PHYSICAL REVIEW B VOLUME 26, NUMBER 12 15 DECEMBER 1982

Characteristics of the electron traps produced by electron irradiation in n-type germanium

F. Poulin and J. C. Bourgoin
Groupe de Physique des Solides de l'Ecole Normale Supérieure, Université Paris VII, Tour 23,
2 Place Jussieu, 75251 Paris Cedex 05 France

(Received 6 May 1982)

The free energies of ionization, the emission rates, and the cross sections for electron trapping have been measured for the four majority carrier traps which are produced in n-type germanium by electron irradiation at room temperature and which are stable at this temperature. These traps, labeled E_1, E_2, E_4, and E_5, which exhibit an emission rate of 140 s^{-1} at 145, 200, 185, and 170 K, are situated at 260, 410, 380, and 370 meV below the conduction band, respectively. The variations of the electron-capture cross sections versus temperature, characterized by the following activation energies: 65, 120, 80, and 50 meV, respectively, indicate that nonradiation recombination occurs through multiphonon emission. From the values of the free energies of ionization and from the variation of the emission rates with temperature, the enthalpies and entropies of ionization have been deduced.

I. INTRODUCTION

The study of irradiation-induced defects has not been developed in germanium as extensively as it has been in silicon. Owing to the fact that spectroscopic techniques could not be applied (electron paramagnetic resonance) while others were not fully used (infrared absorption), practically no defect has been firmly identified in germanium (for a review, see Ref. 1). However, in the last years, the transient capacitance technique, which provides a thermal spectroscopy of defects, has been applied to electron-irradiated n-type germanium (for a review, see Ref. 2). Depending on the energy of irradiation, up to five electron traps (labeled E_1 to E_5) and four hole traps (labeled H_1 to H_4) are observed following electron irradiation at room temperature.[3–6] The introduction rates of all these traps versus the energy of irradiation have been determined, leading to a threshold energy for atomic displacement of ~200 eV and to the identification of three levels associated with the divacancy[4,5] (E_4, E_5, and H_1), because their introduction rates exhibit a threshold equal to two times the threshold energy for atomic displacement. Thermal spectroscopy studies have also been performed after 4-K irradiation[7] showing that the defects present at room temperature are, as expected from the early observations made with conductivity and infrared-absorption measurements, complex defects produced by the association of impurities with the primary defects, unstable in the temperature range 60–200 K.

The aim of this paper is to describe the characteristics of the electron traps E_1, E_2, E_4, and E_5 (the trap E_3, unstable at room temperature has not yet been studied) which are obtained from thermal spectroscopy, i.e., from the study of the kinetics for carrier emission and recombination between the conduction band and the localized levels associated with these traps. As we shall recall next, the characteristics one obtains from such a study are the following: the free energy of ionization ΔG, the corresponding enthalpy ΔH and entropy ΔS, and the carrier capture cross section σ and its temperature dependence. The way these characteristics are obtained is as follows. Consider a defect D in equilibrium with the conduction band

$$D^- \rightleftarrows D^0 + e^- \ . \tag{1}$$

The transition $D^- \rightarrow D^0$ occurs with an emission rate

$$e_n = \sigma(T) v(T) N_c(T) \exp\left[-\frac{\Delta G(T)}{kT}\right] , \tag{2}$$

