra have only been observed for transitions to the conduction band but not for transitions to the valence band. It is interesting to note that the measured binding energy of the  $2s(T_2)$  state for the  $E_C - 0.268$ -eV center in Ge:Se is close to the EMT value for the  $2s$  state (Table III). This result is in good agreement with similar data obtained for chalcogens in silicon<sup>2</sup> and further supports our assignment of the spectra studied.

Though there are reasons to believe that the  $E_C - 0.222$ -eV DLTS level originates from oxygen ( $E_C - 207$  meV) we cannot exclude the possibility that a nearby center ( $E_C - 0.19$  eV), due to tellurium, contributes to the DLTS peak, considering the resemblance with silicon and the fact that the center is charged. Further work is needed for a definite identification.

Whereas in silicon the phonons involved in Fano resonances are intervalley phonons, we have strong reasons to believe that in the case of germanium the  $\Gamma_0$  intravalley phonon is involved.

No pronounced lattice relaxation was found for isolated chalcogens in silicon and no indication of any larger lattice relaxation was observed for the chalcogen-related centers in germanium discussed in this paper. We consider this as further support for our interpretation that the centers studied by us are simple centers.

## V. CONCLUSIONS

Sulfur-, selenium-, and tellurium-doped germanium has been investigated using different types of junction space-charge and Fourier spectroscopy techniques. The results are best understood in terms of double donors with three different charge states. Whereas the tellurium states are all observed in the upper half of the band gap, evidence was found that in the case of sulfur and selenium the charged centers are situated in the lower half of the band gap. This conclusion is supported by a close resemblance between the binding energies of the sulfur and selenium centers in germanium and corresponding energies in silicon. Line spectra indicating the existence of excited states were observed for all neutral centers whereas the line spectrum of a charged center was measured only for

selenium-doped germanium. All energy positions of the centers studied by Fourier spectroscopy are in agreement with capacitance measurements. Finally we have presented optical spectra which, for the first time, give evidence for the existence of Fano resonances in chalcogen-doped germanium.

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