PHYSICAL REVIEW B VOLUME 27, NUMBER 6 15 MARCH 1983

Thermal conductivity of vitreous silica

D. P. Jones and W. A. Phillips
Cavendish Laboratory, University of Cambridge, Madingley Road,
Cambridge CB3 OHE, England

(Received 15 December 1981)

The temperature dependence of the thermal conductivity of vitreous silica has been calculated in the temperature range 0.1 to 100 K using an energy-independent density of states for the tunneling states. In contrast to a recent suggestion, it appears that this model cannot explain the "plateau" seen in the thermal conductivity between 4 and 20 K.

The temperature dependence of the thermal conductivity of glasses has been a subject of considerable interest for many years, but as yet no completely satisfactory explanation of the important physical processes has been found. Strangely, the best understood temperature region is that below 1 K, where complementary acoustic measurements have demonstrated that heat is carried by Debye phonons (sound waves) which are scattered by two-level systems (tunneling states).[1] By contrast, perhaps the least understood region is that between about 1 and 10 K, where the thermal conductivity varies only slightly with temperature, before increasing again above 10 K.[2]

The usual approach to calculations of the thermal conductivity in this intermediate temperature region has been to assume that as at lower temperatures heat is carried by Debye phonons and that the scattering increases rapidly with phonon frequency to offset the increasing number of phonons (which for scattering independent of temperature and frequency gives κ proportional to T^3). In general it has been claimed that scattering additional to that provided by two-level systems is necessary,[2] although none of the proposed explanations is completely satisfactory. However, it has also been suggested that scattering from two-level systems *can* explain the plateau in κ by assuming a density of two-level states that increases at least quadratically with energy.[3] If this explanation is accepted the discussion then centers on the physical origin of this rapidly increasing density of states: A density of states which increases slowly with energy is easy to justify, but a quadratic form is not.

However, in a recent paper Dutta and Jackson[4] claim to have explained the plateau on the basis of scattering by two-level states with an almost constant density of states. Since this appears to conflict with the conclusions of many other authors, the calculation is reexamined in this paper with the use of as simple an approach as possible, in order to make clear the physical principles, and to examine the approximations used by Dutta and Jackson.

The starting point for the calculation is the kinetic formula

$$\kappa=\frac{1}{3}\sum_{\alpha}\int_0^{\omega_{\alpha\max}} C_\alpha(\omega,T)v_\alpha l_\alpha(\omega,T)\,d\omega \ , \tag{1}$$

where α is the phonon branch index, v_α the velocity, $C_\alpha(\omega,T)$ the contribution to the heat capacity, and $l_\alpha(\omega,T)$ the free path of phonons of frequency ω. For the purposes of the calculation given here a mean sound velocity $\bar{v}$ can be used provided the Debye cutoff energy $\hbar\omega_{\alpha\max} >> kT$. Using the explicit Debye form for $C_\alpha(\omega,T)$ and using the reduced variable $\tilde{\omega}=\hbar\omega/k$, Eq. (1) becomes

$$\kappa=\frac{1}{6\pi^2}\frac{k^4}{\hbar^2\bar{v}^2T^2}\int_0^\infty \tilde{\omega}^4 e^{\tilde{\omega}/T}(e^{\tilde{\omega}/T}-1)^{-2}\, l(\tilde{\omega},T)\,d\tilde{\omega} \ . \tag{2}$$

Below 1 K resonant scattering from two-level systems is important, with[5]

$$l_{\mathrm{res}}^{-1}(\tilde{\omega},T)=A\,\tilde{\omega}\tanh\left(\frac{\tilde{\omega}}{2T}\right) \ , \tag{3}$$

where the density of two-level systems has been assumed to have the constant value $\bar{n}_0$ appropriate to an average coupling constant (and not equal to that derived from the heat capacity) and

$$A=\frac{\pi\bar{n}_0\bar{\gamma}^2k}{\rho\bar{v}^3\hbar} \ , \tag{4}$$

where ρ is the density and $\bar{\gamma}$ is an average coupling constant. It is clear by using Eq. (3) in Eq. (2) that resonance scattering gives a T^2 dependence of κ.