where v is the thermal velocity of the electrons in the band, given by

$$\tfrac{1}{2} m^* v^2 = kT \ , \tag{3}$$

N_c the density of states in the conduction band

$$N_c = 2\left[\frac{2\pi m^* kT}{h^2}\right]^{3/2} , \tag{4}$$

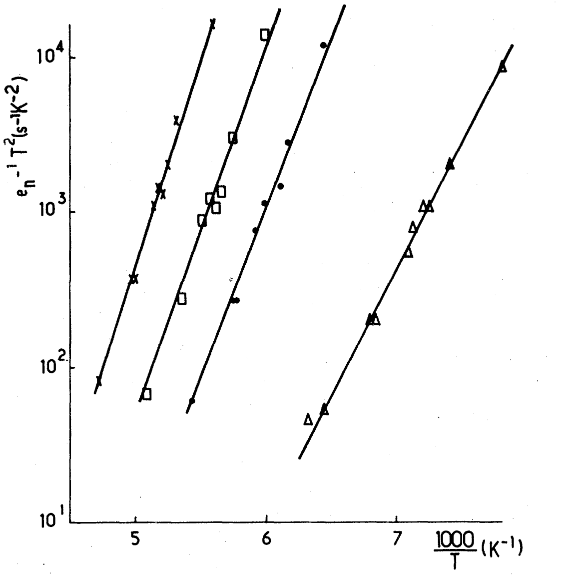

FIG. 1. Variation of the logarithm of the emission rate e_n, corrected for the temperature variation of v and N_c, vs 1000 T^{-1} for the traps E_1 (△), E_2 (×), E_4 (□) and E_5 (●).

TABLE I. Slopes $\Delta H+\Delta E$ of the signatures of Fig. 1 and values of e_n extrapolated to $T^{-1}=0$, from which the quantities $e_\infty=\sigma_\infty\exp(\Delta S/k)$ are calculated for the four traps studied.

Trap	$\Delta H+\Delta E$ (eV)	$e_n^{-1}T^{-2}$ (s K^{-2}) for $T^{-1}=0$	e_∞ (cm$^{2)}$
E_1	0.32 ± 0.02	2×10^8	1×10^{-13}
E_2	0.53 ± 0.04	7×10^{10}	4×10^{-11}
E_4	0.46 ± 0.04	6×10^9	3×10^{-12}
E_5	0.42 ± 0.03	4×10^9	2×10^{-12}

and m^* the effective electron mass ($m^*=0.55m_e$). The quantity ΔG is the free energy of ionization, i.e. the difference between the free energies G for the formation of the detect in its D^0 and D^- states,

$$\Delta G=G(D^-)-G(D^0)\ . \tag{5}$$

This can be easily shown[8] by writing that the condition of equilibrium between the D^- and D^0 states corresponds to the minimization of the free energy for defect formation. Introducing the enthalpy and entropy associated with ΔG,

$$\Delta G=\Delta H-T\Delta S\ , \tag{6}$$

and using the following expression (which will be justified later) for the temperature dependence of the cross section:

$$\sigma=\sigma_\infty\exp[-(\Delta E/kT)]\ , \tag{7}$$

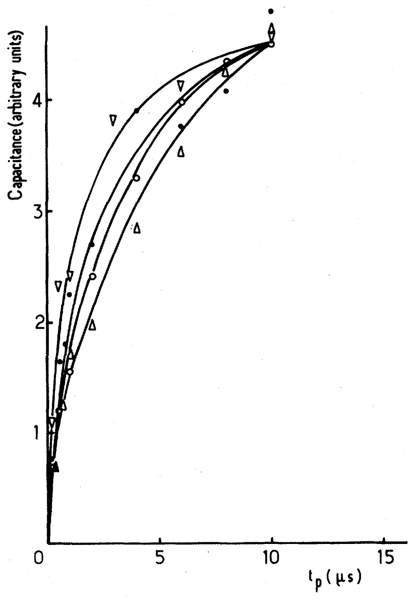

FIG. 2. Variation, vs the pulse width t_p, of the capacitance change due to the emission of electrons from the E_1 trap at: (●) 156 K ($e_n^{-1}=1.82$ ms), (○) 145 K ($e_n^{-1}=14.56$ ms), (△) 139 K ($e_n^{-1}=45.5$ ms), in a diode irradiated with 2×10^{15} cm^{-2} electrons at 2.9 MeV and at (▽) 135 K ($e_n^{-1}=109$ ms) in a diode irradiated with 2×10^{16} cm^{-2} electrons at 0.6 MeV.

