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Effect of internal strains on thermal-phonon scattering in Li-doped Si

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The thermal conductivity of Li-doped Si has been measured down to 0.1 K. It is shown that the observed strong scattering of low-frequency phonons below 2 K can be explained by taking account of the resonant phonon absorption between the ground state of Li donors, which is split at random due to internal strain fields. The Gaussian distribution of the energy-level splitting is found to have a width of about 0.2 meV, with approximately 20% of the Li impurities occupying distorted sites.

I. INTRODUCTION

Scattering of thermal phonons by electrons bound to impurities in semiconductors was shown to account satisfactorily for low-temperature thermal conductivity data in lightly doped materials, and mainly in Si and Ge.[1] The calculated results were obtained by considering elastic and inelastic scattering due to electron transitions between energy levels of the impurity ground state.[2,3] In particular, such analysis has been recently shown to allow the determination of the valley-orbit splitting of the ground state of Li donors in Ge.[4] However, at lower temperatures, the above theoretical approach was found unable to account for some experimental data, that is, the theory underestimates the phonon scattering. In a previous work,[5] Fortier and Suzuki could satisfactorily analyze the thermal conductivity of Si doped with Li (in the isolated impurity concentration range) down to 2.5 K on the basis of scattering processes mentioned above. The disagreement observed at lower temperatures (2.5 to 1 K) between experimental and calculated results was suggested by the authors to arise most likely from the split of the ground state due to internal strains. The effect of the latter has been recently considered and discussed to account for the thermal conductivity data at lower temperatures. Challis *et al.*[6] have interpreted the thermal conductivity of p-type Ge by taking account of the resonant phonon absorption between the acceptor ground-state split due to internal strains. Singh[7] has calculated the effect of internal strains on the thermal conductivity of Li-doped Si. However, his calculation is not adequate because of the following points: (i) No account is taken concerning the effect of internal strains on the donor wave functions, and therefore on the coupling coefficients $C_{\vec{q}t}^{nn'}$ in the donor-phonon interaction. (ii) The strain-induced energy splitting is assumed to be identical for all impurities in the crystal, while one may expect to have a distribution of the splitting of energy levels over a certain energy range because donor electrons are most likely submitted to random strain fields. The assumption of uniformity of the splitting of energy levels leads to resulting adjusted values which are not supported by ir (Ref. 8) and EPR (Ref. 9) data. (iii) The split of the triplet of the donor ground state is not taken into account.

In the present paper, we report the thermal conductivity measurements extended down to 0.1 K on Li-doped Si in the isolated impurity range, and analyze these results by including, in addition to the phonon scattering previously considered,[5] the resonant absorption between the ground state split due to internal strains.

II. EXPERIMENT

The thermal conductivity between 0.1 and 10 K was measured using the usual longitudinal steady-state heat-flow technique. Carbon Speer resistors as well as a compound carbon device[10] were used as thermometers. The starting silicon was a 2500-Ω cm resistivity material with low oxygen concentration ($< 10^{15}$ cm^{-3}). The samples were in the shape of rectangular parallelepipeds 35 mm long and with a cross section s of about 2×3 mm^2. The doping of the samples with Li was carried out on the basis of the previous method used,[5] involving the evaporation of Li on both sides of the sample followed by appropriate heat treatments leading to the different Li concentrations and to a good homogeneity. The Li donor density N was determined from Hall measurements at room temperature.

