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Hopping-conductivity changes with the concentration of compensating centers

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Electrical-conductivity changes due to variation of the concentration of compensating centers are calculated for both the nearest-neighbor hopping and the variable-range hopping regimes. Verification of the formulas obtained in the case of high compensation is made using irradiation with energetic electrons in cadmium telluride (for the nearest-neighbor hopping regime) and in semiconducting diamond (for the variable-range hopping regime).

I. INTRODUCTION

During the characterization process of semiconductors one has to determine the concentration of the deep impurities which compensate partially the doping impurities and the variation of this concentration due to thermal processes such as quenching or diffusion. This determination can be done in principle using electrical or optical techniques. Electrical techniques are macroscopic, i.e., they allow the determination of all the (electrically active) centers while optical techniques are microscopic, i.e., they can detect only a given center; moreover the electrical techniques are more sensitive than the optical techniques. Electrical techniques are therefore better adapted than the optical techniques to the measurements of variations in the concentration of compensating centers.

When the electrical conduction occurs at moderate temperatures, i.e., at temperatures for which the carriers are excited from the doping impurity level into the conduction or valence bands, the variation of the concentration of the compensating centers is given directly by the variation of the carrier concentration in the band. When the temperature is low enough so that the carriers cannot be excited into one of the bands, the conductivity takes place through an hopping mechanism, in which the carriers hop from occupied to unoccupied impurity sites. Such hopping mechanism occurs when the doping concentration is high enough to allow a non-negligible overlap of the wave functions of the carriers bound on the impurities and when part of the impurities are rendered unoccupied because of the compensation by deep centers. The conductivity is then very sensitive to the concentration of these compensating centers and a small variation of this concentration can be easily detected.

The aim of this paper is: (i) to provide relations giving the variations, assumed to be small, of the concentration of compensating centers corresponding to changes of conductivity when this conductivity occurs through both a nearest-neighbor-hopping (NNH) and a variable-range-hopping (VRH) mechanism; (ii) to verify experimentally these relations. The verification will be done in cadmium telluride (where it has been shown that the conductivity occurs through a NNH mechanism below[1] 10 °K) and in synthetic boron-doped diamond (where it has been shown that the conductivity occurs through a VRH mechanism below[2] 100 °K) using irradiation with energetic electrons as a tool to introduce extra compensating centers. Because the samples available present a high compensation, this verification is performed only in this case.

In Sec. II we briefly recall the formula which give the expression of the conductivity versus doping and compensation in the NNH and VRH regimes and we calculate in these two regimes the variations of conductivity due to a variation in the concentration of the compensating centers. In Sec. III we study the effect of an electron irradiation upon the conductivity of cadmium telluride and diamond. The comparison between the experimental results obtained and the calculations of Sec. II is discussed in Sec. IV. The experimental setups used in these experiments, described elsewhere[1-3] will not be repeated here.

II. CALCULATION OF CONDUCTIVITY VARIATIONS

In an hopping regime the probability P for carrier hopping is given by

$$P = \gamma_{ph} \exp(-2\alpha R - W/kT), \qquad (1)$$

where γ_{ph} is a factor depending upon the phonon frequency (in the approximation of shallow impurity conduction and sufficiently low temperature[4]). The first term $2\alpha R$ depends upon the overlap of the wave functions: α^{-1} is a length characterizing the extension in space of a wave function and R is the hopping distance. The second term depends upon the energy difference W between the states through which the carriers hop.

A. Nearest-neighbor-hopping (NNH) regime

In case of strong localization ($\alpha R \gg 1$) and small dispersion in energy ($W \ll kT$), P is maximum when R is minimum, the carriers hop from one site to the nearest site and the conductivity is characterized by a constant activation energy ϵ_3:

$$\sigma = \sigma_3 e^{-\epsilon_3/kT}, \tag{2}$$

where ϵ_3 is the energy necessary for a carrier to hop from one site to a neighboring unoccupied site. This energy has been calculated by Miller and Abrahams,[5] in case of low compensation ($K \ll 1$),

$$\epsilon_3 = 1.61(e^2/X)N_D^{1/3}|1 - 1.35(N_A/N_D)^{1/3}| \tag{3}$$

and by Shklovskii *et al.*[6,7]

$$\epsilon_3 = 0.99(e^2/X)N_D^{1/3}|1 - 0.3(N_A/N_D)^{1/4}| \quad \text{for } K \ll 1 \tag{4}$$

and

$$\epsilon_3 = V_1(e^2/X)N_D^{1/3}(1 - N_A/N_D)^{1/3} \quad \text{for } 1 - K \ll 1. \tag{5}$$