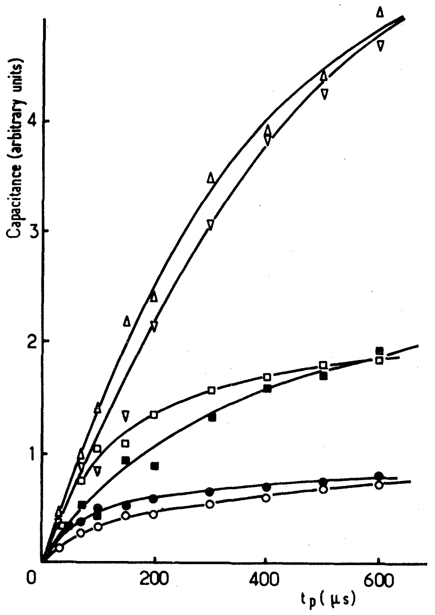

FIG. 3. Variation, vs the pulse width t_p, of the capacitance change due to the emission of electrons from traps E_2, E_4, and E_5 in a diode irradiated with 10^{15} cm^{-2} electrons at 1.6 MeV for the emission rates $e_n^{-1}=9.1$ ms (△,E_2; □, E_4; ○, E_5) and 2.03 s (▽, E_2; ■, E_4; ●, E_5).

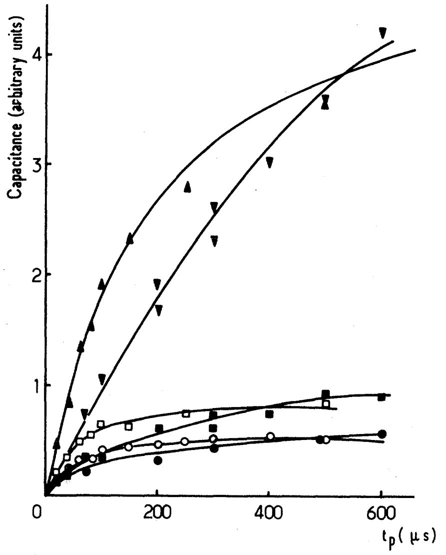

FIG. 4. Variation, vs the pulse width t_p, of the capacitance change due to the emission of electrons from traps E_2, E_4, and E_5 in a diode irradiated with 10^{15} cm^{-2} electrons at 1.6 MeV for the emission rates $e_n^{-1}=1.82$ ms (▲, E_2; □, E_4; ○, E_5) and 109 ms (▼, E_2; ■, E_4; ●, E_5).

we finally write the emission rate as

$$e_n=\sigma_\infty v N_c \exp\left[\frac{\Delta S}{k}\right] \times \exp\left[-\left[\frac{\Delta H+\Delta E}{kT}\right]\right] . \tag{8}$$

The entropy of ionization ΔS contains two terms. One, k lng, is due to the degeneracy g of the level. The other is due to the fact that the change of charge state induced by the transition modifies the bonding of the defect with the surrouding lattice and, consequently, changes the associated localized modes of vibration.[9]

We have first determined, for each trap, the variation of the emission rate with temperature in order to obtain the quantities $\Delta H+\Delta E$ and $e_\infty=\sigma_\infty \exp(\Delta S/k)$. Then, we measured capture rates, from which we deduced the capture cross sections and their evolution with temperature to get σ_∞ and ΔE. Finally, we measured directly the free energy of ionization ΔG. The knowledge of all these quantities allowed us to deduce ΔH and ΔS by two independent ways (from e_∞,σ_∞ and from ΔG,ΔH).

This study has been performed on n-type lightly doped material ($\sim 10^{13}$ cm^{-3}) in order to obtain sufficiently slow capture rates.

II. EMISSION RATES

The measurement of emission rates has been performed using deep-level transient spectroscopy (DLTS). A p^+n diode is reverse biased to a potential V_0 and the time constant e_n^{-1} of the capacitance change, which follows the application of a voltage pulse (of amplitude ΔV, in forward direction, and of duration t_p long compared to the cap-

TABLE II. Capture rates C_n of various traps, as determined from Figs. 5–7, and calculated cross sections σ_n at various temperatures fixed by the chosen emission rate.

Trap	e_n^{-1} (ms)	T (K)	C_n (s^{-1})	σ_n (cm^{-2})
E_1	109	135	9.90×10^5	2.77×10^{-14}
	45.5	139	3.50×10^5	3.12×10^{-14}
	14.56	145	5.00×10^5	4.37×10^{-14}
	1.82	156	6.60×10^3	5.51×10^{-14}
E_2	2030	167	8.04×10^2	3.64×10^{-17}
	109	188	1.60×10^3	6.60×10^{-17}
	9.1	201	2.42×10^3	9.60×10^{-17}
	1.82	214	6.98×10^3	2.65×10^{-16}
E_4	2030	157	2.86×10^3	1.35×10^{-16}
	109	174.5	4.30×10^3	1.90×10^{-16}
	9.1	187	6.25×10^3	2.61×10^{-16}
	1.82	200	1.38×10^4	5.50×10^{-16}
E_5	2030	146	3.90×10^3	1.93×10^{-16}
	109	162	5.64×10^3	2.60×10^{-16}
	9.1	174	6.33×10^3	2.78×10^{-16}
	1.82	186	1.19×10^4	4.98×10^{-16}

ture rate), is measured with the help of a double boxcar.