At higher temperatures a relaxation contribution is important, usually given by[4,5]

$$l_{\mathrm{rel}}^{-1}=\frac{\bar{\gamma}^2}{2kT\rho\bar{v}^3}\int_0^{E_{\max}} dE\,\bar{n}_0\,\mathrm{sech}^2\left(\frac{E}{2kT}\right)\int_{\tau_{\min}}^\infty d\tau\left(1-\frac{\tau_{\min}}{\tau}\right)^{1/2}\frac{\omega^2}{1+\omega^2\tau^2} \ , \tag{5}$$

where E is the energy of the tunneling state and τ is the one-phonon relaxation time, with

$$\tau_{\min}^{-1}=\sum_{\alpha}\frac{\gamma_{\alpha}^{2}}{v_{\alpha}^{5}}\frac{E^{3}}{2\pi\hbar^{4}\rho}\coth\left(\frac{E}{2kT}\right) . \tag{6}$$

The maximum value of τ is assumed to be very large. The integral over τ in Eq. (5) can be evaluated in the limits $\omega\tau_{\min} >> 1$ and $\omega\tau_{\min} << 1$. For $\omega\tau_{\min} << 1$,

$$l_{\mathrm{rel}}^{-1}=\frac{\pi\bar{\gamma}^{2}\omega}{4\rho\bar{v}^{3}kT}\int_{0}^{E_{\max}}\bar{n}_{0}\operatorname{sech}^{2}\left(\frac{E}{2kT}\right)dE=\frac{\pi}{2}\frac{\bar{n}_{0}\bar{\gamma}^{2}\omega}{\rho v_{l}^{3}}=\frac{A}{2}\tilde{\omega},\quad \omega\tau_{\min} << 1 . \tag{7}$$

In the other limit

$$l_{\mathrm{rel}}^{-1}=\frac{\bar{\gamma}^{2}\omega}{2\rho\bar{v}^{3}kT}\int\bar{n}_{0}\operatorname{sech}^{2}\left(\frac{E}{2kT}\right)\frac{2}{3\omega}\frac{E^{2}\coth(E/2kT)}{2\pi\rho\hbar^{4}}\sum_{\alpha}\frac{\gamma_{\alpha}^{2}}{v_{\alpha}^{5}}dE=\frac{\pi^{3}}{24}\frac{\bar{n}_{0}\bar{\gamma}^{2}(kT)^{3}}{\rho^{2}\hbar^{4}\bar{v}^{3}}\sum_{\alpha}\frac{\gamma_{\alpha}^{2}}{v_{\alpha}^{5}} . \tag{8}$$

This agrees with the result obtained by integrating Eq. (14) of Dutta and Jackson for a constant density of states, but does not agree with their Eq. (15), which is larger by a factor of 3. Equation (8) can be rewritten as

$$l_{\mathrm{rel}}^{-1}=\frac{A}{2}BT^{3} \tag{9}$$

with

$$B=\frac{\pi^{2}k^{2}}{12\rho\hbar^{3}}\sum_{\alpha}\frac{\gamma_{\alpha}^{2}}{v_{\alpha}^{5}}=3\times10^{-3}K^{-2} ,$$

using measured values of γ_{α}^{2} and v_{α}.[6] The two limits can be combined in the interpolation formula[7]

$$l_{\mathrm{rel}}^{-1}=\frac{A}{2}\left(\frac{1}{\tilde{\omega}}+\frac{1}{BT^{3}}\right)^{-1} , \tag{10}$$

giving for the total inverse free path

$$l^{-1}(\tilde{\omega},T)=\frac{A}{2}\left[2\tilde{\omega}\tanh\left(\frac{\tilde{\omega}}{2T}\right)+\left(\frac{1}{\tilde{\omega}}+\frac{1}{BT^{3}}\right)^{-1}\right] . \tag{11}$$

The importance of this formula is that it shows in a direct way the relative importance of the resonance and relaxation, a relation which is almost unchanged for other forms of the density of states, which appears simply as a prefactor. Equation (11) is implied in the discussion following Eq. (15) of Dutta and Jackson, apart from the factor of $(E/kT)^3$ in their expression for the relaxation scattering rate, a factor which does not appear explicitly after integration over the tunnel-state energy E. However, their use of the high-frequency limit means that they use a term BT^3 to represent the l_{rel}^{-1} for all frequencies. The importance of this approximation is shown in Fig. 1, where