In these formula V_1 is a constant factor whose value is on the order of 1, X is the dielectric constant, e the electronic charge, N_D the doping concentration, N_A the concentration of the compensating centers, and $K = N_A/N_D$ the compensation.

A change ΔN_A in N_A induces a change $\Delta\epsilon_3$ in ϵ_3; the expression of $\Delta\epsilon_3$ is

$$\begin{aligned}\Delta\epsilon_3 = {} & 1.61(e^2/X)N_D^{1/3} \\ & \times \{|1 - 1.35[(N_A + \Delta N_A)/N_D]|^{1/3} \\ & \quad - |1 - 1.35(N_A/N_D)|^{1/3}\}\end{aligned}$$

in case of Eq. (3). Similar expressions give $\Delta\epsilon_3$ in case of Eqs. (4) and (5). In the approximation $\Delta N_A \ll N_A$ for $K \ll 1$ and $\Delta N_A \ll N_D - N_A$ for $1 - K \ll 1$, then the expressions for $\Delta\epsilon_3$ reduce to

$$\Delta\epsilon_3 = 0.72(e^2/X)N_A^{-2/3}\Delta N_A, \tag{6}$$

$$\Delta\epsilon_3 = -0.07(e^2/X)N_D^{1/12}N_A^{-3/4}\Delta N_A, \tag{7}$$

$$\Delta\epsilon_3 = 0.33V_1(e^2/X)N_D^{2/3}(N_D - N_A)^{-4/3}\Delta N_A \tag{8}$$

for Eqs. (3)–(5), respectively.

Since the preexponential factor σ_3 in the expression of the conductivity varies only with N_D, the conductivity σ, corresponding to $N_A + \Delta N_A$ can be expressed in terms of the initial conductivity σ_i corresponding to N_A in the following way:

$$\sigma = \sigma_i e^{-\Delta\epsilon_3/kT}. \tag{9}$$

Since $\Delta\epsilon_3$ is proportional to ΔN_A, σ varies exponentially with ΔN_A, decreasing in case of high compensation ($\Delta\epsilon_3 > 0$) and increasing in case of low compensation ($\Delta\epsilon_3 < 0$):

$$\ln\sigma = \ln\sigma_i - \gamma\Delta N_A, \tag{10}$$

with

$$\gamma = -0.72(e^2/X)N_A^{-2/3}(kT)^{-1} \tag{11}$$

or

$$\gamma = -0.07(e^2/X)N_D^{1/12}N_A^{-3/4}(kT)^{-1} \quad \text{for } K \ll 1, \tag{12}$$

and

$$\gamma = 0.33V_1(e^2/X)N_D^{2/3}(N_D - N_A)^{-4/3}(kT)^{-1} \quad \text{for } 1 - K \ll 1. \tag{13}$$

B. Variable-range-hopping (VRH) regime

In diamond the doping concentration can reach considerably larger values than in other semiconductors before the conduction becomes of metallic type because the extension in space of the wave function associated with the impurity is smaller. As a result the dispersion in energy W can be larger than kT even for relatively high temperature (for a 10^{20}-cm^{-3} concentration W is of the order of 200 meV). In such case W/kT cannot be anymore neglected in front of $2\alpha R$ and P is maximum for hops between sites separated by a distance R such that $2\alpha R + W/kT$ is minimum. In such a regime the conductivity follows the Mott's law[7]:

$$\sigma = \sigma_0 e^{-A/T^{1/4}}, \tag{14}$$

where

$$A = 2(\alpha^3/kN_F)^{1/4},$$

where N_F is the density of states at the Fermi level.

