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Thermal phonon scattering in Li-doped Si

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Experimental results are presented for thermal conductivity of Si containing between 5×10^{15} and 7×10^{17} Li donors cm^{-3} in the temperature range 1.2–50 °K, which show that Li donors scatter phonons very effectively at low temperature. The Li donor in Si has an "inverted" ground state in which the lowest level is degenerate and the split-off level is a singlet in contrast with group-V donors. Is is shown that strong scattering of phonons is due to the degenerate lowest state and the small valley-orbit splitting. A theory on the basis of a simple model for the donor ground state is formulated in which possible splitting of the degenerate state is ignored. It can fairly well explain the experimental results for lightly doped samples in the low-temperature region ($T \leq 10$ °K), without using adjustable parameters. However, it cannot explain the stong scattering of phonons observed at very low temperatures. Discussions of this are given.

I. INTRODUCTION

The strength of phonon scattering by electrons or holes bound to impurity centers depends strongly on the structure of the impurity state. It is well known that group-V donors, particularly Sb donor, in Ge and shallow acceptors in semiconductors[1] give rise to a strong scattering of thermal phonons[2] below 10 °K. For the former, it is due to the fact that 1S-like excited states lie just above the 1S-like lowest state.[3,4] (The energy difference is called the valley-orbit splitting.) For the latter, it is due to the fourfold-degenerate ground state of the acceptor.[5] Shallow donors in III-V semiconductors with a direct energy gap scatter thermal phonons very weakly. This is due to the fact that these donors have no 1S-like excited state and cannot couple with transverse phonons as long as we consider the electron-phonon interaction to be via the deformation-potential coupling. Although group-V donors in Si have 1S-like excited states as in Ge, they give rise to only a small thermal resistance[4,6] because of their large valley-orbit splitting.[7]

The Li donor in Si has an "inverted" ground state, that is, the lowest state being the fivefold-degenerate state and the 1S-like excited state being a singlet.[8] The valley-orbit splitting is small. Although it is not clear at the present time that Li donors occupy the tetrahedral (T_d) site[8,9] or the D_{3d} site,[10] it is expected that they scatter phonons very effectively because of their peculiar level structure.[2,11] Indeed, the experiment on the thermal conductivity of Li-doped Si shows that Li donors are very strong scatterers of phonons.

In this paper, we present for the first time the experimental results of the thermal conductivity in Si containing between 5×10^{15} and 7×10^{17} Li donors/cm^3, and the theory of phonon scattering by the Li donors, which can fairly well explain the experimental results for lightly doped samples at $T \leq 10$ °K, without using adjustable parameters. In Sec. II, the experimental procedure and data are given. In Sec. III, the expressions of the relaxation rate of phonons scattered by an isolated Li donor on the basis of an idealized model for the ground state are derived, using second-order perturbation theory. In Sec. IV, comparison and discussion are given. Our simple theory cannot explain the strong scattering of phonons at lower temperatures. Speculations on this are presented. It is pointed out that the donor-electron state contributing to phonon scattering in samples with Li concentrations 5 and 7×10^{17} cm^{-3} seems to be different from that in samples with lower donor concentration. A brief discussion on the dynamic Jahn-Teller effect is also given.

II. EXPERIMENTAL

The thermal conductivity was measured in the temperature region 1.2–50 °K using the usual longitudinal steady-state heat-flow technique, as previously described elsewhere.[12] Indium sheets were used to ensure intimate thermal contacts between the specimen and the heater and between the specimen and the cryostat and at the same time to avoid any excess mechanical stress on the specimen. Allen-Bradley carbon resistors were used as thermometers. They were attached at two points along the long dimension of the specimen by means of small copper clamps. For all the samples, the heat flow was along the ⟨111⟩ direction. The uncertainty of the measured values was evaluated to be ±10% in the range 1.2–20 °K and less than 15% at higher temperatures.

The Li-doped samples were prepared as follows. Silicon with a resistivity of 2500 Ω cm and low oxygen concentration (< 10^{15} cm^{-3}) was used as a starting material. After evaporation of Li on both

TABLE I. Sample characteristics.

Samples and symbols	Number of donors (cm^{-3}) at $T = 300\,°K$	Casimir's length (cm)
1 △	5.0×10^{15}	0.186
2 ▲	9.0×10^{15}	0.166
3 ●	2.4×10^{16}	0.177
4 ○	3.25×10^{16}	0.250
5 □	5.0×10^{16}	0.258
6 ■	9.0×10^{16}	0.235
7 ♦	1.85×10^{17}	0.159
8 ◇	2.0×10^{17}	0.265
9 ▽	5.2×10^{17}	0.260
10 ▼	8.0×10^{17}	0.262

sides, the samples were sealed in a quartz tube under vacuum and subsequently heated at appropriate temperatures and times in order to obtain the different Li concentrations and a good homogeneity.[13] The latter in each sample was found from resistance measurement to be better than 5%. Surfaces of the samples were prepared by lapping with 400-grit SiC on a glass block. The samples were in the shape of rectangular parallelepipeds 35-mm long and with a cross section s of about 3.5–5 mm^2. The donor contents were evaluated by means of resistivity measurements at room temperature. The donor concentrations and Casimir's length ($L = 2\pi^{-1/2}s^{1/2}$) of samples are given in Table I. The measured thermal conductivity is shown in Figs. 1 and 2.

