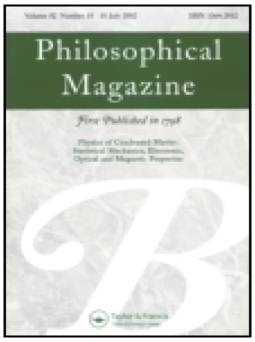

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The low-temperature thermal properties of amorphous arsenic

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Abstract

Below 1 K the heat capacity $C(T)$ of bulk amorphous As is proportional to the cube of the absolute temperature T, in marked contrast to the behaviour of other amorphous solids. Above 1 K $C(T)/T^3$ increases rapidly to a maximum at about 5 K, decreasing more gradually at higher temperatures, in a way that resembles other amorphous solids. The thermal conductivity κ varies as T^3 below 0·3 K, shows a plateau centred at about 5 K, and increases again above 10 K. The T^3 variation below 0·3 K is shown to be a result of phonon scattering by small holes in the sample, giving a constant phonon mean free path of 25 μm.

The temperature dependence and magnitude of κ are discussed in terms of two different theories, neither of which is completely satisfactory. The effects of dispersion are included with the help of parameters derived from the heat capacity, but this is shown to have little effect on the strength of scattering needed to explain the plateau. Finally, it is suggested that phonon–phonon scattering may account for the temperature variation of κ in amorphous solids above 1 K.

§ 1. Introduction

Over the last few years low-temperature thermal measurements have been made on a wide range of amorphous solids. Similar features have been observed in all of them. Below 1 K the heat capacity $C(T)$ is considerably larger than that calculated from measured sound velocities, and although measurements down to 25 mK have shown that the temperature dependence of the excess heat capacity cannot be described by a simple power law, between 0·1 and 1 K it can be adequately described by a term proportional to the temperature T together with a term proportional to T^3. The thermal conductivity κ varies roughly as T^2 below 1 K, shows little temperature dependence between 1 and 10 K, and then increases again at higher temperatures.

Although a variety of explanations have been proposed to account for the results below 1 K, the most widely used model is based on the idea of tunnelling states in the glass. In this model (Phillips 1972, Anderson, Halperin and Varma 1972) the quantum mechanical tunnelling of an atom or a small group of atoms from one potential minimum to a neighbouring one gives rise to a small energy splitting ϵ between the ground and excited states. This energy ϵ can be comparable to thermal energies at 1 K and below. A wide range of such energy splittings is to be expected as a general feature of the amorphous solid, and can be described by a density of states $n(\epsilon)$. Originally it was argued on general grounds that $n(\epsilon)$ would be a slowly increasing function of energy which over a limited range can be represented by a constant term n_0. This constant density of states gives rise to the term proportional to T in the heat capacity. Each tunnelling state can also interact with, and scatter, phonons. Resonance scattering occurs when the phonon energy, $\hbar\omega$, is equal to ϵ, and leads to a thermal conductivity proportional to T^2 for a constant density of tunnelling-state energies. (Expressions for the phonon free path are given in §3.)

A test of this, or any other, theory requires measurements on amorphous insulators with as wide a range of structures as possible. However, almost all the measurements up to now have been on glasses, bulk amorphous solids prepared by quenching from the melt. The only exceptions are results obtained from thin films of amorphous germanium (King, Phillips and de Neufville 1974, Löhneysen and Steglich 1977), but neither κ nor C has been measured to sufficiently low temperatures to allow a detailed comparison with bulk glasses. This is unfortunate, since the four-fold coordinated Ge network provides a very different disordered structure on which to test out theories of the thermal properties.

This paper presents measurements of the thermal properties of amorphous arsenic (a-As), which can be prepared in bulk form but cannot be obtained by quenching from the melt. The structure is three-fold coordinated (Greaves and Davis 1974), providing a useful contrast to that of most bulk glasses. A preliminary account of the heat capacity results below 1 K has already been presented (Phillips and Thomas 1977) and, more recently, heat capacity data at higher temperatures has been published by Lannin, Eno and Luo (1977).

The main result of this paper is that the thermal conductivity of a-As has a similar temperature dependence to that of other amorphous solids, except below 0·5 K where κ varies as T^3. This T^3 behaviour is shown to arise from the presence of small holes in the bulk samples. The specific heat varies as T^3 below 1 K, but C/T^3 shows a peak at about 5 K. These results are presented in § 2, together with details of the experimental techniques, and are discussed fully in § 3.

§ 2. EXPERIMENTAL TECHNIQUES AND RESULTS

Samples of bulk a-As were obtained from Mining & Chemical Products, where it is prepared by condensing As in the presence of hydrogen onto a heated substrate. These samples were similar to those used by Lannin *et al.* (1977) and indeed to all samples of bulk a-As, which are obtained from the same source or made in a similar way. It appears, from a variety of private communications, that the hydrogen concentration is less than 0·1% in bulk a-As (Lannin *et al.* 1977). The bulk density of the samples was 4770 kg m^{-3}.

The heat capacity $C(T)$ was measured between 0·35 and 18 K by means of a small-sample pulse technique described fully by Bachmann and his collaborators†. For the measurements above 1·5 K the sample, weighing about 100 mg, was stuck onto a doped silicon chip which acted as a thermometer, and also carried an evaporated nichrome or copper heater. Below 1·5 K a sapphire disk was used instead of the silicon chip, and the temperature was monitored by a thin slice cut from an Allen Bradley resistor. The random error is apparent from the figures, and any systematic errors are believed to be less than 5%.

