Thermal Conductivity of p-Ge down to 50 mK

L. J. Challis
Department of Physics, University of Nottingham, Nottingham, United Kingdom

and

A. M. de Goër
Service Basses Températures, Centre d'Etudes Nucléaires, Grenoble, France

and

S. C. Haseler
Department of Physics, University of Nottingham, Nottingham, United Kingdom

(Received 16 May 1977)

Thermal conductivity measurements on samples of p-Ge down to 50 mK indicate the presence of an approximately Gaussian distribution of resonant scattering frequencies which has a width $\Delta \sim 30$ GHz. The data suggest that this is due to about half of the acceptors which are in distorted sites while the other half are relatively free from distortion. The "two-site" model reconciles disagreements in linewidth from different types of experiment. We obtain a value for $D_{u'}{}^{a}$ (dynamic) = 4.1 ± 0.4 eV.

The nature of the acceptor ground state in Ge has recently been the subject of some debate. If the Jahn-Teller effect can be neglected, the ground state is fourfold degenerate, Γ_8, although random strains would split this into two Kramers doublets. If the Jahn-Teller effect cannot be neglected, there may also be vibronic states associated with the ground state. In this Letter we present information on the distribution of resonant frequencies $N(\omega_0)$ arising from these low-lying levels which has been obtained from thermal conductivity measurements down to 50 mK.

Measurements were made on three specimens doped with Ga or In (Table I).[1] Below 1 K the sample contacts were indium-faced copper clamps, spring loaded to minimize strains. One experiment was repeated with the sample ends indium soldered to copper posts and with thermometer contacts attached with epoxy resin. The data agree to within experimental error indicating that strains due to sample mounting have no significant effect on the results. A selection of the data is shown in Fig. 1. This is plotted both as the conductivity $K(T)$ and as K/T^3 which shows the temperature variation of an average phonon mean free path. Below 10 K, the mean free path decreases with acceptor concentration n_a. The broken curve shown is calculated using the standard conductivity integral with $\theta_D = 310$ K and a phonon relaxation rate which includes both "intrinsic" and acceptor scattering. The "intrinsic" rates τ_B^{-1}, $A\omega^4$, and $B_N\omega^2T^3$ describe scattering by boundaries, isotopes, and phonons, respectively, and account for the conductivities above 10 K. τ_B^{-1} (see Table I) and $A = 2.1\times10^{-44}$ s^3 are the theoretical values and $B_N = 7\times10^{-23}$ (s K^{-3}) is

TABLE I. Specimen details. The samples were Czochralski grown at the Royal Radar Establishment from germanium supplied by Metallurgie Hoboken. Undoped crystals obtained from the same source contain $n_d \sim 2\times10^{13}$ cm^{-3} and $n_a \sim 1.6\times10^{13}$ cm^{-3}. Samples II 1 and IV were grown in argon with no encapsulant while VII 1 was grown in a 90% N_2, 10% H_2 mixture with a B_2O_3 encapsulant. The surfaces of II 1 and VII 1 for which boundary scattering was of most importance were sandblasted before the measurements were made. The sample axes were along ⟨110⟩ directions. The acceptor concentrations n_a were determined from Hall measurements at 77 K and τ_B^{-1} was calculated with allowance for phonon focusing.

Sample	Doping	Cross section (mm^2)	τ_B^{-1} (s^{-1})	n_a (cm^{-3})	$D_{u'}{}^{a}$ (dynamic) (eV)	$N_0\bar{D}^2$ (eV^2 GHz^{-1} cm^{-3})	Δ (GHz)
VII 1	Ga	3.33×3.43	1.13×10^6	5×10^{14}	4.3	8.0×10^{12}	28
II 1	Ga	3.41×3.42	1.13×10^6	3×10^{15}	3.8	2.5×10^{13}	35
IV	In	3.10×3.21	1.21×10^6	1.1×10^{16}	4.2	7.8×10^{13}	38

