

THEORY OF THE THERMAL CONDUCTIVITY OF AMORPHOUS SOLIDS

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Thermal conduction by means of lattice waves in glasses will be discussed. Random arrangements of molecular units can be treated as point defects which scatter phonons, with possible enhancement of the scattering due to correlations over longer distances. However, such a model does not result in sufficient scattering at low frequencies and accounts neither for the thermal resistivity at ordinary temperatures nor at low temperatures, unless correlations over unlikely long distances are assumed. An additional interaction mechanism is provided by phonon-assisted transitions between the states of two-level systems, with a wide distribution of level spacings. These systems, whose presence in amorphous systems are postulated, also give rise to an excess specific heat at low temperatures, linear in temperature. This model also accounts for saturation effects in the absorption of high-frequency ultrasonic waves. Unfortunately we know too little about the basic structure of amorphous solids to derive the density, the level-spacing distribution and the phonon interaction strength of these centers. In a simpler case of crystalline Ti-V alloys, where such centers have also been observed, it is possible to derive the first two of these parameters, and hence the excess specific heat, from the known size difference of the two ions.

INTRODUCTION

The thermal conductivity of amorphous dielectric solids is less than that of the corresponding crystals. This can be ascribed to their disorder, which causes additional phonon scattering. Defining an average phonon mean free path ℓ in terms of the thermal conductivity λ by

$$\lambda = (1/3) C v \ell \quad (1)$$

where C is the specific heat per unit volume and v the sound velocity, one can deduce ℓ from measurements of λ . Kittel[1] pointed out that in glass ℓ is roughly constant above 50K, but increases at lower temperatures. This seemed reasonable, since the phonons have long wavelengths at low temperatures, so that amorphous solids should then approach the behavior of homogeneous elastic media. Subsequent measurements, starting with those of Berman[2], confirmed that ℓ continues to increase as T decreases.

A detailed explanation of the behavior of ℓ in terms of phonon scattering by structural disorder has proved far from easy. The most obvious model of disorder would consider each molecular unit as a phonon scattering center, because the local phonon velocity fluctuates from point to point. For point-defect scattering, this change occurs over an elementary volume a^3 . If δv is the root mean square velocity fluctuation, one can show that the attenuation probability per unit length, or the reciprocal of the mean free path, is given by [3]

$$1/\ell_p(\omega) = c(\delta v/v)^2(a^3/\pi v^4)\omega^4 \quad (2)$$

where c is the concentration of point defects (per atom or molecule) and ω the (angular) phonon frequency. If δv is due to a relative mass fluctuation $\Delta M/M$, then $\delta v/v = -\Delta M/2M$.

In the case of glasses such as vitreous silica, δv arises not from fluctuations in mass or density but from a variation of the orientation of molecular units. We can estimate $\delta v/v$ from the variability with direction of the ultrasonic wave velocity in crystalline quartz; thus we take $\delta v/v \approx 0.15$ and $c=1$.

The effects on the thermal conductivity due to atoms differing in mass have been extensively studied. For crystalline Ge-Si of 50-50 composition, $c=1$ and $|\Delta M|/M=1/3$, so that $\delta v/v=0.16$. Thus one would expect vitreous silica and mixed crystals of 50-50 Ge-Si to have comparable point defect scattering for phonons of the same wavelength, except that a^3 is larger for SiO_2 , so that ℓ_p should be correspondingly smaller. At 500K the thermal conductivity of vitreous silica is $1.6 \text{ W-m}^{-1}\text{-K}^{-1}$, while that of 50Ge-50Si is $6 \text{ W-m}^{-1}\text{-K}^{-1}$. It thus appears that the thermal conductivity of vitreous silica is slightly lower than one would expect from the ratio of the point defect mean free paths.

However, the disagreement rapidly worsens as the temperature is lowered, since the thermal conductivity of the mixed crystal increases with decreasing temperature, while that of glass decreases. Therefore in amorphous solids, there must be a further scattering

mechanism which becomes relatively more important at low temperatures, hence at low frequencies, and which becomes overwhelmingly important at very low temperatures where the thermal conductivity of glass is orders of magnitude lower than that of the corresponding crystal.

