Resonant scattering and thermal transport in orientational glasses

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(Received 30 June 1988)

In the orientational glass KBr:KCN, we provide a natural explanation for the plateau in the thermal conductivity, which is a universal feature of all amorphous insulators. We show that the angular oscillation modes of the CN ions have a sharply peaked density of states in the THz range. These modes, in addition to contributing to the specific heat, resonantly scatter the thermal phonons in the plateau region. We discuss the possibility of localization of phonons in a narrow band due to this strong scattering. We speculate about the applicability of these ideas to structural glasses.

I. INTRODUCTION

Crystals and glasses have very different thermal properties at low temperatures.[1] Below 1 K, glassy materials[2] have a specific heat that grows linearly with the temperature T and a thermal conductivity $\Lambda \propto T^2$; these properties may be understood[3] in terms of two-level systems (TLS). Between 1 and 10 K, glasses have two other "universal" properties[4] which have thus far resisted a convincing theoretical explanation.[5] These are (1) a temperature-independent thermal conductivity, often called the "plateau," and (2) an excess specific heat over the Debye T^3 contribution, best seen as a bump in C/T^3.

Recently, we have proposed[6] a common explanation of these two features in the orientational glass KBr:KCN, in terms of harmonic excitations in the THz region. Subsequently, Grannan, Randeria, and Sethna (GRS) have analyzed[7] a model glass consisting of randomly located elastic-dipole defects interacting via their strain fields. This has led to a quantitative understanding of the "intermediate" temperature properties of KBr:KCN. However, the GRS analysis[7] requires an extensive numerical simulation to determine the density of states of the defect modes. In view of this, we consider it especially important to have a simple intuitive picture[6] of the physics underlying the thermal conductivity plateau and the excess specific heat. This is what we aim to provide in the present paper.

There have been several recent suggestions linking the plateau in the thermal conductivity with localization of short-wavelength normal modes in amorphous materials either due to strong scattering from structural disorder,[8,9] or to the postulated fractal nature[10] of glasses. All these approaches need to introduce a new characteristic length scale which is roughly ten times the lattice spacing. The fraction theory needs to assume that amorphous materials are self-similar below this correlation length, an assumption for which there is little direct evidence in bulk glasses. Certainly no such length is plausible[11] in KBr:KCN. The localization proposals require a matching of length scales between the structural disorder and the thermal phonon wavelength in the plateau region, as shown below. We do not believe that there is any independent evidence for, say, density fluctuations, on such a length scale.

In our model the strong scattering required for the plateau is due to a matching of energy scales, rather than that of length scales, i.e., resonance between the phonons and additional vibrational excitations in a glass. Arguments similar in spirit to ours, but considerably different in detail, have recently been given by several authors[12] who have postulated the "extra" modes without a microscopic identification. There is also mounting experimental evidence for the existence of localized harmonic excitations in glasses, in addition to the acoustic phonons, primarily from the neutron-scattering work[13] of Buchenau and collaborators on vitreous silica.

In this paper, we focus on the orientational glass KBr:KCN, whose low-temperature properties[14] are indistinguishable from those of structural glasses, but whose structure is sufficiently well understood to enable us to make a simple model and to estimate the parameters needed in our theory. In this material we identify the harmonic resonant modes as the small angular oscillations, or *librations*, of the individual CN molecules. In the remainder of this paper we will first estimate the density of states for these excitations. After a brief review of the known phonon-scattering mechanisms in glasses, we discuss the resonant scattering of phonons from librations. We show that the thermal phonons in the THz frequency region are so strongly scattered that they do not contribute significantly to thermal transport. This, together with a temperature-independent scattering rate for the low-frequency phonons, leads to a plateau in the thermal conductivity. We also discuss the possibility of a narrow band of localized phonons within our harmonic

model. We conclude with some remarks on the applicability of these ideas to "real" (i.e., structural) glasses.