III. THEORY

A. Ground state of Li donor in Si

We shall briefly review the structure of the Li donor in Si on the basis of the effective-mass approximation.[1] The ground state of shallow donors in Si is sixfold degenerate reflecting the six equivalent conduction-band minima. We assume, hereafter, that the Li donor occupies the T_d site like group-V donors, though the former is in an interstitial site and the latter in a substitutional site. The ground-state wave functions of a shallow donor are as follows:

$$\Psi_n(\vec{r}) = \sum_j \alpha_n^{(j)} F^{(j)}(\vec{r}) \psi_{\vec{k}_0^j}(\vec{r}) , \tag{1}$$

where

$$\begin{aligned}
&A_1: \quad \alpha_0 = \frac{1}{\sqrt{6}}(1,1,1,1,1,1) ,\\
&E: \quad \alpha_1 = \frac{1}{\sqrt{12}}(1,1,1,1,-2,-2) ,\\
&\qquad \alpha_2 = \tfrac{1}{2}(-1,-1,1,1,0,0) ,\\
&T_2: \quad \alpha_3 = \frac{1}{\sqrt{2}}(1,-1,0,0,0,0) ,\\
&\qquad \alpha_4 = \frac{1}{\sqrt{2}}(0,0,1,-1,0,0) ,\\
&\qquad \alpha_5 = \frac{1}{\sqrt{2}}(0,0,0,0,1,-1) .
\end{aligned} \tag{2}$$

Here, $\alpha_n^{(j)}$ is the coefficient representing a contribution of the jth valley to the donor state n, $\psi_{\vec{k}_0^j}(\vec{r})$ denotes the Bloch function at the jth valley and $F^{(j)}(\vec{r})$ is the envelope function. We assume that $F^{(j)}(\vec{r})$ is isotropic, that is,

$$F(\vec{r}) = (\pi a^{*3})^{-1/2} e^{-r/a^*} \text{ for all } j , \tag{3}$$

where a^* denotes the effective Bohr radius.

The degenerate ground state is partially split by the valley-orbit interaction and the central-cell correction. The lowest level of Li donor, according to Aggarwal *et al.*,[8] has a fivefold degeneracy

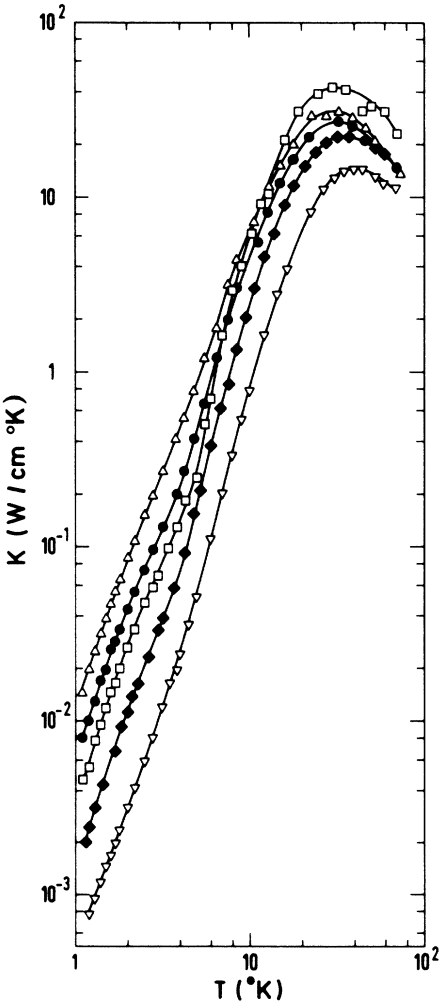

FIG. 1. Thermal conductivity K of Li-doped Si as a function of temperature.

in contrast with other shallow donors. Thus the Li donor has an "inverted" ground state. The energy separation between the lowest $(E+T_2)$ and split-off (A_1) levels, Δ, is 1.8 meV.