THE LOW-FREQUENCY MECHANISM

One cannot treat the thermal conductivity as mainly due to phonons of one dominant frequency at any given temperature, but must consider that λ is made up of contributions from a wide frequency spectrum, i.e.

$$\lambda = \int \kappa(\omega) d\omega \quad (3)$$

where

$$\kappa(\omega) = (1/3) C(\omega) v l(\omega) \quad (4)$$

and where $C(\omega)d\omega$ is the contribution to C from modes in the frequency interval ω , $d\omega$. At low frequencies $C(\omega) \propto \omega^2$, so that point defects, for which $l(\omega) \propto \omega^{-4}$, cannot by themselves yield a finite thermal conductivity, for the integral of equation (3) would diverge at low frequencies. One must always treat point defects in combination with some other scattering mechanism which varies more slowly at low frequencies.

In the case of disordered crystals, such as Ge-Si, at ordinary temperatures, the low-frequency divergence is removed by anharmonic processes, with a mean free path $l_1 \propto \omega^{-2} T^{-1}$. This makes $\kappa(\omega)$ independent of ω but varying as T^{-1} at frequencies well below ω_0 , where ω_0 is defined by $l_p(\omega_0) = l_1(\omega_0)$. Thus $\omega_0 \propto (T/c)$, and one can show[4] that, based on a simple Debye model

$$(\lambda/\lambda_1) = (\omega_0/\omega_D) \arctan(\omega_D/\omega_0) \quad (5)$$

where λ_1 is the intrinsic thermal conductivity and ω_D the Debye frequency. At ordinary temperatures for strong point defect scattering ($\omega_0 < \omega_D$), $\lambda \propto T^{-2} c^{-1/2}$. This simple theory accounts in a rough manner for the thermal conductivity of mixed crystals, including Ge-Si alloys, but neglects the effect of normal three-phonon processes and tends to underestimate the reduction in λ due to point defects[5].

In the case of amorphous solids too, point defect scattering must be supplemented by another scattering process at low frequencies. However, since λ decreases with decreasing temperature, it seems that anharmonic processes, which depend on T , do not contribute significantly to that unknown process. The unknown scattering seems to be

a function of frequency - but varying more slowly than ω^3 - and seems to be practically independent of temperature.

More information about this scattering mechanism is provided by observations of the thermal conductivity at low temperatures, where only low-frequency modes are excited. In general[6] if $\ell(\omega)$ depends on frequency but not on temperature, and if $\ell(\omega) \propto \omega^{-n}$, where $n < 3$, $\lambda(T) \propto T^{3-n}$. Berman's observations above 1K suggest $n=2$, but later measurements below 1K suggest $n=1$ for the low-frequency scattering process[7].

STRUCTURAL CORRELATIONS

It was pointed out[8] that scattering due to a local velocity fluctuation δv can be enhanced if there are correlations in the values of δv at neighboring locations. If the fluctuations δv vary randomly from one elementary volume a^3 to the next, scattering is like point-defect scattering and varies as $a^3 \delta v^2 \omega^4$. If δv at one location is correlated with δv at a location a distance r away, scattering of waves of wave-number q is enhanced by a factor

$$a^{-3} \langle \delta v \rangle^{-2} \int \langle \delta v(0) \delta v(r) \rangle \sin(qr) r q^{-1} dr \quad (6)$$

where the pointed brackets denote averages, and the integral is the q 'th Fourier transform of a spherically symmetrical correlation function $f(r)$. If $f(r) \propto r^{-m}$, $\ell(\omega) \propto \omega^{-(m+1)}$ and $\lambda(T) \propto T^{2-m}$. In the liquid helium range where $\lambda(T) \propto T$, we require $m=1$, and quantitatively one requires [9]

$$f(r) \sim 0.01 a/r \quad (7)$$

for r below about 300\AA . Since such correlations are not seen in small-angle X-ray scattering, they would have to be orientational correlations, possibly arising from residual crystallinity over distances governed by the grain size of the precursor material.