The characteristics (carrier density N and Cas-

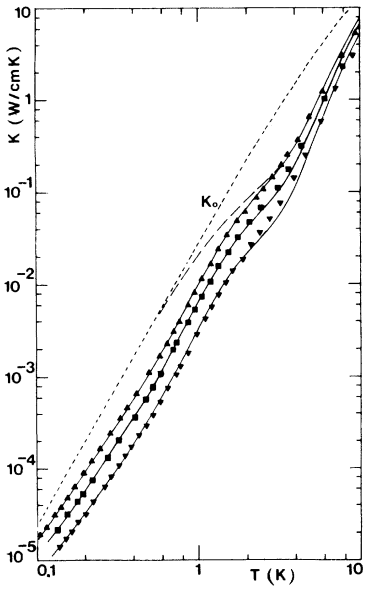

FIG. 1. Thermal conductivity K of Li-doped Si samples. Experimental data: S_{I} ($N=1.6\times10^{16}\,\mathrm{cm}^{-3}$), points ▲▲; S_{II} ($N=3\times10^{16}\,\mathrm{cm}^{-3}$), points ■■; S_{III} ($N=7.5\times10^{16}\,\mathrm{cm}^{-3}$), points ▼▼. Solid lines: calculated curves taking into account the effect of internal strains. The fits were obtained for a Gaussian strain distribution of half-width corresponding to a doublet level splitting of 0.2 meV, the impurity rate being in distorted sites (the "two-site" model) is about 20%. Dotted line ---: calculated thermal conductivity K_0 for "pure" sample. Dashed line ———: calculated thermal conductivity for sample S_{I}, without including the effect of internal strains (previous analysis, see Ref. 5).

imir's length $L=2\,\pi^{-1/2}S^{1/2}$) of the three samples measured were for S_{I}, $N=1.6\times10^{16}\,\mathrm{cm}^{-3}$, $L=0.26$ cm; for S_{II}, $N=3\times10^{16}\,\mathrm{cm}^{-3}$, $L=0.25$ cm; for S_{III}, $N=7.5\times10^{16}\,\mathrm{cm}^{-3}$, $L=0.26$ cm. The carrier concentrations considered correspond to the isolated impurity range. The thermal-conductivity data relative to the above three samples are shown on Fig. 1.

III. THEORY

The ground state of Li-donors in Si consists of the nearly degenerate triplet (T_2) and doublet (E) and the higher-lying singlet (A_1).[8,9] Internal fields with lower symmetry than T_d, for example strain fields due to dislocations, can lift the degeneracy of the triplet and doublet states.[9] Internal strains are considered to have finite values of the following components[9]:

$$e_1=-e_\theta=\tfrac{1}{2}\,(e_{xx}+e_{yy})-e_{zz},\qquad e_2=-e_\varphi=\tfrac{3}{2}\,(e_{yy}-e_{xx}), \tag{1}$$

where e_{xx}, e_{yy}, and e_{zz} are the diagonal components of the strain tensor. It is assumed for simplicity that e_1 and e_2 are independent, and the distributions of their magnitude, $P(e_1)$ and $P(e_2)$ have a Gaussian or Lorentzian form. The energy splitting resulting from these strains are for the triplet

$$\Delta E_3=\tfrac{1}{3}\,E_u\,(e_1-\sqrt{3}\,e_2)$$
$$\Delta E_4=\tfrac{1}{3}\,\Xi_u\,(e_1+\sqrt{3}\,e_2) \tag{2}$$
$$\Delta E_5=-\tfrac{2}{3}\,\Xi_u\,e_1\,,$$

and for the doublet

$$E_\pm=\pm\tfrac{1}{3}\,\Xi_u\,(e_1^2+e_2^2)^{1/2}\,. \tag{3}$$

The wave functions of the triplet are unchanged, and those of the doublet become[11]

$$|+\rangle=a\,|1\rangle+b\,|2\rangle,\quad |-\rangle=b\,|1\rangle-a\,|2\rangle\,, \tag{4}$$

where

$$a=\sin(\tfrac{1}{2}\phi),\quad b=\cos(\tfrac{1}{2}\phi),\quad \cos\phi=e_1(e_1^2+e_2^2)^{1/2}\,,$$
and (5)
$$\sin\phi=e_2(e_1^2+e_2^2)^{1/2}.$$

Here $|E_\pm|\ll\Delta$ is assumed, where Δ denotes the energy difference (1.8 meV) between the A_1 and the T_2 and E states in absence of strain, $|1\rangle$ and $|2\rangle$ denote the E states in the absence of strain, and Ξ_u is the deformation potential for shear strain.