It is shown in Ref. 2 that the conductivity, in the samples studied here, follows this law and that the associated activation energy decreases as $T^{3/4}$, indicating that the conductivity occurs through a VRH mechanism below 100–150 °K.

Shklovskii[8] has given approximate expressions for N_F, in cases of low and high compensation (we introduce a factor 2 to account for spin degeneracy):

$$N_F = 2(X/e^2)N_A N_D^{-1/3} \quad \text{for } K \ll 1 \tag{15}$$

and

$$N_F = 2(X/e^2)(N_D - N_A)^{4/3}N_D^{-2/3} \quad \text{for } 1 - K \ll 1. \tag{16}$$

A change ΔN_A in N_A induces therefore the following change ΔA in A:

$$\begin{aligned}\Delta A = {} & 2(\alpha^3/k)^{1/4}(2X/e^2)^{-1/4} \\ & \times |(N_A + \Delta N_A)^{-1/4} - N_A^{-1/4}|N_D^{1/12} \quad \text{for } K \ll 1;\end{aligned}$$

for $1 - K \ll 1$, the expression obtained using Eq. (16) is similar. These expressions reduce to

$$\Delta A = -0.5(\alpha^3 e^2/2kX)^{1/4} N_D^{1/12} N_A^{-5/4} \Delta N_A \quad \text{for } \Delta N_A \ll N_A \ll N_D \tag{17}$$

and to

$$\Delta A = 0.66(\alpha^3 e^2/2kX)^{1/4} N_D^{1/6} (N_D - N_A)^{-4/3} \Delta N_A \quad \text{for } \Delta N_A \ll N_D - N_A \ll N_D. \tag{18}$$

As a result, the conductivity σ due to the change in N_A, which, in terms of ΔA is

$$\sigma = \sigma_i e^{-\Delta A / T^{1/4}} \tag{19}$$

(σ_i is the initial conductivity), varies exponentially with ΔN_A:

$$\ln\sigma = \ln\sigma_i - \beta \Delta N_A, \tag{20}$$

with

$$\beta = -0.5(\alpha^3 e^2/2kX)^{1/4} N_D^{1/2} N_A^{-5/4} \quad \text{for } K \ll 1 \text{ [Eq. (17)]} \tag{21}$$

and

$$\beta = 0.66(\alpha^3 e^2/2kX)^{1/4} N_D^{1/6} (N_D - N_A)^{-4/3} \quad \text{for } 1 - K \ll 1 \text{ [Eq. (18)]}. \tag{22}$$

III. EXPERIMENTAL VERIFICATION

The experimental verification of these formulas has been attempted by irradiating strongly compensated cadmium telluride and synthetic boron-doped diamond at low temperature with energetic electrons. Irradiation introduces defects which, at least partly, play the role of compensating centers; the concentration of these compensating centers ΔN_A is proportional to the dose ϕ of the energetic electrons, for low doses of irradiation and at low temperature where the defects are not mobile since there is no interaction possible between the defects themselves or between defects and impurities. The samples used (cadmium telluride as well as diamond) are "thick" samples, compared to the penetration depth of the electrons; as a consequence, the distribution in depth of the concentration of the defects introduced is not uniform (it can vary within a factor of 2 approximately), and the value of ΔN_A determined can only be considered as an averaged value over the whole sample thickness. The averaged value ΔN_A depends therefore upon the energy of the electrons and, consequently, the limit of validity for the approximation $\Delta N_A \ll N_A$ or $\Delta N_A \ll N_D - N_A$ varies with this energy.

