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Chemical shift and donor-electron radius for lightly doped *n*-Ge

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Optimized values of the valley-orbit splitting 4Δ and the donor-electron radius a_0 for the different Sb-, As-, and P-doped Ge samples are obtained from the analysis of the resonance scattering of phonons which play a dominant role in the phonon resistivity of these materials in the liquid-helium range. Both elastic and inelastic scatterings from the singlet and triplet states as well as phonon-assisted absorption processes are considered in the calculations for the entire resonance region. Excellent agreement between theory and experiment is obtained for the optimized values of a_0 and 4Δ.

Certain types of impurities, when introduced in the host lattice of semiconductors of the fourth group, produce bound states with binding energies much smaller than the band gap and orbits large in comparison with the lattice constant within the band gap. These states are called shallow impurity states.[1] For example, when donor impurities such as Sb, P, or As are introduced into Ge or Si, donor-electron bound states are formed within the energy gap for donor-electron concentrations N_{ex} less than 10^{17} cm^{-3}. The binding energies associated with such states usually lie between 0.01 and 0.1 eV and the orbits are of the order of 50 Å. Shallow impurity states are usually treated within the framework of the effective-mass approximation.[1] In this approximation the complicated impurity potential is replaced by a simple Coulombic potential, that is, the potential of a point charge screened by the dielectric polarization of the host lattice.

In the effective-mass approximation the donor-electron ground-state wave functions $\Psi_n(\vec{r})$ are given by

$$\Psi(\vec{r}) = \sum_{t=1}^{N} \alpha_n^{(t)} F_n^{(t)}(\vec{r}) \psi_{kt}(\vec{r}) . \qquad (1)$$

Here the suffix n refers to the state n of the ground state. For example, in n-Ge, the suffix n can refer to the singlet ($n = 0$) or triplet state ($n = 1, 2, 3$ triply degenerate), which arises from the splitting of the fourfold degenerate donor-electron groundstate. In Ge there are four equivalent conduction-band minimas in $\langle 111 \rangle$ directions, and t, which refers to the conduction-band minima, can take values $t = 1, 2, 3, 4$. Thus the summation over t for n-Ge is the summation over four equivalent conduction-band minimas and $N = 4$. Further $\psi_{kt}(\vec{r})$ is the Bloch wave function for the tth band, $F(\vec{r})$ is the envelope wave function, and $\alpha_n^{(t)}$ are the numerical coefficients. The amplitudes $\alpha_n^{(t)}$ are fixed entirely by the symmetry of the Hamiltonian of the impurity state (the full tetrahedral group).

One usually makes use of the isotropic approximation and approximates the envelope wave function by a valley-independent function

$$F(r) = (\pi a_0^3)^{-1/2} e^{-r/a_0} , \qquad (2)$$

where a_0 is the effective radius of the ground-state donor-electron wave function. It seems appropriate to regard a_0 as a parameter to be fixed by experiment.

As mentioned earlier, the donor-electron ground state is fourfold degenerate reflecting four equivalent conduction-band minima. The valley-orbit interaction and the central cell correction split the fourfold-degenerate ground state in n-Ge into a lower-energy singlet state (A_1) and the higher-energy triply degenerate state (T_2). The energy difference between these two states is denoted by $4\Delta = E(T_2) - E(A_1)$ and is known as the "chemical shift." The splitting 4Δ depends on both the donor and the host semiconductor.

Any physical process involving donor-electron singlet and triplet states and hence their energy difference 4Δ, or donor-electron ground-state wave function involving a_0, require their accurate estimates under dynamic conditions. These resonance characteristic parameters such as 4Δ and a_0 are directly involved in the resonance scattering of phonons by bound donor electrons in the liquid-helium range where one observes resonance dips in the phonon conductivity versus temperature curves. In the present work we have obtained the optimized values of 4Δ and a_0 from the analysis of phonon conductivity results of Sb-, P-, and As-doped Ge in the temperature range 0.3 to 4 K. We feel that these values of the resonance scattering parameters 4Δ and a_0 can be used in explaining other physical processes, which may need an independent estimate of these quantities.

It may not be out of place to mention here that the present estimates of 4Δ and a_0 are based on a theory which takes into account not only the elastic and inelastic scatterings of phonons from both the singlet and triplet states but also the phonon-assisted absorption processes. Such a theory has been proposed by Kwok[2] and later on extended by Suzuki and Mikoshiba[2] to include also the inelastic scattering from the singlet state, which was not considered by Kwok. The earlier calculations in the resonance scattering region were based on the theories of Keyes[4] and of Griffin and Carruthers.[5] Keyes as well as Griffin and Carruthers have considered only the elastic phonon scattering by the donor electrons in the singlet state. Their results, however, are too small to account for the observed phonon conductivity.