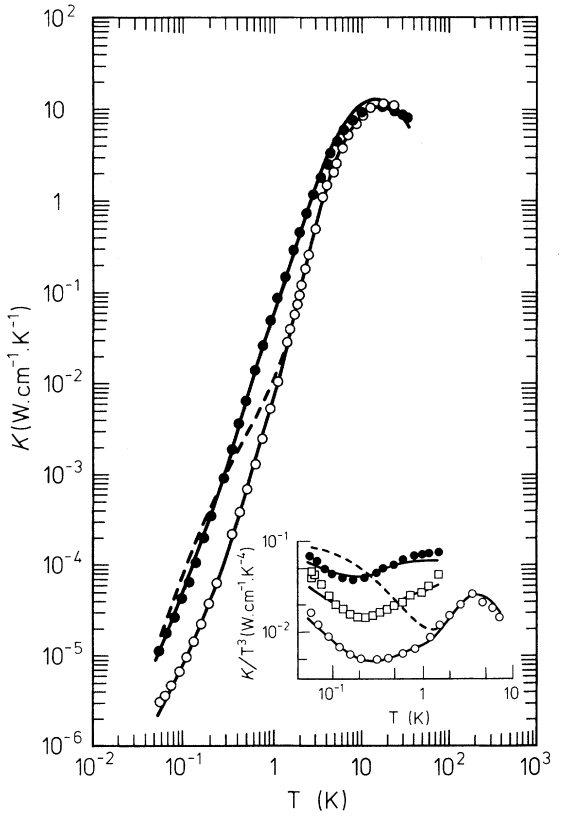

FIG. 1. The thermal conductivity and K/T^3 for the germanium samples. ●, VII 1 (5×10^{14} Ga cm^{-3}); □, II 1 (3×10^{15} Ga cm^{-3}); ○, IV (1.1×10^{16} In cm^{-3}). The broken line is calculated including τ^{-1} (intrinsic) and τ_{SM}^{-1} The effect of adding resonant scattering τ_R^{-1} is shown by the solid lines.

chosen to fit the high-temperature data.

The phonon-scattering rate by acceptors $\tau_{SM}^{-1} = M\omega^2(1+a^{*2}\omega^2/4v^2)^{-8}$ has the form calculated by Suzuki and Mikoshiba[2] for a degenerate quartet. a^* is the Bohr radius of the acceptor wave function and v is a mean phonon velocity defined by $3v^{-3} = v_l^{-3} + 2v_t^{-3}$. The term in parentheses in τ_{SM}^{-1} acts as a cutoff function which describes the reduction in the scattering from $M\omega^2$ that occurs when the phonon wavelength λ falls below a^*. This expression for τ_{SM}^{-1} is an average of expressions for longitudinal and for transverse modes[2] and in this average

$$M = n_a(2D_{u'}^{\,a}/3)^4(v_l^{-5} + \tfrac{3}{2}v_t^{-5})W/100\pi\rho^2\hbar^2v^2,$$

where ρ is the density of germanium and $D_{u'}^{\,a}$ is the deformation potential for T_2-type lattice distortions. The potential $D_u^{\,a}$ for E-type distortions enters through a function $W(D_{SM}) = \frac{1}{3}(W_1 + W_2 + W_3)$, where $D_{SM} = D_u^{\,a}/D_{u'}^{\,a}$, and W_1, W_2, and W_3, are defined in Ref. 2. Both potentials should have their "dynamic" values since τ_{SM}^{-1} is only really significant at the higher phonon frequencies, $\omega \sim v/a^*$. The numerical values of the parameters used including $D_{SM} = 0.86$ are those of Ref. 2 with the exception of a^*; to improve the fit to the experimental data we use a value of $a^* = 35$ rather than 37 Å.

The broken curve in Fig. 1 was obtained by adjusting the value of M to fit the data above 1 K for for sample IV. The effect of the cutoff function is seen in the rise of K/T^3 as the temperature increases from 1 to 4 K. Below 1 K the cutoff weakens and $\tau_{SM}^{-1} \sim \omega^2$. Hence as T falls, K/T^3 rises and would eventually saturate at the boundary-scattering limit. The values of M for the three specimens give the values of $D_{u'}^{\,a}$ (dynamic) shown in Table I which have a mean of 4.1 ± 0.4 eV. (Previous values are 4.9,[2] 3.9 ± 0.4,[3] and 5.1 ± 0.7 eV[3]). Figure 1 suggests that the theory provides a good description of the acceptor scattering in the range 1.5–5 K, that is, for frequencies ~100–400 GHz. Below 1 K the scattering still correlates with n_a and so is presumably due to the acceptors but its strength is much greater than that indicated theoretically. We conclude that the ground-state structure is no longer a good approximation to a degenerate quartet for frequencies $\gtrsim$100 GHz.