A. Cadmium telluride (NNH regime)

In *n*-type cadmium telluride, synthetized by the Bridgman method and refined by zone melting, it has been shown[1] that the conductivity occurs through a NNH mechanism below 10 °K. Using resistivity and Hall effect measurements in the temperature range 20–100 °K, the doping and compensating concentrations have been determined to

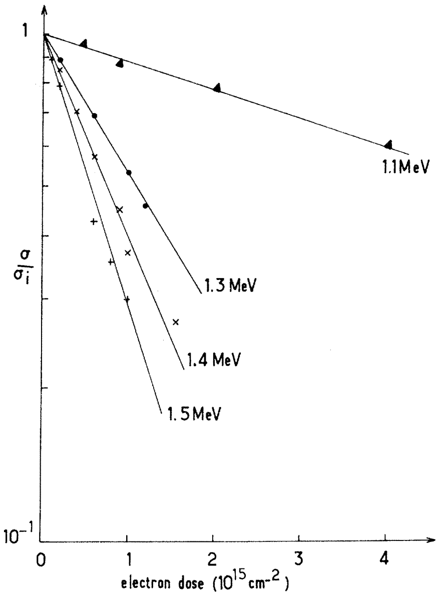

FIG. 1. Variation of the conductivity at 4.2° K vs the dose of electrons for different energies of irradiation in cadmium telluride.

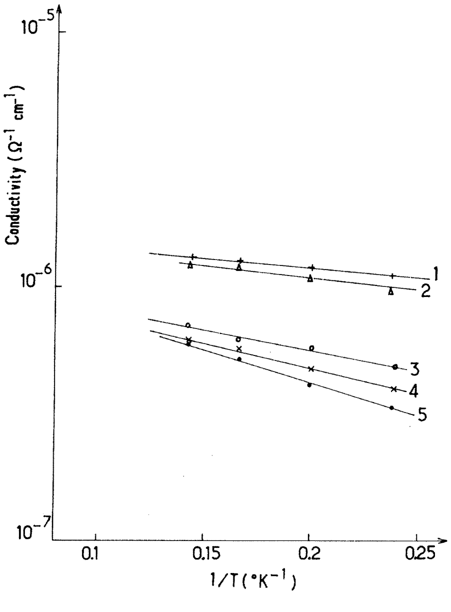

FIG. 2. Variation of the conductivity vs temperature after irradiation with 1.5-MeV electrons in cadmium telluride: 1—before irradiation; 2—10^{14} cm^{-2}; 3—4 × 10^{14} cm^{-2}; 4—8 × 10^{14} cm^{-2}; 5—10^{15} cm^{-2}.

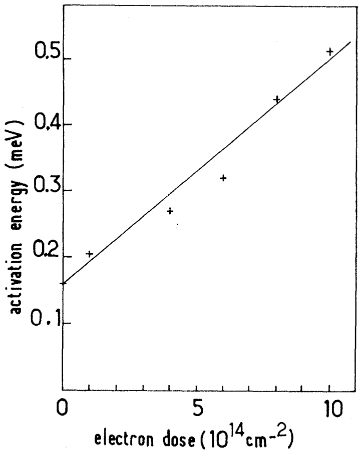

FIG. 3. Variation of the activation energy ϵ_3 vs electron dose for 1.5-MeV electron irradiation in cadmium telluride.

be: $N_D = 5\times10^{14}$ cm^{-3} and $N_A = 4.5\times10^{14}$ cm^{-3}, respectively (i.e., $K \simeq 90\%$). The samples are irradiated at liquid-helium temperature and the measurements (conductivity and Hall effect) performed at this temperature.

Figure 1 shows the variation of $\ln(\sigma/\sigma_i)$ versus the dose of electrons whose energy ranges from 1.1 to 1.5 MeV. The conductivity is measured versus temperature after the equilibrium of the carrier population has been restored by heating the sample around 40 °K (temperature at which no annealing has still taken place[9]). The activation energy ϵ_3, having a slope of $\ln\sigma(T^{-1})$ is then measured (Fig. 2) and plotted versus the dose of irradiation (Fig. 3).

