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[9]Passage of a boojum on the surface or a 4π vortex (for definition, see Ref. 8) in the bulk across L means that an area 4π has been swept though by the line $\hat{l}(L)$ in S_l^2.

[10]This configuration in the bulk, apart from some twisting along $\hat{z}$, corresponds to the 0-π-0 soliton in Ref. 3. Note that when the rectangles *abcda* and *adefa* in Fig. 1(a) cover the lower hemisphere of S_l^2 [Fig. 1(b)] once but with + and − orientation, they can be viewed as a pair of $\pm 2\pi$ vortices. The whole configuration in *adefa* is then deformable into an uniform one (see Ref. 8).

[11]In our discussions, we have only talked about the textures but not the order parameters $\hat{\varphi}$. The reason is that in simply connected containers, deformations of $\hat{\varphi}$ subject to the usual boundary condition are characterized by the deformations of their textures. Suppose the textures $\hat{l}_a$ and $\hat{l}_b$ of order parameters $\hat{\varphi}_a$ and $\hat{\varphi}_b$ are connected by a deformation $\hat{l}_t = R(t)\hat{l}_a$, $0 \leq t \leq 1$, which satisfies the boundary condition for all t, where $R(t)$ is a rotational matrix satisfying $R(0)=1$, $R(1)\hat{l}_a = \hat{l}_b$. Using the $\vec{\nabla}\times\vec{v}_s$ equation [N. D. Mermin and T. L. Ho, Phys. Rev. Lett. 36, 594 (1976)], it is easy to see that $\hat{\varphi}_a' \equiv R(1)\hat{\varphi}_a$ differs from $\hat{\varphi}_b$ only by a phase factor $e^{i\chi}$. The family $\hat{\varphi}^t = e^{it\chi} R(t)\hat{\varphi}_a$ hence carries $\hat{\varphi}_a$ continuously into $\hat{\varphi}_b$.

[12]Our conclusions, however, do not depend on this particular choice of boundary texture.

[13]In case we change the boundary texture in Ω and put a boojum on the curved surface (the line $\overline{bc}$ in Fig. 2), the texture between the contour Λ_1 and the boundary $\overline{s_1bcd}$ in Fig. 2 will then be time dependent because the boojum will move on the surface. However, the bulk texture (that enclosed by Λ_1) is still decoupled from that near the surface.

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Valley-Orbit Splitting of Li in Ge

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The thermal conductivity of germanium doped with lithium in the isolated impurity range has been measured between 0.4 and 20 K. The analysis of the electron-phonon scattering leads, for the first time, to a determination of the valley-orbit splitting (0.12 meV) of the ground state of the interstitial Li donor in Ge.

It is well known that in semiconductors phonon scattering by electrons bound to shallow impurities depends strongly on the electronic structure[1] of the latter. This was particularly emphasized in recent works on Li and other donors in silicon.[2-5] Therefore phonon scattering is useful in the study of unknown impurity states. Among shallow donors in Ge and Si, only the ground state of a Li donor in Ge is still not known. The electronic structure of the ground state of Li in Si, which was suggested theoretically[6] to be of the D_{3d} symmetry, was found[7,8] to correspond to the T_d site with an "inverted" Group-V–like ground state and a valley-orbit splitting of 1.8 meV. The ground state of Li in Ge, which is fourfold degenerate in the effective-mass approximation, involves a singlet A_1 and a triplet T_2 in case of the T_d symmetry, and two singlets A_{2u} and a doublet E_u for the D_{3d} site. No convincing experimental evidence for a splitting of the ground state is so far available. However, the calculations of Nara and Yamazaki[9] indicate that the ground state is expected, in the case of the T_d site, to exhibit an "inverted" structure (the triplet lying below the singlet) with a singlet-triplet interval of 0.15 meV, and to be nearly degenerate in the case of the D_{3d} symmetry. In this Letter, we present for the first time a determination of

the valley-orbit splitting of the ground state of Li in Ge, obtained from low-temperature thermal conductivity results.