II. LIBRATIONS: DENSITY OF STATES

The glassy crystal $(KBr)_{1-x}(KCN)_x$, for x between 0.1 and 0.6, is known to freeze into an orientational glass state at low temperatures with the cyanides frozen in random orientations. We focus on the case $x=0.5$ which has been studied experimentally in most detail. We shall use data from the dielectric loss experiment of Birge *et al.*,[15] to estimate the density of libration modes.

The local potential for a cyanide has a double-well structure as a function of the angular displacement from its frozen orientation (see Fig. 1). There are two local minima 180° apart, which are more or less degenerate in energy, to the extent that one may neglect[16] the weak effects of electric-dipole interactions and crystal-field effects relative to the elastic interactions between the cyanides. The very wide log-normal dielectric-loss peak in $(KBr)_{0.5}(KCN)_{0.5}$ is thought to arise from individual cyanides reorienting by 180° via thermal activation over a range of barriers. A Gaussian distribution of barrier heights, with a mean $V_0=660$ K, and a standard deviation $\sigma_V=212$ K provides an excellent fit[15] to the data, and has also been subsequently obtained within a simple mean-field theory.[17] Given this distribution, only a very small fraction of the cyanides have sufficiently small barriers that they can reorient by 180° via quantum tunneling on experimental time scales. These have been identified[17] as the tunneling centers, or TLS, in KBr:KCN. In this paper, however, we shall use for simplicity the standard[3] TLS distributions, since our main interest here is not the rare (few ppm) cyanides which are tunneling, but rather the typical cyanides and how they affect the intermediate temperature properties.

We will find that the parameters of the double-well potentials are such that the majority of cyanides cannot reorient by 180°, on experimental time scales, either via quantum tunneling or via thermal activation in the temperature range of interest ($T \lesssim 10$ K). The only important degree of freedom for these cyanides is then small angular oscillations[18] about their frozen orientations. Now, in the real material, the librational motion of different cyanides would be coupled to each other and to the phonons (see below). We make the simplest possible assumption and model each cyanide as an independent Einstein oscillator,[19] with a distribution of frequencies to be determined below.

We further make the simplest choice for the form of the potential energy of a single cyanide molecule, namely,

$$E(\theta)=V\sin^2\theta\ , \tag{1}$$

where V is the barrier height and θ is the angular dispacement from its frozen orientation. The small oscillation frequency Ω within each of the wells is then related to the barrier height by

$$\Omega=(2V/I_{\text{eff}})^{1/2}\ , \tag{2}$$

where I_{eff} is the effective moment of inertia of the librational oscillator. We expect I_{eff} to be of the same order of magnitude as the moment of inertia[20] of an isolated CN^- embedded in a lattice. We shall, however, treat I_{eff} as our only free parameter, lumping our ignorance of the real normal modes into an "effective mass."

A peaked distribution of barrier heights now directly translates into a peaked density of states for the libration modes $p(\hbar\Omega)$. We approximate[21] $p(\hbar\Omega)$ by a Gaussian with mean $\Omega_0=(2V_0/I_{\text{eff}})^{1/2}$, standard deviation $\sigma=\sigma_V\Omega_0/2V_0$, and normalized to the total density of cyanides 7.1×10^{21} cm^{-3}. We have chosen $I_{\text{eff}}=14.6\times10^{-39}$ g cm^2, roughly 2–5 times larger than the single-cyanide value,[20] which gives a mean libration frequency $\Omega_0=3.5\times10^{12}$ rad/sec ~ 30 K and $\sigma=5.6\times10^{11}$ rad/sec ~ 4 K. This choice of I_{eff} (or equivalently Ω_0) gives the thermal conductivity plateau at the right temperature. We will discuss in the following section the sensitivity of the plateau to the value of Ω_0.