As one goes to lower temperatures, well below 1K, one finds $\lambda \propto T^2$, so that $m=0$. No reasonable model of spherically symmetric structural correlations would yield such a dependence; one would have to invoke correlations of cylindrical symmetry. Furthermore, the low temperature values of λ for any single material do not show the variability as function of specimen history that one would expect if long-range structural correlations were the sole factor governing phonon scattering[10]. One must conclude that another mechanism dominates below 1K. At higher temperatures structural correlations may be significant in phonon scattering and they may be responsible for the variability in thermal conductivity around the plateau region (10 to 20K), but they may not be the major mechanism, and they are not important below 1K. There are strong arguments in favor of another mechanism, a distribution of two-level centers, proposed by

Phillips[11] and by Anderson, Halperin and Varma[12]. Perhaps the strongest argument in favor of this mechanism is that the same model also predicts an excess specific heat linear in T and a saturation in the absorption of high-frequency ultrasonic waves, both of which have been observed.

DISTRIBUTION OF TWO-LEVEL CENTERS

Consider a solid which contains a number of defect centers, each of which can be in two distinct quantum-mechanical states, separated by a level difference $E = \hbar\omega_0$, where \hbar is the reduced Planck constant. If the energy of the defect can be perturbed by strain, transitions between the two levels occur with the emission or absorption of a phonon of frequency ω_0 . This will reduce the mean free path of phonons of that frequency, and since the process is of first order in the local strain produced by the phonon, this reduction will be stronger than that due to phonon scattering by the same defect, since the latter is second order in strain, by a factor of order $(v/a\omega_0)^2$.

However, if all defects had the same level spacing E, the reduction in thermal conductivity would be minor, since only a small portion of the phonon spectrum would be affected. To account for the reduction in $\ell(\omega)$ over a wide range of frequencies, one must assume a distribution of E-values for different centers, no doubt because of the stochastic nature of amorphous structures.

Let us assume that the number of centers per unit volume with E in the range E, dE is given by a Gaussian

$$n(E)dE = 2ca^{-3} \pi^{-\frac{1}{2}}\sigma^{-1} \exp(-\omega_0^2/2\sigma^2) d\omega_0 \quad (8)$$

so that $a^{-3}c$ is the total number of such centers per unit volume and σ is the root mean square width of the corresponding ω_0 distribution. If the level population is in thermal equilibrium at temperature T, and if $\hbar\sigma \gg kT$, where k is the Boltzmann constant, there is an excess specific heat per unit volume due to these centers given by

$$C_E = a^{-3}c(\pi^{3/2}/3) k^2T/\hbar\sigma. \quad (9)$$

Glasses do show an excess specific heat linear in T over the corresponding crystalline phase, and one can treat both c and σ as adjustable parameters. Typical values of C_E/T are $30 \text{ erg-cm}^{-3}\text{-K}^{-2}$, whence one can deduce values of $ck/\hbar\sigma$ of the order of 10^{-6} per degree Kelvin. It was assumed, of course, that the two quantum states are distinct, which requires a potential barrier between them of some minimum height[11].

The phonon mean free path is limited by processes in which a phonon is absorbed in the transition between the levels and subsequently re-emitted in a random direction, thus restoring thermal

equilibrium. If the two levels are linked by a phenomenological perturbation Hamiltonian

$$H' = Ae \quad (10)$$

where e is the strain at the center due to the phonon and A is a parameter having the dimensions of energy, one obtains the following expression for the reciprocal mean free path of the phonons

$$1/\ell(\omega) = 8\pi^{\frac{1}{2}}cA^2(Mv^2/\sigma)^{-1}(e^x-1)(e^x+1)^{-1}\omega/v \quad (11)$$

where $x = \hbar\omega/kT$. Except at the very bottom of the thermal phonon distribution, equation (11) makes $\ell(\omega) \propto \omega^{-1}$, so that $\lambda(T) \propto T^2$, as observed below 1K. The phonon mean free path, and thus λ , varies inversely as the factor c/σ , which appears as an empirical parameter in the excess specific heat; however it also varies inversely as A^2 , and thus depends on a second parameter.

The role of these distributed two-level systems in limiting the thermal conductivity of glasses has been reviewed by A.C. Anderson [13]. The temperature dependence of the thermal conductivity is explained in terms of three mechanisms:-

(a) At lowest frequencies $\ell(\omega)$ is limited by interactions with the two-level systems, with a reciprocal mean free path given by (11).