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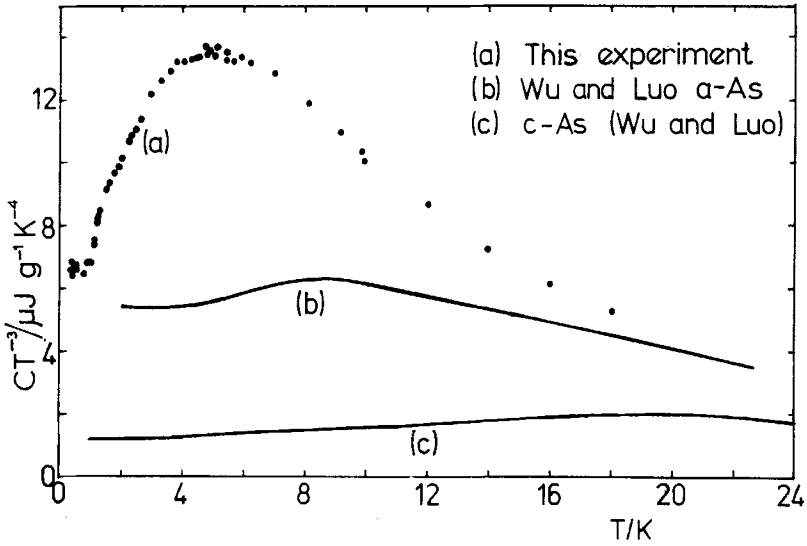
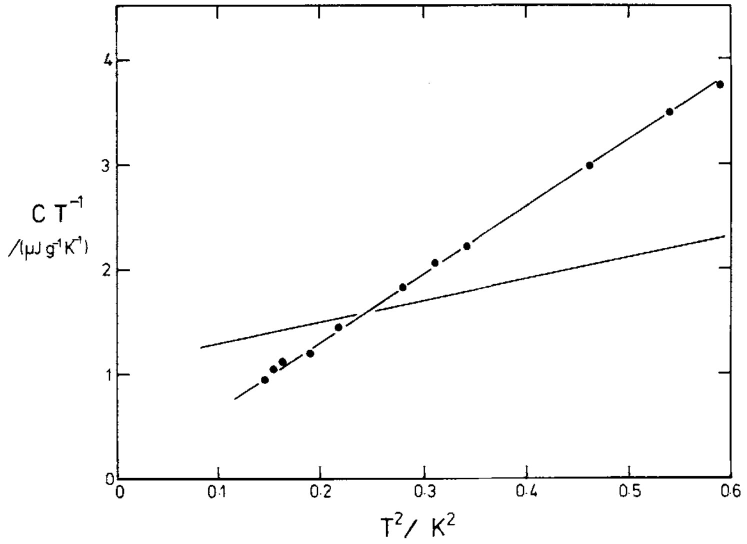
† Bachmann, Di Salvo, Geballe, Greene, Howard, King, Kirsch, Lee, Schwall, Thomas and Zubeck (1972).

Fig. 1



Specific heat of various forms of arsenic, plotted as C/T^3 against T. (a) Bulk a-A —this work. (b) Compacted thin film a-As from Wu and Luo (1974). (c) Lattice specific heat of crystalline rhombohedral As from Wu and Luo. The densities of the three materials are 4770, 4950 and 5730 kg m^{-1}, respectively.

Fig. 2

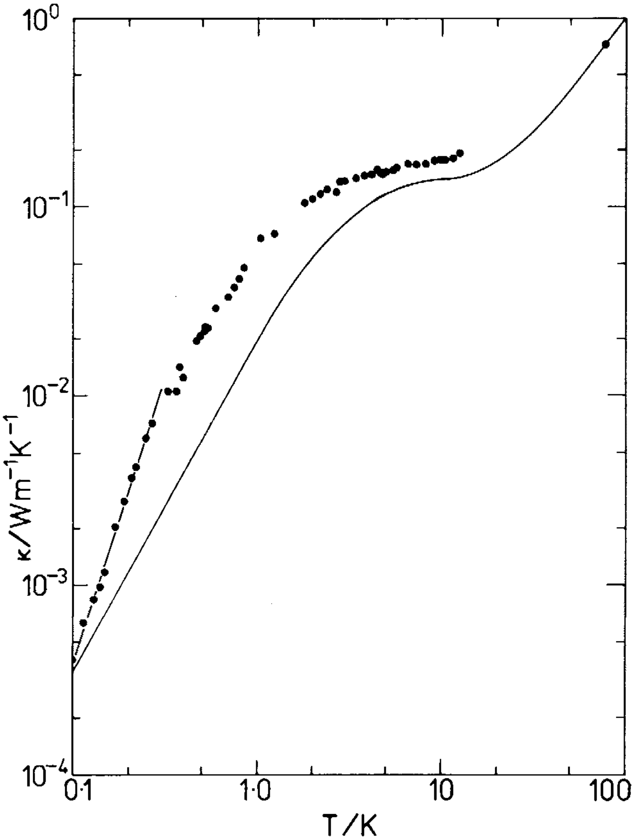


Specific heat of a-As plotted as C/T versus T^2 (solid circles). Also shown in the curve for vitreous silica (Zeller 1971).

The results are plotted in fig. 1 as $C(T)/T^3$ against T. A marked peak in this form of plot is typical of amorphous solids, but unlike these other solids there is no sign of an upturn in $C(T)/T^3$ below 1 K. This is confirmed by replotting the data as $C(T)/T$ against T^2 in the temperature range 0·35 to 0·7 K. As shown in fig. 2 this gives a straight line plot with a very small intercept: a regression analysis gives $0{\cdot}05 \pm 0{\cdot}05$ μJ g^{-1} K^{-2}.

The thermal conductivity $\kappa(T)$ was measured using a two-heater steady-state technique with a single thermometer (Zaitlin and Anderson 1975). This has two advantages over the more common two-thermometer method: narrow strip heaters define the geometry of the sample more precisely than do thermometers, and the method requires only a single thermometer calibration. The samples were rectangular prisms about 10 mm long, 4 mm wide and 1 mm thick, with one polished face. Two thin copper or nichrome heaters were evaporated across this face about 4 mm apart, and one end of the sample was clamped between two copper plates. Vacuum grease was used to improve thermal contact. A carbon thermometer, again cut from a resistor, was mounted at the other end.

Fig. 3



Thermal conductivity κ of a-As (solid circles). The line drawn through the low-temperature points is proportional to T^3. Also shown is κ for vitreous silica (Zeller 1971).

Power P dissipated in a heater increases the thermometer temperature by ΔT above the equilibrium temperature T_0. The fractional change $\Delta T/T_0$ was always less than 10%, and in this range of temperature throws there was no evidence for any non-linear dependence of ΔT on P. Any boundary resistance between the sample and the copper was small even at the lowest temperatures, since the ratio of $\Delta T/P$ (at a fixed T_0) for the two heaters was within 10% of that estimated from the sample geometry, and did not vary with temperature. The thermal conductivity was calculated from values of $\Delta T_1/P_1$ and $\Delta T_2/P_2$ for heaters 1 and 2 evaluated at the same temperature T. Corrections to the measured values of κ resulting from the finite thickness of the sample were shown to be less than 2% by modelling the heat flow on conducting paper. A gold–iron/chromel thermocouple was used in place of the carbon thermometer to give the thermal conductivity at 77 K. The points have an average error of about 5%.

The results are shown in fig. 3. Below 0·25 K, the temperature dependence of κ is given by T^η, with $\eta = 3{\cdot}0 \pm 0{\cdot}2$. This is in marked contrast to the temperature dependence of κ in other amorphous solids in this temperature range (the thermal conductivity of vitreous SiO_2 is also shown in fig. 3), but at higher temperatures the behaviour is similar.