The form of K/T^3 suggests that the additional scattering is resonant and we suppose that the resonant frequencies have a distribution $N(\omega_0)$. For first-order scattering when, as here, $\hbar\omega \gg kT$ for most of the phonons, we may write[4] $\tau_R^{-1}(\omega) = \pi\bar{D}^2\omega N(|\omega_0| = \omega)/\hbar\rho v^2$, where $\bar{D}$ is a deformation potential. $N(|\omega_0|) = 2N(\omega_0)$ for a symmetrical distribution and $n_a = \int_{-\infty}^{+\infty} N(\omega_0)d\omega_0$. Now since $\tau_R^{-1}(\omega) \propto \omega N(\omega) \propto (K/T^3)^{-1}$ for the dominant phonons of frequency $\omega \sim 4kT/\hbar$, $N(\omega) \propto T^2/K$ and the data for sample IV plotted in this form in Fig. 2 suggest that $N(\omega)$ might be approximately Gaussian: $N(\omega) = N_0 \exp(-\omega_0^2/\Delta^2)$. By adding a $\tau_R^{-1}(\omega)$ of this form to τ_{SM}^{-1} and τ^{-1} (intrinsic) and adjusting $N_0\bar{D}^2$ and Δ we obtain the solid lines in Fig. 1. The values of the parameters are given in Table I and are similar to values obtained using a Lorentzian although this gave a slightly poorer fit.

The distribution width Δ is large, ~30 GHz, for all three samples. It appears to depend only weakly if at all on n_a and is similar for Ga and In acceptors and for samples grown under different conditions. Its value is strikingly different from values of $\Delta \sim 1$ GHz obtained from magnetoacous-

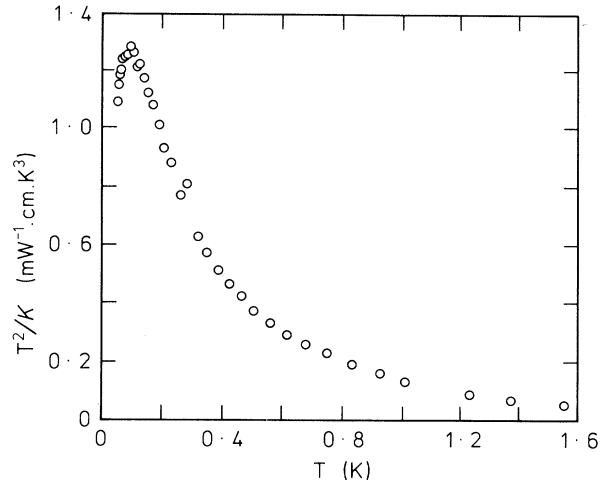

FIG. 2. The experimental values of T^2/K for specimen IV.

tic resonance linewidths in samples of comparable doping.[5] It is comparable, however, with optical linewidths Δ_0 for transitions from the ground state measured on sample VII using the photoconductivity technique.[6] Thus Δ_0 is 40 GHz for the lowest transition G and 70 GHz for C and D in the usual notation and with Δ_0 defined as $1/e$ times the full width at maximum height for proper comparison with Δ. Now although Δ and Δ_0 are roughly comparable this is also very surprising since the broadening mechanisms are believed to have much larger effects on the excited states than on the ground state[7] so that the ground-state widths should be very much less than Δ_0.

The likely reason for this disagreement is suggested by a comparison of the values $N(\omega_0)\overline{D}^2$ obtained in the present work with those obtained in recent work on ultrasonic attenuation,[8] $[N(\omega_0)\overline{D}^2]_u$. From the ultrasonic work $[N(\omega_0)\overline{D}^2]_u$ was found to be constant from 0.5 GHz and equal to 6.5×10^{14} eV^2 GHz^{-1} cm^{-3} in sample 10 which is a neighboring slice from the same ingot as sample IV. This is 8.4 times larger than our low-frequency limit $N_0\overline{D}^2 = 7.8\times10^{13}$ eV^2 GHz^{-1} cm^{-3} for IV. Now the ultrasonic values are for longitudinal phonons traveling along the $\langle 110\rangle$ direction for which $\overline{D} = 1.1\overline{D}_{\rm av}$, where $\overline{D}_{\rm av}$ is an average over all modes and directions,[9] so that $N(\omega_0)_u = 8.4N_0/1.1^2 = 6.9N_0$.