B. Donor-electron-phonon interaction

The matrix elements of the electron-phonon interaction between two donor states n and n' is given by[14]

$$\langle n|\mathcal{H}_{e-p}|n'\rangle=\sum_{\vec{q}t}\left(\frac{\hbar\omega_{\vec{q}t}}{2Mv_t^2}\right)^{1/2} f(q)(\Xi_d\vec{e}_t\cdot\hat{q}\delta_{nn'}+\tfrac{1}{3}\Xi_u\vec{e}_t\cdot\underline{D}^{nn'}\cdot\hat{q})(a_{\vec{q}t}+a_{\vec{q}t}^{\dagger}), \tag{4}$$

$$f(q)=(1+\tfrac{1}{4}a^{*2}q^2)^{-2}, \tag{5}$$

where M is the mass of crystal, $\omega_{\vec{q}t}$ is the angular frequency of the phonon with wave vector $\vec{q}$ in the t branch, v_t is the velocity of sound, $\vec{e}_t$ is the polarization vector, $\hat{q}$ is the unit vector along $\vec{q}$, Ξ_d and Ξ_u are the deformation potential constants, $a_{\vec{q}t}^{\dagger}$ and $a_{\vec{q}t}$ are the creation and annihilation operators of $(\vec{q}t)$ phonon. The tensors $\underline{D}^{nn'}$ defined by Hasegawa[14] are as follows:

$$\underline{D}^{nn'}=3\sum_j \alpha_n^{(j)}\alpha_{n'}^{(j)}\underline{U}^{(j)}, \tag{6}$$

and we take the following set of $\underline{U}^{(j)}$

$$\underline{U}^{(1)}=\underline{U}^{(2)}=\begin{pmatrix}1&0&0\\0&0&0\\0&0&0\end{pmatrix},\quad \underline{U}^{(3)}=\underline{U}^{(4)}=\begin{pmatrix}0&0&0\\0&1&0\\0&0&0\end{pmatrix},\quad \underline{U}^{(5)}=\underline{U}^{(6)}=\begin{pmatrix}0&0&0\\0&0&0\\0&0&1\end{pmatrix}, \tag{7}$$

where superscripts 1, 2, 3, 4, 5, and 6 denote the valley along the $\langle 100\rangle$, $\langle\bar{1}00\rangle$, $\langle 010\rangle$, $\langle 0\bar{1}0\rangle$, $\langle 001\rangle$, and $\langle 00\bar{1}\rangle$ directions, respectively. From Eqs. (2), (6), and (7), we obtain the following expressions for $\underline{D}^{nn'}$,

$$\underline{D}^{11}=\underline{D}^{00}-\frac{1}{\sqrt{2}}\underline{D}^{01},\quad \underline{D}^{22}=\underline{D}^{00}+\frac{1}{\sqrt{2}}\underline{D}^{01},\quad \underline{D}^{12}=\frac{1}{\sqrt{2}}\underline{D}^{02},\quad \underline{D}^{0i}=\underline{D}^{1i}=\underline{D}^{2i}=\underline{D}^{ij}\ (i\neq j)=0\ (i,j=3,4,5),$$

$$\underline{D}^{33}=3\begin{pmatrix}1&0&0\\0&0&0\\0&0&0\end{pmatrix}=\underline{D}^{00}-\begin{pmatrix}-2&0&0\\0&1&0\\0&0&1\end{pmatrix},\quad \underline{D}^{44}=3\begin{pmatrix}0&0&0\\0&1&0\\0&0&0\end{pmatrix}=\underline{D}^{00}-\begin{pmatrix}1&0&0\\0&-2&0\\0&0&0\end{pmatrix}, \tag{8}$$

$$\underline{D}^{55}=3\begin{pmatrix}0&0&0\\0&0&0\\0&0&1\end{pmatrix}=\underline{D}^{00}-\sqrt{2}\,\underline{D}^{01},$$

$$\underline{D}^{00}=\begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix},\quad \underline{D}^{01}=\frac{1}{\sqrt{2}}\begin{pmatrix}1&0&0\\0&1&0\\0&0&-2\end{pmatrix},\quad \underline{D}^{02}=\sqrt{\tfrac{3}{2}}\begin{pmatrix}-1&0&0\\0&1&0\\0&0&0\end{pmatrix}. \tag{9}$$

C. Phonon relaxation rate

We consider the processes of phonon scattering by donor electrons as shown in Fig. 3. Figure 3(a) represents elastic scattering for $E_n=E_{n'}$ and inelastic scattering for $E_n\neq E_{n'}$ and Fig. 3(b) represents "thermally assisted" phonon absorption.[15] In Fig. 3, n, m, and n' denote initial, intermediate, and final states, respectively.

We neglect, for simplicity, the splitting of the fivefold-degenerate ground state $(E+T_2)$ owing to the strain field due to dislocation, the interaction among impurities, the interaction with lattice vibration, and so on. The single-mode relaxation rate $\tau(\vec{q}t)^{-1}$ by the processes of Fig. 3 can be calculated by using Eqs. (4), (8), and (9) in the same way as one of the present authors has done in previous papers.[16,17] Therefore we show here only the final results of the calculations of $\tau(\vec{q}t)^{-1}$:

$$\bar{\tau}_e^{-1} = B_t\omega^4[\bar{v}_1^{-5}f^2(\omega/\bar{v}_1) + \tfrac{3}{2}\bar{v}_2^{-5}f^2(\omega/\bar{v}_2)]\left\{\frac{4\Delta^2}{(\Delta^2-\hbar^2\omega^2)^2}(N_0+N_1) + N_1\left[\left(-\frac{1}{\hbar\omega}+\frac{1}{\Delta+\hbar\omega}\right)^2 + \left(\frac{1}{\hbar\omega}+\frac{1}{\Delta-\hbar\omega}\right)^2\right]\right\}, \tag{10}$$