§ 3. DISCUSSION

3.1. *Specific heat*

There are three main features of the results shown in figs. 1 and 2 that should be emphasized. The specific heat of this bulk sample of a-As is much larger than that of the films of a-As which were measured earlier by Wu and Luo (1974); significant departures from Debye behaviour can be seen at the surprisingly low temperature of 1 K; and below 0·7 K the specific heat varies as T^3 and shows no sign of the linear anomaly that has been seen in all other bulk amorphous solids. These features will be discussed in turn, even though Lannin *et al.* (1977) have discussed the first two points in some detail. Their results on bulk a-As agree with those of fig. 1 within about 10%.

a-As is probably the first amorphous solid for which specific heat data are available in both thin film and bulk samples. A comparison of the data (fig. 1) shows that the bulk sample has a heat capacity which is larger by a factor of about two at 6 K, although the differences are much less marked at high and low temperatures. Such differences are much greater than those observed between different samples of bulk glasses (White and Birch 1965) and provide strong evidence that the properties of thin films are very sensitive to the method of preparation.

One simple observation can be made from the data. The number of modes at low frequencies does appear to increase with decreasing density. Although such a trend is seen in other systems, for example, germanium (King *et al.* 1974) or neutron-irradiated silica (White and Birch 1965), the unusually large magnitude of the effect in As suggests that it may be a property of the unusual bonding of As atoms. The effect of the bonding can be understood from a generalization of an argument put forward for a-Ge by Weaire and Alben (1972). If it is assumed that the vibrational modes in a topologically disordered random network can be adequately described by bond-stretching and bond-bending force constants alone, a proportion of the modes depend only on the much weaker bond-bending force constant. In the limit where this force constant tends to zero, the number of such modes can be calculated. The condition that the bond lengths remain constant in a z-fold coordinated network places $zN/2$ constraints (one per bond) on the $3N$ normal modes, where N is the number of atoms. In a-Ge this gives one mode per atom. As long as the bond-bending force constant is much weaker than the bond-stretching one, these modes give the observed low-frequency peak in the density of states.

Each As atom in rhombohedral crystalline As forms three short bonds with three neighbouring As atoms on one side, and three long, weaker, bonds with neighbours on the other. This effectively six-fold coordinated structure should not show a marked low-frequency peak in the density of states, a conclusion which agrees with experiment. In the disordered solid the ability to form the three long bonds is much reduced, partly because of the disordered structure and partly because the density is less. The As is then effectively three-fold coordinated and should show the low-frequency peak. The extent to which the atoms are three- or six-fold coordinated will depend on the density, and this in turn will give rise to large changes in the low-frequency peak with density.

The appearance of a low-frequency peak in an effectively three-fold coordinated structure provides a qualitative explanation for the departure from a T^3 temperature dependence of the specific heat at a few degrees K. A quantitative explanation, however, requires a detailed knowledge of the density of states $g(\omega)$. The difficulty of the reverse process, calculating $g(\omega)$ from the heat capacity, is illustrated in the paper by Lannin *et al.* (1977), who do, however, show that $g(\omega)$ departs from a quadratic variation with ω at very low frequencies.

One point must be stressed before discussing the thermal conductivity later in this section. The departures from the quadratic density of states at 10 cm^{-1} and above (equivalent to C/T^3 departing from a constant value at 2 K or so) casts serious doubts of the validity of the Debye approximation in this frequency range. This is of some importance, in view of the fact that almost all analyses of thermal conductivity assume that the Debye approximation is valid, and discuss any unusual behaviour of κ in terms of the scattering of sound waves. Direct evidence for the existence of non-dispersive sound waves in amorphous solids has been obtained only for frequencies below 1 cm^{-1}, and the peak in C/T^3 is strong evidence that such modes do *not* exist at higher frequencies.

One possible interpretation of the data shown for bulk a-As in fig. 1 is to say that the sharp rise in C/T^3 marks the limit of the Debye approximation for the lowest frequency group of phonons, those equivalent to transverse acoustic waves at long wavelengths. The modes that contribute to the heat capacity near 5 K are non-propagating or localized, just as the modes that contribute to the peak in C/T^3 in crystalline germanium are non-propagating by virtue of their very small group velocity. This interpretation then leads to a natural cut-off in the Debye model for these modes at about 10 cm^{-1}, although of course the other type of low-frequency phonon, corresponding to a longitudinal acoustic mode at long wavelengths, may still be adequately represented by the Debye model up to much higher frequencies.

The final point concerns the difference between these results on bulk a-As and those obtained for other bulk amorphous solids below 1 K. As shown in fig.

2, C is proportional to T^3, with a slope which gives an average sound velocity of $1{\cdot}6 \times 10^3\,\mathrm{m\,s^{-1}}$. Measurements of sound velocities are not available in a-As, but this value appears to be a reasonable estimate of the thermally averaged sound velocity in view of the value of $1{\cdot}36 \times 10^3\,\mathrm{m\,s^{-1}}$ found in As_2Se_3 (Soga, Kunugi and Ota 1973). A more precise comparison with a measured average velocity would of course be desirable in order to establish that the Debye model gives a complete description of the heat capacity below 0·7 K, and that no other modes are contributing.

The experimental results shown in fig. 2 are consistent with the absence of a 'linear term'. The measured intercept is smaller than that measured in SiO_2 by a factor of over 15, and smaller than that in very pure As_2S_3 by a factor of about six. Converted to the number of additional states per As atom, bulk a-As compared to As_2S_3 contains fewer additional states by a factor of four. It is difficult to give firm reasons for this smaller value. For example, it may be a continuation of the trend seen in As_2S_3 where purer samples give a smaller linear term in the heat capacity (Stephens 1976), since the method of preparation of a-As should give very pure samples. On the other hand, it may be that the result supports the tunnelling model, as the local rearrangements of a few atoms which give rise to the linear heat capacity in this model may not be possible in the rigid a-As structure, containing no two-fold coordinated atoms.

