Low-Temperature Specific Heat of Germanium*

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Electronic and lattice contributions to the specific heat are reported for several *n*-type degenerate Ge ingots. The electronic effective mass, calculated on the assumption of a parabolic conduction band, is not strongly dependent on donor concentration in Ge. The Debye temperature decreases as donor or acceptor impurities are added, from 371°K for pure Ge to 362°K for the most heavily doped ingot. However, this marked decrease did not occur in silicon-doped Ge. It is suggested that the effect is due to screening of long-range lattice forces by free electrons or holes.

INTRODUCTION

UNTIL recently, there had been significant disagreement in the Debye temperature of germanium as calculated by De Launay from the elastic constants[1,2] and as obtained from the specific heat. At the acoustic frequencies used to measure the elastic constants, phonon velocities are independent of the magnitude of the wave vector, and the Debye temperature calculated from the low temperature elastic constants, $374.0°\mathrm{K}=\theta_0$, should characterize the specific heat at absolute zero. For temperatures below about 1% of θ_0, the lattice specific heat is usually expressed with sufficient accuracy by

$$(12\pi^4/5)R(T/\theta_0)^3=\alpha T^3. \qquad (1)$$

Keesom and Pearlman measured a variety of Ge specimens,[3] obtaining $362\pm6°\mathrm{K}$ for θ_0, but it is likely that effects of helium exchange gas desorption in these measurements resulted in too low a θ_0. Lately, the technique has been improved through the use of a helium-three cryostat employing a mechanical heat switch,[4] so that there is no longer exchange gas to contribute a heat of desorption. Because measurements were now extended to $\frac{1}{2}°\mathrm{K}$ or lower, a more accurate lattice term as well as an electronic term could be observed. Still, the measurement by Keesom and Seidel of a Ge single crystal doped with 5.4×10^{19} cm^{-3} gallium[5] yielded $362\pm2°\mathrm{K}$ for θ_0. About the same time, Flubacher, Leadbetter, and Morrison published the first specific heat value in accurate agreement with the elastic constants, $374\pm2°\mathrm{K}$ for a pure single crystal.[6] The disagreement between these two specific heat measurements is well outside the combined errors and appears to be related to impurity concentration. One of the aims of the present and continuing series of measurements is to study that relationship.

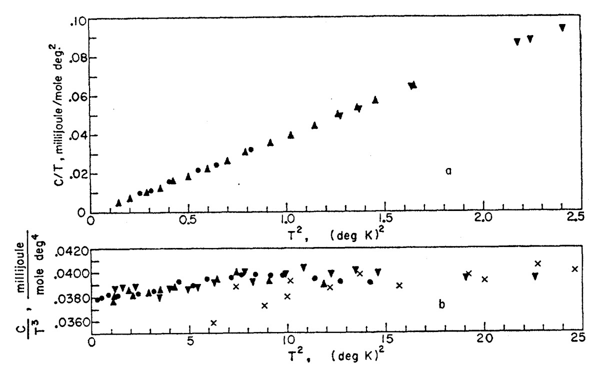

FIG. 1. Specific heat of pure germanium. The points designated by ▼, ▲, and ● are for separate measurements of the same ingot. Results of Flubacher, Leadbetter, and Morrison are denoted by ×.

RESULTS

The specific heat data for each specimen could be represented by

$$C/T=\gamma+\alpha T^2+\beta T^4, \qquad (2)$$

within the precision of the measurement. References 4 and 5 give details of the experimental apparatus and procedure. Figure 1 shows the result from a pure polycrystalline ingot of 563 g which was cast in a high-purity graphite crucible and cooled to a solid over 1.3 hr. The points in Fig. 1(a) are well fitted by a straight line through the origin so that γ is zero within a microjoule/mole deg². The value of α was determined graphically as in Fig. 1(b), where $\lim (C/T^3)$ as $T\rightarrow0$ has the value 0.0380 ± 0.005 mjoule/mole deg⁴ and θ_0 is $371\pm2°\mathrm{K}$ by Eq. (1). The slight upward slope in Fig. 1(b) indicates that $\beta=(0.00015\pm0.00005)$ mjoule/mole deg⁶. Three other specimens were measured, Ge single crystals pulled from the melt, doped with 0.44×10^{18} cm^{-3} Sb, 1.00×10^{18} cm^{-3} Sb, and 3×10^{19} cm^{-3} Si. The Ge(Sb) ingots were sliced after measurement and Hall coefficients determined at intervals along their axes. From these, the impurity concentration n was calculated, and it varied by about a factor of 2 from top to bottom. Following the procedure of Keesom and Seidel,[5] n was then averaged over the volume of the ingot. The

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TABLE I. Results on germanium.