The variations of $\ln e_n$ versus temperature, corrected for the T^2 dependence of N_c and v, are given in Fig. 1 for each trap. According to (8), $\ln(e_n T^{-2})$ varies linearly with T^{-1}; the slope provides the quantity $\Delta H + \Delta E$, and the extrapolation to $T^{-1}=0$, the quantity e_∞. These values are given in Table I.

III. CAPTURE CROSS SECTIONS

When the diode is biased, the application of the voltage pulse has for effect to fill the electron traps. Such filling occurs with a capture rate

$$C_n = \sigma v n \ , \tag{9}$$

where n is the free-carrier (electron) concentration. The concentration n_t of the traps filled after a time t_p, the solution of

$$\frac{dn_t}{dt} = C_n (N_T - n_t) \ , \tag{10}$$

is therefore

$$n_t = N_T \{1 - \exp[-(C_n t_p)]\} \ , \tag{11}$$

where n_T is the total trap concentration. Because the capacitance change $\Delta C(t_p)$ associated with the emission from the filled traps (the DLTS peak amplitude) is proportional to n_t, the determination of C_n can be made from the variation of $\Delta C(t_p)$ vs t_p.

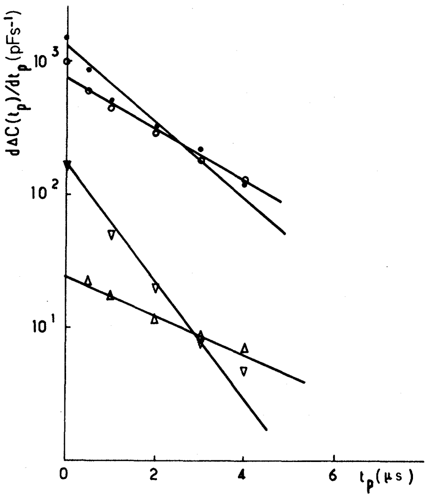

FIG. 5. Variation of the logarithm of dn_t/dt_p vs t_p for the E_1 trap in a diode irradiated with 2×10^{15} cm^{-2} (2.9 MeV) electrons at 156 K (●), 145 K (○), 139 K (△), and in a diode irradiated with 2×10^{16} cm^{-2} (0.6 MeV) electrons at 135 K (▽).

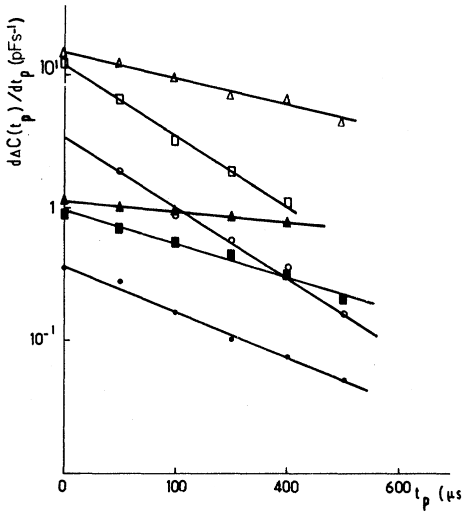

FIG. 6. Variations of the logarithm of dn_t/dt_p vs t_p for the E_2, E_4, and E_5 traps in a diode irradiated with 10^{15} cm^{-2} (1.6 MeV) electrons for the emission rates $e_n^{-1}=9.1$ ms (△, E_2; □, E_4; ○, E_5) and 2.03 s (▲, E_2; ■; E_4; ●, E_5).