$$\bar{\tau}_i^{-1} = N_0B_t\omega(1-e^{-\hbar\omega/kT})(\Delta/\hbar+\omega)^3[\bar{v}_1^{-5}f^2(q_1^+) + \tfrac{3}{2}\bar{v}_2^{-5}f^2(q_2^+)]\left(\frac{1}{\hbar\omega}-\frac{1}{\Delta+\hbar\omega}\right)^2\left[1-\exp\left(-\frac{\Delta+\hbar\omega}{kT}\right)\right]^{-1}, \tag{11}$$

$$\bar{\tau}_2^{-1} = N_1B_t\omega(1-e^{-\hbar\omega/kT})\,|\Delta/\hbar-\omega|^3[\bar{v}_1^{-5}f^2(q_1^-) + \tfrac{3}{2}\bar{v}_2^{-5}f^2(q_2^-)]\left(\frac{1}{\hbar\omega}+\frac{1}{\Delta-\hbar\omega}\right)^2\left|\left[\exp\left(\frac{\Delta-\hbar\omega}{kT}\right)-1\right]^{-1}\right., \tag{12}$$

$$B_t \equiv \frac{w_t}{10\pi\rho^2\bar{v}_t^2}\left(\tfrac{1}{3}\Xi_u\right)^4 f^2\left(\frac{\omega}{\bar{v}_t}\right), \tag{13}$$

$$q_t^{\pm} \equiv (\Delta \pm \hbar\omega)/\hbar\bar{v}_t, \tag{14}$$

$$w_1 = \tfrac{4}{5}, \quad w_2 = \tfrac{7}{10}, \quad w_3 = \tfrac{1}{2}, \tag{15}$$

$$N_0 = Ne^{-\Delta/kT}/(5+e^{-\Delta/kT}), \quad N_1 = N_0e^{\Delta/kT}, \quad N_1 = N_2 = N_3 = N_4 = N_5, \tag{16}$$

where ρ is the density of mass, N and N_i are the number of donors and electrons in the ith level per unit volume, respectively, $\bar{v}_1$ and $\bar{v}_2$ $(=\bar{v}_3)$ denote the average velocity of sound for the longitudinal and transverse modes,[14] $\omega \equiv \omega_{\vec{q}t}$, $\bar{\tau}_e^{-1}$ and $\bar{\tau}_i^{-1}$ are the angular average of phonon relaxation rate for elastic and inelastic scattering, respectively and $\bar{\tau}_2^{-1}$ is that for thermally assisted phonon absorption ($\hbar\omega < \Delta$) and inelastic scattering ($\hbar\omega > \Delta$). It should be emphasized that electrons in T_2 states cannot scatter phonons by the processes considered above because inelastic scattering and "thermally" assisted phonon absorption are forbidden by a selection rule ($\underline{D}^{0n} = 0$, $n = 3, 4, 5$) in Eq. (8) and the relaxation rate for elastic scattering turns out zero due to cancellation [see Eq. (8) and Eq. (3.5) of Ref. 16 or Eq. (2.1) of Ref. 17]. Therefore the phonon scattering occurs only from transitions of electrons among the A_1 and E states. Equations (10)–(16) also hold even when we assume that Li donor occupies the D_{3d} site as has been considered by Nara and Morita[10] (see Appendix).

As $\Delta \to \infty$, the total relaxation rate, τ_0^{-1}, for the phonon scattering by Li donors is simply given by the second term in the large curly bracket of Eq. (10):

$$\tau_0^{-1} = 2N_1B_t\omega^2\hbar^{-2}[\bar{v}_1^{-5}f^2(\omega/\bar{v}_1) + \tfrac{3}{2}\bar{v}_2^{-5}f^2(\omega/\bar{v}_2)]. \tag{17}$$

This represents the phonon relaxation rate by elastic scattering when we consider only electrons in the E state. The strong scattering of phonons by shallow acceptors in Ge, Si, and InSb has been explained by the equation similar to Eq. (17).[2,5] In order to show the difference between the aspect of phonon scattering due to this and a resonant-type scattering proposed by Griffin and Carruthers,[4] that is, the first term in the large curly bracket of Eq. (10), we have calculated the