The concentration ΔN_A of the defects introduced is also measured (using conductivity and Hall-effect measurements) at 20 °K, temperature at which the conductivity occurs in the conduction band. In this regime the free carrier concentration is related to N_A and N_D by the relation

$$n(N_A + n)(N_D - N_A - n)^{-1} = gN_C e^{-E_D/kT},$$

where E_D is the ionization energy of the (donor) impurity ($E_D = 7$ meV), N_C the density of states in the conduction band, and g a degeneracy factor ($g = \frac{1}{2}$). This reduction of the donor activation energy, compared to the usual one (~11 meV), is due to distant defect pairing.[10] The variation of the free carrier concentration Δn, due to the introduction of the defects, is

$$\Delta n = -\Delta N_A\left(\frac{n + gN_C e^{-E_D/kT}}{N_A + 2n + gN_C e^{-E_D/kT}}\right) .$$

At 20 °K n (~10^{12} cm^{-3}) is negligible in front of $N_A(4.5\times10^{14}$ cm$^{-3})$ and $gN_C e^{-E_D/kT}(1.1\times10^{14}$ cm$^{-3})$; therefore

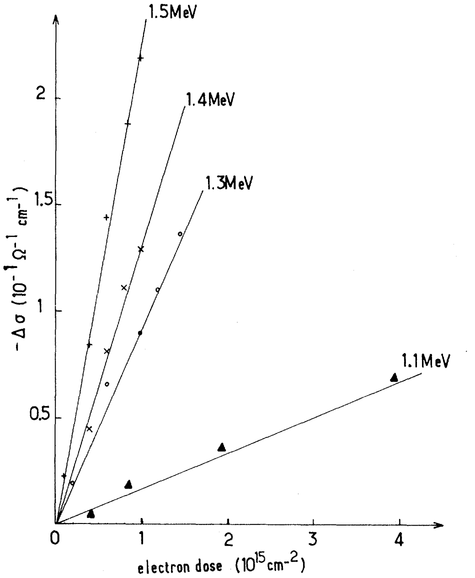

FIG. 4. Variation of the conductivity at 20° K vs dose of electrons for various energies of irradiation in cadmium telluride.

$$\Delta n = -\Delta N_A(1 + N_A/gN_C e^{-E_D/kT})^{-1} \simeq -0.2\Delta N_A .$$

The corresponding variation of conductivity

$$\Delta\sigma = \Delta n e \mu$$

(μ electron mobility) is linear with ΔN_A. This is verified in Fig. 4 giving $\Delta\sigma$ versus the dose ϕ of irradiation (since ϕ is proportional to ΔN_A). The knowledge of the electron mobility ($\mu \simeq 10^5$ cm^{2}V^{-1}sec^{-1} at 20 °K) allows to calculate ΔN_A.

B. Diamond (VRH regime)

In synthetic boron-doped (p type) diamond it has been shown that the conductivity occurs through a VRH mechanism below approximately 100 °K.[2] In the sample studied N_A and N_D have been estimated (from conductivity measurements and from the comparison between optical-absorption and conductivity measurements[2]) to be[11] $N_A = 1.7\times10^{18}$ cm^{-3} and $N_D = 1.6\times10^{18}$ cm^{-3} (i.e., $K \simeq 96\%$). In this case N_A is the doping concentration and N_D the compensating concentration.[11] The variation ΔN_D of the compensating centers can be again obtained using irradiation with energetic electrons; indeed it has been shown[12] that, in semiconducting diamond, electron irradiation introduces donor centers which trap the free holes present at high enough temperature.

The temperature of irradiation is approximately 20 °K. The conductivity measurements are performed after the sample has been heated up to about 230 °K for several minutes[13]; this treatment

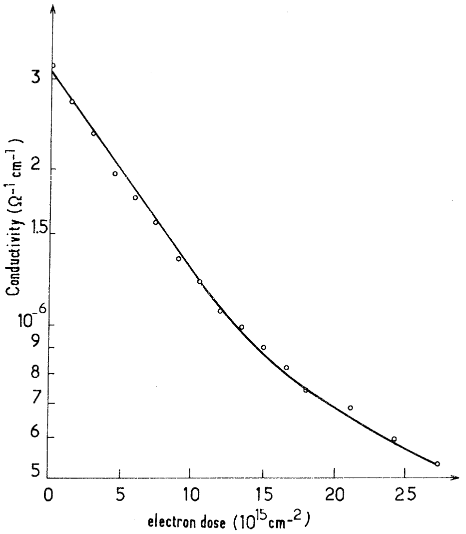

FIG. 5. Variation of the conductivity at 12° K vs the dose of irradiation with 0.5-MeV electrons in diamond.

allows the thermal deexcitation of some of the traps present before or after irradiation (and playing the role of compensating centers) which otherwise perturb the measurements; it also allows to make all the measurements in the same metastable states of the compensating centers (the irradiation, through ionization, results in the excitation of some of the compensating centers and consequently changes the compensation).