Thermal conductivity measurements were performed between 0.4 and 20 K on Ge samples doped with Li in the concentration range of isolated impurities. The Ge samples used were initially p type with an acceptor concentration of 1×10^{14} cm^{-3}. The doping with Li was carried out using the diffusion technique previously adopted for silicon.[2,5] The lithium concentrations were determined from Hall-coefficient measurements (Table I). The homogeneity in the samples was checked electrically to be better than $\pm5\%$. The experimental data for starting and Li-doped Ge samples are shown separately in Figs. 1(a) and 1(b) for clarity. In the low-temperature interval, the thermal conductivity K decreases with increasing Li doping, as a result of phonon scattering by electrons bound to Li donors.

The experimental results were analyzed on the basis of the standard conductivity integral, using the Holland model[10] with the two polarization modes. For the low-temperature interval considered, the contribution of the umklapp transverse term, K_{tu}, to K is negligible. Thus the phonon relaxation rates used for scattering by boundaries (τ_B^{-1}), isotopes (τ_I^{-1}), and phonons (τ_{ph}^{-1}) were, respectively, v_t/L, $A\omega^4$, and $B_t\omega T^4$ for transverse phonons, and v_l/L, $A\omega^4$, and $B_l\omega^2T^3$ for longitudinal phonons. The following numerical values of the parameters were used,

TABLE I. Doping and the Casimir length ($L=2\pi^{-1/2}\times s^{1/2}$) for a selection of Ge samples measured.

Sample	Doping (cm^{-3})	L (cm)
Ge(Ga) I	1×10^{14} (Ga)	0.26
Ge(Li) I	1.5×10^{15} (Li)	0.26
Ge(Li) II	3.5×10^{15} (Li)	0.255
Ge(Li) III	4.8×10^{15} (Li)	0.26

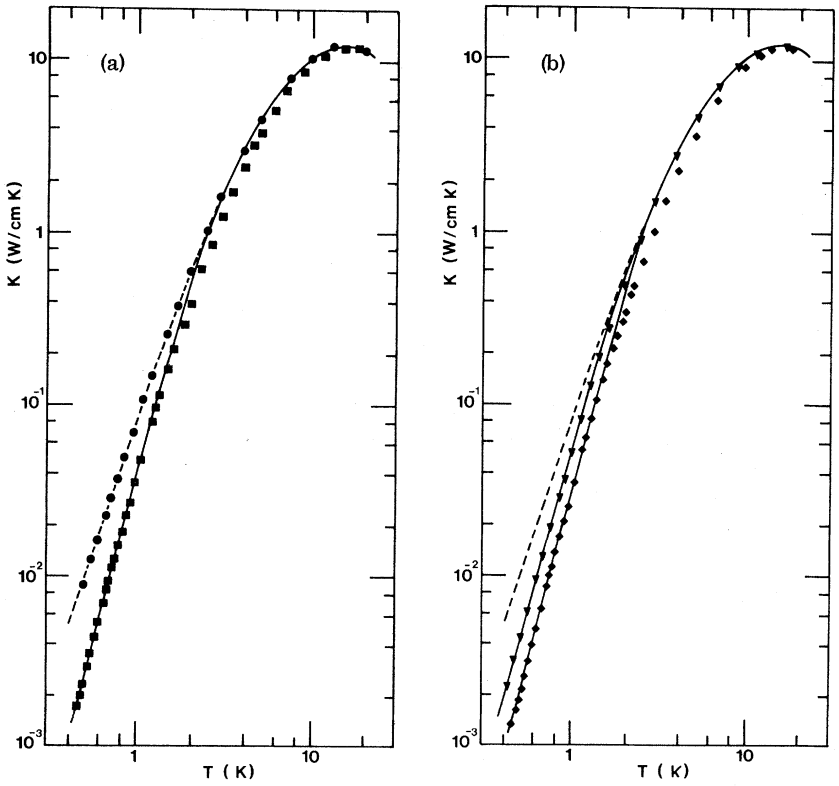

FIG. 1. The thermal conductivity K of starting and Li-doped germanium samples. (a), (b) Experimental points: starting, closed circles; Li doped, closed triangles (1.5×10^{15} cm^{-3}), squares (3.5×10^{15} cm^{-3}), closed diamonds (4.8×10^{15} cm^{-3}). Dotted line, calculated K for starting sample. Full lines, calculated curves for Li-doped samples, assuming a symmetry T_d and an inverted structure for the Li donor. The fits were obtained for a value $\Delta=0.12$ meV of the singlet-triplet interval, considered as an adjustable parameter. (Practically, equivalent fits were obtained, assuming a T_d symmetry and a normal structure, with $\Delta=0.11$ meV.)