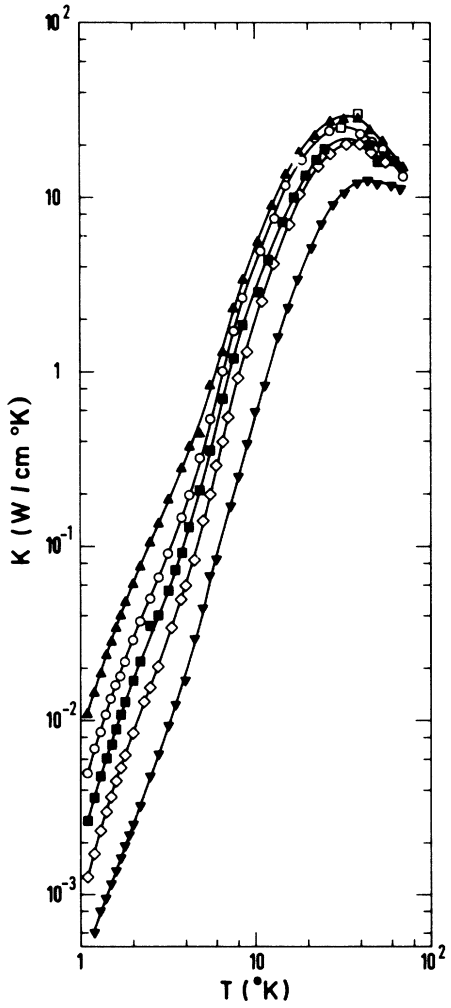

FIG. 2. Thermal conductivity K of Li-doped Si as a function of temperature.

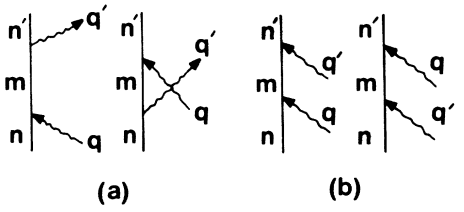

FIG. 3. Phonon scattering by second-order processes n, m, and n' denote initial, intermediate, and final states, respectively.

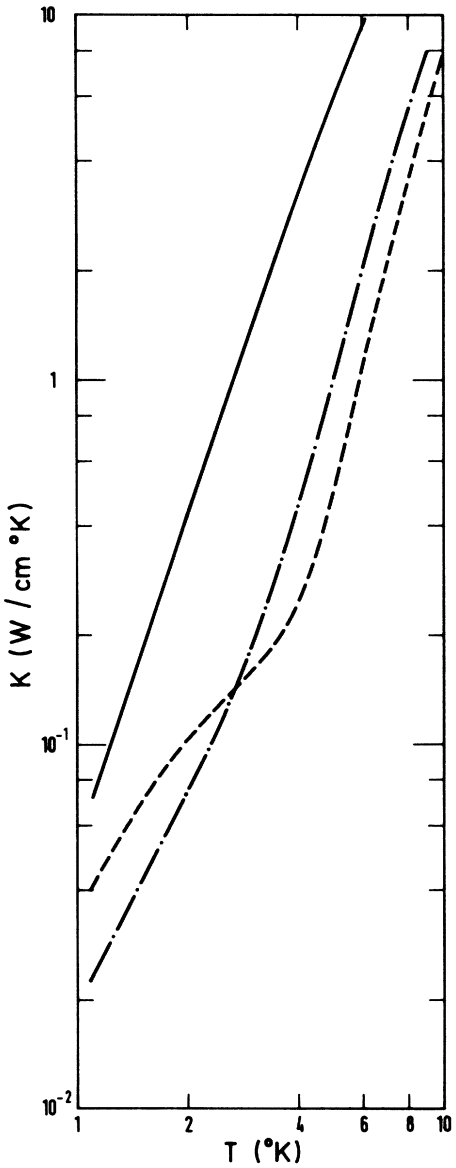

FIG. 4. Calculated thermal conductivity when only nonresonant- or resonant-type scattering is taken into account as the donor-phonon interaction. ---: nonresonant; -·-·-· : resonant; and ——: K for $N_1 = 0$.

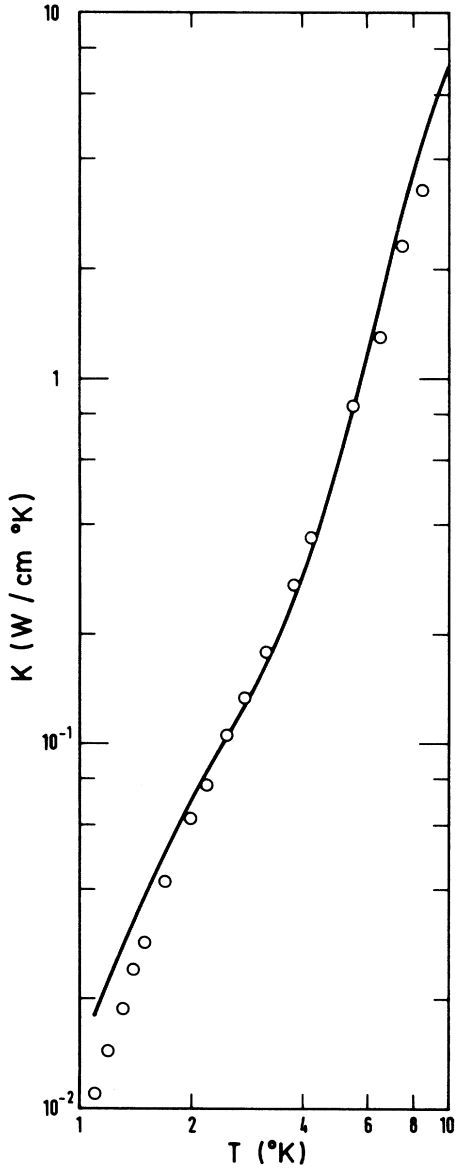

FIG. 5. Experimental and calculated K for sample 2. The solid line represents the calculated K.

