Cooperation of free- and bound-electron—phonon scatterings in Sb-doped Ge

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The cooperation of free- and bound-electron—phonon scatterings are studied in detail for Sb-doped Ge in the intermediate range of donor concentrations. It has been shown that the cooperation of free- and bound-electron—phonon scatterings in the intermediate range of donor concentrations explains the anomalous variation of the phonon-conductivity ratio $\mathscr{K}_D/\mathscr{K}_P$ (doped to pure host) with temperature for Sb-doped germanium which could not be explained so far by previous workers.

I. INTRODUCTION

Bird and Pearlman[1] measured the phonon conductivity of three Sb-doped germanium samples in the liquid-helium range of temperature having donor-impurity concentrations from 3×10^{14} to 3×10^{16} atoms/cm^3. It is now well established that the drastic reduction in the phonon conductivity of n-type germanium can be explained on the basis of the scattering of phonons by donor electrons. Previous workers have considered that for donor concentrations less than 10^{17} cm^{-3}, the phonons are scattered by the bound donor electrons. Keyes[2] was first to propose a theory for such a scattering. Later on, a detailed theory was given by Griffin and Carruthers[3] and by Kwok,[4] and finally the scattering relaxation rates were given in a form suitable for the evaluation of phonon conductivity by Suzuki and Mikoshiba.[5] In the final version of the theory, phonons are scattered both from the donor-electron ground state and the next-higher-energy state, which is a triplet state and is separated from the ground state by an energy 4Δ, known as the chemical shift. Phonons are scattered by the virtual transitions of the donor electrons between the singlet and the triplet states separated by 4Δ. As far as the resonance scattering of phonons is concerned, Sb-doped Ge provides the most interesting situation. The Suzuki-Mikoshiba theory[5] for the resonance scattering of phonons by bound donor electrons explains the experimental results of two Sb-doped Ge samples[6] having donor-impurity concentrations 3.4×10^{14} and 3.6×10^{16} cm^{-3}. However, it has not been possible to explain the experimental results of the third sample for which the donor-electron concentration is 3.0×10^{16} cm^{-3}. The discrepancy occurs both at temperatures lower and higher than the resonance temperature T_R, where a dip occurs in the $\mathscr{K}_D/\mathscr{K}_P$-versus-temperature curve. The failure of the Suzuki-Mikoshiba theory in explaining the $\mathscr{K}_D/\mathscr{K}_P$-versus-temperature curve for Sb-doped Ge sample (designated as Sb-306) having donor concentration 3.0×10^{16} cm^{-3} is reviewed. Earlier workers considered the electrons to be completely bound with the impurity atoms, and they tried to explain the experimental results with the assumption that the crystal is strained either by external stress applied along the $\langle 111\rangle$ direction[7] or by internal random strains[8] that take into account the modified values of valley-orbit splitting.

In the present work, it has been found that the upper limit of donor concentration for bound-electron—phonon scattering is 4×10^{15} cm^{-3} instead of 10^{17} cm^{-3} as considered by all earlier workers. Thus revising the range of donor concentrations for bound- and free-electron—phonon scatterings, we have been able to explain successfully the anomalous variation of the $\mathscr{K}_D/\mathscr{K}_P$-versus-temperature curve for the Sb-306 Ge sample.

II. THEORY

According to Mikoshiba's "inhomogeneity model,"[9] the impurity states in the intermediate range of concentrations are regarded as spatial mixtures of metallic and nonmetallic regions. In the low-concentration region, the concentration of this nonmetallic type of impurities is given by

$$N_n = N\exp(-t_c)\ . \tag{1}$$

In the higher-concentration region they are purely metallic, and the concentration of metallic impurities in which the electrons are in the isolated state is given by

$$N_m = N[1-\exp(-t_c)]\ , \tag{2}$$

where

$$t_c=(4\pi/3)Nr_c^3 \ ,$$

$$r_c=(144/\pi^2)^{1/3}a \ ,$$

where a is the donor electron radius and N is the total donor-impurity concentration. Here a is treated as an adjustable parameter, and its value is obtained for the best fit between theory and experiment. The values of a and t_c are given in Sec. III.

Mikoshiba has shown that his model explains in the intermediate-concentration region the electrical properties such as activation energy, the Hall effect, and the electrical resistivity. Here, we have applied the inhomogeneity model to explain the anomalous behavior of the $\mathcal{K}_D/\mathcal{K}_P$-versus-temperature curve for Sb-doped Ge having an impurity concentration of 3×10^{16} cm^{-3} (see Fig. 1). Concentrations of nonmetallic impurities (N_n) are considered as the concentration of bound donor impurities, and the concentration of metallic impurities (N_m) are considered as the concentration of free impurities.