which give a very satisfactory fit to the data for the starting germanium (Fig. 1): $v_t = 3.28 \times 10^5$ cm s^{-1} and $v_l = 5.37 \times 10^5$ cm s^{-1} (Ref. 11); $A = 2.4 \times 10^{-44}$ s^3, $B_t = 1 \times 10^{-11}$ K^{-4}, and $B_l = 6.9 \times 10^{-24}$ s K^{-3} (Ref. 10). It is known that the low-temperature lattice thermal conductivity is essentially due to transverse phonons.

In addition to the above usual phonon-scattering mechanisms, three types of second-order processes were considered for the electron-phonon interaction[12,13]: the elastic ($\bar{\tau}_e^{-1}$) and inelastic ($\bar{\tau}_1^{-1}$) scatterings, and the thermally assisted phonon absorption ($\bar{\tau}_2^{-1}$). The corresponding angular average of the relaxation rates were calculated by Suzuki and Mikoshiba[13] for the T_d symmetry and a normal structure. For an inverted structure, the occupation rates of the singlet (N_S) and the triplet (N_T) levels in the expressions of the relaxation rates $\bar{\tau}_1^{-1}$ and $\bar{\tau}_2^{-1}$ must be permuted, and replaced by the following relations (with inclusion of $\bar{\tau}_e^{-1}$):

$$N_S = \frac{N}{1+3\exp(\Delta/kT)}, \quad N_T = \frac{N}{3+\exp(-\Delta/kT)},$$

where N is the impurity concentration. For the electron-phonon interactions considered in the present Letter, the deformation potential Ξ_u was taken equal[13] to 16 eV, and the effective Bohr radius adopted ($a^* = 44$ Å), for Li in Ge was determined in the effective-mass approximation. The behavior of the relaxation rates τ_B^{-1}, τ_I^{-1}, $\bar{\tau}_e^{-1}$, $\bar{\tau}_1^{-1}$, and $\bar{\tau}_2^{-1}$ as a function of the angular frequency ω is shown in Fig. 2. This was calculated for $T = 0.6$ K, a donor concentration $N = 3.5 \times 10^{15}$ cm^{-3}, and a singlet-triplet separation $\Delta = 0.12$ meV for both normal and inverted structures. It is to be noticed that $\bar{\tau}_1^{-1}$ and $\bar{\tau}_2^{-1}$ are always masked by τ_B^{-1} or $\bar{\tau}_e^{-1}$. Similar conclusions were obtained for donors in Si.[2-5] Thus the influence of $\bar{\tau}_2^{-1}$ in the calculation of K is very small. In addition it can be seen that the $\bar{\tau}_e^{-1}$ of the normal structure is slightly higher to the $\bar{\tau}_e^{-1}$ of the inverted structure for $\omega > 2 \times 10^{11}$ s^{-1} and lower to it for $\omega < 2 \times 10^{11}$ s^{-1}. This leads for $T > 0.4$ K to a thermal conductivity slightly higher for an inverted structure than for a normal one, and to an opposite behavior for $T < 0.4$ K.