3.2. *Thermal conductivity*

The thermal conductivity of glasses is usually interpreted by means of a general form of the kinetic equation

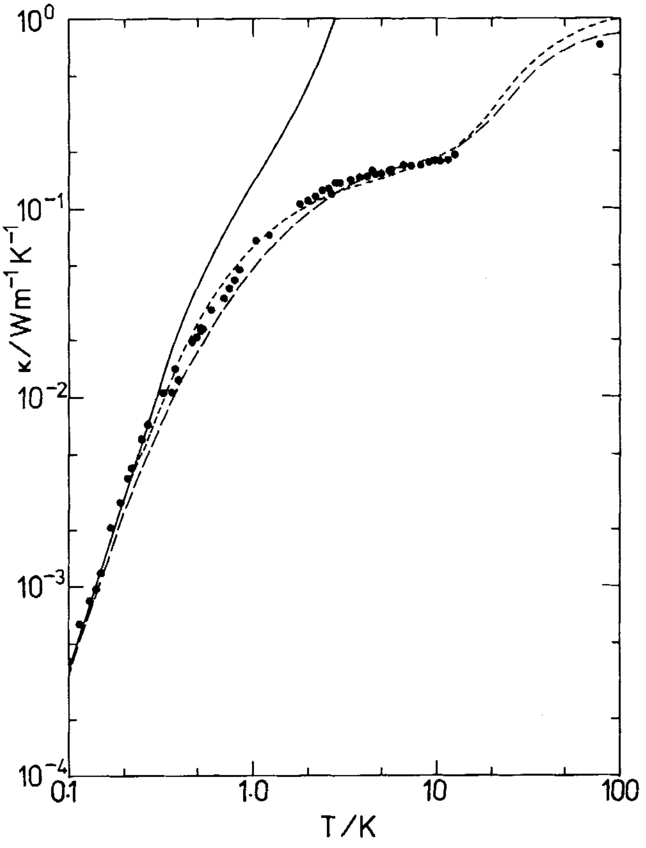
$$\kappa(T)=\tfrac{1}{3}\int_0^{\omega_D} C(\omega, T)\bar{v}l(\omega, T)\,d\omega. \tag{1}$$

$C(\omega, T)\,d\omega$ is the contribution to the heat capacity from the propagating modes with frequencies between ω and $\omega+d\omega$. These modes are invariably taken as acoustic modes, with cut-off frequency ω_D, and with an average velocity $\bar{v}$, assumed independent of ω. The mean free path of these phonons is written as $l(\omega, T)$ to include the explicit temperature dependence which must be present in some glasses to explain a minimum in κ as a function of T (Leadbetter, Jeapes, Waterfield and Maynard 1977). The inverse mean free paths resulting from different scattering mechanisms are assumed to add to give a total $l^{-1}(\omega, T)$. If $l(\omega, T)$ does not vary rapidly with ω, then, since $C(\omega, T)$ has a maximum for $\hbar\omega \sim 4kT$, the integral can be replaced by the expression, $\kappa(T)=\frac{1}{3}C(T)\bar{v}\,l$, where l is evaluated at a frequency given by $\hbar\omega=4kT$. This is known as the dominant phonon approximation.

It has been suggested that dispersion may play a part in the temperature dependence of κ (Jäckle 1976). (Dispersion is perhaps not an appropriate term to use in a disordered solid, since it assumes a well-defined wavevector, but the physical interpretation of the effect is clear; a large number of the modes contributing to $C(T)$ in the disordered solid are effectively non-propagating.) Equation (1) must be generalized to include the real vibrational spectrum $g(\omega)$. $C(\omega, T)$ can of course be related to $g(\omega)$ but, in addition, the velocity must be written so as to account not only for different types of modes but also to allow for any variations with ω.

A simple prescription for including the effects of ' dispersion ' is to say that the modes are either sound waves with the appropriate velocity or non-propagating, in which case they make no contribution to the integral in eqn. (1). This requires the introduction of two separate cut-off frequencies in (1), and these can be chosen with reference to the vibrational density of states, as far as it is known. For example, from the discussion of the heat capacity data in a-As, the cut-off for the transverse acoustic modes might be taken as 10 cm^{-1}, while the corresponding cut-off for the longitudinal modes would be much higher, say 100 cm^{-1} or above. This figure is obtained from the position of the second pronounced peak in the vibrational density of states as measured by neutron or Raman scattering (Leadbetter, Smith and Seyfert 1976, Lannin 1977).

