

Eqs. (1.7a) and (1.7b) by

$$\tau = n_{12}/c_{p2}N_2P_0 = [2(2\pi m_n^*k)^{3/2}/c_{p2}N_2p_0h^3]T^{3/2} \times \exp[(E_2 - E_c)/kT], \quad (5.3a)$$

or

$$\tau = p_{12}/c_{p2}N_2p_0 = [2(2\pi m_p^*k)^{3/2}/c_{p2}N_2p_0h^3]T^{3/2} \times \exp[(E_v - E_2)/kT]. \quad (5.3b)$$

A least-squares fit of the data gives

$$\tau = 4.1T^{3/2} \exp(-0.13/kT). \quad (5.4)$$

The recombination center lies 0.13 eV from one of the band edges. For this case, it is not possible to differentiate between Eqs. (5.3a) and (5.3b) since the constant low-temperature lifetime  $1/c_{n2}N_2$  is masked by the presence of the trap.

At temperatures below  $1000/T=4.06$ , the excess carrier lifetime increases, which is characteristic of a trapping process. The slope in the trapping region indicates that the trap lies 0.05 eV from one of the band edges.

The measurement of lifetime as a function of pressure was performed at  $1000/T=3.10$ , which is well into the region dominated by the recombination center. The results are shown in Fig. 9. A fit of the data to Eqs. (5.3a) and (5.3b) (substituting the pressure-dependent terms) results in a pressure coefficient of

$$\gamma = -1.5 \times 10^{-6} \text{ eV cm}^2 \text{ kg}^{-1},$$

and the recombination level approaches the nearest band edge at the above rate. No pressure measurements were made in the trapping region, since the temperatures well into the trapping region where the measurements should be made are too low to permit the high-pressure system to function properly.

## VI. DISCUSSION

In order to interpret the experimental results, it is necessary to examine the various types of flaws and

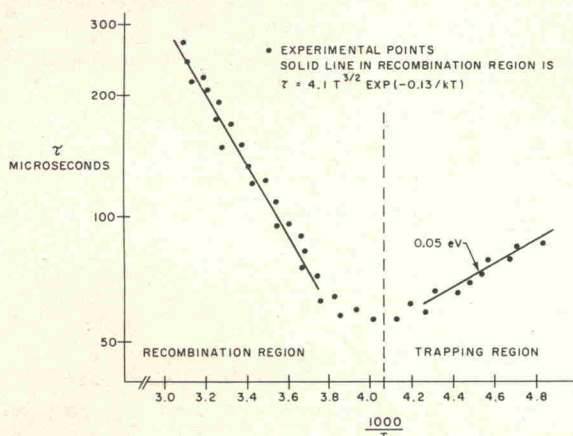


FIG. 8. Excess carrier lifetime for 5- $\Omega$  cm  $p$ -type sample as a function of temperature, showing both a recombination center and a trap.

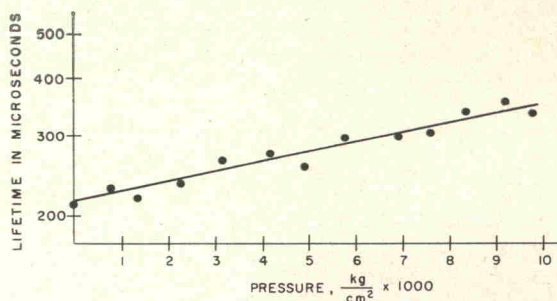


FIG. 9. Excess carrier lifetime versus pressure for 5- $\Omega$  cm  $p$ -type sample at  $T=322^\circ\text{K}$ .

dislocations which may function as recombination and trapping centers.

Consider first the introduction of chemical impurities in the germanium lattice. Depending upon their size and nature, these impurity atoms may be incorporated in the lattice either substitutionally or interstitially. Atoms which are easily ionized, and known to be partially present interstitially in germanium such as copper, nickel, and lithium are expected to act as donors, since none of the electrons of these atoms are required for bonding purposes. Unfortunately, a general theory of the electrical effects of interstitial atoms in semiconductors is nonexistent, and it is difficult to infer anything about the depth of these donor levels. However, when metal ions such as these are substitutionally placed, they act as acceptors, since there is then a deficiency of electrons. Table I shows the position and character of the energy levels associated with the more common chemical impurities in germanium.<sup>9</sup>

The effect of hydrostatic pressure on these impurity levels may be deduced in a simple manner by assuming that a hydrogenic atom model is applicable. The ionization energy is then given by

$$E_i = me^4/2K^2\hbar^2, \quad (6.1)$$

where  $K$  is the dielectric constant. The applicability of this picture, particularly in a quantitative sense, is circumscribed by the fact that the Bohr radii for levels as deep lying as these are so small that the region of the crystal enclosed by them is not very well represented as a uniform linear dielectric. Nevertheless in the absence of any more sophisticated theory (and there appears to be none applicable to deep-lying states) we shall use this simple picture as a basis for discussion of our experimental results. The dielectric constant for germanium is known to decrease with pressure.<sup>10</sup> Therefore, on the basis of this admittedly naïve and oversimplified model, a donor level would be expected to shift toward the valence band, and an acceptor level toward the conduction band. Dislocation defects, due to the unpaired or "dangling" bond which inevitably results, are expected to act as acceptor centers.