A peaked density of states will surely make its presence felt in the specific heat of the material. Note, however, that these excitations exist in addition to the usual acoustic phonons. Given the rather soft elastic constants of KBr:KCN, and correspondingly large Debye density of states, the effect of the librations on the specific heat is not dramatic. The bump in C/T^3 in KBr:KCN is considerably weaker than in structural glasses. As discussed in detail in Ref. 6, the simple analysis presented here is unable to fit the C/T^3 data quantitatively; while the choice of Ω_0 given above leads to a bump at the correct temperature, its magnitude is too high. From the detailed study of GRS,[7] where the librational density of states is obtained from a numerical simulation, it becomes clear that the C/T^3 plots are highly sensitive to the exact shape of the density of states. The GRS analysis takes into account two important features: first, the interaction between the cyanides and hence the collective motion of the librations, and second, the modification of the phonon density of states due to their interaction with the librations. By numerically including

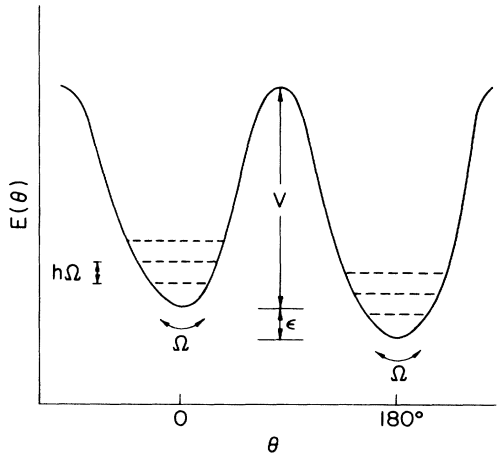

FIG. 1. Double-well potential for a cyanide, sketched as a function of the libration coordinate θ. The barrier height is V, the asymmetry is ε, and Ω is the small oscillation frequency in each well.

these two features, GRS obtained quantitative agreement with the experimental specific heat as well as the thermal conductivity. In the simple model presented here, the first effect is crudely modeled by an "effective" moment of inertia for our independent Einstein oscillators, and the second is ignored altogether. We shall find below that the thermal conductivity plateau is rather insensitive[22] to details of the librational density of states, and is essentially due to its peaked nature.

III. THERMAL TRANSPORT

We now turn to the calculation of the thermal conductivity $\Lambda(T)$. We shall assume that acoustic phonons, with a Debye density of states, are responsible for thermal transport. The relaxation-time approximation to the phonon Boltzmann equation gives

$$\Lambda(T)=\int_0^{\omega_D} d\omega\, C_{\rm ph}(\omega,T)v^2\tau(\omega,T)\ , \tag{3}$$

with v the speed of sound and ω_D the Debye frequency. $C_{\rm ph}$ is the specific-heat contribution of the phonons given by

$$C_{\rm ph}(\omega,T)=\frac{\omega^2}{2\pi^2v^3}\frac{k_Bx^2e^x}{(e^x-1)^2}\ , \tag{4}$$

where $x=\hbar\omega/k_BT$. The total scattering rate $\tau(\omega,T)^{-1}$ in (3) is approximated by Matthiesen's rule of adding the rates due to independent scattering mechanisms.

We shall begin by briefly reviewing various known phonon-scattering mechanisms in glasses and the regimes in which they dominate, and emphasize their inability to explain the plateau in the thermal conductivity. While this inadequacy has been recognized (see, e.g., Refs. 23 and 24) for a long time, there is still some controversy about whether the plateau can be understood in terms of the traditional scattering mechanisms.

For temperatures below 1 K, the dominant scattering mechanism is resonant scattering[1,3] from TLS. Assuming a broad distribution of TLS, with a constant density of states $\bar{P}$, this scattering rate is given by

$$\tau_{\rm res}^{-1}=A\omega\tanh(\hbar\omega/2k_BT),\quad A\equiv\pi\gamma^2\bar{P}/\rho v^2 \tag{5}$$

where γ is the coupling of the strain field to TLS and ρ the density of the material. As is well known,[1,3] this leads to a T^2 temperature dependence of the thermal conductivity at very low temperatures.