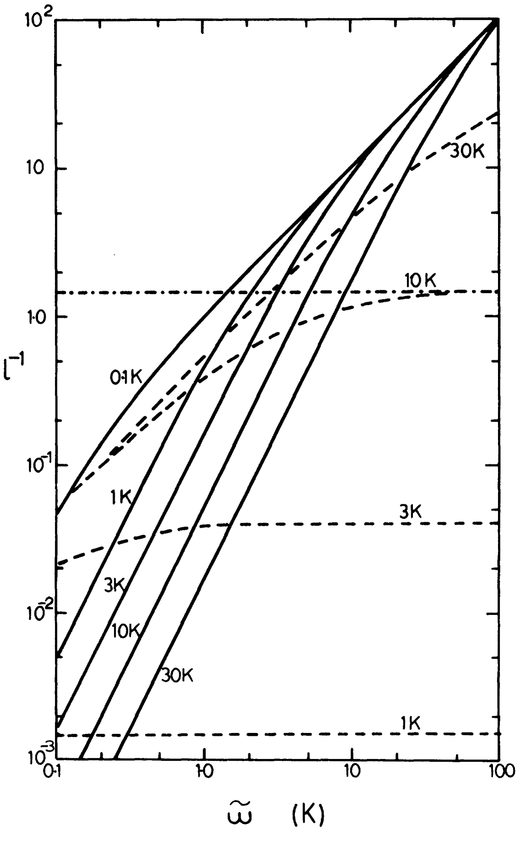

FIG. 1. Contributions of relaxation (dashed line) and resonance scattering (solid line) to the free path at various temperatures as a function of reduced phonon frequency. The values are normalized to unity at $\tilde{\omega} = 1.0$ K in the low-temperature limit ($T < 0.1$ K). A dash-dotted line is drawn to show at 10 K the effect of the high-frequency limit used in Ref. 4.

l^{-1} given by Eq. (11) is plotted as a function of $\tilde{\omega}$ for various temperatures. It can be seen that use of the high-frequency approximation overestimates the scattering of low-frequency phonons at high temperatures, although as will be shown later the effect on κ is not dramatic.

The thermal conductivity as a function of temperature, calculated using Eq. (11) in Eq. (2), is shown as curve b in Fig. 2. Also shown is the thermal conductivity calculated using resonance scattering alone (curve a) and, following Dutta and Jackson, using the high-frequency limit for the relaxation term (curve c). Clearly the relaxation term cannot reduce the thermal conductivity sufficiently to produce a plateau. Agreement with experiment can only be obtained by using a density of two-level states which increases rapidly with energy, or by introducing additional scattering as shown in curve d, where a term proportional to $\tilde{\omega}^4$ has been included to represent Rayleigh scattering. The parameters used in this fit (given in the figure caption) are in close agreement with those of Jäckle.[7]

The effect of the approximation of a mean sound velocity used in deriving Eq. (2) can be easily examined by using Eq. (1). Below 1 K the value of A required for agreement with experiment can be divided into $A_L = 6.3 \times 10^4$ m^{-1}K^{-1} and $A_T = 1.2 \times 10^5$ m^{-1}K^{-1} on the basis of measured parameters.[6] The upper limits $\omega_{\alpha \max}$ can be chosen consistently within the Debye model as 360 and 240 K, respectively, on the basis that in the closest crystalline form of SiO$_2$, cristobalite, the acoustic modes comprise $\frac{1}{6}$ of the total number. In fact both neutron studies and measurements of the low-temperature heat capacity of vitreous silica indicate that a lower cutoff for the transverse modes of about 60 K is more appropriate,[9] although it must be emphasized that this is not consistent with the use of the Debye model. A calculation which includes a "dispersive" effect has already been published.[10] However, ignoring this inconsistency, the thermal conductivity was calculated for both values of the transverse cutoff frequency. With the use of $\tilde{\omega}_{L \max} = 360$ K, $\tilde{\omega}_{T \max} = 240$ K, κ at 50 K was reduced from 40 W m^{-1}K^{-1} (given by curve b) to 33 W m^{-1}K^{-1}, and with $\tilde{\omega}_{L \max} = 360$ K, $\tilde{\omega}_{T \max} = 60$ K, κ was reduced to 15 W m^{-1}K^{-1}. In neither case was there any sign of a plateau, so that it is clear that the use of mean velocity does not lead to serious error.