The splitting of energy levels within the lowest quintet ($E+T_2$) is distributed over a certain range reflecting $P(e_1)$ and $P(e_2)$. In this case the resonant phonon absorption of low-frequency phonons contributes considerably to the thermal resistance at low temperatures. For a given e_1 and e_2, the relaxation rate per donor for this process, τ_r^{-1}, can be easily calculated[2]

$$\tau_r^{-1}=\frac{\pi\omega}{\rho v_t^2}\left(\frac{\Xi_u}{3}\right)^2 f^2\left(\frac{\omega}{v_t}\right)N(T)\,w_t(1-e^{-\beta\hbar\omega})\delta(\hbar\omega-2\delta), \tag{6}$$

where

$$w_1=\tfrac{1}{5}(1+4a^2b^2)\,,$$
$$w_2=\tfrac{1}{20}(1+4\,a^2b^2)\,, \tag{7}$$
$$w_3=\tfrac{1}{4}(1-4\,a^2b^2)\,,$$
$$2\delta=E_+-E_-=\tfrac{2}{3}\,\Xi_u(e_1^2+e_2^2)^{1/2}\,. \tag{8}$$

Here $\beta=1/k_BT$ and $N(T)$ is the occupation rate of the state $|-\rangle$. The notations are the same as in Ref. 5: ρ is the density of mass, v_t is the velocity of sound for the t mode, and

$$f(\omega/v_t)=\left(1+\tfrac{1}{4}\,a^{*2}\,\frac{\omega^2}{v_t^2}\right)^{-2}\,,$$

where a^* is the effective Bohr radius.

An averaging relaxation rate per donor is given by

$$\langle \tau_r^{-1} \rangle = \int\int \tau_r^{-1} P(e_1) P(e_2) de_1 de_2 \quad . \tag{9}$$

Furthermore in order to analyze the experimental results, we will approximate this equation by a combination of two limiting cases: (i) $e_1 \neq 0$, $e_2 = 0$ and (ii) $e_1 = 0$, $e_2 \neq 0$. We have

$$\langle \tau_r^{-1} \rangle = (1-x)\langle \tau_r^{-1} \rangle_1 + x \langle \tau_r^{-1} \rangle_2 \quad \text{with } 0 \leq x \leq 1 , \tag{10}$$

$$\langle \tau_r^{-1} \rangle_{i=1,2} = \frac{\pi\omega}{\rho v_t^2}\left(\frac{\Xi_y}{3}\right) f^2 \left(\frac{\omega}{v_t}\right)(N_i^+ + N_i^-) w_t^i (1 - e^{-\beta\hbar\omega}) P(\hbar\omega), \tag{11}$$

where

$$w_1^1 = \tfrac{1}{5}, \quad w_2^1 = \tfrac{1}{20}, \quad w_3^1 = \tfrac{1}{4}, \quad w_1^2 = \tfrac{2}{5}, \quad w_2^2 = \tfrac{3}{5}, \quad w_3^2 = 0 , \tag{12}$$

and

$$\begin{aligned} N_1^+ &= e^{\beta\hbar\omega/2}/(e^{-\beta\Delta} + e^{-\beta\hbar\omega/2} + 3e^{\beta\hbar\omega/2} + e^{-\beta\hbar\omega}) , \\ N_1^- &= e^{\beta\hbar\omega/2}/(e^{-\beta\Delta} + 3e^{-\beta\hbar\omega/2} + e^{\beta\hbar\omega/2} + e^{\beta\hbar\omega}) , \\ N_2^+ = N_2^- &= e^{\beta\hbar\omega/2}/(e^{-\beta\Delta} + e^{-\beta\hbar\omega/2} + e^{\beta\hbar\omega/2} \\ &\quad + e^{-\beta\sqrt{3}\hbar\omega/2} + e^{\beta\sqrt{3}\hbar\omega/2} + 1) , \end{aligned} \tag{13}$$

and

$$P(\hbar\omega) = \frac{1}{\sqrt{2\pi}} \frac{1}{\sigma} e^{-\hbar^2\omega^2/2\sigma^2}$$

or (14)

$$P(\hbar\omega) = \frac{1}{\pi} \frac{\sigma}{\sigma^2 + \hbar^2\omega^2} \quad .$$