Relaxational scattering[25] is another mechanism by which the TLS can scatter phonons, and has been well tested in ultrasound experiments when the resonant processes are saturated by a large acoustic intensity. While it is well known[24] that this scattering is much too weak to affect the low-temperature thermal conductivity, we shall show below that there are circumstances under which it plays an important role. An approximate expression for the phonon lifetime due to the relaxation of TLS is[24]

$$\tau_{\rm rel}\simeq(aT^3)^{-1}+(b\omega)^{-1}\ , \tag{6}$$

where

$$a=\pi^3\bar{P}\gamma^4k_B^3/8\rho^2\hbar^4v^7\ \text{ and }\ b=A/2\ . \tag{7}$$

Equation (6) is an interpolation formula between two regimes: the first term represents the low-temperature scattering rate where the TLS are relaxing slowly compared with the incident phonon frequency, and the second term dominates at high temperatures when the TLS relax fast on the phonon time scale.

Finally, we consider Rayleigh scattering from density fluctuations. While there may be some questions about the validity of various estimates of Rayleigh scattering in structural glasses, for KBr:KCN, at least, the microscopic nature of the density fluctuations is clearly well understood.[26] Here the scattering is simply due to substitutional disorder in the anion sublattice, and is given by

$$\tau_{\rm fluc}(\omega)^{-1}\simeq(\tau_{\rm min}+1/R\omega^4)^{-1}\ . \tag{8}$$

The Rayleigh term is[27]

$$R\omega^4=a_0^3F\omega^4/4\pi v^3\ \text{ with }\ F=\sum_i f_i(\Delta M_i/\bar{M})^2\ , \tag{9}$$

where ΔM_i is the deviation from the average mass $\bar{M}$ in a cell of "type" i occurring with probability f_i, and a_0^3 is the volume of the primitive cell. In (8) the Rayleigh cross section is cut off at very short wavelengths by a minimum phonon lifetime $\tau_{\rm min}\sim a_0/v$, so that the mean free path cannot become smaller than roughly a_0.

For $(KBr)_{0.5}(KCN)_{0.5}$, we use[14] the density $\rho=2.2$ g/cc, the Debye temperature $\Theta_D=135$ K and the speed of sound $v=1.48\times10^5$ cm/sec. We also use the TLS parameter values given in DeYoreo *et al.* (Ref. 14), which have been estimated from specific heat and ultrasound experiments. For the TLS resonant interaction we obtain $A=4.8\times10^{-4}$ [see Eq. (5)] and for the relaxational scattering parameters [Eq. (7)] $a=7\times10^5$ cgs units and $b=A/2$. Using a primitive cell volume $a_0^3=72$ Å^3 and estimating $F\simeq0.08$ [from Eq. (9)], the Rayleigh scattering rate is $R\omega^4\simeq1.5\times10^{-40}\omega^4$ sec^{-1}. We take the maximum scattering rate to be $(\tau_{\rm min})^{-1}=3.7\times10^{12}$ sec^{-1}.

We can now compute the thermal conductivity using (3) taking the total scattering rate to be

$$\tau^{-1}=\tau_{\rm res}(\omega,T)^{-1}+\tau_{\rm rel}(\omega,T)^{-1}+\tau_{\rm fluc}(\omega)^{-1}\ . \tag{10}$$

The result is compared with experiment in Fig. 2. Low temperature ($T<1$ K) resistance is determined by resonant scattering from TLS, and at higher temperatures Rayleigh scattering is dominant in this calculation; these results are essentially unaffected by relaxational scattering. While the very-low-temperature T^2 behavior is well accounted for by the TLS model, the calculated thermal conductivity in the plateau region is much too high. Clearly, much more scattering is required for phonons in the 1–10 K range.