Fig. 4

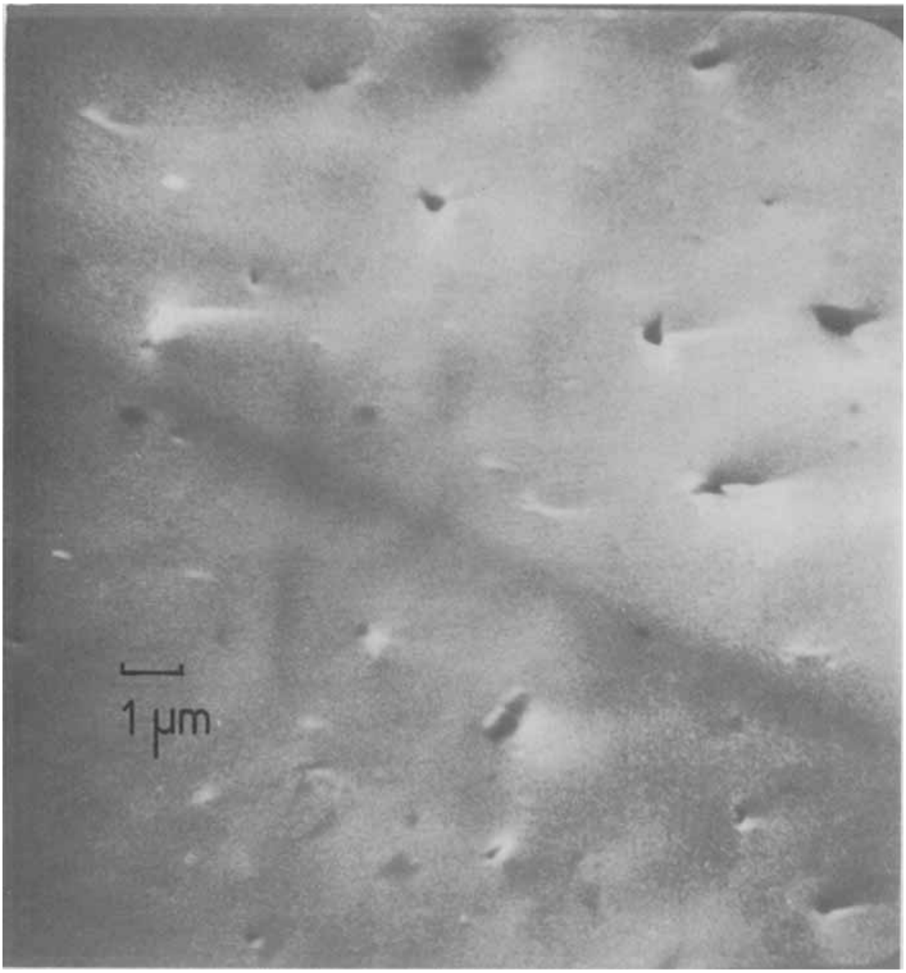


Calculations of the thermal conductivity of a-As (see text). Solid line = modelling the effect of dispersion (with a constant mean free path of 25 μm) using a cut-off frequency for the transverse phonons of 3 cm^{-1}. Long dashes = calculated assuming phonon scattering from a quadratic density of tunnelling states, using eqns. (4) and (5) with $B = 10^4$ m^{-1} K^{-3}, $\beta = 5\times10^{-3}$ K^{-2} and a minimum mean free path l_0 of 1·5 nm. Short dashes = calculated using eqn. (6), with $D = 1{\cdot}9\times10^3$ m^{-1} K^{-4} and $l_0 = 1{\cdot}5$ nm, together with a constant mean free path of 25 μm.

The results of a calculation that includes dispersion depend on the form of $l(\omega, T)$, but a simple example is shown in fig. 4 for a constant mean free path of $25\,\mu$m. Both at high and low temperatures κ varies as T^3, but the graph does show an intermediate regime where κ varies more slowly with temperature. (It has been assumed that the ratio of longitudinal to transverse velocity has the typical value of two.) This result, which would be similar for other types of scattering, is not sufficient by itself to explain the plateau in κ. What it does show, however, is that the strength of scattering required to produce a plateau is less than would be expected in the absence of dispersion.

Returning to the results shown in fig. 3, the temperature dependence of the thermal conductivity of bulk a-As can be seen to be very similar to that of other glasses, with the exception of the very low-temperature region. Below 0·5 K, κ varies as T^3. From the measurements, using an average sound velocity

Fig. 5



Cleaved surface of a-As viewed with the scanning electron microscope.

deduced from the specific heat data, a value of 25 μm is calculated for the temperature-independent mean free path. Since this is much less than any dimensions of the sample, it must be concluded that scattering arises from internal cracks or voids in bulk a-As.

A microscopic examination of cleaved surfaces of a-As, both with the optical and with the scanning electron microscope, shows structure which can account for the constant phonon mean free path. Figure 5 shows a surface in which small holes are clearly visible, each of diameter about 0·5 μm. The number of these holes can be estimated as about 10^{17} m^{-3}. Each hole is larger than the dominant phonon wavelength above 0·1 K, so that a simple argument can be used to give a mean free path of about 40 μm, in reasonable agreement with the value needed to fit the data below 0·5 K. The presence of these holes in a-As means that the measured density is likely to be too low by about 1%.

The measurements of κ were started in the hope that the absence of a linear term in the heat capacity might be associated with a κ having a different temperature dependence to that found in other bulk amorphous solids. Certainly κ varies as T^3 below 0·5 K, but the complete curve shown in fig. 3 looks very similar to the corresponding curve for SiO_2, with the addition of a constant mean free path of 25 μm.

Perhaps the most complete interpretation of the thermal conductivity of amorphous solids, both at low temperatures and through the plateau region, has been made by Anderson in a number of papers (Zaitlin and Anderson 1975, Smith, Anthony and Anderson 1978). He has extended the tunnelling-state model, originally suggested to account for the thermal properties below 1 K, to higher temperatures. In the original model, described in the introduction, each tunnelling state can provide both a resonant and a relaxation contribution (Jäckle 1972) to the scattering of phonons. The resonant process occurs when the energy of the phonon $\hbar\omega$ is equal to ϵ, and the relaxation process is important when the relaxation time τ of the state satisfies $\omega\tau \sim 1$.

Formally, the expressions for the mean free paths arising from the two scattering mechanisms are (Zaitlin and Anderson 1975).

$$l_{\mathrm{res}}^{-1} = A\left(\frac{\hbar\omega}{k}\right)\tanh\frac{\hbar\omega}{2kT}, \quad \text{with } A = \frac{\pi\bar{n}M^2k}{\rho v^3\hbar}, \tag{2}$$

and

$$\left.\begin{aligned} l_{\mathrm{rel}}^{-1} &= \frac{A}{4}\left(\frac{\hbar\omega}{k}\right) \quad \omega < \omega_1, \\ l_{\mathrm{rel}}^{-1} &= \frac{A}{4}\left(\frac{\hbar\omega_1}{k}\right) \quad \omega > \omega_1, \end{aligned}\right\} \tag{3}$$

where $\hbar\omega_1/k = \beta T^3$ and $\beta = 2{\cdot}46\ M^2k^2/\rho\bar{v}^5\hbar^3$. Strictly speaking, eqns. (3) are true only in the extreme limits $\omega \leqslant \omega_1$ and $\omega \geqslant \omega_1$ but the two expressions given here provide a convenient, and fairly accurate, interpolation. In these expressions M is a constant representing the coupling between the tunnelling states and the phonons, $\bar{v}$ is the average sound velocity, ρ is the density and $\bar{n}$ is an effective density of states. Both types of scattering give at low temperatures a mean free path for the thermal phonons that varies as ω^{-1} if the density of states is constant and so a thermal conductivity that varies as T^2.

If the thermal conductivity of a-As between 0·5 and 1·0 K is limited by scattering from tunnelling states, a value of about $2 \times 10^4\,\mathrm{m^{-1}\,K^{-1}}$ is found for A. This leads to a value of $\bar{n}$ which is smaller than that derived from the thermal conductivity of SiO_2 by a factor of about 20, assuming the same value of coupling constant.

κ does not give a direct measure of $\bar{n}$ but of $\bar{n}M^2$, in contrast to the linear term in the heat capacity which gives a direct measure of a different density of states n_0. M can be chosen to bring $\bar{n}$ and n_0 into agreement, but this is unsatisfactory because not all states of a given energy are equally effective in scattering phonons. n_0 is the number of states with a given energy, while $\bar{n}$ is an effective average which takes into account the different scattering strengths of the states. For a given energy, the tunnelling states with the shortest relaxation times are the strongest scatterers. The effect of this averaging is to give a value of n_0 larger than $\bar{n}$ by a factor of between 10 and 100 (Phillips 1972, Smith *et al.* 1978). The relationship between $\bar{n}$ and n_0 is known in SiO_2; if the same relationship is assumed in a-As then no linear term would be detected in the measurements of the heat capacity between 0·3 and 1 K. Notice that the value of $\bar{n}$, which is an average over longitudinal and transverse modes, is not very sensitive to the precise value chosen for $\bar{v}$; the factor of $\bar{v}$ in A compensates for a similar factor in the Debye heat capacity in eqn. (1).