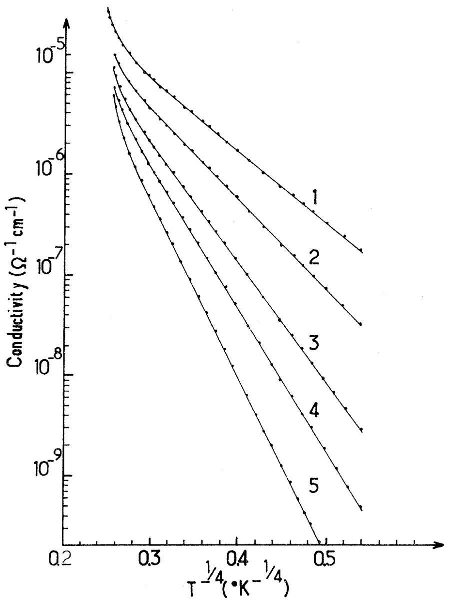

FIG. 6. Variation of the conductivity vs temperature in diamond: 1—before irradiation; 2—after irradiation at 0.7 MeV with 2×10^{16} cm^{-2}; 3—4×10^{16} cm^{-2}; 4—6×10^{16} cm^{-2}; 5—8.5×10^{16} cm^{-2}.

Figure 5 shows the variation of the conductivity, measured at 12 °K, with the dose of irradiation. As illustrated in Fig. 6, the conductivity, before and after successive doses of irradiation, follows the Mott's law; the slope A of the plots $\ln\sigma(T^{-1/4})$ is given versus electron dose in Fig. 7.

IV. DISCUSSION OF THE RESULTS

The concentration ΔN_A of the defects introduced is proportional to the electron dose ϕ. Then the conductivity should vary exponentially with ϕ; $\Delta\epsilon_3$ and ΔA should be linear with ϕ.

A. NNH regime (cadmium telluride)

This is indeed the case in the NNH regime, as illustrated in Figs. 1 and 3. Using Eqs. (10) and (13), ΔN_A in the hopping regime is calculated (assuming $V_1=1$) and the results obtained are compared in Fig. 8 with the corresponding values of ΔN_A obtained at 20 °K when the conduction occurs in the conduction band. This comparison shows that the correlation expected between ΔN_A (hopping) and ΔN_A (conduction band) is verified; however the slope of ΔN_A (hopping) vs ΔN_A (conduction band) is approximately 2 instead of 1. The full agreement between the two determinations of the concentration of the compensating centers would have been obtained by taking $V_1=0.5$ instead of 1. For large doses, i.e., for large values of ΔN_A, the linarity of ΔN_A (hopping) vs ΔN_A (conduction band) is no longer verified; this can be explained in terms of the approximation taken in the calculation ($\Delta N_A \ll N_D - N_A$) since $\Delta N_A \simeq 10^{13}$ cm^{-3} while $N_D - N_A \simeq 5\times10^{13}$ cm^{-3} when the deviation from linearity occurs.

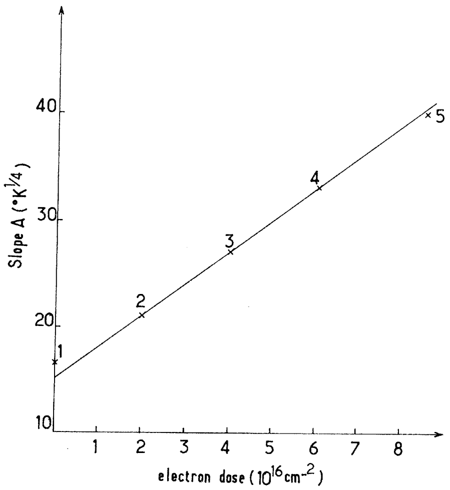

FIG. 7. Variation of the slope A of $\ln\sigma(T^{-1/4})$ vs the dose of irradiation at 0.7 MeV in diamond.