As noted by a number of authors, if one increases, by hand, the magnitude of the Rayleigh scattering term by 2 orders of magnitude, then that alone is sufficient to give the plateau. This is, in fact, related to the postulated existence (see e.g., Ref. 9) of a new "structural correlation length" R_0 in glasses, which is several times larger than the microscopic length scale a_0. If the density fluctuations are on the scale of R_0, then it is R_0^3 that enters in

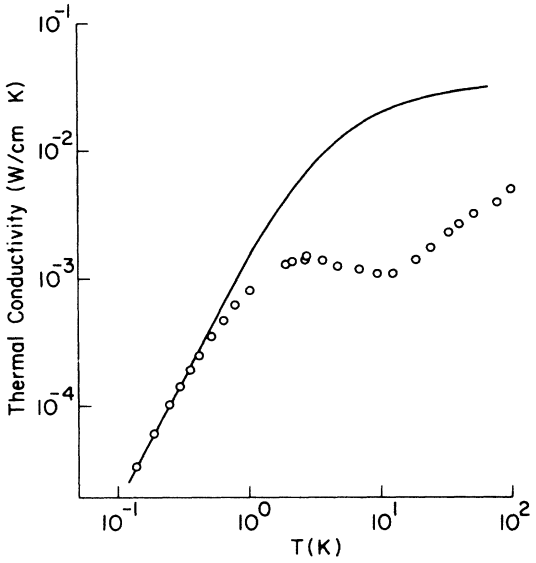

FIG. 2. Thermal conductivity of $(KBr)_{0.5}(KCN)_{0.5}$. Data are from De Yoreo *et al.* (Ref. 14). The calculated curve includes TLS resonant and relaxational scattering and Rayleigh scattering from density fluctuations (see text). Libration scattering is *not* included.

Eq. (9), and one easily obtains a dramatic increase in the Rayleigh scattering.

A related issue is the connection between the Ioffe-Regel localization criterion[28] and the length scale R_0. Let $k=\omega/v$ be the magnitude of the phonon wave vector. For very-long-wavelength phonons ($kR_0 \ll 1$) we have the Rayleigh cross section $\sigma \sim R_0^2 (kR_0)^4$. The mean free path is then given by $l=(n_i\sigma)^{-1}$, where n_i is the density of impurities. But this means that the Ioffe-Regel criterion, $kl \sim 1$, can never be satisfied for $kR_0 \ll 1$, since $kl \sim [n_i R_0^3 (kR_0)^3]^{-1} \gg 1$. Similarly, for very-short-wavelength phonons ($kR_0 \gg 1$) we are in the "geometrical optics" limit with $\sigma \sim R_0^2$ and $kl \sim kR_0/(n_i R_0^3) \gg 1$. Thus the only phonons which can be strongly scattered ($kl \approx 1$), and possibly localized, are those whose wavelength matches the scale R_0 of the density fluctuations, so that $kR_0 \approx 1$.

However, as stated in the Introduction, there is no independent evidence for such a length scale in glasses. In any case, we have microscopic knowledge of the density fluctuations in KBr:KCN and we do not find enhanced scattering from density fluctuations a viable explanation for the plateau in this material.

IV. PHONON SCATTERING FROM LIBRATIONS

We will now show that the resonant scattering of the acoustic phonons from the libration modes leads to the thermal conductivity plateau. Note that we are assuming that the librations are localized and do not contribute to thermal transport, rather they degrade the heat current by scattering the phonons. Since the phonons and the librations are both harmonic oscillators, the simplest coupling[29] between them is bilinear in their displacements, namely,

$$H_{\rm int} = \sum_{\mathbf{k}} \lambda_{\mathbf{k}} q_{\mathbf{k}} \theta \ , \tag{11}$$

where $q_{\mathbf{k}}$ is the displacement of the phonon mode with wave vector $\mathbf{k}$, and θ is the angular displacement of a libration mode. Further, $\lambda_{\mathbf{k}} \sim \lambda_0 k$, in the long-wavelength limit, where λ_0 is directly related to the (experimentally measured) elastic dipole moment[30] of the cyanide molecule; thus (11) is the coupling of the phonon strain field to the libration coordinate θ.