thermal conductivity $K(T)$ for the same number of scatters using Eq. (18). They are shown in Fig. 4. In calculations we have used $N_1 = 10^{16}$ cm^{-3} and $L = 0.5$ cm. The curves 1 and 2 have been calculated by using Eq. (17) and Eq. (10) putting $N_0 = N_1$ in the first term and neglecting the second term in the large curly bracket, respectively. For comparison, the curve for $N_1 = 0$ is also given in Fig. 4.

D. Calculation of thermal conductivity

We shall calculate $K(T)$ using the usual semiphenomenological expression for the lattice thermal conductivity[4,18]:

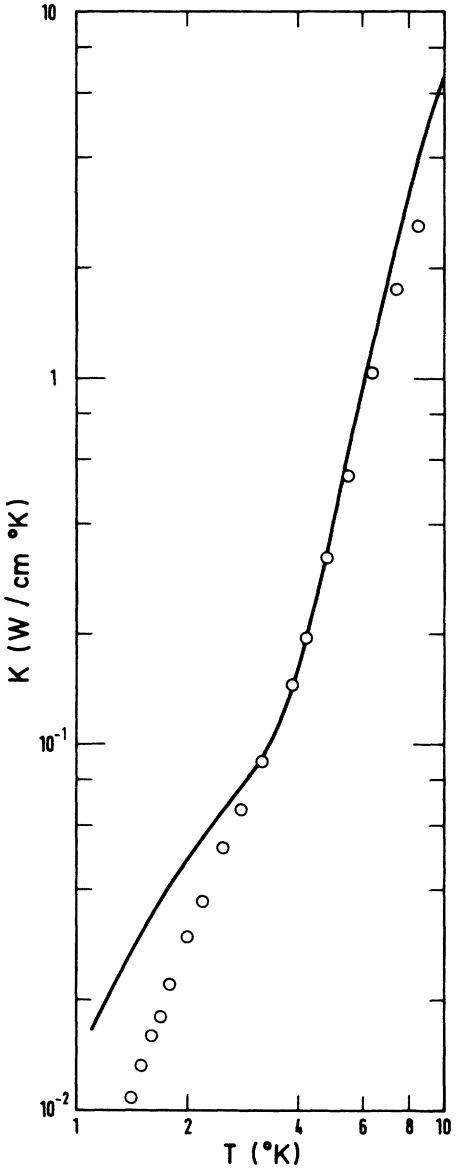

FIG. 6. Experimental and calculated K for sample 4. The solid line represents the calculated K.

$$K(T) = \frac{k^4 T^3}{6\pi^2 \hbar^3} \sum_t \frac{1}{\bar{v}_t} \int_0^\infty \frac{x^4 e^x}{(e^x - 1)^2} \tau \, dx \,, \tag{18}$$

$$\tau^{-1} = \tau_{B_t}^{-1} + \tau_I^{-1} + \tau_{e\text{-}p}^{-1} \,, \tag{19}$$

where

$$\tau_{B_t}^{-1} = \bar{v}_t / L \,, \tag{20}$$

$$\tau_I^{-1} = A\omega^4 = A(k/\hbar)^4 x^4 T^4 \,, \tag{21}$$

$$x \equiv \hbar\omega / kT \,. \tag{22}$$

Here $\tau_{B_t}^{-1}$, τ_I^{-1} and $\tau_{e\text{-}p}^{-1}$ are the phonon relaxation rate due to boundary scattering, isotopic scattering, and scattering by donor electrons, respectively, L is the Casimir's length.

The values of physical parameters used in the calculation of $K(T)$ are as follows:

$\rho = 2.33$ g cm^{-3}, $\bar{v}_1 = 9.33 \times 10^5$ cm sec^{-1},

$\bar{v}_2 = 5.42 \times 10^5$ cm sec^{-1}, $A = 1.32 \times 10^{-45}$ sec^3,

$a^* = 20$ Å, $\Xi_u = 11.4$ eV (Ref. 7).