The data imply then that as ω_0 falls, $N(\omega_0)$ rises from its approximately constant value of N_0 at $\omega_0 \gtrsim 5$ GHz to a near-flat central peak below 2.5 GHz. The central peak has a height $N_0{}^c \sim 7N_0$ and must have a width $\Delta^c \sim 4$ GHz $\sim \Delta/7$ so that if it is also approximately Gaussian it will contain an acceptor concentration of $\pi^{1/2}N_0{}^c\Delta^c \sim \pi^{1/2}N_0\Delta$. So both distributions contain approximately equal concentration $\frac{1}{2}n_a$.[10]

A rough check on this conclusion is provided by calculating a value for $D_u{}'^a$ (static: $\omega \ll v/a^*$) from $\pi^{1/2}N_0\Delta = \frac{1}{2}n_a$. For sample IV, $\Delta = 38$ GHz, so that $N_0 = 8.2\times10^{13}$ GHz^{-1} cm^{-3} and, since $N_0\overline{D}_{\rm av}{}^2 = 7.8\times10^{13}$ eV^2 GHz^{-1} cm^{-3}, we obtain a value $\overline{D}_{\rm av} = 0.98$ eV. Now $\overline{D}_{\rm av} = \alpha_{\rm av}(\frac{2}{3}D_u{}'^a)$, where $\alpha_{\rm av} = 0.77$[9] so that $D_u{}'^a = 1.9$ eV. This is in reasonable agreement with previous measurements for $D_u{}'^a$ (static) of 2.2 ± 0.3 eV (and $D_{\rm SM} = 0.95 \pm 0.2$)[11] and 2.3 ± 0.2 eV.[3]

We propose, then, a "two-site" model for acceptors in germanium. We suggest that about half the acceptors are in largely undistorted sites with ground-state splittings $\lesssim 4$ GHz—that is, splittings too small to be seen by the present technique. These acceptors are responsible for most of the optical absorption and for the peaks in the magnetoacoustic measurements. The other half of the acceptors are in distorted sites. They would only be seen in the wings of the optical absorption peaks and hardly at all in the magnetoacoustic work since in most cases their levels would anticross with minimum separations greater than the phonon energy. However, they are selected from the rest by the present experiments since the resonance scattering they give rise to lies within the measurement range. They would also be responsible for the additional scattering seen or inferred in a number of other phonon experiments on p-Ge.[3,1] The distortions could possibly be due to charged or neutral impurities[12] or to dislocations if the distorted acceptors are in Cottrell atmospheres around them but the near independence of Δ on n_a tends to eliminate acceptor-acceptor interactions as the cause. We cannot rule out the possibility that there is scattering by vibronic states though in this case we should expect $N(\omega_0)$ to increase with ω_0 to $\sim v/a^*$ unless the structure were very anharmonic. Finally we note that the strong scattering up to ~30 GHz together with the very small g values recently determined[5] can probably explain the remarkably small magnetothermal conductivity of p-Ge.[1]

We are very grateful to M. Locatelli and M. W. S. Parsons for help with the measurements, R. Cooke and R. A. Stradling for their kindness in making the optical measurements, H. Tokumoto and T. Ishiguro for helpful discussions and for sending us their data prior to publication, and J. R. Fletcher, O. Jones, K. Lassmann, A. Ramdane, and several other colleagues for helpful

discussions. We also wish to acknowledge support for this collaborative project from the Ministère des Affaires Etrangères and the Science Research Council.

[1]Measurements above 1 K on a number of other samples are given by L. J. Challis, S. C. Haseler, M. W. S. Parsons, and J. Rivallin, in *Phonon Scattering in Solids*, edited by L. J. Challis, V. W. Rampton, and A. F. G. Wyatt (Plenum, New York and London, 1976), p. 328; and on one sample down to 0.2 K by J. A. Carruthers, J. F. Cochran, and K. Mendelssohn, Cryogenics 2, 160 (1962). See also L. J. Challis and L. Halbo, Phys. Rev. Lett. 28, 816 (1972); L. Halbo and L. J. Challis, in *Proceedings of the International Conference on Phonon Scattering in Solids, Paris, 1972*, edited by H. J. Albany (Commissariat à l'Energie Atomique, Saclay, 1972), p. 139. The explanation of these data in terms of a small g value is given in H. Tokumoto and T. Ishiguro, Phys. Rev. B 15, 2099 (1977), on the assumption that Δ is large.

[2]K. Suzuki and N. Mikoshiba, Phys. Rev. B 3, 2550 (1971).