In the case of resonant scattering from TLS, the homogeneous broadening of the TLS distribution made it unnecessary to compute the exact line shape; only the area under the curve was relevant. Here we have a peaked density of libration states and a more careful treatment is required. The line shape for phonons of frequency ω scattering off a libration mode of frequency Ω is given by[6,31]

$$\tau_l(\omega;\Omega)^{-1} = \frac{1}{L^3}\frac{4\pi v^3}{\omega^2}\frac{\omega^2\Gamma^2(\omega)}{(\Omega^2-\omega^2)^2+\omega^2\Gamma^2(\omega)} \ , \tag{12}$$

where L^3 is the volume of the system. The width of the resonance is determined by the broadening of the libration oscillator

$$\Gamma(\omega) = \hbar\lambda_0^2\omega^2/4\pi\rho I_{\rm eff} v^5 \ . \tag{13}$$

We ignore here the shift in the resonance frequency from the "bare" libration frequency resulting from the coupling to the acoustic phonons. The bare frequency is unknown in any case, so we write the result in terms of the physical ("renormalized") Ω which has been determined using an effective moment of inertia for the cyanides. It is interesting to note that the scattering rate is temperature independent due to the harmonic nature of the libration mode.

The interacting phonon-libration system, although harmonic, is random and thus has a finite thermal conductivity, since the phonon momentum is not a conserved quantity in a system without translational invariance. We assume, to begin with, that the scattering from different libration oscillators is incoherent, so that a Boltzmann equation approach is valid. (We discuss localization effects below.) The total scattering rate for a phonon mode of frequency ω, from all of the libration modes, is then given by the convolution of the density of libration states with the line shape for a given libration oscillator. We thus obtain

$$\tau_l(\omega)^{-1} = \frac{L^3}{3}\int d(\hbar\Omega)\, p(\hbar\Omega)\tau_l(\omega;\Omega)^{-1} \ . \tag{14}$$

The factor of $\frac{1}{3}$ arises because we have assumed above, for simplicity, that a given libration mode couples only to phonons of a single polarization. We thus avoid a complicated average[29] over polarizations of the phonon modes.

The result of (14), using the Gaussian density of states determined earlier, and a coupling constant $\lambda_0 = 1.0$ eV (which is the experimental value[30] for KBr:KCN, and also characteristic of phonon-defect couplings in glasses), gives the librational scattering plotted in Fig. 3. We find that phonons in the THz frequency range are very

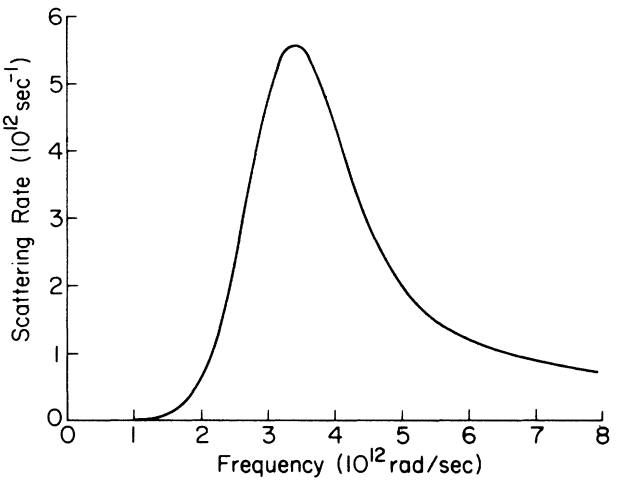

FIG. 3. Total phonon-scattering rate from librations for $(KBr)_{0.5}(KCN)_{0.5}$, plotted as a function of the phonon frequency.

strongly scattered as a result of their resonant interaction with the librations. If we incorporate this scattering in the thermal-conductivity calculation, in addition to the three mechanisms discussed above, we find that we are able to fit the data rather well; see Fig. 4.

