

mental results can be fitted excellently by solving degree.

$$m^* \ddot{z} = -V'(z) - \eta \dot{z},$$

with  $V(z < 0) = \frac{1}{2}K(z+a)^2 - \frac{1}{2}Ka^2$ ,  $V(z > 0) = 0$ , and noting the lowest velocity of incidence which permits escape after one passage. The resulting sticking coefficient takes the universal form

$$s = \text{erf}(T_c/T)^{1/2},$$

where

$$T_c = 2\pi a^2 \eta K^{1/2} / k_B m^{1/2},$$

and  $k_B$  is Boltzmann's constant, and erf is the error function. The model gives results that simulate closely the computer results utilized by Goodman in proposing a formula for  $\alpha(T)$ .<sup>12</sup>

The authors wish to acknowledge the hospitality of the Centre Européen du Calcul Moléculaire, Orsay, France, where this work was begun, and to thank Dr. David Y. Wong and Dr. Lu Jeu Sham for valuable discussions. This work was supported in part by National Science Foundation Grant No. DMR-74-03838 and in part by the Centre Européen du Calcul Moléculaire, Orsay, France. It was submitted by one of us (T.R.K.) in partial fulfillment of the requirements for the doctoral

<sup>1</sup>B. McCarroll and G. Ehrlich, *J. Chem. Phys.* **38**, 523 (1963).

<sup>2</sup>J. E. Lennard-Jones *et al.*, *Proc. Roy. Soc. London, Ser. A* **156**, 6, 36 (1936).

<sup>3</sup>F. O. Goodman, in *Rarefied Gas Dynamics*, edited by J. H. de Leeuw (Academic, New York, 1966), p. 366.

<sup>4</sup>F. O. Goodman, in *Progress in Surface Science*, edited by S. Davidson (Pergamon, New York, 1975), Vol. 5, p. 261.

<sup>5</sup>A. F. Devonshire, *Proc. Roy. Soc. London, Ser. A* **158**, 269 (1937).

<sup>6</sup>T. D. Lee, F. E. Low, and D. Pines, *Phys. Rev.* **90**, 297 (1953).

<sup>7</sup>Here we have used the model of an infinite barrier plus well, with  $m^*$  inside and  $m$  outside the well. Note that  $\psi$  and  $\psi'/m$  are continuous.

<sup>8</sup>The model employs a three-dimensional density of states while restricting motion of the adatom to the  $z$  direction, taken normal to the surface.

<sup>9</sup>C. Caroli, B. Roulet, and D. Saint-James, to be published.

<sup>10</sup>The coupling term in (1) then becomes  $\sum_q (V_q a_q e^{iqz} + V_q^* a_q^\dagger e^{-iqz})$ , hence  $s_q(z) = s_q e^{iqz}$ .

<sup>11</sup>E. Kartheuser, in *Polarons in Ionic Crystals and Polar Semiconductors*, edited by J. Devreese (North-Holland, Amsterdam, 1972), p. 515.

<sup>12</sup>F. O. Goodman, *J. Chem. Phys.* **46**, 2376 (1967).

## Low-Temperature Thermal Conductivity of Amorphous Germanium

H. v. Löhneysen<sup>(a)</sup> and F. Steglich

*II. Physikalisches Institut der Universität zu Köln, Köln, Germany*

(Received 20 June 1977)

The thermal conductivity  $k$  of  $a$ -Ge films has been measured between 0.4 and 10 K. The temperature dependence of  $k$  shows that heat conduction by phonons is limited by some intrinsic scattering mechanism in addition to boundary scattering. Evidence is presented that these scatterers are localized low-energy excitations which are common in glasses.

The thermal properties of amorphous dielectrics show a distinct temperature dependence below 1 K. As discovered by Zeller and Pohl,<sup>1</sup> the specific heat varies as  $C \sim T$  and the thermal conductivity  $k$  is roughly proportional to  $T^2$ , whereas in crystalline dielectrics both quantities vary as  $T^3$ . From these anomalies in the thermal—and similar ones in the acoustic<sup>2</sup>—properties, one infers the existence of localized low-energy excitations (LEE) from which phonons are scattered. However, the microscopic nature of these excitations is far from being understood. Among the phenomenological models proposed, the "tunneling model"<sup>3,4</sup> has proved to be the most successful. This model implies tunneling of atoms

(or groups of atoms) between nearly degenerate equilibrium positions. For this model, an "open structure" (e.g., a wide range of bond angles) seems to be required, as found in glasses, polymers, or amorphous Se.