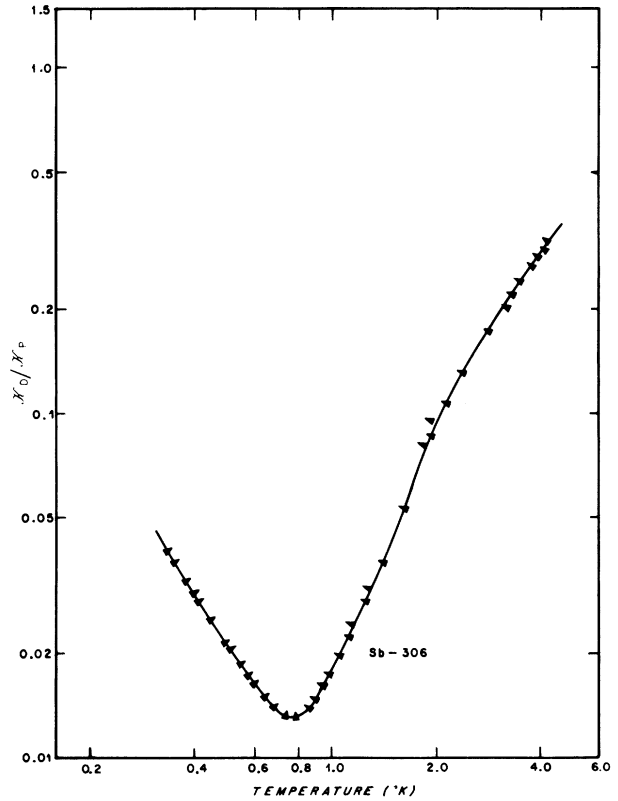

FIG. 1. Variation of $\mathcal{K}_D/\mathcal{K}_P$ with temperature for the Sb-306 Ge sample studied in Ref. 1 with $N=3.0\times10^{16}$ cm^{-3}. Experimental points are shown by the symbol ▲. Theoretical curves are shown by solid lines ($\mathcal{K}_D$ is the phonon conductivity of Sb-doped Ge, $\mathcal{K}_P$ is the phonon conductivity of pure equivalent Ge sample).

The scattering of phonons by electrons both in metallic and nonmetallic states is considered in the phonon conductivity calculations. The phonon conductivity in the Debye approximation is given by Callaway's[10] integral:

$$\mathcal{K}=\frac{k_B}{2\pi^2 v}\left[\frac{k_BT}{\hbar}\right]^3\int_0^{\Theta/T}\tau_c\frac{x^4e^x}{(e^x-1)^2}dx \ , \tag{3}$$

where $x=\hbar\omega/k_BT$ and τ_c^{-1} is the combined relaxation rate given by

$$\tau_c^{-1}=\tau_B^{-1}+\tau_{\rm pt}^{-1}+\tau_{\text{ph-ph}}^{-1}+\tau_{e\text{-ph}}^{-1} \ , \tag{4}$$

where $\tau_B^{-1}=V/L$ is the relaxation rate for the boundary scattering of phonons, $\tau_{\rm pt}^{-1}=A(k_B/\hbar)^4x^4T^4$ is the point-defect relaxation rate, $\tau_{\text{ph-ph}}^{-1}=B(k_B/\hbar)^2x^2T^5$ is the relaxation rate due to phonon-phonon scattering, and $\tau_{e\text{-ph}}^{-1}=\tau_{e\text{-ph(bound)}}^{-1}+\tau_{e\text{-ph(free)}}^{-1}$ is the combined relaxation rate due to bound- and free-electron–phonon scatterings.

The complete expressions for bound-electron–phonon scattering relaxation rates have been given by Suzuki and Mikoshiba,[5]

$$\tau_{e\text{-ph(bound)}}^{-1}=\tau_{\rm el}^{-1}+\tau_1^{-1}+\tau_2^{-1} \ , \tag{5}$$

where $\tau_{\rm el}^{-1}$ represents the relaxation rate due to elastic scattering of phonons both from the triplet as well as the singlet states, τ_1^{-1} represents the relaxation rate due to inelastic scattering of phonons from the triplet state, and τ_2^{-1} represents the relaxation rate due to "thermally assisted" phonon absorption for $\omega_{qt}<4\Delta/\hbar$ and inelastic scattering by electrons in the singlet state for $\omega_{qt}>4\Delta/\hbar$. The complete expressions for free-electron–phonon scattering relaxation rates are given by Ziman[11] and Kosarev,[12]

$$\tau_{e\text{-ph(free)}}^{-1}=(\tau_{e\text{-ph}Z}^{-1})_{q\le2k_F}+(\tau_{e\text{-ph}K}^{-1})_{q>2k_F} \ . \tag{6}$$

