duced in ultrapure Al₂O₃. On the other hand, when Al₂O₃ containing trace impurities is subjected to the proper heat treatment the impurities precipitate along certain crystallographic axes. This is the manner in which synthetic star sapphires are manufactured, and a great deal of effort has been put into developing the correct conditions of heating. Evidently in the experiments described in this paper the same phenomenon resulted without regard for the type of heat treatment employed. It may be that the irradiation produced enough residual stress in the crystal to make the stress resulting from the heat treatment much less important than it is in an unirradiated crystal. With regard to the impurities, it is not known at present whether they precipitate on dislocations or on clusters of defects or whether some other mechanism is responsible for their agglomeration. It is not difficult to imagine that various defects are introduced during crystal growth, and that these migrate to the center of the crystal during the heating process forming complex centers upon which the impurities precipitate.

V. CONCLUSIONS

In conclusion, this work on aluminum oxide is considered to represent only a beginning on the study of

radiation effects in this material. A much more detailed study is necessary to determine the exact behavior of simple defects in this crystal structure, particularly as a function of temperature, before neutron transmission studies will be more fruitful. The outstanding factor which remains to be determined is the reason for the low fraction of defects retained at room temperature after irradiation. This, of course, speaks well for corundum as a stable structural material under the stress of high bombardment fluxes. A future experiment with the material irradiated and examined at low temperatures would be a profitable study and is contemplated as the equipment becomes available.

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Thermal Conductivity of Selenium at Low Temperatures

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Measurements are reported of the thermal conductivity of glassy selenium and polycrystalline metallic (hexagonal) selenium at temperatures from 2° to above 100°K. At the higher temperatures, the heat conductivity, λ , for the glassy solid is about 1 mw/cm deg. If we write $\lambda \approx \frac{1}{2}lCv$, then l, the mean free path, is of the order of the interatomic distance. On the other hand, for the high-purity metallic samples, $\lambda \cong 5/T$ w/cm deg. At low temperatures in metallic selenium, λ varies approximately as T^2 , while in the glassy modification λ behaves in a similar fashion to that expected from earlier observations on soft glass and Pvrex.

INTRODUCTION

HE hexagonal form of selenium consists, like tellurium, of long spiral chains of atoms arranged in such a way that for each atom, in addition to the two nearest neighbors lying 2.316 A away in the same chain, four next-nearest neighbors lie in adjacent chains 3.467 A distant. This form has a density of 4.80 g cm^{-3} compared with about 4.30 g cm⁻³ for amorphous or glassy selenium. Some years ago one of us (GKW), at the suggestion of Dr. P. G. Klemens, measured¹ the heat conductivity below 100°K of a rod of glassy

selenium (called Se 1) in order to see whether the dependence of its conductivity on temperature showed the same characteristic form found by Berman² for quartz glass, Phoenix glass, and Perspex and discussed in detail by Klemens.³ This dependence is determined by the fact that at high temperatures, the disorder in the glass results in a phonon mean free path which is independent of the phonon frequency (and therefore of temperature), so that in the Debye expression for heat conductivity, $\lambda \simeq \frac{1}{3} C v l$, where C is the specific heat per unit volume, v is the phonon velocity, and l, the mean free path for phonons, is of the order of the lattice

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¹ Performed at the Commonwealth Scientific and Industrial Research Organization, Division of Physics, National Standards Laboratory, Sydney, Australia.

 ² R. Berman, Proc. Roy. Soc. (London) A208, 90 (1951).
 ³ P. G. Klemens, Proc. Roy. Soc. (London) A208, 108 (1951).



FIG. 1. Thermal conductivity of selenium. Data for "soft" glass are from G. K. White and S. B. Woods (unpublished) and for "hard" glass are from Berman² and Stephens.¹² \triangle Se 1, □ Se 2, • Se 3, ■ Se 4, • Se 5. A. and A.: see reference 11; Joffe: see reference 10; K. and M.: see reference 9; Sayce: see reference 8; g-Se: glassy, m-Se: metallic.

constant. With decreasing temperature, λ first diminishes to some extent as C falls but at low temperatures, when the wavelength of the phonons becomes long in comparison with the interatomic distance, the mean free path for the longitudinal lattice waves then *increases* with decreasing temperature. As discussed by Klemens,³ this can lead to a region of temperature where λ is fairly constant, but below which it is ultimately expected to fall linearly with temperature. In Fig. 1 some earlier results on soft glass and Pyrex are shown to illustrate the behavior.