In contrast, amorphous germanium ( $a$ -Ge) was not expected to show such low-temperature anomalies since its structure is rather closed.<sup>4</sup> Experimental support for this assumption comes from specific heat measurements on  $a$ -Ge above 2 K, which yielded an enhanced  $T^3$  term as compared to crystalline Ge, but did not give evidence for a linear term.<sup>5</sup> Thus, the question whether LEE do or do not exist in  $a$ -Ge appears to be of great importance with respect to the physical na-

ture of the low-temperature tunneling process in amorphous solids.

In this Letter we present the first measurements of the thermal conductivity of *a*-Ge between 0.4 and 10 K. The films were prepared by evaporation at 300 K onto a 12.5- $\mu\text{m}$ -thick Kapton foil which served as substrate. The thickness of the *a*-Ge films varied between about 2 and 6  $\mu\text{m}$  as determined by weight, where a density of 4.7 g/cm<sup>3</sup> for *a*-Ge was assumed.<sup>6</sup> The structure of the films has been verified to be amorphous by x-ray analysis.

The thermal conductivity was measured in the standard stationary method; however, a radial heat flow in a circular geometry was employed.<sup>7</sup> A resistive heater was glued to the center of the substrate. The substrate, which carried three concentric Ag rings ( $\approx 5000$  Å thick, evaporated prior to Ge), was clamped at its circumference on the outermost Ag ring to the cold part of a He<sup>3</sup> cryostat. The inner Ag rings served as isotherms. In the steady state the heater input  $\dot{Q}$  produced a temperature difference  $\Delta T_H$  which was measured by carbon resistors. The thermal conductance of all resistor leads (70- $\mu\text{m}$  Manganin wire) comprised less than 1.5% of the substrate's conductance at the available temperatures. The power dissipated in the resistors was always kept below 0.01 $\dot{Q}$ . Because of spurious radiative heating there was a  $\Delta T_0$  even when the heater was turned off, presumably because of the small mass (150 mg) and low thermal conductance of the sample arrangement. This (temperature-dependent)  $\Delta T_0$  was also measured, yielding a thermal conductance  $K = \dot{Q}/(\Delta T_H - \Delta T_0)$ . Each datum point was acquired with an accuracy of about 1.5%.

The thermal conductance  $K_s$  of the substrate was determined *each* time before evaporation of Ge and was subtracted from the thermal conductance of the Kapton-Ge sandwich. This way we could minimize the uncertainties in the absolute values of the thermal conductance  $K$  of *a*-Ge.  $K/K_s$  varied between 0.15 and 1, depending on  $T$  and the sample thickness. Thus the maximum error in the results for the thermal conductivity of *a*-Ge,  $k = Kg$ , varied between 20% and 3%, where  $g$  is the geometric factor of the arrangement.

The thermal conductivity data we report on are presented in Fig. 1 in a plot of  $\log k$  vs  $\log T$  for three *a*-Ge films of thickness  $d = 2.3, 3.0,$  and  $5.7 \mu\text{m}$ . Two other films with  $d \approx 2 \mu\text{m}$  gave the same results as the 2.3- $\mu\text{m}$  film within accuracy

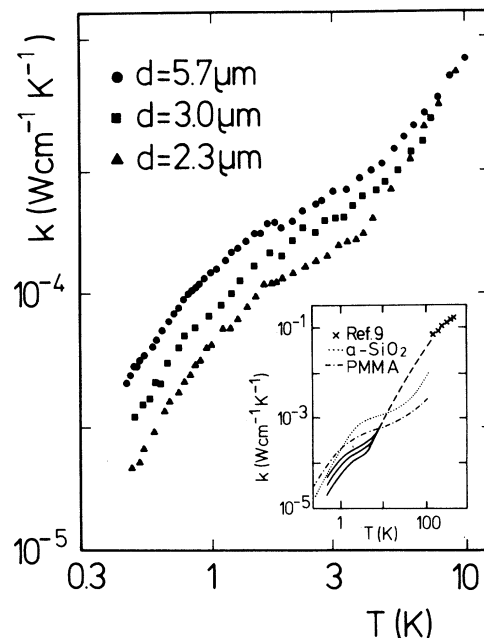


FIG. 1. Thermal conductivity  $k$  as a function of temperature  $T$  for amorphous germanium films of different thickness  $d$ . Inset shows the same data as compared to high-temperature data on *a*-Ge (Ref. 8) and to  $k$  vs  $T$  curves of a standard glass ( $\text{SiO}_2$ ) (Ref. 9) and standard polymer (PMMA) (Ref. 9).