The use of radiation as a method of introducing rec-



TABLE I. Activation energies of chemical impurities in germanium.  $E_c$ : Energy of conduction band edge.  $E_v$ : Energy of valence band edge.  $E_i$ : Energy of impurity level.  $A$ : Acceptor.  $D$ : Donor.

Element	Type	$E_c - E_i$ (eV)	$E_i - E_v$ (eV)
Cu(1)	A	...	0.32
Cu(2)	A	...	0.04
Cu(3)	A	0.26	...
Au(1)	D	...	0.05
Au(2)	A	...	0.15
Au(3)	A	0.20	...
Au(4)	A	0.04	...
Ag(1)	A	...	0.14
Ag(2)	A	0.28	...
Ag(3)	A	0.09	...
Ni(1)	A	...	0.22
Ni(2)	A	...	0.30
Fe(1)	A	...	0.34
Fe(2)	A	0.27	...
Co(1)	A	...	0.25
Co(2)	A	0.31	...
Mn(1)	A	...	0.16
Mn(2)	A	0.35	...

tain types of defects has resulted in a wealth of information on the nature of defect structures. The subject has been extensively reviewed.<sup>11,12</sup> The energy levels which have been observed in germanium irradiated by deuterons, electrons, neutrons, and gamma rays have been discussed by Fan and Lark-Horowitz.<sup>13</sup> A donor level appearing at 0.18 eV above the edge of the valence band has been attributed to an interstitial atom.<sup>14</sup>

The recombination center in the  $n$ -type sample was found to be a donor-type level 0.18 eV from the valence band. If the donor level is associated with a chemical impurity, then Eq. (6.1) can be used to calculate the change in ionization energy with pressure. The fractional change in dielectric constant with pressure  $(1/K)(dK/dP)$ , is  $-1.2 \times 10^{-6}$  cm<sup>2</sup>/kg, and the fractional change in the effective mass is  $(1/m)(dm/dP) = 5 \times 10^{-6}$  cm<sup>2</sup>/kg. Equation (6.1) may be differentiated and written in the form

$$dE_i/dP = (mc^4/2K^2\hbar^2) \times [(1/m)(dm/dP) - (2/K)(dK/dP)]. \quad (6.2)$$

If the factor multiplying the right-hand side of Eq. (6.2) is assumed to be 0.18 eV, then

$$\begin{aligned} dE_i/dP &= 0.18(5 \times 10^{-6} + 2 \times 1.2 \times 10^{-6}) \\ &= 1.3 \times 10^{-6} \text{ eV cm}^2 \text{ kg}^{-1} \end{aligned}$$

which is a value remarkably close to that found from the measurements.

The agreement between the above results and the measurements must be regarded as somewhat

fortuitous, since it is not at all clear that Eq. (6.1) is applicable to deep-lying levels. For example, if one calculates the radius of the first Bohr orbit corresponding to an energy of 0.18 eV and a dielectric constant of 16, the result is a radius of about 3 Å, or just slightly more than the interatomic distance in germanium (2.44 Å). The concept of a dielectric constant loses its meaning under these circumstances. Reference to Table I shows that none of the common chemical impurities behave as a donor level 0.18 eV from the valence band. It is therefore regarded as unlikely that the recombination process proceeds via a substitutional chemical impurity.

The donor nature of the recombination center mitigates against an edge (or any other) dislocation acting as a recombination center since, due to the "dangling" bonds which are present in such dislocations, they are expected to act as acceptors.

It is known from the effects of neutron radiation that heavy particle radiation can result in an atom moving to an interstitial site, and it is also quite possible that such an interstitial results during the growth of the crystal.<sup>15</sup> The interstitial atom may act as a donor, and may result in a donor level 0.18 eV from the valence band. The application of pressure, resulting in a compression of the lattice and an increase in the interaction between neighboring atoms, is expected to increase the activation energy of the recombination level, and the measurements show this to be the case. Therefore, it is suggested that for the  $n$ -type sample the recombination process occurs via a center which is associated with an interstitial atom.

The other terms in the expression for the lifetime [Eq. (3.5a)] which may contribute to a change in the excess carrier lifetime, are the electron capture coefficient  $c_n$  and the hole effective mass  $m_p^*$ . The change in effective mass is approximately 2% in 10 000 kg/cm<sup>2</sup>. This increase is not nearly enough to account for the increase in lifetime by approximately 60%. In addition, Fig. 7 shows that the hole capture coefficient is independent of pressure. It is considered unlikely, then, that the electron capture coefficient is strongly pressure dependent. It is possible to explain the results of Fig. 7 using a simple model of carrier capture.<sup>4</sup> An estimate of the capture coefficient can be made by assuming that the carrier will be captured if the Coulomb binding energy is comparable to  $kT$ . Then there will be some capture "radius"  $r$  such that

$$e^2/Kr = kT.$$

The capture cross section is then

$$\sigma = \pi r^2 = \pi [e^4/K^2(kT)^2].$$

The capture cross section and the capture coefficient are related by the thermal velocity of the carrier, i.e.,  $c = \sigma \langle v \rangle$ , where  $\langle v \rangle = (8kT/\pi m)^{1/2}$ . The above equation