These measurements have been performed at various temperatures for each trap (see Figs. 2–4). Usually, the capture rate C_n is taken as the slope of the plot $\ln[(N_T - n_t)/N_T]$ vs t_p, with the use of the fact that

$$\frac{N_T - n_t}{N_T} = 1 - \frac{\Delta C(t_p)}{\Delta C(\infty)} \ , \tag{12}$$

where $\Delta C(\infty)$ is the amplitude of the DLTS peak for pulse widths very long compared to $C_n^{-1} N_T^{-1}$,

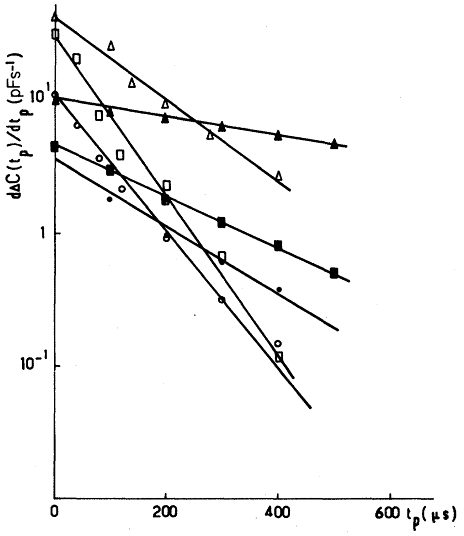

FIG. 7. Variations of the logarithm of dn_t/dt_p vs t_p for the E_2, E_4, and E_5 traps in a diode irradiated with 10^{15} cm^{-2} (1.6 MeV) electrons for the emission rates $e_n^{-1}=109$ ms (▲, E_2; ■, E_4; ●, E_5) and 1.82 ms (△, E_2; □, E_4; ○, E_5).

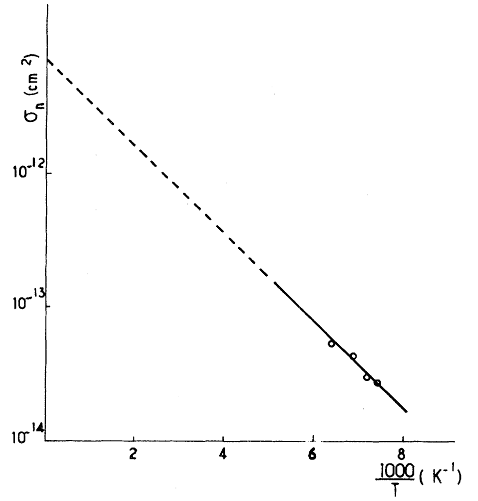

FIG. 8. Variation of the logarithm of the cross section for trap E_1 vs 1000 T^{-1}.

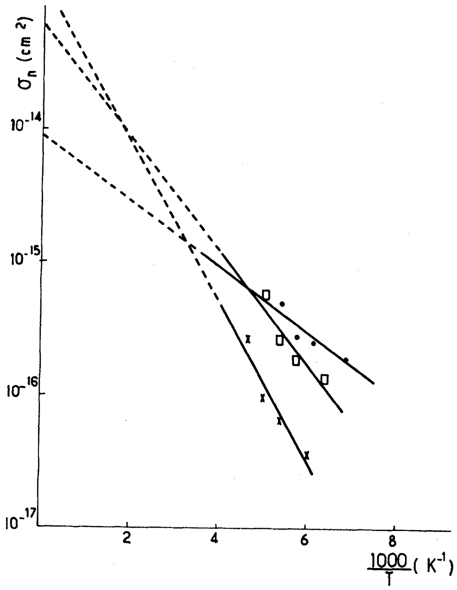

FIG. 9. Variation of the logarithm of the cross sections for traps E_2 (×), E_4 (●), and E_5 (□) vs 1000 T^{-1}.

i.e., corresponding to $n_t = N_T$. However, this method necessitates the precise knowledge of the total trap concentration, which is difficult to obtain. Indeed, a small uncertainty on N_T leads to a large error on $N_T - n_t$ when n_t tends to N_T. The reason it is difficult to measure precisely N_T is as follows: Even for very long pulse widths the traps of the space charge region are not completely filled, due to residual band bending. This effect is noticed by the fact that, for pulses such that $t_p \gg C_n^{-1} N_T^{-1}$, the capacitance change $\Delta C(t_p)$ is not completely saturated as can be seen for instance in Figs. 3 and 4 for the E_2 and E_4 traps.