Anderson has extended this model by using a density of states $n(\epsilon)$ that contains, in addition to the almost constant term, a contribution varying as the second (or higher) power of ϵ. This, of course, leads to a much greater scattering at higher phonon energies and can be used to explain the plateau in κ. Zaitlin and Anderson (1975) derive the equivalents of eqn. (2) and (3) for a quadratic density of states by replacing the constant $\bar{n}$ by a factor of the form $\bar{n}_2(\hbar\omega)^2$. This seems oversimplified. A more complete treatment involves a calculation, similar to that of Jäckle (1972) for a constant density of states, in which the total scattering is the integrated contribution from all the tunnelling states using the correct energy dependent $n(\epsilon)$. If this is done for a quadratic density of states the resonance scattering involves a divergent integral. Using the generalized expression for l_{res}^{-1} given by Jäckle, Piché, Arnold and Hunklinger (1976) and choosing a cut-off for $\bar{n}_2(\epsilon)$ at the very high energy of kT_g, where T_g is the glass transition, the expression

$$l_{\mathrm{res}}^{-1} = B\left(\frac{\hbar\omega}{k}\right)^3 \tanh\frac{\hbar\omega}{2kT}, \tag{4}$$

with $B = \pi\bar{n}_2M^2k^3/\rho\bar{v}^3\hbar$, is valid to within a few per cent. (The result depends on T_g if the density of states varies more rapidly than ϵ^2.) A similar calculation for the relaxation terms gives

$$\left.\begin{aligned} l_{\mathrm{res}}^{-1} &= 0{\cdot}17B\frac{\hbar\omega}{k}T^2 \qquad \omega < \omega_1, \\ l_{\mathrm{res}}^{-1} &= 0{\cdot}17B\frac{\hbar\omega_1}{k}T^2 \qquad \omega > \omega_1, \end{aligned}\right\} \tag{5}$$

where $\hbar\omega_1/k = 30\beta T^3$.

These expressions are very similar to those used by Zaitlin and Anderson, and a suitable combination of eqns. (2), (3), (4) and (5) give an equally good fit to the thermal conductivity of SiO_2. The only significant change is in the ratio $\bar{n}_2/\bar{n}$, which is reduced from Zaitlin and Anderson's value by about 30%. It should be noted that the total mean free path in SiO_2 is of the form $l(\omega, T) = (l_{rel}^{-1} + l_{res}^{-1})^{-1} + l_0$ where l_0 must be included to prevent l from reaching unphysically small values.

A similar procedure can be used for the thermal conductivity of a-As, except that the constant term $\bar{n}$ need not be included. The resulting fit, which includes a constant mean free path of 25 μm to fit the low-temperature date, is shown in fig. 4. The curve is drawn for $B = 1 \times 10^4\,\mathrm{m^{-1}\,K^{-3}}$ and $\beta = 5 \times 10^{-3}\,\mathrm{K^{-2}}$. From eqn. (4), a value is found for $\bar{n}_2M^2$ comparable to that obtained from a similar fit to the thermal conductivity of SiO_2.

In SiO_2 this quadratic term leads to a difference between the measured T^3 term in the heat capacity and that calculated from the sound velocity. The link between $\bar{n}_2$ and the quadratic density of states derived from the heat capacity is again not direct. If the same link is assumed in a-As as is assumed in SiO_2, then the term $\bar{n}_2\epsilon^2$ would lead to a term in C/T^3 of about $0{\cdot}5\,\mu\mathrm{J\,g^{-1}\,K^{-4}}$ in the low-temperature heat capacity. In the absence of accurate values for the sound velocity, the presence of such a term, amounting to less than 10% of the total heat capacity, cannot be ruled out.

Even though this extension of the tunnelling model provides an adequate fit to the data in a-As as well as in SiO_2, it is not altogether satisfactory. The quadratic density of states has no natural cut-off in the model, and to prevent the scattering of high-frequency sound waves from becoming unphysically strong, an arbitrary effective cut-off is introduced in the form of a limiting frequency-independent mean free path l_0. In SiO_2, for example, this l_0 implies that the density of states is cut off at an equivalent frequency, $\hbar\omega/k$, of about 80 K. If the total number of tunnelling states is calculated by integrating $n_2\epsilon^2$ up to an energy equivalent to 80 K, where n_2 is calculated from the ' excess ' T^3 term in the heat capacity, the number turns out to be only one order of magnitude less than the number of atoms in the solid. Modifications to the theory, including the effect of dispersion, might reduce this figure, but the number will remain uncomfortably large. A similar conclusion is probably true for As, although in the absence of any knowledge of the sound velocities the equivalent calculation is not possible.

One further point concerns the generality of the model. Although it provides a satisfactory fit to κ in a-As and SiO_2, it has not been possible to fit the plateau in As_2S_3. The scattering does not increase sufficiently rapidly with frequency to allow the temperature dependent term in the relaxation scattering to produce a sufficiently sharp maximum and minimum. This is in contrast to the model described below, where the addition of a mean free path varying as ω^{-4} can give a good fit to the data in As_2S_3 (Jäckle 1976). In its present form, therefore, the model does not seem capable of explaining the behaviour of all glasses, although the addition of Raman scattering from the tunnelling states might make it generally applicable (Leadbetter *et al.* 1977).

The tunnelling model with a quadratic density of states is not the only one that attempts to account for the plateau in κ. Any model in which the scattering increases rapidly with phonon frequency will fit the data in most amorphous solids when combined with the constant density of states tunnelling model.

One way of obtaining this rapid increase of scattering strength with frequency is by structure scattering. Sound waves are scattered by the local variations in structure, and in the limit of long wavelengths the scattering, which is similar to Rayleigh scattering, varies as ω^4. In the high-frequency limit the mean free path is constant, and over the complete frequency range the scattering can be described by the interpolation formula

$$l_{\mathrm{struc}} = \left[D^{-1} \left(\frac{\hbar\omega}{k} \right)^{-4} + l_0 \right]. \tag{6}$$

A combination of a constant free path of 25 μm (to fit the data below 0·5 K) together with eqn. (6) gives a good fit to the thermal conductivity data in a-As as shown in fig. 4. The fitting parameters are $D = 1{\cdot}9 \times 10^3\,\mathrm{m^{-1}\,K^{-4}}$ and $l_0 = 1{\cdot}5$ nm. This value of D is about an order of magnitude greater than that needed to fit the data in SiO_2, 170 $\mathrm{m^{-1}\,K^{-4}}$ (Jäckle 1976), while l_0 is comparable to the SiO_2 value of 1 nm. The significance of the curve in fig. 4 lies in the fact that no tunnelling state scattering is needed to explain the temperature dependence of κ. This, in combination with the result shown in fig. 2, means that there is no firm evidence for the existence of tunnelling states in a-As.

