The results indicate that a simple thermally activated process cannot explain the observed changes. In particular, the fast increase in the number of centers which annealed at, e.g., 400°C after failing to anneal in 16 hours at 370°C requires an activation energy of about 5 ev. This activation energy is exceedingly high for a thermally activated process. It is interesting to add that the characteristics of the annealing are qualitatively similar to those observed by Logan[6] in germanium. One has to conclude that the process responsible for the observed changes is probably a complex one, possibly involving interactions between crystal imperfections of more than one kind.

ACKNOWLEDGMENTS

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[6] R. Logan, Phys. Rev. 101, 1455 (1956).

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Thermal Conductivity of Germanium and Silicon at Low Temperatures

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Measurements are reported of the thermal conductivity, K, of high-purity n- and p-type germanium, and of a single crystal of n-type silicon at temperatures between 2 and 150°K. These confirm that in silicon and in annealed germanium the thermal conductivity is limited only by boundary scattering at temperatures below about $\theta/100$, where θ is the Debye characteristic temperature; while at temperatures above $\theta/10$, $K\propto T^{-n}$ where $n\simeq 1.3$ for germanium and $n\simeq 1.0$ for silicon. In the range of temperature just above the conductivity maximum, that is, from $\theta/20$ to $\theta/10$, no particularly rapid rate of change of K with T is observed, in contrast with the behavior found in pure dielectric crystals and bismuth. These features are discussed.

I. INTRODUCTION

RECENTLY, we reported[1] on the thermal conductivity of a high-purity single crystal of germanium, and since then further measurements on thermal conductivity and thermoelectric power have been made and some of the results published.[2,3] The thermal conductivity measurements, together with those just completed on an annealed specimen of germanium and a single crystal of silicon,[4] serve to emphasize some singular features of the thermal conductivity of these semiconductors.

Owing to the high electrical resistance of these elements, we should expect the heat to be carried almost wholly by the lattice waves and consequently the conductivity should exhibit the type of temperature dependence which is shown by crystalline dielectric solids (see, e.g., comprehensive reviews by Berman[5] and Klemens[6]). Previous work, particularly on germanium,[7–9,1] certainly suggests that lattice conduction is dominant, but even high-purity single crystals of germanium have not shown the marked rise in conductivity with decreasing temperature exhibited by such materials as diamond, sapphire, bismuth, or solid helium and ascribed to an exponential decrease in the thermal resistance due to phonon-phonon interaction at temperatures below $\theta/10$ (θ being the Debye characteristic temperature), where the probability of the so-called "umklapp-processes"[10,11,5] is decreasing rapidly as the temperature falls.

Thus it would appear that some fundamental reason exists for the behavior of germanium and silicon or that some physical impurity must be present which masks or obliterates an otherwise very high maximum in the conductivity at about $\theta/20$. In order to investigate the latter possibility, measurements were carried out on germanium specifically to determine the effect of annealing and on a single crystal of pure silicon.

2. EXPERIMENTAL

The specimens were mounted in a cryostat similar to that described previously[1] and the thermal conductivity

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[1] G. K. White and S. B. Woods, Can. J. Phys. 33, 58 (1955).

[2] E. Mooser and S. B. Woods, Phys. Rev. 97, 1721 (1955).

[3] Pearson, Mooser, and Woods, *Conference de Physique des Basses Temperatures* (Centre National de la Recherche Scientifique and UNESCO, Paris, 1956), p. 420.

[4] We are greateful to Dr. W. F. Leverton of the Research Division, Raytheon Manufacturing Company, Ltd., who supplied us with specimens cut from an n-type crystal of silicon.

[5] R. Berman, Phil. Mag. Suppl. 2, 103 (1953).

[6] P. G. Klemens, *Handbuch der Physik* (Springer-Verlag, Berlin, 1956), Vol. 14.

[7] H. M. Rosenberg, Proc. Phys. Soc. (London) A67, 837 (1954).

[8] H. M. Rosenberg, *Conference de Physique des Basses Temperatures* (Centre National de la Recherche Scientifique and UNESCO, Paris, 1956), p. 464.

[9] I. Estermann and J. E. Zimmerman, Carnegie Institute of Technology Technical Report No. 6, 1951 (unpublished).

[10] R. Peierls, Ann. Physik 3, 1055 (1929).

[11] R. Peierls, *Quantum Theory of Solids* (Oxford University Press, New York, 1955).

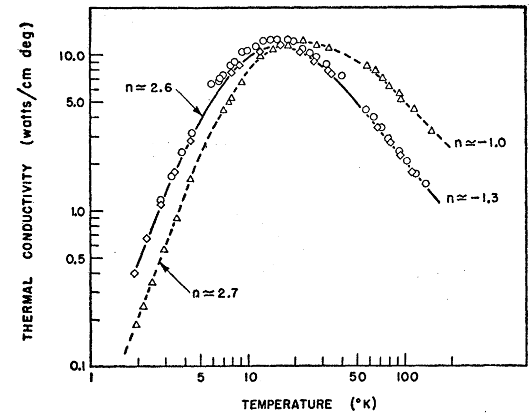

FIG. 1. Thermal conductivity of germanium and silicon at low temperatures. ○ Ge3*a*, polycrystalline *p*-type; ——◇—— Ge3*b*, 3*a* after annealing; – – –△– – – Si 1, single crystal *n*-type.

was measured at temperatures from 1.8°K to 150°K. The *n*-type silicon crystal was nickel-plated near the ends and small copper connectors were soldered to the plating with a 90/10 (atomic percent) lead-bismuth alloy.