The calculations of Suzuki and Mikoshiba for the phonon conductivity of Sb-, P-, and As-doped Ge are incomplete in the sense that the lowest temperature which they have considered is 1 K. Figure 1 shows that the resonance dip in Sb-doped Ge occurs at 0.6 K. Thus the calculations of Suzuki and Mikoshiba are in the off-resonance region and cannot provide any correct information regarding the resonance characteristic parameters 4Δ and a_0. Moreover, their calculations in the temperature range 1 to 5 K show deviations between theory and experiment towards the lower-temperature side and hence any extrapolation to still lower temperatures can not explain the low-temperature (<1 K) results shown in Fig. 1. As is evident from Fig. 2 for P- and As-doped Ge, the low-temperature data below the resonance region are as important as the results beyond 1 K. Hence the correct estimate of 4Δ and a_0 demands that the entire resonance region should be explored. The present calculations take into consideration elastic and inelastic scatterings of phonons both from the singlet and triplet states as well as phonon-assisted absorption processes in the entire resonance region, and hence the present estimates of 4Δ and a_0 are significant and relevant from theoretical considerations.

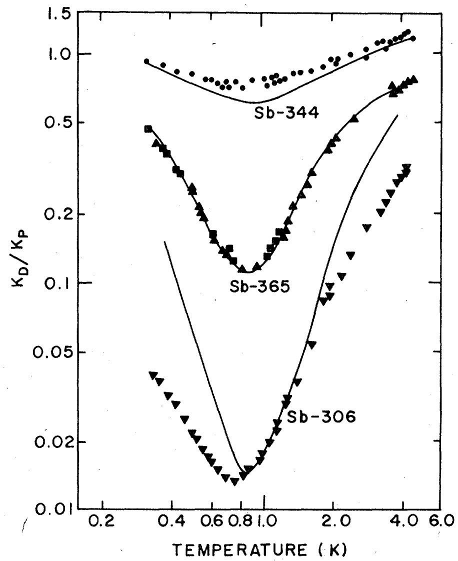

FIG. 1. Plot of (K_D/K_P) vs temperature for Sb-doped Ge samples. Solid lines represent the theoretical curves and experimental points (Ref. 6) are shown by ●, ■, ▲, and ▼. K_D is the phonon conductivity of doped Ge, while K_P is the same for undoped Ge.

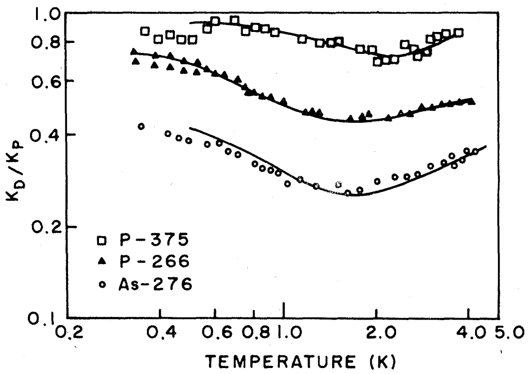

FIG. 2. Plot of (K_D/K_P) vs T for the samples (Ref. 6) Ge(P)-375 ($N_{ex}=3.7\times10^{15}$ cm^{3}), Ge(P)-266 ($N_{ex}=2.6\times10^{15}$ cm^{-3}), Ge(As)-276 ($N_{ex}=2.7\times10^{16}$ cm^{-3}). Experimental results are shown by □, ▲, and ○. Theoretical curves are shown by solid lines.

The results of calculations of the optimized values of a_0 and 4Δ for the different n-type Ge samples are summarized in Table I. Figures 1 and 2 show the comparison between theory and experiment.[6] Except for the sample Sb 306, which is believed to be strained and has been discussed elsewhere,[7] agreement is excellent when one considers both elastic and inelastic scatterings both from the singlet and triplet states as well as from phonon-assisted absorption processes. The detailed expressions of the relaxation rates for

TABLE I. Optimized values of 4Δ and a_0 for different n-type Ge samples.

Sample (Ref. 6)	N_{ex} (cm^{-3})	4Δ (meV)	a_0 (Å)	E_u (eV)
P-375	3.7×10^{15}	2.83	37	16
P-266	2.6×10^{16}	2.83	33	16
As-276	2.7×10^{16}	4.23	36	16
Sb-344	3.4×10^{14}	0.34	44	14
Sb-365	3.6×10^{15}	0.32	44	14

the different phonon scattering processes for lightly doped n-type semiconductors used in the present calculations were given in an earlier paper.[8] The phonon conductivity is evaluated in the framework of Callaway's theory. Since phonon-phonon scattering is negligible in the liquid-helium range, there is no adjustable parameter in the calculations. Only the quantities 4Δ and a_0 are optimized for the best agreement between theory and experiment. Calculations have been performed with the help of an IBM-7044 computer.

However, the estimate of a_0 is meaningful only if one wants to use isotropic envelope wave functions. The use of anisotropic wave function makes the phonon resistivity calculations very complicated and no attempt has been made to incorporate these features into our estimates of the optimized values of 4Δ and a_0.

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