V. THERMAL CONDUCTIVITY PLATEAU

We now wish to understand the physics of the processes that give rise to the plateau. For temperatures $T < 1$ K, very low energy phonons transport heat. There are essentially no libration modes at such low frequencies and thus this regime is dominated, as in the usual TLS description, by resonant scattering from TLS. The onset of the plateau corresponds to the dramatic increase in the libration density of states, and thus in the scattering of phonons on resonance with these modes. In fact, thermal phonons, i.e., those with $\hbar\omega \sim k_B T$, are so strongly scattered [$\omega\tau \sim O(1)$] that they transport essentially no heat. It is then the low-frequency phonons, with $\hbar\omega \ll k_B T$, which dominate thermal transport. Thus one can see that the often used "dominant-phonon approximation," which amounts to replacing $\hbar\omega$ by $k_B T$, breaks down completely in the plateau region; see also Ref. 23. Different phonon modes act like parallel channels for thermal transport, as is apparent from Eq. (3); when certain channels are blocked, due to strong scattering, it is the others that carry the heat current.

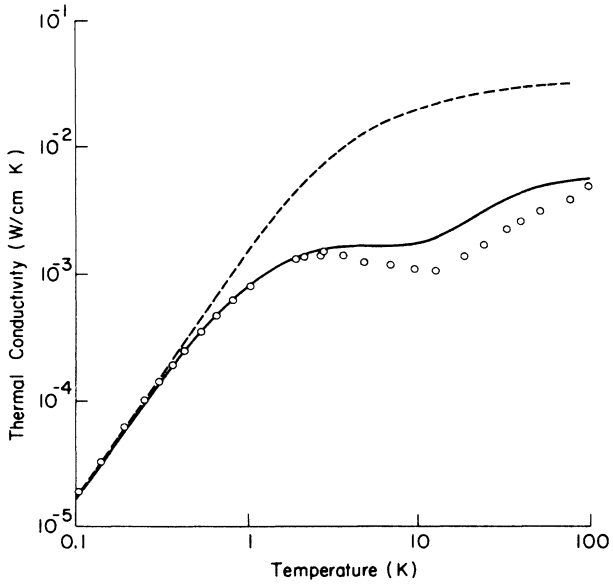

FIG. 4. Thermal conductivity of $(KBr)_{0.5}(KCN)_{0.5}$ calculated with librational scattering, in addition to the TLS resonant and relaxational contributions and the calculated Rayleigh scattering included in Fig. 2. The dashed curve is the same as in Fig. 2.

Now it turns out that it is *not* resonant scattering by the TLS which limits thermal transport by these low-energy phonons. To see this most clearly, let us make some simplifying assumptions to understand the onset of the plateau (not worrying about temperatures above the plateau regime, for the moment). Assume, for the sake of argument, that phonons with energy greater than $\hbar\omega_c = k_B\Theta_c$ are so strongly scattered by the librations that their contribution to thermal transport is strictly zero. This amounts to cutting off the thermal conductivity integral in Eq. (3) at a frequency ω_c roughly 2 orders of magnitude smaller than the Debye frequency. Thus very low-frequency phonons transport heat even for temperatures $T > 1$ K.

The resonant interaction of these low-frequency phonons with the TLS becomes very weak for temperatures much larger than the phonon frequency, or equivalently, the TLS level splitting; see Eq. (5). Physically this arises due to an equalization of the populations in the two levels. We can estimate the effect of this weak resonant scattering on the conductivity from

$$\Lambda(T) \sim T^2 \int_0^{\Theta_c/T} dx \frac{x^3 e^x}{(e^x-1)^2} \coth(x/2) \sim T \quad \text{for } T \gg \Theta_c \ , \qquad (15)$$

where, as usual, $x = \hbar\omega/k_B T$. This clearly shows the need for an additional scattering mechanism for low-frequency phonons, since even if the librations scatter the dominant phonons as strongly as they possibly can, all we get is a T^2 to T crossover in the thermal conductivity instead of a plateau, i.e., a T^2 to constant crossover.