(b) At intermediate frequencies, ℓ is controlled by point defect scattering with a reciprocal mean free path given by (2). However, $\delta v/v$ is treated as an adjustable parameter, and is larger than the value of 0.15 suggested by the anisotropy of the phonon velocity in the crystal.

(c) There is therefore a relatively wide range of high frequencies such that (2) breaks down because it would make ℓ_p less than the molecular diameter. Over that range, ℓ is chosen to be independent of frequency and of the order of 5\AA .

I propose a modification of the model. Point defect scattering is not as strong, but of strength appropriate to $\delta v/v$ 0.15. The frequency where ℓ_p reaches its constant limiting value is reached only at high frequencies ($\omega > \omega_D/2$). To compensate for this increase in λ , one needs an additional scattering mechanism, namely intermediate-range correlations in the orientation of molecular units, given by (7) over distances of up to perhaps 100 to 300 \AA , but rapidly disappearing over greater distances. This enhances point-defect scattering by the factor of expression (6), and effectively adds a scattering mechanism at frequencies intermediate between those of (a) and (b). In this range $1/\ell(\omega) \propto \omega^2$. Until we know more about orientational correlations in amorphous solids, this enhancement factor has to be treated as an empirical function of phonon frequency. It could well vary between specimens of the same glass and account for the modest variability between specimens seen at intermediate temperatures. I regard point defect scattering as weaker, which

would allow one to explain the lower thermal conductivity at ordinary temperatures of lead-containing glasses[14] in terms of additional point-defect scattering.

We must still explain the magnitude of the mean free path at lowest frequencies, where phonons interact with two-level systems of distributed level spacing. There is good support for this mechanism from the excess specific heat and the saturation of the absorption of ultrasonic waves, but we need a way of explaining the parameters in equation (11) from basic principles.

A CALCULABLE TWO-LEVEL SYSTEM

The following illustrates how one can calculate parameters of a two-level system in a better-defined situation: a solid solution of two atoms of different size. Consider a Ti-V alloy; the atomic radius of Ti is 15% larger than that of V. The thermal conductivity of Ti-V containing 34% V has been measured by Chandrasekhar et al. [15] below 0.1K. At those low temperatures the superconducting alloy has the thermal conductivity of a dielectric crystal: it is entirely due to lattice waves, and the phonon mean free path is not influenced by interactions with free electrons. These authors found a thermal conductivity proportional to T^2 , and a specific heat[16] well above the expected lattice specific heat and proportional to T . It thus appears that the alloy contains a distribution of two-level systems, which the authors attribute to some atoms being in a bistable configuration as a result of the size difference between the atoms.

Let us assume that the only bistable configuration is one in which a Ti atom (surrounded by 8 atoms in that lattice) is surrounded by 6 Ti atoms and 2 V atoms, and that the two V atoms are diagonally opposite each other. The central Ti atom has then two stable positions on either side of its normal position at the center of its atomic cage. If x is the V concentration, the number of such sites per atom site is

$$c = 4 x^2 (1-x)^7 \quad (12)$$

provided there is no short-range order.

To find σ we use elasticity theory to calculate the fluctuating strain, and hence the strain energy, seen by the Ti atom due to the fluctuations in size of all the atoms beyond the nearest neighbor shell. This depends on the difference in atomic size and also on x . In the case considered here

$$\hbar\sigma/k \approx 8000 \text{ K} \quad (13)$$

while the observed excess specific heat $C_E/T = 1.4 \times 10^{-4} \text{ J-mole}^{-1}\text{-K}^{-2}$

would demand a value of 6000K. Furthermore we would expect the specific heat for the complementary 67%V alloy to be less by a factor 32, because σ is the same, but c changes according to (12). Observations[16] show a reduction by at least a factor of 7.

To calculate the phonon scattering we must estimate A of equation (10). The effects of strain due to phonons can be related to the effects of static strains, hence to σ . However, there is an additional factor in A due to the quantum-mechanical overlap integral between the atomic wave-functions centered on the two stable sites. This factor is very model-sensitive, and only crude estimates seem possible at present. Thus we can calculate the excess specific heat with greater confidence than the thermal conductivity. Whether similar considerations can be used in amorphous systems remains to be seen.

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