[3]T. Fjeldly, T. Ishiguro, and C. Elbaum, Phys. Rev. B 7, 1390 (1972). The interaction Hamiltonian used by these authors differs from that used here in that $(\frac{2}{3}D_{u'})f(q)$ replaces $(\frac{2}{3}D_{u'}{}^{a})(1+a^{*2}\omega^2/4v^2)^{-2}$, where $f(q)$ is a more complicated cutoff function allowing for the d-like parts of the acceptor wave functions. We obtain a value of $D_{u'}{}^{a}$ (dynamic) by taking the high-frequency limit, $f(q)=0.74(1+a^{*2}\omega^2/v^2)^{-2}$, which is a reasonable approximation for $\nu \gtrsim 150$ GHz, and so $D_{u'}{}^{a}$ (dynamic) $=0.74D_{u'}$ (dynamic). The value of $D_{u'}{}^{a}$ (static) comes directly from the zero-frequency value of $f(q)$ giving $D_{u'}{}^{a}$ (static) $=0.61D_{u'}$ (static).

[4]J. Jäckle, Z. Phys. 257, 212 (1972).

[5]Tokumoto and Ishiguro, Ref. 1.

[6]R. Cooke and R. A. Stradling, private communication.

[7]J. J. White, Can. J. Phys. 45, 2695 (1967); D. M. Larsen, Phys. Rev. B 8, 535 (1973); see also K. K. Bajaj, J. R. Birch, L. Eaves, R. A. Hoult, R. F. Simmonds, and R. A. Stradling, J. Phys. C 8, 530 (1975).

[8]E. Ortlieb, H. P. Schad, and K. Lassmann, Solid State Commun. 19, 599 (1976), and private communication. We note that their theoretical expression α_{res} refers to the ratio of ultrasonic amplitudes and that the concentration of Ge(10) should be 1.1×10^{16} cm^{-3}. Their published figure of 8×10^{15} cm^{-3} was incorrectly supplied by us with the sample.

[9]L. J. Challis and A. M. de Goër, Centre d'Etudes Nucléaires, Grenoble, Internal Report No. SBT 437/77, 1977 (unpublished). $\bar{D}$ depends on the eigenstates of the strain-split levels which are determined by the symmetry of the strains. Writing $\bar{D}=\alpha(\frac{2}{3}D_{u'}{}^{a})$, we have $\alpha_u{}^2$ ($\langle 100\rangle$, longitudinal) $=(D_{SM}{}^2+6)/8$ (E) and $(D_{SM}{}^2+2)/4$ (T^2) and $\alpha_{av}{}^2$(averaged over all modes and directions) $=(D_{SM}{}^2+3)/6$ (E) and $(D_{SM}{}^2+1)/3$ (T_2). For $D_{SM}=0.86$ these values become 0.84, 0.68, 0.62, and 0.58, respectively, giving an average value of $\alpha_u{}^2/\alpha_{av}{}^2$ of 1.3.

[10]This assumes that the dominant symmetry of the strains is the same in both distributions. The proportions of acceptors in each will differ somewhat if this is not the case. We note too that the distribution appears to have a flatter top than a Gaussian.

[11]R. L. Jones and P. Fisher, Phys. Rev. B 2, 2016 (1970).

[12]Mass-spectrographic analysis of vacuum-grown germanium showed that the concentration of O_2 and C were $\sim 2\times10^{15}$ at cm^{-3} and those of other impurities were less than $\sim 1\times10^{15}$ cm^{-3}. When GeO_2 was added to the melt the O_2 concentration rose to a maximum of 1×10^{17} cm^{-3}. J. B. Clegg and E. J. Millett, Mullard Research Laboratories, private communication. A sample grown under similar conditions to III and IV had an O_2 concentration of 1.6×10^{16} cm^{-3}. O. Jones, Royal Radar Establishment, private communication.

Deuterium Impurities and the Rayleigh Central Peak in Hydrogen-Bonded Ferroelectrics

Eric Courtens
IBM Zurich Research Laboratory, 8803 Rüschlikon ZH, Switzerland
(Received 18 July 1977)

Results of a mean-field treatment of deuterium impurities in hydrogen-bonded ferroelectrics are compared with observations of the critical central peak in potassium dihydrogen phosphate. The natural abundance of deuterium accounts quantiatively for the relative strength and temperature dependence of the peak. Its slow dynamics and the absence of a similar feature in cesium dihydrogen arsenate are commented on.

The occurrence of a critical central peak (CP) in addition to the normal soft mode in the spectra of materials approaching phase transitions from above has stirred considerable interest. Explanations based either on intrinsic nonlinear cluster dynamics or on impurity effects have been proposed.[1] Halperin and Varma have recently shown within the mean-field approximation (MFA) that a small concentration of defects more susceptible than the host is in principle able to account for observations near displacive transitions.[2] They replaced the isolated defects by a uniform distribution over all lattice sites (effective-crystal approximation or ECA) and postulated the defect