A method we propose to overcome this difficulty consists of plotting the logarithm of the derivative of n_t, (dn_t/dt_p), i.e., $\ln[\Delta C(t_p)/dt_p]$ vs t_p. According to (11),

$$\ln\left[\frac{dn_t}{dt_p}\right] = \ln(C_n N_T) - C_n t_p \ . \qquad (13)$$

Thus the slope of this plot provides directly C_n. The experimental results presented in Figs. 2–4 are plotted in this way in Figs. 5–7. The values of C_n thus determined are given in Table II together with the deduced cross sections. These cross sections are calculated once the carrier concentration has been determined, from capacitance-voltage measurements, at the temperature at which C_n is measured. The resulting variations of the cross sections with temperature for the various traps are given in Figs. 8 and 9. As shown in these figures, these variations fit reasonably the exponential law.[7] The values of σ_∞ and ΔE which are obtained for the four traps are given in Table III.

IV. FREE ENERGY OF IONIZATION

In principle the free energy of ionization can be obtained by independently measuring emission and capture rates since these two quantities are related to ΔG through the detailed balance principle. However, such determination requires a precise knowledge of N_T and the direct measurement of C_n is long and difficult to perform. We applied here a method which overcomes these difficulties. It consists[10] of determining the distribution of the occupied traps in the depletion region. The free energy ΔG is deduced from the depth $W_0 - \lambda$ at which the Fermi level E_F crosses the localized level

TABLE III. Values of the parameters σ_∞ and ΔE which define the temperature dependence of the cross sections, as deduced from Figs. 8 and 9.

Traps	E_1	E_2	E_4	E_5
σ_∞ (cm^2)	$(7\pm3)\times10^{-12}$	$(1\pm0.5)\times10^{-13}$	$(1.2\pm0.8)\times10^{-14}$	$(6\pm3)\times10^{-14}$
ΔE (meV)	65 ± 10	120 ± 20	80 ± 15	50 ± 10

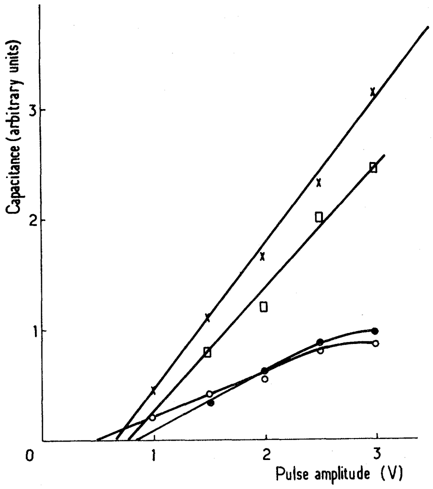

FIG. 10. Amplitude of the DLTS peak vs the amplitude of the filling pulse for the four traps E_1 (○), E_2 (×), E_4 (□), and E_5 (●) in a diode irradiated with 10^{15} cm^{-2}, 1.6 MeV, electrons. The diode is reverse biased at $V_0=3.5$ V. The pulse width is 100 μs, the repetition rate 50 ms and the emission rate 14.4 ms.

associated with the trap

$$W_0-\lambda=2\epsilon\frac{(E_F-E_c+\Delta G)}{qn}, \tag{14}$$

where q is the electron charge, ϵ the dielectric constant, E_c the bottom of the conduction band, and W_0 the width of the depletion region under the reverse bias V_0. To perform this determination, the amplitude ΔC of the capacitance transient is monitored as a function of the amplitude ΔV of the filling pulse (whose width t_p is chosen small compared to e_n^{-1} and large compared to $C_n^{-1}N_T^{-1}$). A threshold voltage ΔV_0 is observed (see Fig. 10), from which λ is calculated, because it is necessary for ΔV to have a minimum value before the width of the space charge region reduces to a value smaller than $W_0-\lambda$, at which traps are empty. The various quantities which are necessary to perform the calculation of λ are given in Table IV.

TABLE V. Experimental free energies of ionization ΔG and activation energies ΔE associated with the capture cross sections, calculated enthalpies of ionization ΔH (difference between the activation energies associated with the emission rates and ΔE), and ionization entropies ΔS. These entropies are determined in two ways: (a) from $\Delta H-\Delta G$ and (b) from $\ln(e_\infty/\sigma_\infty)$. The temperatures at which the entropy terms are calculated correspond to the observation of the peaks with an emission rate of 9.17 s^{-1}.