The fit to the experimental data was carried out, with the singlet-triplet interval Δ as an adjustable parameter. Good fits for the Li-doped samples with different concentrations were obtained[14] for $\Delta = 0.12$ meV in the case of an inverted structure (a slightly lower value, $\Delta = 0.11$ meV, for a normal structure). This corresponds to the first

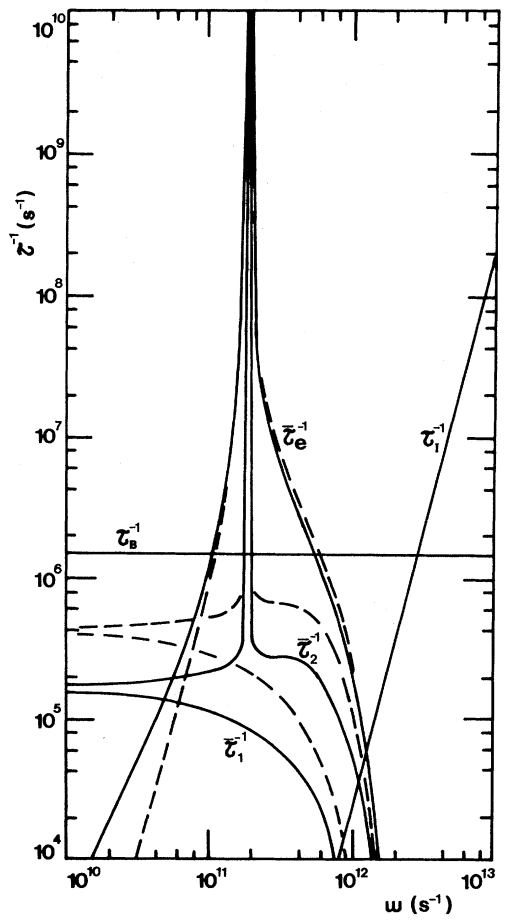

FIG. 2. Variation of different phonon relaxation rates as function of the angular frequency ω, assuming a T_d symmetry. (This was calculated for $T = 0.6$ K, donor concentration $= 3.5 \times 10^{15}$ cm^{-3}, and $\Delta = 0.12$ meV). Dashed and full lines correspond, respectively, to normal and inverted structures.

experimental determination of the chemical splitting, a value which is close to the theoretical one ($\Delta = 0.15$ meV) estimated by Nara and Yamazaki.[9] Small or acceptable modifications (up to about $\pm 20\%$) of the values adopted for the deformation potential and the Bohr radius do not lead to a variation of more than about $\pm 10\%$ of the deduced value of Δ. The difference between the calculated K for normal and inverted structures is not significant enough to distinguish between the two structures. For Li concentrations higher than approximately 6×10^{15} cm^{-3}, no acceptable fit to the experimental data could be obtained on the basis of the above analysis. This is in agreement with the fact that Li impurities can no more be considered as isolated.

As the site of Li in Ge is presently not estab-

lished, it was of interest to investigate the effect of the D_{3a} symmetry on the phonon scattering, and to compare it to that observed for the T_d site. The expressions of the relaxation rates calculated for D_{3d} symmetry,[15] using the Nara and Yamazaki wave functions,[16] are similar to the corresponding ones for the T_d site. They become zero for a completely degenerate ground state. Therefore, since the theory of Nara and Yamazaki[9] predicts a nearly degenerate ground state for the D_{3d} symmetry, the present experiment is in favor of the T_d symmetry as long as we accept the above theory. However, if we consider the value of the splitting in the D_{3d} site as an adjustable parameter, the analyses of the experimental data[15,17] give practically the same value of the splitting as for the T_d symmetry, for both normal and inverted structures.

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[17]Using Nara and Yamazaki's approximation, the analyses of the experimental data for the D_{3d} site were carried out using the deduced relaxation rates, and assuming the value of the splitting as an adjustable parameter. The allowed transitions were found to take place between the doublet E_u and the singlet $A_{2u}{}^2$. However the position of the $A_{2u}{}^1$ state has an effect on the electronic populations. Satisfactory fits were again obtained for an energy separation $\Delta \simeq 0.12$ meV between E_u and $A_{2u}{}^2$, for both normal and inverted structures. The singlet $A_{2u}{}^1$ was found to lie between E_u and $A_{2u}{}^2$, with an energy separation Δ' from $A_{2u}{}^2$ of about 0.07 and 0.05 meV for the normal and inverted structures, respectively. The calculated thermal conductivity K is much less sensitive to Δ' than to Δ. The equivalent result ($\Delta = 0.12$ meV) obtained for both symmetries arises from the fact that the relaxation rates for electron-phonon interaction are similar for both T_d and D_{3d}.