More recently we have made a series of measurements on metallic or hexagonal selenium. As we are aware of no previous experimental studies of heat conduction on selenium below room temperature, it seems of interest to present these results and discuss briefly their significance. Although hexagonal selenium does conduct electricity weakly, it seems fairly certain that heat transport is almost solely by lattice waves and thermal resistance is produced by anharmonic interaction between lattice waves themselves or by scattering due to physical and chemical impurities. We discussed this latter behavior in relation to tellurium⁴ in an earlier paper and detailed discussions of heat conductivity in insulating crystals have been given in reviews by Berman⁵ and Klemens.⁶

EXPERIMENTAL DETAILS

The heat conductivity of the rod-shaped specimens listed below was measured in a cryostat described previously,⁷ at temperatures from 2° to about 100°K.

Se 1 was a rod about 3 cm long and 1 cm diameter, prepared by melting selenium powder (of probable purity >99.9%) in a split brass mold at about 250° C and quenching it rapidly in ice water to produce a glassy specimen. Copper potential and current leads were inserted into the mold before melting so that they were cast integrally with the rod.

Se 2 was of similar dimensions and was prepared in a similar fashion, being intended as a glassy rod, but because of unwitting variations in heat treatment it was found to be finely polycrystalline.

Se 3 was a rod of crystalline selenium (6 cm long $\times 1$ cm diam) supplied by the Fairmount Chemical Company, Newark (New Jersey). Copper leads were attached by coating narrow regions of the rod with silver-conducting paste and fixing the leads with Wood's allov solder to this coated area.

Se 4 and Se 5 were both produced by melting 99.999%pure selenium powder from Canadian Copper Refiners Ltd., under vacuum in a glass tube, chilling the melt rapidly to produce solid rods of glassy selenium, and later annealing the rods in vacuo at about 210°C for 50 or 60 hours to give polycrystalline specimens. Copper leads were attached to the rods with cold-setting Araldite cement. Se 4 was about 4 cm long and 4 mm diameter. Se 5 was of similar length but greater diameter; because of shrinkage on annealing, its cross section became irregular and so was reduced to a regular triangular section (area $\simeq 0.26$ cm²) by grinding with emery paper.

For specimens Se 4 and Se 5 the average grain dimensions were about 20μ .

RESULTS

The results of measurements are shown in Fig. 1 together with various room temperature values found by previous workers.8-11 Data of Berman² on Phoenix glass are inserted for comparison purposes and are extrapolated from 100° to 300°K using earlier data of Stephens¹² on Pyrex glass. Although Kurtener and Malyshev⁹ do not specify the form of selenium on which they obtained measurements at 28°C and 48°C, it appears probable that it was glassy or at least principally glassy. On the other hand, the value of conductivity quoted by Abdullaev and Aliev¹¹ for glassy selenium at about 26°C seems rather high, suggesting

 ⁴ Fischer, White, and Woods, Phys. Rev. 106, 480 (1957).
 ⁵ R. Berman, Suppl. Phil. Mag. 2, 103 (1953).
 ⁶ P. G. Klemens, *Handbuch der Physik* (Springer-Verlag, Berlin, 1956), Vol. 14, p. 198.

⁷ G. K. White and S. B. Woods, Can. J. Phys. 33, 58 (1955).
⁸ E. D. Sayce, J. Roy. Soc. N. S. Wales 51, 356 (1917).
⁹ A. V. Kurtener and E. K. Malyshev, J. Tech. Phys. (U.S.S.R.) 13, 641 (1943).

A. B. Joffe and A. F. Joffe, J. Tech. Phys. (U.S.S.R.) 22, 2005 (1952).

¹¹G. B. Abdullaev and M. I. Aliev, Doklady Akad. Nauk. S.S.S.R. 114, 995 (1957).

¹² R. W. B. Stephens, Phil. Mag. 14, 897 (1932).

that the specimen was partly polycrystalline or possibly that an error of an order of magnitude occurs in the ordinate scale of their figure; in the latter case their value would agree well with that of Sayce.