For the electrons in the metallic state (N_m) Ziman's expression for the relaxation rate for the scattering of phonons and free electrons is given by

$$(\tau_{e\text{-ph}Z}^{-1})_{q\le2k_F}=\frac{m^{*2}C^2k_BT}{2\pi\hbar^4V}L_n \times\frac{1+\exp(\eta^*-N/T-PTx^2+\frac{1}{2}x)}{1+\exp(\eta^*-N/T-PTx^2-\frac{1}{2}x)} \ , \tag{7}$$

where $N=m^*V^2/2k_B$, $P=k_B/8m^*V^2$, $\eta^*=\pi^2\hbar^2\times(3N/\pi)^{2/3}/2m^*k_BT$, m^* is the density-of-states effective mass, and C is the dilatation deformation potential constant, $x=\hbar\omega/k_BT$. Owing to the cutoff function, Ziman's expression becomes zero for

phonon wave vector $q > 2k_F$, where k_F is the Fermi wave vector. Kosarev has shown that in the presence of the electric field due to the ionized impurity atoms, the phonons with wave vector $q > 2k$ can also interact with the electrons, and he obtained a relaxation rate for the scattering of phonons with $q > 2k_F$,

$$(\tau^{-1}_{e\text{-ph}\,K})_{q>2k_F} = \frac{185 N_m m^{*2} C^2 \eta^2}{\hbar^3 \rho q^5 a^3} , \quad (8)$$

where η^2 is the square of the cosine of the angle between the phonon wave vector q and the polarization vector eq.

III. RESULTS AND DISCUSSIONS

As discussed in Sec. II, Mikoshiba's inhomogeneity model has been applied to data from the Sb-306 Ge sample. The values of N_n, nonmetallic donor impurities, and N_m, metallic donor impurities, are calculated using Eqs. (1) and (2), respectively. The results obtained are $N_n = 2.5660 \times 10^{16}$ cm^{-3} and $N_m = 4.3400 \times 10^{15}$ cm^{-3}. The adjustable value of a used in evaluating N_n and N_m is $a = 44$ Å, corresponding to $t_c = 0.156\,26$.

It is obvious from the above that the Sb-306 Ge sample contains both bound donor electrons as well as free donor electrons. However, it has been shown that for donor concentrations less than 4.5×10^{15} cm^{-3}, the Sb-doped Ge samples contain bound donor impurities only and phonons are scattered by bound donor electrons only, and for donor concentrations more than 3×10^{17} cm^{-3} the Sb-doped Ge samples contain free donor impurities only and the phonons are scattered by free donor electrons only. Therefore there is a range of donor concentrations from 4.0×10^{15} to 3×10^{17} cm^{-3} in which phonons are not only scattered by bound donor electrons but also scattered by free donor electrons. It is concluded that in this range of donor concentrations the donor electrons are not completely bound with the impurity atoms, but some of them are completely bound with impurity atoms and some are completely free from impurity atoms. The sample as such can be regarded as the spatial mixture of free and bound donor-impurity atoms. The bound donor impurities are greater than the free donor impurities when the donor concentration is closer to 4.0×10^{15} cm^{-3}, and free donor impurities are greater than the bound donor impurities when the donor concentration is closer to 3×10^{17} cm^{-3}. But at any time, irrespective of their relative values, both types of impurities are present in Sb-doped Ge samples having donor concentrations from 4×10^{15} to 3×10^{17} cm^{-3}. For donor concentrations less than 4×10^{15} cm^{-3} the donor-electron bound states are formed within the energy gap; for donor concentrations more than 3×10^{17} cm^{-3} the impurity states merge into the conduction band, making the donor electrons completely free from impurity atoms.

From the above discussion, it is concluded that the Sb-306 Ge sample lies in the intermediate region of metal-nonmetal transition, and the $\mathscr{K}_D/\mathscr{K}_P$-versus-temperature curve for this sample could not be explained by earlier workers because they considered the electrons to be completely bound with the impurity atoms.

So it is necessary to use phonon scattering by free and bound electrons simultaneously. For evaluation of the bound-electron–phonon scattering relaxation rates, the calculated values of N_n are used as the bound donor-electron concentration, and for evaluation of the free-electron–phonon scattering relaxation rates the calculated values of N_m are used as the free donor-electron concentration. Good agreement between theoretical and experimental values of the $\mathscr{K}_D/\mathscr{K}_P$-versus-temperature curve for the Sb-306 Ge sample is obtained. Thus it has been shown that the cooperation of free- and bound-electron–phonon scatterings resolve the anomaly of the $\mathscr{K}_D/\mathscr{K}_P$-versus-temperature curve for Sb-doped Ge having donor concentrations of 3.0×10^{16} cm^{-3}, which could not be explained by previous workers. The values of the various parameters used in the calculations are given in Table I.

TABLE I. Values of the various parameters used in the evaluation of the phonon conductivity.

$V_1 = 5.37 \times 10^5$ cm/sec
$V_2 = 3.28 \times 10^5$ cm/sec
$A = 2.40 \times 10^{-44}$ sec^3
$B_1 + B_2 = 2.80 \times 10^{-23}$ sec deg^{-3}
$4\Delta = 0.32$ meV
$a = 44$ Å
$E_u = 15$ eV
$C = 1.05$ eV
$m^* = 0.22 m_0$

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