Here σ denotes the variance and the half-width for the Gaussian form (and the Lorentzian one) of the distribution of 2δ [see Eq. (8)]. x and $(1-x)$ denote the percentage of donor electrons feeling strains of e_1 type and e_2 type, respectively.

Now we will adopt a "two-site" model considered by Challis *et al.*[6] in which a part of the impurities occupy the distorted sites and the rest the undistorted sites. The relaxation rate due to internal strain fields finally becomes

$$\langle \tau_R^{-1} \rangle = N_R \langle \tau_r^{-1} \rangle ,$$

where N_R is the donor density in distorted sites.

The relaxation rates for elastic and inelastic scattering are very complicated for donors in distorted sites. However, we will use the expressions given in Ref. 4 for donors in both distorted and undistorted sites. This approximation is good as long as $|E_\pm| \ll \Delta$.

The thermal conductivity was calculated by using Holland's expression with boundary and isotope scattering and the electron-phonon and phonon-phonon interactions. Values of physical parameters are the same as in Ref. 4.[12]

IV. RESULTS AND DISCUSSION

The parameters x, N_R, and σ have been considered as adjustable parameters. The best fits of the experimental data, assuming a Gaussian form for $P(e_1)$ and $P(e_2)$, were obtained for $x = 0.5$, $N_R/N = 0.2$, and $\sigma = 0.2$ meV, where N is the donor concentration (Fig. 1). A Lorentzian distribution gives less satisfactory fits.

In Fig. 2 is shown the ω dependence of various relaxation rates using values of parameters which give the best fit. On the other hand, the effect of different values for the adjusted parameters x, N_R, and σ on the calculated thermal conductivity is illustrated in Fig. 3. It is worth noting that the ratio N_R/N (and also σ) depends little on samples used here.

We will briefly remark on the values of parameters obtained by the present analysis. The value of x is reasonable, since x and $1-x$ should be almost the same. Watkins and Ham[9] obtained a

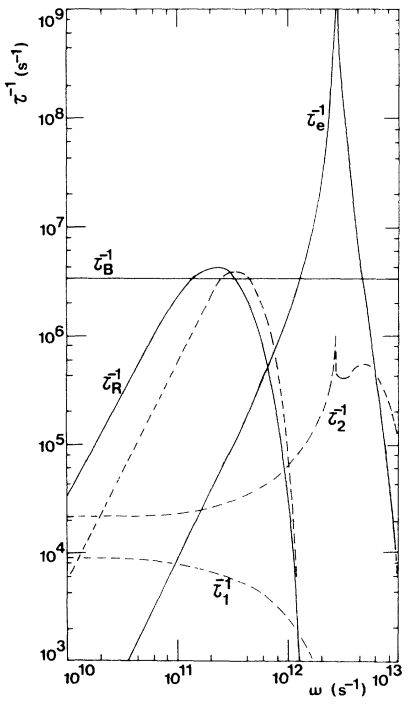

FIG. 2. Relaxation rates as a function of pulsation ω of phonons due to the second-order electron-phonon elastic (τ_e^{-1}) and inelastic (τ_1^{-1} and τ_2^{-2}) processes, and to the first-order processes (τ_R^{-1}) due to internal strains. The calculations were obtained for the temperatures $T = 0.5$ K (solid lines) and $T = 3$ K (broken lines) and the parameter set giving the best fit for K, that is, $\sigma = 0.2$ meV; $N_R/N = 20\%$. (τ_1^{-1} and τ_2^{-2} are negligible at 0.5 K; τ_e^{-1} is not affected by temperature variation.)