IV. COMPARISON AND DISCUSSION

Figures 5 and 6 show comparisons of the calculated $K(T)$ with the experimental ones for lightly

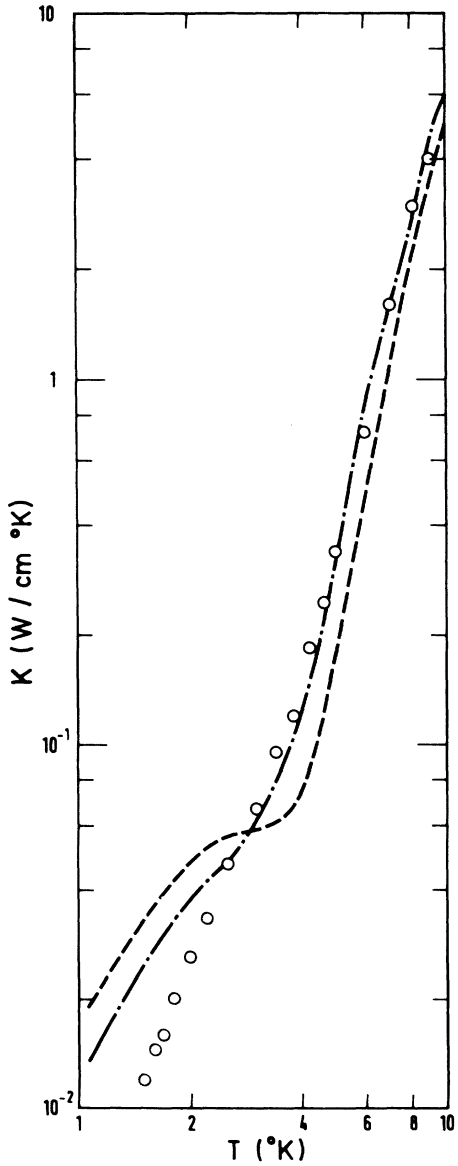

FIG. 7. Calculated K of sample No. 5 for Li donor with a "normal" ground state (- - -) and "inverted" ground state (-·-·-). The experimental data are also shown.

doped samples (Nos. 2 and 4) at low temperatures ($T \leq 10\,^{\circ}$K). In calculating $K(T)$ we have used no adjustable parameters. Our theory on the basis of a simple model for the ground state of the Li donor can fairly explain the experimental data over a concentration range 5×10^{15} to 2×10^{17} cm^{-3}. The deviation of the calculated $K(T)$ from the experimental ones at higher temperatures is due partly to the form of the donor wave function used in the calculations. The population of phonons with frequency $\omega > \bar{v}_t/a^*$ increases with temperature. [Note that $\hbar\bar{v}_t/ka^* \simeq 21\,^{\circ}$K for transverse phonons and the maximum of the factor $x^4e^x/(e^x-1)^2$ is at $x \simeq 3.8$.] For these phonons the coupling strength with a donor depends strongly on the donor wave function [see Eq. (5)] and then in the calculation of $K(T)$ we should use the true wave function which we don't know at present. Therefore we will not further discuss this.

It should be emphasized that if the Li donor has a "normal" ground state, the strong scattering of phonons cannot be expected at lower temperatures. Figure 7 shows the calculated $K(T)$ for the Li donor with a "normal" and an "inverted" ground state for sample No. 5 ($N = 5\times10^{16}$ cm^{-3} and $L = 0.258$ cm). For comparison, the experimental data are also given there. It is noted that the strength of the phonon scattering per one electron at $T \lesssim 3\,^{\circ}$K is stronger for an "inverted" ground state than for a "normal" ground state. (Recall that in the former only $\frac{2}{5}$ of the total donor electrons contribute to the phonon scattering at $T \ll \Delta/k$.) This is due to the contribution of a nonresonant-type scattering by electrons in the E state as mentioned in Sec. III C (see Fig. 3).

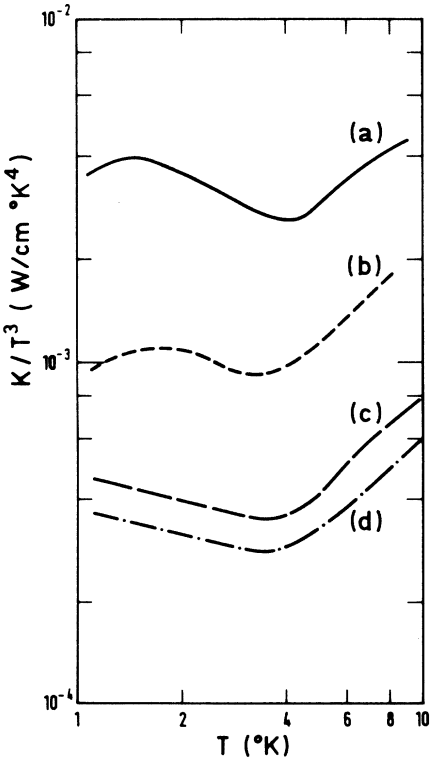

FIG. 8. Experimental curves of K/T^3 as a function of T. (a), (b), (c), and (d) represent K/T^3 for samples 4, 7, 9 and 10, respectively.

Larger thermal resistance at the lower temperature might be expected in the following cases.

(a) The small splitting between the E and T_2 states exists and the E state is the lowest.

(b) The small splitting of the E state exists and it distributes over a certain energy range, for example, in a Gaussian or Lorentzian form as has been considered to explain the ultrasonic attenuation of p-Si.[19] In this case, the strong scattering of low-frequency phonons via the resonance process may occur and this scattering become rapidly ineffective with increasing temperature, though of course this depends on the form of the distribution of the splitting energy. This kind of splitting may be caused by, for example, dislocation and the scattering of low-frequency phonons by electrons depends on the dislocation density in the sample as has recently been shown by Ishiguro.[20] However we don't know the dislocation density in our samples.