The uncertainty in the absolute conductivity values obtained by us may be as much as 5% due to uncertain geometry but errors in relative values should be much smaller, except in the case of Se 1 (glassy Se) which was an extremely poor conductor, so that equilibrium times were very long, the influence of small temperature drifts was correspondingly greater, and errors in the radiation corrections applied may have been serious above 50 or 60°K.

DISCUSSION

Glassy Selenium

In view of the detailed discussion by Klemens^{3,6} and Berman² of the heat conductivity of glassy solids, we believe it will be sufficient to point out the apparent resemblance in the behavior of Se 1 to that of the other two glasses shown in Fig. 1 and to compare λ with that given by the relation $\lambda = \frac{1}{3}Cvl$. A crude estimate of velocity v, obtained from the compressibility and density, is about 1.5×10^5 cm/sec and specific heat values are given by Anderson.¹³ If then we equate l to an average interatomic distance of 3×10^{-8} cm, we obtain $\lambda \simeq 1.4$ mw/cm deg at about 100°K and 2.1 mw/cm deg at 300°K. The agreement with Fig. 1 makes it appear that the mean free path is, indeed, similar in magnitude to the interatomic distance.

Crystalline Selenium

For Se 4 and Se 5 we observe that $\lambda \simeq 5/T$ watts per cm deg for $T \ge 50^{\circ}$ K and $\lambda \propto T^{2.2}$ for $T < 6^{\circ}$ K. If we regard these specimens as being truly representative of high-purity hexagonal selenium crystals, we may compare the magnitude of λ in the higher temperature range with that obtained for Te and that given by simplified theoretical models of Dugdale and Mac-Donald¹⁴ or Leibfried and Schlömann,¹⁵ since at higher temperatures phonon-phonon interaction is the domi-

nant cause of thermal resistance and λ is here rather insensitive to physical or chemical defects (if in sufficiently low concentration). For tellurium we observed $\lambda \simeq 10/T$ watts per cm deg and for both Se and Te we calculate that $\lambda \simeq 40/T$ watts per cm deg assuming for Se that $\theta_D \simeq 250^{\circ}$ K and that γ (the Grüneisen parameter) $\simeq 2$. In view of the very simplified theoretical models adopted, it is hardly surprising that the observed value is rather different from the theoretical; although a doubt is raised in our minds whether large crystals of selenium might not be found to show a conductivity as high as that of tellurium.

It is difficult to compare our data below 10°K with a theoretical model, e.g., with Casimir's¹⁶ theory of boundary scattering, as there appears to be no specific heat data extending below 12° or 15°K. We do, however, find that if we assume $\theta_D \simeq 200^{\circ}$ K (i.e., that a T^3 region in the specific heat exists at sufficiently low temperatures for which $\theta_D \simeq 200^{\circ}$ K), then Casimir's formula leads to $\lambda_B \simeq DT^3$ where D is the effective diameter of the crystals. At 2°K this ¹⁷ would give a value of λ about 3 times higher (using $D \simeq 20 \mu$) than that observed, but in any case λ decreases rather less rapidly with T than would be expected if boundary scattering predominates.

We tried to produce larger crystals but grain growth in the rods appeared to stop after one or two days annealing, and did not seem to be increased by any alteration in temperatures. We did consider the method used by Henkels,¹⁸ and also the possibility of condensation from the vapor phase but felt that the crystals produced would not be large enough individually to use and that no compact mass of large crystals could be obtained from which rods or bar could be cut. However, this problem may be solved in the future and measurements on large selenium crystals would certainly be of great interest.

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 ¹⁴ J. S. Dugdale and D. K. C. MacDonald, Phys. Rev. 98, 1751

^{(1955).} ¹⁵ G. Leibfried and E. Schlömann, Nachr. Akad. Wiss. Göttingen

¹⁶ H. B. G. Casimir, Physica 5, 495 (1938). ¹⁷ The Debye formula $\lambda \simeq \frac{1}{3}Cvl$ gives a similar magnitude if we assume $v \simeq 1.5 \times 10^{5}$ cm sec⁻¹.

¹⁸ H. W. Henkels, Phys. Rev. 76, 1737 (1949).