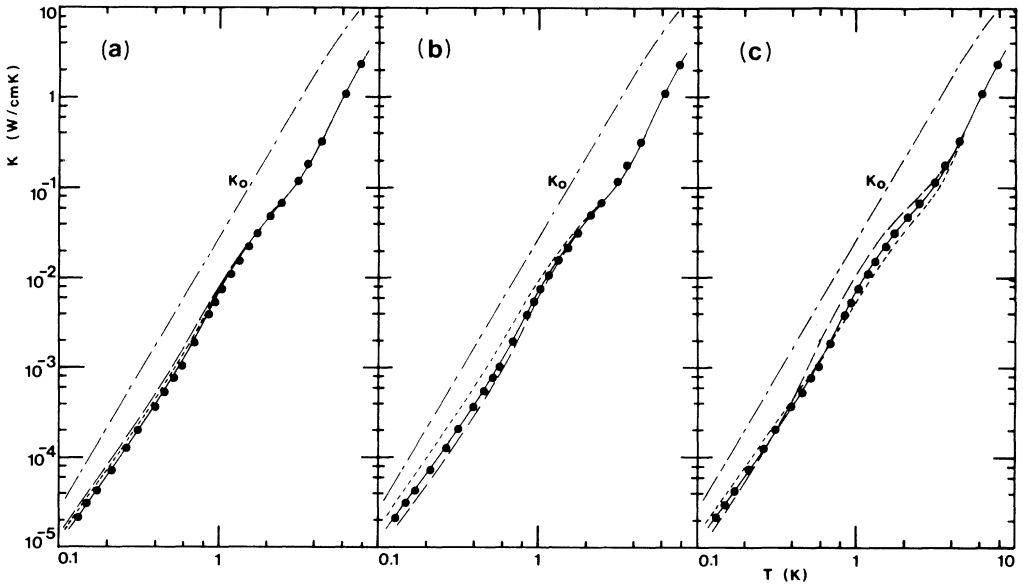

FIG. 3. Calculated thermal conductivity relative to sample S_{II} [($N = 3 \times 10^{16}$ cm^{-3} and $L = 0.25$ cm); experimental data: points (●●)] for different values of the adjustable parameters x, N_R, and σ (K_0 is the calculated thermal conductivity for "pure" sample). (a) $\sigma = 0.2$ meV, $N_R/N = 20\%$; $x = 0.8$ (dashed line ———), 0.5 (solid line), 0.2 (dotted line ---). (b) $\sigma = 0.2$ meV, $x = 0.5$; $N_R/N = 10\%$ (dotted line ---), 20% (solid line ——), 30% (dashed line ———). (c) $N_R/N = 20\%$, $x = 0.5$; $\sigma = 0.3$ meV (dotted line ---), 0.2 meV (solid line ——), 0.12 meV (dashed line ———).

root-mean-square strain of $\sim 1-2 \times 10^6$ for internal strains. This value of $\langle e_1 \rangle_{\rm rms}$ and $\langle e_2 \rangle_{\rm rms}$ leads to $\sigma \sim 0.01$ meV which is much smaller than our value. However, donor electrons in distorted sites are expected to feel much larger strain fields than an average value. Therefore $\sigma = 0.2$ meV is not unreasonable. According to the results of Challis *et al.*[6] and Wilson,[13] the above behavior can also be found in doped Ge.

We have shown a model which can well explain a large thermal resistance of Li-doped Si at lower temperatures. In this model 20% of the donors are in distorted sites and the rest, 80%, are in undistorted sites, and the energy splitting due to internal fields is small, since σ is such that the condition $\sigma \ll \Delta$ (with $\Delta = 1.8$ meV) holds true. These results (small values of N_R and σ) are compatible with ir (Ref. 8) and EPR (Ref. 9) data, since the additional optical transitions induced by internal strains have unobservable or negligible effects in comparison with the linewidths and the random noise of spectra.

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