Specimen	Impurity in 10^{18} cm^{-3}	Temp. range deg K	θ_0, deg K	γ, $\frac{\text{mjoule}}{\text{mole deg}^2}$	$\mu=\frac{(m_t^2 m_l)^{\frac{1}{3}}}{m_0}$	$(\zeta^{\frac{1}{2}})_{av}^2$ ev
122B2[a]	4.7 As	0.5–4.2	364±3	0.0215	0.23	0.018
152H[b]	1.00 Sb	0.4–1.4	365±3	0.0146±0.0008	0.27	0.0055
185A[b]	0.44 Sb	0.4–1.1	367±3	0.0098±0.0006	0.23	0.0036
⋯	54 Ga[a]	0.5–4.2	362±2	0.0272	0.33	0.16
240A[b]	30 Si	0.5–4.2	368±2	0	⋯	⋯
Ge 563 g[b]	pure polycrystalline	0.5–4.5	371±3	0±0.001	⋯	⋯
Ge 208 g[c]	pure single crystal	2.5–300	374±2	⋯	⋯	⋯
Theory[d]	pure single crystal	0	374.0	0	⋯	⋯

[a] Reference 5.
[b] Present work.
[c] Reference 6.
[d] References 1 and 2.

concentration of Si could be estimated only from the net amount of Si added to the melt, and is believed to be much less uniform. As the Hall coefficient was -7×10^3 cm^3/coul at 80 and 300°K at one end and the order of -10^5 at the other, the concentration of impurities other than Si was estimated as less than 10^{15} cm^{-3} throughout.

The summary of results in Table I shows that θ_0 and γ vary monotonically with donor concentration. The Fermi energy ζ (relative to the band edge) and density-of-states effective mass ratio, $\mu=m_d/m_0=(m_l m_t^2)^{\frac{1}{3}}/m_0$, are calculated from n and γ on the assumption of a degenerate Fermi gas of electrons in a parabolic conduction band.[5] That μ is roughly constant and close to the value obtained from cyclotron resonance[7] (0.22) indicates that the energy at the band edge, as a function wave vector, is not greatly affected by these donor concentrations.

Uncertainties given here are three times the standard error when (2) is fitted to the data by the least mean squared deviation method, and do not include systematic errors. Among these, the uncertainty in correction for the heat capacity of heater and thermometer is prominent. The heater wire was about 10 mg of constantan, for which we have approximated the data of Guthrie *et al.*[8] by $0.18\,T-0.004\,T^3$ mjoule/g deg±20%. The thermometer was a tenth-watt, 10-ohm Allen-Bradley carbon composition resistor whose heat capacity, $0.0016\,T+0.00036\,T^3$ mjoule/deg±30%, was measured directly. Heater and thermometer were glued to the specimen with less than 30 mg of red glyptal for which the measured correction[5] is $0.027\,T^3$ mjoule/deg ±20%. The uncertainty in heat capacity of the addenda is therefore about $0.001\,T+0.0003\,T^3$ mjoule/deg, as compared with the heat capacity of at least two moles of Ge. This contributes chiefly to the error in γ. Other systematic errors, such as appear in the temperature scale, may amount to about a percent.

Discussion of the Lattice Term

In Fig. 2, θ_0 is plotted against n, the average impurity concentration. The decrease in θ_0 with addition of impurities is significantly greater than experimental error, and corresponds to a softening of the lattice, or decrease in the elastic constants, by an amount larger than was thought possible for such dilute alloys. There are several possibilities which may explain this decrease and are open for investigation: (a) The Ge lattice is strained locally by substitutional impurity atoms of different size than the host atom. (b) Pressure from the electron gas of Coulomb repulsion of ionized donors increases the lattice spacing enough to affect the elastic constants. (c) The ionized donors, each having a charge e, polarize the neighboring Ge atoms, and this polarization in turn weakens the bonds between them. (d) The free electrons screen and weaken the interatomic forces, thus decreasing θ_0.

Though the θ_0 obtained for Ge(Si), which had the next highest impurity concentration, is somewhat lower than our result for pure Ge, it is significantly higher than θ_0 for Ge(Ga). If the cause of $\Delta\theta_0$ were purely mechanical, one would expect from that much Si at least the effect

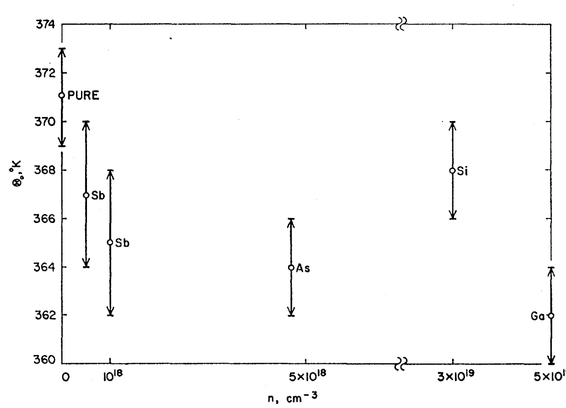

FIG. 2. Debye temperature of germanium as a function of impurity concentration, n. As the electron gas in these samples is degenerate at low temperatures, n is also the free carrier concentration except for pure Ge and Ge(Si), which have virtually no free carriers at liquid helium temperatures.