The specimen Ge3, after the first series of measurements (Ge3*a*) was cleaned with (a) fine emery, (b) concentrated nitric acid and hydrogen peroxide, (c) potassium cyanide solution, and (d) de-ionized water, and was then annealed for three hours at 550°C in an atmosphere of helium, cooled slowly, and finally measured again (Ge3*b*). The purpose of this thorough cleaning was to ensure that all surface impurities were removed before annealing, as traces of certain elements —notably copper—diffuse very rapidly into the germanium at elevated temperatures. The success of the cleaning was indicated by the fact that the electrical resistance appeared unchanged by annealing. Copper connections were soldered directly to the *p*-type germanium specimen with indium solder and to the *n*-type with lead-bismuth solder.

RESULTS

The experimental results on the polycrystalline *p*-type germanium before (Ge3*a*) and after annealing (Ge3*b*), and on the single crystal of *n*-type silicon are shown in Fig. 1, and Table I gives some representative values for the thermal conductivity.

TABLE I. Experimental data on germanium and silicon samples. (K is given in watts/cm deg.)

Specimen	Ge1 Single crystal *p*-type	Ge3*a* Poly-crystalline *p*-type	Ge3*b* Annealed Ge3*a*	Ge4 Single crystal *n*-type	Si1 Single crystal *n*-type
Cross section (mm×mm)	2×4	2.2×2.3	2.2×2.3	1.4×2	1.75×1.5
ρ_{295} (ohm cm)	~30	~30	~30	~50	6.7
K(125°K)	1.6_5	1.6	1.5	1.4_7	4.0
K(75°K)	3.1	3.1	3.0	2.8_5	6.7
K(40°K)	6.7_5	6.8	6.4	6.5	10.2
K(20°K)	11.4	12.0	10.8	9.7	11.9
K(10°K)	12.0	10.7	9.5	7.7	7.8
K(3°K)	1.8	1.3_5	1.3	1.2	6.1

For the various germanium samples above 30°K it is found that $K \propto T^{-1.3}$, the magnitude varying by not more than about 10% among the samples, whereas for Si 1, $K \propto T^{-1}$ above 60°K.

The maximum conductivity, which occurs near 15°K, is about 10 to 12 watts per cm deg in each of the specimens, and below this the conductivity falls rapidly so that at liquid helium temperature $K \propto T^n$ where $n = 2.6 \pm 0.2$.

DISCUSSION

At the lowest temperatures, where the wavelength of the lattice vibrations is relatively large, we expect following Casimir[12] that boundary scattering will limit the conductivity such that

$$K = 2.31 \times 10^3 pRA^{\frac{2}{3}}T^3 \text{ watts/cm deg},$$

where p, a function of the velocity of sound, is about 1.4 for most crystals, R is the effective radius of the crystal, and A is defined by the equation $C_v = AT^3$ joules/cm^3 deg; for crystals of square cross section, R is replaced by $0.56d$ where d is the width of the crystal.

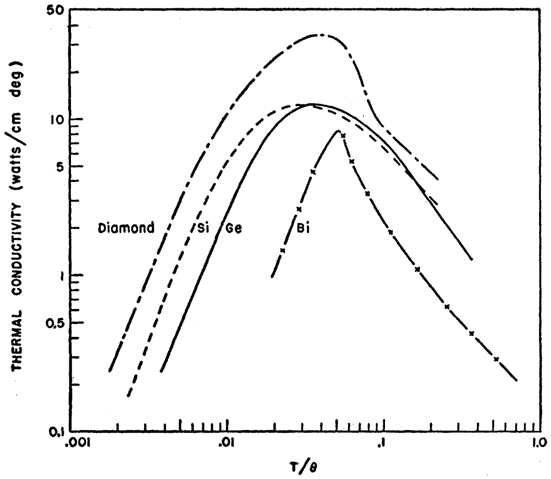

FIG. 2. Variation of thermal conductivity with reduced temperature, T/θ, for silicon ($\theta = 790$°K) and germanium ($\theta = 400$°K). ——— Ge3*a*; - - - - - - Si1; — — — Diamond ($\theta = 1840$°) from Berman, Simon, and Ziman (1953); — × — Bismuth ($\theta = 100$°) from White and Woods (1955).

Using specific heat data from Keesom and Pearlman[13] and Hill and Parkinson[14] (see also review by Blackman[15]), which suggest that at very low temperature $\theta_{\mathrm{Si}} = 668$°K and $\theta_{\mathrm{Ge}} \simeq 300$°K, together with our

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[12] H. B. G. Casimir, Physica **5**, 495 (1938).