of measurement and are not reproduced here. The same data are shown again in the inset and are compared to the high-temperature data (which can be smoothly extrapolated to ours) of a 0.7- $\mu\text{m}$ -thick *a*-Ge film<sup>8</sup> as well as to the thermal conductivities of  $\text{SiO}_2$  glass<sup>9</sup> and polymethylmethacrylate (PMMA).<sup>9</sup>

From the dc resistivity  $\rho = 10^2 \Omega \text{ cm}$  which we obtained for the *a*-Ge films at room temperature (in agreement with the results of other authors<sup>6,8,10</sup>), we conclude that the electronic contribution to  $k$  due to the Wiedemann-Franz law is completely negligible. Thus,  $k$  is readily identified with the thermal conductivity of the *lattice*.

Before commenting in detail, we wish to stress four important results: (1) The absolute values of  $k$  are about 3 to 4 orders of magnitude lower than those for crystalline Ge in the same temperature range.<sup>11</sup> (2) The curves of  $\log k$  vs  $\log T$  are reminiscent of the behavior discovered<sup>1</sup> for glasses and polymers: Coming from high temperatures, the thermal conductivity flattens off around 3 K ("plateau" region) and decreases more strongly below 1 K. (3) At all but the highest temperatures, there is a considerable dependence of  $k$  on

the film thickness. (4) Below 1 K we find  $k \sim T^n$ , where the exponent varies between 1.5 and 1.7.

We comment on these last two features first. Together they indicate that *boundary* as well as *intrinsic* (bulk) scattering limits the thermal conductivity. This interplay inhibits observation of a  $k \sim T^3$  law which one should find in the case of *dominating* boundary scattering and expect to exist at sufficiently low temperatures. The latter was established by Zaitlin and Anderson<sup>12</sup> who have studied glasses with holes, i.e., internal boundaries, and found curves of  $k$  vs  $T$  very similar to those in Fig. 1. The intrinsic scattering cannot be provided by dislocations, since they are usually thought to be absent in amorphous materials. Impurity or isotopic scattering is too weak at these low temperatures and furthermore would yield a different temperature dependence of  $k$ . We suggest that the phonons are scattered by LEE mentioned above, since the temperature dependence of  $k$  is close to the  $T^{1.8}$  law often found in glasses.<sup>1</sup>

To give a more quantitative analysis we evaluate the temperature dependence of the phonon mean free path (mfp)  $l$ . The mfp is obtained through  $k = \frac{1}{3} C_D l \bar{v}$ , where

$$C_D = \frac{2\pi^2 k_B^4 T^3}{5 \hbar^3 \bar{v}^3} = 55.5 T^3 \text{ erg K}^{-4} \text{ cm}^{-3}$$

is the Debye specific heat as calculated from the measured sound velocity<sup>13</sup>  $\bar{v} = 2.8 \times 10^5 \text{ cm s}^{-1}$  of  $a$ -Ge. In this calculation the dominant-phonon approximation ( $\hbar\omega_{\text{dom}} = 4k_B T$ ) is used. Between 0.4 and 10 K the wavelength,  $\lambda_{\text{dom}}$ , of the dominant phonons varies between 850 and 35 Å. In the same range the mfp varies between 10  $\mu\text{m}$  and 150 Å, as is seen from the bilogarithmic plot of  $l$  vs  $T$  in Fig. 2.