It has been argued that structure scattering cannot give sufficiently large values of D (Zaitlin and Anderson 1975, Jäckle 1976) although the argument is not universally accepted (Walton 1977). The various calculations of D in the long wavelength limit use either a microscopic of a macroscopic approach to the problem, but all require two parameters to describe the strength of the scattering. One is a measure of the magnitude of the fluctuations, and the other is a correlation length describing the scale of the fluctuations. Fluctuations in density, in force constants and in the relative orientations of molecular groups forming the glass have all been used in the calculations. These different approaches give different values for D, and in order to test the validity of the structure scattering model they will be discussed using SiO_2 as an example. An early calculation by Pekeris (1947), in which he concentrated on the resulting fluctuation in the velocity of sound $\langle(\Delta v/v)^2\rangle$, is a convenient starting point for the calculation. His result is

$$l_{\mathrm{struc}}^{-1} = 8\langle(\Delta v/v)^2\rangle a^3 k^4 \quad ka \ll 1, \tag{7}$$

where k is the wavevector of the sound waves and a the correlation length. The more recent calculations give results which can usually be recast into the form of eqn. (7). This equation gives

$$D = 8\langle(\Delta v/v)^2\rangle \frac{a^3}{v_s^4} \left(\frac{k}{\hbar} \right)^4 \quad \frac{\omega a}{v_s} \ll 1. \tag{8}$$

In the short wavelength limit the free path l_0 might be expected to take the form

$$a\langle(\Delta v/v)^2\rangle.$$

The effect of density fluctuations has been considered by Jäckle (1976) using a microscopic approach. His estimate of the magnitude of the density fluctuations in SiO_2, for which data is available, is based on a combination of light scattering data and thermodynamic results for the density fluctuations frozen into the solid when quenched from a temperature T_0 corresponding to the liquid state. Simplifying his argument slightly, the density fluctuations in volume V are given by

$$\langle(\Delta\rho/\rho)^2\rangle = kT_0\beta_T(T_0)/V, \qquad (9)$$

where β_T is the isothermal compressibility. Strictly speaking this result includes both static and dynamic fluctuations giving Rayleigh and Brillouin scattering, respectively. Only the former is relevant to structure scattering and an estimate of the magnitude of the Rayleigh term alone can be found from the experimentally measured ratio of the intensity of Rayleigh scattered light to the intensity of Brillouin scattered light. This ratio, the Landau–Placzek ratio. is at least ten in vitreous SiO_2 in the liquid state (Bucaro and Dardy 1974) so that eqn. (9) does give a good measure of the *static* fluctuations. Replacing the volume V by $4\pi a^3/3$, and writing $\langle(\Delta v/v)^2\rangle = \gamma^2\langle(\Delta\rho/\rho)^2\rangle$ where γ is a Grüneisen constant, eqn. (8) becomes

$$D = \frac{1{\cdot}5}{\pi}\frac{\gamma^2}{v_s^4}kT_0\beta_T(T_0)\left(\frac{k}{\hbar}\right)^4, \qquad (10)$$

using a value of β_T of $8{\cdot}5\times10^{-11}$ m^2 N^{-1} at 1700 K (Bucaro and Dardy 1974), this equation gives a value of 4 m^{-1} K^{-4} for D. γ is taken as $-2{\cdot}15$, a value calculated from experimental values of the pressure dependence of the sound velocities in vitreous SiO_2 (Kurkjian, Krause, McSkimin, Andreatch and Bateman 1972). This value for D is over an order of magnitude smaller than the value needed to fit the thermal conductivity in SiO_2.

An alternative approach is taken by Walton (1977) and by Morgan and Smith (1974) who calculate the scattering produced by the fluctuations of force constant, produced in turn by the fluctuations in bond length. Both calculations are microscopic, but the main result can be derived macroscopically. The fluctuations of force constant are proportional to the fluctuations in velocity, which can be written as

$$\langle(\Delta v/v)^2\rangle = (3\gamma)^2\langle(\Delta R/R)^2\rangle, \qquad (11)$$

where γ is the Grüneisen constant and $\langle(\Delta R/R)^2\rangle$ is the fractional mean-square variation in bond length. This leads to an expression for D from eqn. (8);

$$D = 8(3\gamma)^2\left\langle\left(\frac{\Delta R}{R}\right)^2\right\rangle\frac{a^3}{v_s^4}\left(\frac{k}{\hbar}\right)^4. \qquad (12)$$

Using $\langle(\Delta R/R)^2\rangle = 10^{-3}$, and $4\pi a^3/3$ equal to the volume of a molecule of SiO_2, $3{\cdot}76\times10^{-29}$ m^3, this gives a value of D equal to about 5 m^{-1} K^{-4}, comparable to the value given by eqn. (10).

It is worth comparing the estimates of $\langle(\Delta v/v)^2\rangle$ which follow from eqns. (9) and (11) using the molecular volume for V in (9). The two values are 0·1 and 0·04, respectively, a result which agrees with Walton's assertion that Jäckle's calculation underestimates the magnitude of the fluctuations. Walton's published calculation in fact leads to a value of $\langle(\Delta v/v)^2\rangle$ equal to 0·7. This unreasonably large value (corresponding to mean-square fractional fluctuations in force constant greater than one) is a result of choosing γ to be the thermal value of -9, instead of the value that is known to apply to sound waves. The only way in which D could be increased in eqn. (12) is by increasing a, and there seems to be no evidence for any correlation of bond lengths in amorphous solids.

A third type of scattering, discussed by Jäckle (1976), is closely related to scattering of sound waves in polycrystalline solids. At a boundary between two crystallites of different orientation the sound wave must satisfy continuity equations for both particle displacement and pressure. In general, these stringent conditions can only be satisfied if the incident wave is matched with scattered waves of differing polarizations (Bhatia 1967). This mode conversion gives an additional contribution to the scattering, which cannot be calculated solely on the basis of the different velocities of sound in the two crystallites. Calculations of the attenuation of sound waves in polycrystals give results which contain explicitly the anisotropy of the elastic constants, and which agree with experiment (Papadakis 1968). These calculations (Bhatia 1967) can be interpreted to give an effective value for the magnitude of $\langle(\Delta v/v)^2\rangle$:

$$\langle(\Delta v/v)^2\rangle \sim \frac{1}{400}\left(\frac{\mu^2}{\rho^2 v^4}\right), \tag{13}$$

where μ is a measure of the anisotropy of the elastic constants and ρ is the density. μ can be evaluated explicitly from the known elastic constants of quartz, and used in eqn. (13) to give a value of about 0·02 for $\langle(\Delta v/v)^2\rangle$ in the case of shear waves in polycrystalline quartz.