What is not clear is the difference between the results presented here and those given by Dutta and Jackson.[4] Equation (11) shows clearly that there is little scope for any adjustment of the parameters, and a comparison of curves b and c in Fig. 2 implies that the use of the high-frequency limit for l_{rel} is not a major effect. The results presented here show that the experimental data cannot be explained by scattering from a constant density of tunneling states. Any successful fit to the data must therefore involve a density of states which increases with energy.

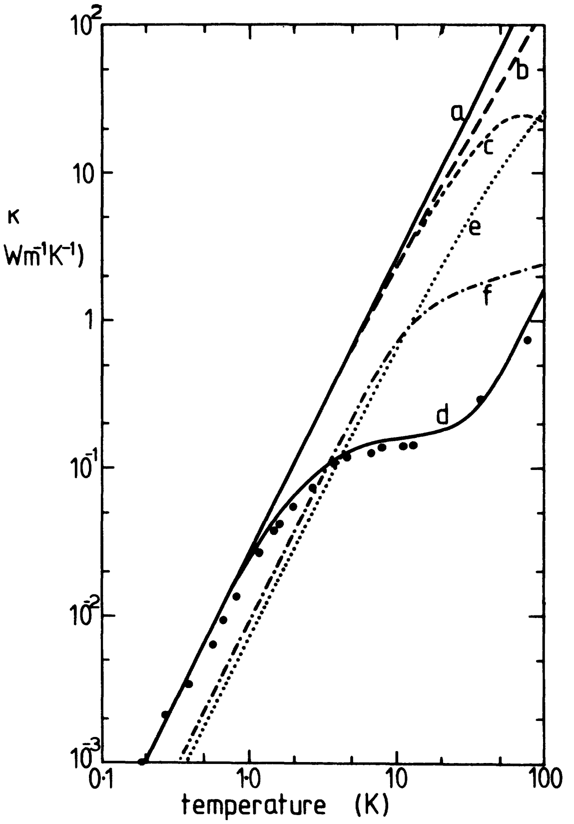

FIG. 2. Experimental values (Ref. 8) for the thermal conductivity of SiO$_2$ together with various calculated curves. Curves a to d are calculated using a mean sound velocity of 4.1×10^3 m s^{-1}, together with values $A = 3.5 \times 10^4$ m^{-1}K^{-1} and $B = 3 \times 10^{-3}$ K^{-2}; a: resonance scattering alone; b: resonance and relaxation contributions included as in Eq. (11); c as in b, but with the high-frequency limit for the relaxation contribution; d as b, but including a term $D\tilde{\omega}^4$ to represent Rayleigh scattering with $D = 110$ m^{-1}K^{-1}. Curves e and f show the longitudinal and *one* transverse contribution to the thermal conductivity, each calculated as in curve b but with upper cutoffs $\tilde{\omega}_{L \max} = 360$ K, $\tilde{\omega}_{T \max} = 60$ K. The values of A are $A_L = 6.3 \times 10^4$ m^{-1}K^{-1} and $A_T = 1.2 \times 10^5$ m^{-1}K^{-1}, while the value of B is unchanged.

---

[1] A. C. Anderson, in *Amorphous Solids; Low Temperature Properties*, edited by W. A. Phillips (Springer, Berlin, 1981), Chap. 5.

[2] D. P. Jones, N. Thomas, and W. A. Phillips, Philos. Mag. 38, 271 (1978).

[3] T. L. Smith, P. J. Anthony, and A. C. Anderson, Phys. Rev. B 17, 4997 (1978).

[4] M. Dutta and H. E. Jackson, Phys. Rev. B 24, 2139 (1981).

[5] S. Hunklinger and W. Arnold, in *Physical Acoustics,* edited by W. P. Mason and R. N. Thurston (Academic, New York, 1976), Vol. 12, p. 155.

[6] B. Golding, J. E. Graebner, and R. J. Shutz, Phys. Rev. B 14, 1660 (1976).

[7] J. Jäckle, in *The Physics of Non-Crystalline Solids,* edited by Frischat (Trans Tech, Rockport, Mass., 1976), p. 568.

[8] R. C. Zeller, M.S. thesis (Cornell University, New York, 1971) (unpublished).

[9] A. J. Leadbetter, Phys. Chem. Glasses 9, 1 (1968).

[10] D. P. Jones, J. Jäckle, and W. A. Phillips, in *Phonon Scattering in Condensed Matter,* edited by H. J. Maris (Plenum, New York, 1980).