The influence of film thickness on  $l$  is attributed to a fraction  $1 - p$  of phonons which are *diffusely* scattered from the (rough) surfaces of the evaporated  $a$ -Ge films. Such "geometrically diffuse" boundary scattering was observed in etched glass fibers<sup>14</sup> and also in the above-mentioned glasses with holes.<sup>12</sup> For "geometrically diffuse" boundary scattering of phonons (like electrons<sup>15</sup>) one expects  $l^{-1} = l_i^{-1} + (1 - p)0.375d^{-1}$  to hold reasonably well if  $d/l_i > 0.1$ , where  $l_i$  is the mfp according to intrinsic scattering.<sup>16</sup> For a fixed temperature,  $l_i$  can be obtained rather accurately from a plot of  $l^{-1}$  vs  $d^{-1}$  by extrapolating  $d^{-1} \rightarrow 0$ . At 0.5 K, we find  $l_i \approx 10 \mu\text{m}$  (see inset of Fig. 2). Since  $l_i$  decreases at higher temperatures, it is, in fact, smaller than  $10d$  in the entire thickness and

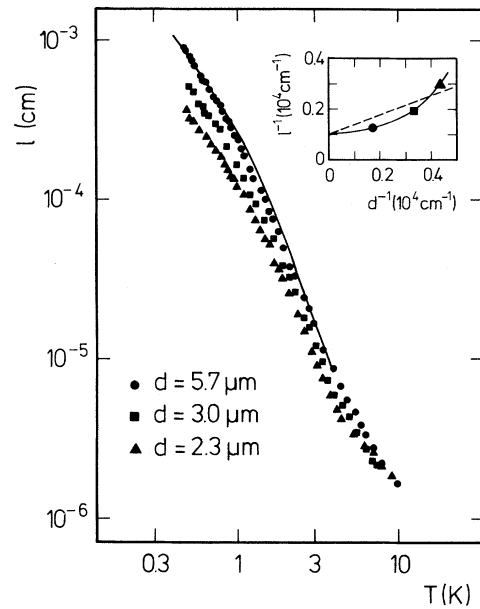


FIG. 2. Phonon mean free path (mfp)  $l$  as function of temperature  $T$  for  $a$ -Ge films. The solid line is a fit to the 5.7- $\mu\text{m}$  film as described in the text. Inset shows inverse mfp  $l^{-1}$  at 0.5 K as a function of inverse film thickness  $d^{-1}$ . Dashed line represents  $l^{-1} = l_i^{-1} + 0.375d^{-1}$  (see text).

temperature range available.

The nonlinear  $l^{-1}$  vs  $d^{-1}$  dependence (as compared to the dashed straight line for  $p = 0$ ) is very likely caused by the poor transport of condensation energy from the film to the (300 K) heat sink during evaporation, yielding an increasing (with thickness) actual deposition temperature. Hence, the density of *voids* (responsible for the above-mentioned surface roughness) is expected<sup>17</sup> to decrease upon increasing  $d$ . For the thinnest film ( $d = 2.3 \mu\text{m}$ ),  $l^{-1}$  exceeds the  $p = 0$  straight line suggesting that internal boundary scattering from voids (probably with inhomogeneous distribution profile) is present in addition to diffuse scattering from the film surfaces. On the other hand, for the thickest film ( $d = 5.7 \mu\text{m}$ )  $l^{-1} \approx l_i^{-1} + (1 - 0.7)0.375d^{-1}$ , which indicates that phonon boundary scattering is mainly specular and hints at a considerable reduction of void density.

The temperature dependence of  $l$  can be analyzed for this  $a$ -Ge film in the same way as proposed by Zaitlin and Anderson.<sup>12</sup> They obtained for borosilicate glass the correct mfp in the "plateau" regime from their *low-temperature* data by assuming scattering from localized excitations with a parabolic density of states,<sup>9</sup>  $n(\epsilon) = n_0 [1 + \alpha(\epsilon/k_B)^2]$ . This form of  $n(\epsilon)$  is inferred from

specific heat measurements to account for the linear term as well as the enhanced cubic term, typical of glasses.<sup>9</sup>