(c) The phonon scattering by a molecule-ion-type center or a molecule-type center. For simplicity, let us suppose a homopolar pair. The scattering of low-frequency phonons by this for low donor concentrations may be stronger for Li donor than for group-V donors. This is due to the following reasons. In the former the level splitting among bonding states and among antibonding states as well as between bonding and antibonding states occurs because a pair has lower symmetry than a single impurity center has. On the other hand, in the latter, only the transition between bonding and antibonding states occurs and the scattering of transverse phonons is quite weak as long as the valley-orbit splitting is much larger than the resonance energy of a pair.[21] It is remarked that electrons in T_2 state can also scatter phonons by the transition between bonding and antibonding states because of $\underline{D}^{ii} \neq 0$ ($i = 3, 4, 5$). The same things would be expected for a molecule-type center. Note that the magnitude of the level splitting distributes over a certain range due to a random distribution of impurities and then we need consider only the resonance scattering by these centers.[22]

We have given K/T^3 as a function of T for samples 4 and 8, in Fig. 8 which reflects the temperature dependence of τ [see Eq. (18)]. As the relaxation rate varies as T^2 at lower temperatures where only the elastic scattering becomes effective,

$f(q) \simeq 1$ and N_1 become independent of T in our simple model [see Eq. (10) or Eq. (17)], Fig. 8 shows that another factor or other scattering process becomes more effective with decreasing temperature. Such an aspect of phonon scattering would be expected for a, b, and c mentioned above. K/T^3 for samples 9 and 10 have also been shown in Fig. 7 which shows that the state of electrons contributing to phonon scattering at lower temperatures appears to be different from that in samples with lower donor concentration.

Finally we shall briefly discuss on the dynamic Jahn-Teller effect. Recently, Morgan stressed the importance of this effect on a shallow impurity state with the degenerate level in semiconductors.[23,24] Challis and Halbo have suggested that this effect has a considerable effect on the thermal conductivity of p-Ge.[25,26] As Watkins and Ham have pointed out,[9] however, the coupling strength of electrons in the E state with lattice vibration is very weak. (The Jahn-Teller energy is smaller than 1 °K.) Then it seems to us that this effect has not a considerable effect on the present problem and also on p-Ge in which the Jahn-Teller energy is about 0.1 °K.[27]

In conclusion, measurements of the thermal conductivity at the temperature region lower than 1 °K and the ultrasonic attenuation would be of interest to understand the scattering of low-frequency phonons by a Li donor in Si.

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APPENDIX

For the D_{3d} symmetry, α_n's in Eq. (2) are as follows[10]:

$$\begin{aligned}
A_{1g}&: \frac{1}{\sqrt{6}}(1,1,1,1,1,1)\,,\\
E_g^{(1)}&: \frac{1}{\sqrt{12}}(1,1,1,1,-2,-2)\,,\\
E_g^{(2)}&: \tfrac{1}{2}(-1,-1,1,1,0,0)\,,\\
A_{2u}&: \frac{1}{\sqrt{6}}(1,-1,1,-1,1,-1)\,,\\
E_u^{(1)}&: \frac{1}{\sqrt{12}}(1,-1,1,-1,-2,2)\,,\\
E_u^{(2)}&: \tfrac{1}{2}(-1,1,1,-1,0,0)\,.
\end{aligned} \tag{A1}$$

Therefore the $\underline{D}^{nn'}$s are given by

$$\begin{aligned}
&\underline{D}^{11}=\underline{D}^{44}=\underline{D}^{00}-\frac{1}{\sqrt{2}}\underline{D}^{01}\,,\quad \underline{D}^{22}=\underline{D}^{55}=\underline{D}^{00}+\frac{1}{\sqrt{2}}\underline{D}^{01}\,,\\
&\underline{D}^{12}=\underline{D}^{45}=\frac{1}{\sqrt{2}}\underline{D}^{02}\,,\quad \underline{D}^{ij}=0\ (i=0,1,2,\ j=3,4,5)\,,
\end{aligned} \tag{A2}$$

where $\underline{D}^{00}$, $\underline{D}^{01}$, and $\underline{D}^{02}$ are given by Eq. (9).

If $(A_{2u}+E_u^{(1)}+E_u^{(2)})$ states are degenerate, only the elastic scattering is allowed due to energy conservation and the selection rule in Eq. (A2) and the relaxation rate by this process turns out zero [see Eqs. (10)–(12) which become zero when $\Delta \to 0$].

It is noted that when T_2 or $(A_{2u}+E_u^{(1)}+E_u^{(2)})$ states are split, the scattering strength of phonons depends on the site symmetry of the Li donor and it is stronger for the D_{3d} symmetry than for the T_d symmetry as can be seen from Eqs. (8) and (A2).

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