Traps	E_1	E_2	E_4	E_5
ΔG (eV)	0.27	0.39	0.35	0.32
ΔE (eV)	0.065	0.120	0.080	0.050
ΔH (eV)	0.26	0.41	0.38	0.37
$\Delta S/k$ (a)	−0.8	1.5	1.9	3.5
$\Delta S/k$ (b)	−1.9	5.9	5.5	3.5

V. DISCUSSION

From the values of the free energy of ionization ΔG, the parameters σ_∞ and ΔE, which characterize the variation of the capture cross section with temperature, and e_∞ and $\Delta H+\Delta E$, which characterize the variation of the emission rate with temperature, we are now able to deduce the enthalpies ΔH and the entropies ΔS of the various traps studied. The results are summarized in Table V.

Only orders of magnitude are obtained for the entropies, as can be noticed from the difference between the results provided by the two independent ways we use to determine them. This is not surprising in view of the following reasons. First, the technique of characterization is a thermal spectroscopy whose resolution in energy is limited to few kT, i.e., typically 2×10^{-2} eV for the traps considered here. Thus the difference between ΔG and ΔH, which are of the same order of magnitude, cannot be obtained with a good accuracy. Second, the estimations of ΔH and ΔS assume a temperature dependence of the cross section given by (7). This dependence is experimentally reached only in a small temperature range and the quanti-

TABLE IV. Threshold values ΔV_0 of the pulse amplitude as obtained from Fig. 10, positions of the Fermi level E_c-E_F, and ratios λ/W_0 from which the free energies of ionization ΔG are calculated for the various traps.

Traps	E_1	E_2	E_4	E_5
T (K)	139	199	188	171
ΔV_0 (V)	0.53	0.65	0.76	0.83
E_c-E_F (eV)	0.18	0.26	0.25	0.22
λ/W_0	0.143	0.163	0.148	0.137
ΔG (eV)	0.27±0.03	0.39±0.02	0.35±0.02	0.32±0.02

ties which characterize it cannot be determined accurately.

Finally, the fact that the capture cross sections are thermally activated suggests that electron recombination on the traps occurs via a multiphonon emission process.[11] The existence of the activation energy reflects the energy barrier an electron of the conduction band must overcome to relax on the defect energy curve of the configuration coordinate diagram. It therefore indicates that non-negligible lattice distortions are present around the defects.

ACKNOWLEDGMENT

Groupe de Physique des Solides de l'Ecole Normale Supérieure is associated with CNRS.

---

[1] T. V. Mashovets, in *International Conference on Radiation Effects in Semiconductors, Dubrovnik, 1976* edited by N. B. Urli and J. W. Corbett (Institute of Physics, Bristol, 1977), p. 30.

[2] J. C. Bourgoin, P. M. Mooney, and F. Poulin, in *International Conference on Defects and Radiation Effects* in Semiconductors, Oiso, 1980, edited by R. R. Hasiguti (Institute of Physics, London, 1981), p. 33.

[3] P. M. Mooney, M. Cherki, and J. C. Bourgoin, J. Phys. (Paris) Lett. 40, L19 (1979).

[4] F. Poulin and J. C. Bourgoin, Rev. Phys. Appl. 15, 15 (1980).

[5] F. Poulin and J. C. Bourgoin, in *Recent Developments in Condensed Matter Physics,* edited by J. T. Devreese, L. F. Lemmens, V. E. Van Doren, and J. Van Royen (Plenum, New York, 1981), Vol. 3, p. 83.

[6] N. Fukuoka and H. Saito, Jpn. J. Appl. Phys. 20, L519 (1981).

[7] Preliminary results are described in Ref. 2.

[8] For a demonstration, see M. Lannoo and J. C. Bourgoin, *Point Defects in Semiconductors* (Springer, Berlin, 1981), Vol. I, Chap. 6.

[9] M. Lannoo and J. C. Bourgoin, Solid State Commun. 32, 913 (1979).

[10] D. Pons, Appl. Phys. Lett. 37, 413 (1980).

[11] C. H. Henry and D. V. Lang, Phys. Rev. B 15, 989 (1977).