Carrying over these assumptions to the thickest *a*-Ge film and using the dominant-phonon approximation, we can calculate  $l_i \sim [T(1 + 16\alpha T^2)]^{-1}$ . Adjusting to the measured  $l$  at 0.5 K and choosing  $\alpha = 0.1 \text{ K}^{-2}$ , one obtains for  $l$  vs  $T$  the solid curve in Fig. 2 which describes satisfactorily the measured mfp below 4 K. Bearing in mind that the choice of a "dominant phonon" is only a crude approximation in the "plateau" region,<sup>12</sup> the agreement between calculated and measured mfp in Fig. 2 lends *additional* support to the existence of LEE in *a*-Ge. The value of  $\alpha$  obtained from the fit of the thermal conductivity data is comparable to that of glasses.<sup>12</sup> Unfortunately, a comparison with specific heat results is not possible since  $C_D$ , as calculated from the sound velocity of *a*-Ge,<sup>13</sup> is *larger* than the  $T^3$  specific heat as measured,<sup>5</sup> and a linear term could not be detected so far, since the measurement was confined to temperatures above 2 K.<sup>5</sup>

Above the "plateau" regime ( $T \gtrsim 5 \text{ K}$ ) the temperature dependence of the thermal conductivity sharpens (Fig. 1) and the phonon mfp tends to flatten off (Fig. 2). It should become constant as it approaches interatomic distances and the increase of  $k$  is then exclusively attributed to the rise in specific heat with temperature.

In summary, we have presented data of the low-temperature thermal conductivity of *a*-Ge which were analyzed in terms of boundary and intrinsic scattering of phonons. The temperature dependence of the phonon mfp provides strong evidence for the existence of localized excitations from which phonons are scattered. Our measurements show that these excitations also occur in an amorphous solid with "closed" structure.

Therefore, a future microscopic explanation must also account for this observation, which seems to go beyond the "atom in a double well" picture. On the experimental side, specific heat measurements on tetrahedrally bonded amorphous

semiconductors below 1 K are highly desirable.

We are grateful to W. Franz for performing the x-ray analysis, Dr. D. Sonder for valuable discussions, and Dr. S. Krebs for her help in preparing the manuscript. This work was performed under the auspices of the Sonderforschungsbereich 125.

<sup>(a)</sup> Present address: Centre de Recherches sur les Très Basses Températures, B. P. 166X, 38042 Grenoble-Cedex, France.

<sup>1</sup>R. C. Zeller and R. O. Pohl, Phys. Rev. B **4**, 2029 (1971).

<sup>2</sup>For a review see S. Hunklinger and W. Arnold, in *Physical Acoustics*, edited by R. N. Thurston and W. P. Mason (Academic, New York, 1976), Vol. 12, p. 155.

<sup>3</sup>P. W. Anderson, B. I. Halperin, and C. M. Varma, Philos. Mag. **25**, 1 (1972).

<sup>4</sup>W. A. Phillips, J. Low Temp. Phys. **7**, 351 (1972).

<sup>5</sup>C. N. King, W. A. Phillips, and J. P. Deneufville, Phys. Rev. Lett. **32**, 538 (1974).

<sup>6</sup>K. L. Chopra and S. K. Bahl, Phys. Rev. B **1**, 2545 (1970).

<sup>7</sup>A. W. Bjerkaas, D. M. Ginsberg, and B. J. Mrstik, Phys. Rev. B **5**, 854 (1972).

<sup>8</sup>P. Nath and K. L. Chopra, Phys. Rev. B **10**, 3412 (1974).

<sup>9</sup>R. B. Stephens, Phys. Rev. B **8**, 2896 (1973).

<sup>10</sup>W. Beyer and J. Stuke, J. Non-Cryst. Solids **8-10**, 321 (1972).

<sup>11</sup>T. H. Geballe and G. W. Hull, Phys. Rev. **110**, 773 (1958).

<sup>12</sup>M. P. Zaithlin and A. C. Anderson, Phys. Rev. B **12**, 4475 (1975).

<sup>13</sup>L. R. Testardi and J. J. Hauser, Solid State Commun. **21**, 1039 (1977).

<sup>14</sup>R. B. Stephens, Ph.D. thesis, Cornell University, 1974 (unpublished).

<sup>15</sup>W. Bausch and W. Waidelich, Phys. Status Solidi **37**, 187 (1970).

<sup>16</sup>The deviation from the exact equation is at most 7% [K. Chopra, *Thin Film Phenomena* (McGraw-Hill, New York, 1969), p. 345ff.]

<sup>17</sup>The "void density" was found by electron microscopy to change strongly with deposition temperature  $T_d$ ; no voids were observed for  $T_d \gtrsim 200^\circ\text{C}$  [M. Donovan and K. Heinemann, Phys. Rev. Lett. **26**, 1794 (1971)].