This scattering in polycrystals has a close parallel in amorphous solids as a result of variations in relative orientations of the basic structural units. An estimate of the strength of the scattering can be made by combining the above value of $\langle(\Delta v/v)^2\rangle$ for microcrystalline quartz with an estimate of the correlation length a in eqn. (8).

Even though this value of $\langle(\Delta v/v)^2\rangle$ is of the same order of magnitude as the values arising from fluctuations in density and force constant, it can lead to larger values of D because the correlation length can be longer. However, the correct choice of correlation length is not obvious. X-ray measurements (Mozzi and Warren 1969, Konnert and Karle 1972) show that significant structure can exist in the radial distribution function only out to about 10 Å, and this sets an upper limit on a. At the other extreme, correlation in orientation can only be completely lost with more than two SiO_4 tetrahedra, in a minimum distance of about 4 Å. A reasonable compromise between the two limits is 7 Å (also equal to the size of the unit cell in the high-temperature form of cristobalite). With this value, eqn. (8), gives a value of $90\,m^{-1}\,K^{-4}$ for D, much larger than the values given by eqn. (10) and (12) but still smaller than the value needed to fit the data in vitreous silica.

It might be argued that if the extreme value of 10 Å is chosen for a, the scattering is just strong enough to explain the data in SiO_2. However, it appears that eqn. (7) does contain a larger numerical factor than do similar expressions given by other authors. For example, Jäckle (1976) give an equation similar to eqn. (10) but containing a factor of $1/4\pi$ instead of $1{\cdot}5/\pi$, with the result that the strength of the scattering predicted by eqn. (10) is about a factor of five greater than that given by Jäckle's calculation. In conclusion, although eqn. (8) may overestimate the strength of structure scattering, the calculated values are too small to explain the data in vitreous silica. This failure of the structure scattering in the one glass for which values can be estimated, casts serious doubts on its use in other amorphous solids, including a-As.

It was mentioned earlier in this paper that the inclusion of dispersion in the theory allows a reduction in the strength of the scattering needed to produce a plateau in κ. A significant effect of this kind would clearly make the structure-scattering model more plausible. To test the magnitude of the effect in a-As, dispersion was included according to the prescription given earlier. With a cut-off for the transverse modes of 10 cm^{-1} in eqn. (6), D was reduced by only 20%. (This assumes a ratio of two for the sound velocities.) To reduce D by an order of magnitude, the cut-off must be taken at the unreasonably small value of 2 cm^{-1}. This conclusion is based on the assumption that the constant D is the same for the longitudinal and transverse modes. If, as an alternative assumption, the parameters $\langle(\Delta v/v)^2\rangle$ and a are assumed equal, then the factor of v^4 in eqn. (8) means that, if structure scattering is dominant, the transverse modes carry only about 20% of the heat. In this case the introduction of a cut-off for the transverse modes can never lead to a reduction in the strength of structure scattering by more than 20%. Dispersion cannot, therefore, make the structure-scattering model any more plausible in a-As.

The same conclusion should be true in other amorphous solids. Although the onset of the plateau is higher in most other amorphous solids, the appropriate cut-off to the transverse modes should also be taken at a higher frequency. In those amorphous solids for which reliable data are available, the departures from Debye behaviour, or the position of the peak in C/T^3, show some correlation with the position of the plateau†.

This possibility of a connection between the plateau in κ and the density of states is supported by measurements of κ in complex boron compounds by Slack, Oliver and Horn (1971). These authors measured the thermal conductivity of single crystals of YB_{66}, a crystalline solid containing a considerable degree of disorder. κ varies as T^2 below 10 K, is less than that of SiO_2 at 1 K, and shows a plateau at about 50 K. The T^2 variation presumably arises from the presence of tunnelling states, since it is known that YB_{66} contains a linear term in the heat capacity comparable to that in SiO_2 (Bilir, Phillips and Geballe 1975). Higher-temperature heat capacity data is not available for YB_{66}, but both heat capacity and infra-red measurements in boron (Johnston, Heish and Kerr 1951, Slack *et al.* 1971) indicate a peak in the density of states at about 100 cm^{-1}. Since the basic bonding in these various boron compounds is very similar, a peak at about the same frequency is expected in YB_{66}. This material then falls into the pattern apparent in other amorphous solids.

In summary, the fact that the plateau in κ occurs at about the same temperature as a peak in C/T^3 in all amorphous solids suggests that the plateau is linked in some way to the vibrational modes responsible for this peak. One such link is implicit in the earlier discussion of dispersion, but as has been seen, using the peak to provide a cut-off to thermal transport by transverse modes is not sufficient to explain the plateau.

A mechanism which might tie κ to the heat capacity is phonon–phonon interaction. In crystals, U-processes are necessary to give a thermal resistivity, whereas in amorphous solids, the equivalent effect has been shown to be small

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† This correlation has also been noticed by Leadbetter (1972).

(Morgan and Smith 1974). Normal processes acting alone in a crystal cannot destroy a heat current, but in an amorphous solid this scattering should be important because the lack of periodicity means that the selection rules for phonon–phonon interactions are relaxed, and because a significant proportion of the phonons may be non-propagating or localized (Bell, Dean and Hibbins-Butler 1970).

In a-As the plateau in κ would then arise in the following way. Below 1 K both longitudinal and transverse sound waves carry heat. At higher temperatures, where higher-frequency phonons are excited, the ‘ transverse ’ modes are non-propagating, and, concentrated into a narrow frequency range, give the peak C/T^3. The longitudinal modes, which still behave as sound waves, interact with this concentration of non-propagating modes through the normal phonon–phonon coupling, and are heavily scattered. The gradual rise in κ above 10 K is a result of the relatively poor thermal transport by the remaining modes in the solid. High-frequency longitudinal modes may also contribute : if the scattering by non-propagating ‘ transverse ’ modes has any resonant character (since both transverse and longitudinal modes have the same frequency), the scattering may well decrease as the longitudinal frequency increases. Careful calculations are, of course, necessary to establish if the strength of this phonon–phonon scattering is sufficient to explain the plateau in κ.

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