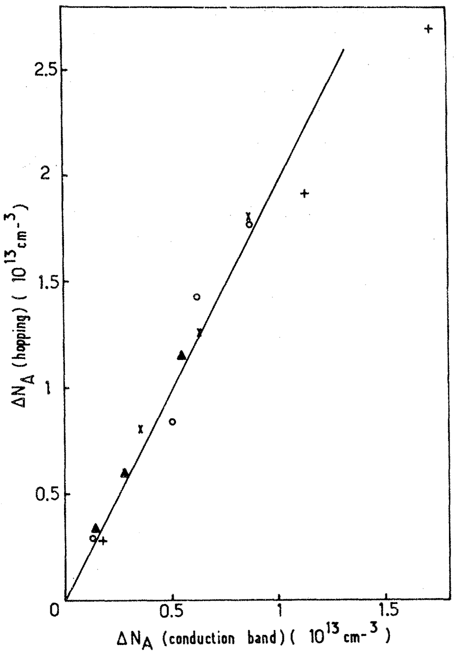

FIG. 8. Correlation between the concentration of the compensating centers introduced in cadmium telluride by irradiation, determined from conductivity measurement in the hopping regime and from conductivity and Hall-effects measurements in the regime of conduction in the conduction band: △—1.1 MeV; ○—1.3 MeV; ×—1.4 MeV; +—1.5 MeV.

B. VRH regime (diamond)

As illustrated on Figs. 5 and 7 both σ and ΔA follow the relations deduced in Sec. II B. Only for high doses of irradiation ($\phi \simeq 1.2\times 10^{16}$ cm^{-2}) $\ln\sigma(\phi)$ deviates from a straight line; this could still be explained, as already discussed, in terms of the approximation taken in the calculation; the deviation from the linearity occurs for lower does at 0.7 MeV (Fig. 7) than at 0.5 MeV (Fig. 5) because the defect introduction rate, and consequently the concentration of the compensating centers introduced, is lower for smaller energies.

In order to calculate ΔN_A it is necessary to know the parameter α. It has been shown[2] that the magnitude of the conductivity as well as its variations with N_A and N_D can be accounted for, in boron-doped diamonds, using a value of α^{-1} on the order of the Bohr radius of the fundamental state of boron: $\alpha^{-1} = 2\times 10^{-7}$ cm. With this value of α, the defect introduction rate ζ, defined as $\zeta = \Delta N_A/\phi$, i.e., $\zeta = (1/\beta\phi)\ln(\sigma/\sigma_i)$ is $\zeta \simeq 0.6$ cm^{-1} ($\beta = 1.25\ 10^{-16}$ cm^3). It has not been possible to verify this result, as in the case of cadmium telluride, by making the determination of ΔN_A at temperatures at which the conduction takes place in the valence band; indeed the variations of the conductivity at these temperatures are too small to be accurately measured.

V. CONCLUSION

We have shown that, in a semiconductor, when the (dc) electrical conductivity occurs through an hopping (nearest-neighbor hopping or variable-range hopping) mechanism, this conductivity varies exponentially with the concentration of the compensating centers, provided that the variation of this concentration is small. We have verified this law in cadmium telluride in which the conductivity occurs through the NNH mechanism below 10 °K and in boron-doped diamond, in which the conductivity occurs through the VRH mechanism below 100 °K, using electron irradiation as a tool to introduce extra compensating centers.

The sensitivity of the determination of the concentration of the compensation centers in the hopping regime is such that it allows the measurement of very low defect creation rates.[14] Such determination could be performed in all semiconductors when conveniently doped provided that they exhibit a non-negligible hopping conduction at low temperatures. The relations obtained in Sec. II permit a choice of the suitable doping concentration and compensation to maximise the sensitivity of this determination.

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