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produced by Ga, which is closer in size to the Ge atom. The lattice might be expected to collapse around the site of a substitutional Si atom, but might be compressed in the neighborhood of the larger Sb atoms, so a Debye-Scherrer x-ray pattern was taken to compare their lattice constants, a, with pure Ge, yielding $a=5.6460 \pm 0.0002$ kxu for both Ge(Si) and Ge(10^{18} Sb) and 5.6458 ± 0.0003 kxu for pure Ge. An estimate of the maximum $\Delta\theta$ which could come from lattice dilation may be obtained from the Grüneisen relationship between the lattice frequencies ω_q and the atomic volume V,[9]

$$\partial \ln\omega_q / \partial \ln V = -\Gamma. \tag{3}$$

Grüneisen's constant Γ is about 2, so that inserting $\theta \propto \omega_{\max}$, $V \propto a^3$ and $\Delta a < 7\times10^{-4}$ kxu into (3) we have $\Delta\theta < \frac{1}{4}$°K, an insignificant change. That there is no observable change in lattice parameter does not itself eliminate (a) or (b), for x-ray techniques are fairly insensitive to local disturbances in the lattice. However, the drop in θ_0 from the pure Ge value (Fig. 2) appears to become saturated for large values of n. This behavior would not be expected for mechanisms of the type (a) or (b). Moreover, the bulk modulus of the electron gas ($\sim 10^5$ d/cm^2), as well as of the ionized donors, is very small compared with that of the Ge lattice, 10^{12} d/cm^2. We feel that the foregoing arguments are sufficient to eliminate the first two possibilities and that either (c) or (d) may be an adequate explanation.

If the donors were ionized through compensation by acceptors rather than by giving their electrons to the conduction band, one could test for the effect on θ_0 of randomly distributed fixed charges while excluding free electrons. If it is true that the charged donors induce dipole moments on near neighbors which in turn weaken the electrostatic interactions in their vicinity, then heavy compensation would be expected to increase the effect by introducing charged acceptors as well. If, on the other hand, the free electrons are more influential, their removal by compensation should bring θ_0 back toward the value for pure Ge. The effectiveness of free electron screening depends on their speed and density, and is expressible as a screening radius, r_0. A screened Coulomb potential,[10,11] for instance, can be written $(e/\kappa r)\exp(-r/r_0)$, with

$$r_0 = \frac{\hbar}{e}\left[\frac{\kappa}{4N_c^{\frac{2}{3}}m_d}\left(\frac{\pi}{3n}\right)^{\frac{1}{3}}\right]^{\frac{1}{2}}, \tag{4}$$

where κ, the dielectric constant of Ge, is 16 and N_c, the number of conduction band minima, is 4.

For Ge (4.7×10^{18} As), $r_0 = 1.5\times10^{-7}$ cm or about 6 times the distance of a nearest neighbor. If, as suggested by Herman,[12] interactions of 5th and 6th nearest neighbors are required to get the elastic constants from an interatomic force model of the diamond lattice, then it would appear that under these conditions free carriers can partially screen out the longer range forces. For the p-type Ge(Ga), $m_d N_c^{\frac{2}{3}}$ is replaced by the density-of-states effective mass of holes and n stands for the hole concentration, so that Ge(Ga) is expected to follow nearly the same trend as the n-type samples. On the other hand, the Ge(Si), which has no free carriers at low T, should have θ_0 close to the pure Ge value. It has recently been demonstrated by Giffels, Hinman, and Vosko that a solute atom in dilute alloys of silver can affect the electric field gradient at up to the ninth nearest lattice site and that the number of sites affected is much more correlated with the difference in valence between host and solute atoms than with the distortion of the host lattice by the solute.[13] Fan pointed out that a saturation of $\Delta\theta_0$ toward high concentrations, such as observed in Fig. 2, would be obtained if the free carriers screened only the long-range forces effectively, but did not weaken nearest neighbor bonds. On this hypothesis, as r_0 becomes less than the lattice constant, a further increase in the carrier density would not increase the screening and soften the lattice any further. But according to (4), this condition should not be reached until n becomes greater than 2×10^{21} cm^{-3}.

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