[13] P. H. Keesom and N. Pearlman, Phys. Rev. **85**, 730 (1952).

[14] R. W. Hill and D. H. Parkinson, Phil. Mag. **43**, 309 (1952).

[15] M. Blackman, *Handbuch der Physik* (Springer-Verlag, Berlin, 1955), Vol. 7, p. 325.

data for K at 3°K, Casimir's equation gives

$$\text{for Si1,}\quad d = 1.8_5 \text{ mm,}$$

and

$$\text{for Ge3,}\quad d = 1.2 \text{ mm.}$$

These values for d agree quite well with measured dimensions when we note that in the case of Ge3, the specimen is polycrystalline containing some 8 to 10 crystals inclined slightly to the axis of the rod. As in most cases, the exponent of T is somewhat less than 3, probably because some specular reflection of phonons occurs at the boundaries.[16]

In Fig. 2 we have plotted the thermal conductivity of Ge3*a* and Si1 as a function of reduced temperature T/θ together with data for bismuth and diamond for comparison; the values of θ assumed for germanium and silicon are obtained from data for temperatures of the order of θ. From the extensive work of Berman and his collaborators on dielectric crystals, and that of Wilks and others[17–19] on solid helium, we expect that highly pure dielectric crystals should show a more rapid increase in conductivity as T falls below $\theta/10$. Thus, unless the specimen has a large number of static imperfections, there should be a temperature region between about $\theta/10$ and $\theta/20$ where $K \propto e^{\theta/bT}$ until at lower temperatures imperfections begin to limit the conductivity. This is illustrated in diamond and even in bismuth where there is a small electronic thermal conductivity—no doubt more important than in germanium and silicon. Some recent experiments by Berman[20] on alkali halide crystals also illustrate this rapid rise in conductivity which is usually ascribed to the exponential decay in the frequency of umklapp process as $T/\theta \rightarrow 0$.

Another and possibly related feature is the magnitude of the thermal conductivity of germanium and silicon at temperatures above that of the maximum, when compared with other physical constants for these elements.

The following expressions have been given for the thermal conductivity of simple crystals in the temperature region ($T \gtrsim \theta$), where anharmonic coupling of the lattice waves is the dominant cause of thermal resistance:

$$K \simeq vCA_0/3\alpha\gamma T,$$

by Dugdale and MacDonald,[21] and

$$K = 12k^3MA_0\theta^3/5h^3\gamma^2T,$$

by Leibfried and Schlömann,[22] where v is the velocity of lattice waves, C is the specific heat per unit volume, A_0 is the lattice constant, α is the cubic expansion coefficient, γ is the Grüneisen parameter $(=\alpha/\chi C)$, χ is the compressibility, M is the atomic mass, and k and h are Boltzmann's and Planck's constants.

Initially it was noted that by assuming $\gamma = 2$, good agreement was obtained between the Leibfried-Schlömann formula and the results for Si and Ge at $T \sim \theta/5$. However, using the values for the expansion coefficient, α, and elastic constants given by Conwell[23] to deduce approximate values for v, we then calculated that $\gamma \simeq 0.76$ for Si and Ge and both the above equations then give values for the thermal conductivity several times higher than the experimental figures. In contrast to the case for some of the alkali halides and also solid helium and solid argon,[24] a similar discrepancy appears to occur for diamond so that either the theoretical expressions are poor approximations in the case of diamond-structure elements or possibly temperatures near $\theta/5$ are too low for a satisfactory comparison to be made.

In either case, we are still faced with the fundamental question: why do high-purity crystalline materials such as germanium and silicon not show the same behavior at temperatures between $\theta/10$ and $\theta/20$, i.e., on the immediate high-temperature side of the conductivity maximum, as dielectric crystals? The interesting measurements of Rosenberg[8] on germanium with introduced dislocations also suggest that physical impurities are *not* the major factor limiting the thermal conductivity at these temperatures.

Indeed, if we can then disregard the possible effect of dislocations or of some internal mosaic structure, it appears strange that these elements, containing no more than probably 10^{16} charge carriers per cm^3 and of very high chemical purity, should behave as they do unless the theoretical ideas of phonon-phonon interaction as applied to dielectric solids are not valid here.

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[16] Berman, Simon, and Ziman, Proc. Roy. Soc. (London) **A220**, 171 (1953).

[17] F. J. Webb and J. Wilks, Phil. Mag. **44**, 663 (1953).

[18] Webb, Wilkinson, and Wilks, Proc. Roy. Soc. (London) **A214**, 546 (1952).

[19] K. R. Wilkinson and J. Wilks, Proc. Phys. Soc. (London) **A64**, 89 (1951).

[20] We are most grateful to Dr. Berman for sending us his results before publication.

[21] J. S. Dugdale and D. K. C. MacDonald, Phys. Rev. **98**, 1751 (1955).

[22] G. Leibfried and E. Schlömann, Gött. Nachr. **IIa**, 71 (1954).

[23] E. M. Conwell, Proc. Inst. Radio Engrs. **40**, 1327 (1952).

[24] G. K. White and S. B. Woods, Nature **177**, 851 (1956).