The scattering of the low-frequency phonons[32] comes from two sources: from the relaxation of the TLS and from the wings of the resonance scattering from librations. For the TLS, the situation is similar to that in ultrasound experiments. When the resonant interaction with TLS is suppressed—by the high temperature in our case or by saturation in ultrasound experiments—the relaxation process dominates. As might be expected from the previous discussion, it is only the high temperature form of the relaxational scattering rate (6), namely, $\tau_{\rm rel}^{-1} \simeq b\omega$, that is relevant. In addition, there is the scattering from the low frequency tail of the libration scattering $\tau_l(\omega)^{-1}$. Denoting the sum of these two

temperature-independent terms as $\tau_0(\omega)^{-1}$, the thermal conductivity is given by

$$\Lambda(T)\sim T^3\int_0^{\Theta_c/T} dx \frac{x^4 e^x}{(e^x-1)^2}\tau_0(xk_BT/\hbar)\ . \tag{16}$$

To estimate the integral analytically, notice that for any power law $\tau_0(\omega)^{-1}\sim\omega^n$, the integral[33] goes as T^{-3} (independent of n), for temperatures $T\gg\Theta_c$. Thus Λ goes to a constant value independent of T, i.e., a plateau in the thermal conductivity.

These arguments make it clear that the onset of the plateau, i.e., the crossover from a T^2 regime to one in which the thermal conductivity is roughly independent of temperature, is due to a combination of two effects: the strong resonant scattering of the thermal phonons and a temperature-independent scattering rate for the low-frequency phonons which dominate transport.

The upper edge of the plateau corresponds to a crossover from a regime dominated by the librations to one where Rayleigh scattering is becoming important. The density of libration states decreases and along with it the scattering from these modes, thus leading to an increase in the thermal conductivity. For sufficiently high frequencies, scattering off density fluctuations, with a cross section that grows like the fourth power of frequency, will dominate. While the very concept of a phonon in this regime might be questionable, we do find qualitative agreement with the data in that the thermal conductivity increases above the plateau value.

Note that we disagree with Karpov and Parshin (Ref. 12) on the origin of the thermal conductivity increase above the plateau. These authors suggest that resonant scattering of low-frequency phonons by TLS, weakened by $k_BT\gg\hbar\omega$, limits thermal transport above the plateau and $\Lambda\sim T$ [see Eq. (15) above]. As we have shown above, TLS relaxational scattering dominates under these circumstances, so that this linear temperature dependence will not be seen, and, further, that Rayleigh scattering dominates *above* the plateau.

Finally, it may be useful to comment on the sensitivity of the calculated thermal conductivity on the choice of parameters. The only parameter that we have chosen in the analysis above is the effective moment of inertia for the libration mode $I_{\rm eff}$, or equivalently, the frequency scale $\Omega_0=3.5\times10^{12}$ rad/sec of the density of states. If, for example, we had chosen the mean frequency in the Gaussian density of libration states to be $\Omega_0=8\times10^{12}$ rad/sec, the value obtained from using the dielectric loss data with the single CN moment of inertia, we do not find a plateau. The thermal conductivity in that case goes from a T^2 regime (dominated by resonant scattering from TLS) directly to a regime dominated by the Rayleigh scattering. Thus librational scattering must become important at sufficiently low frequencies if it is to play any role at all. At higher frequencies all mechanisms are swamped by Rayleigh scattering with a cross section that grows as ω^4. We note that in the GRS analysis[7] there is no fit parameter corresponding to Ω_0, since the density of states is obtained from a numerical simulation which uses only experimentally measured quantities as input.

VI. PHONON LOCALIZATION

We have found that, near the peak in the libration density of states, the scattering rate $\tau_l^{-1}(\omega)$ (Fig. 3) is so large that the Ioffe-Regel criterion[28] $[\omega\tau_l\sim O(1)]$ is satisfied. Traditionally, this is taken to be a signal for localization. Our aim, in this section, is to study, within our model, how phonon localization would affect the thermal conductivity. Localization of phonons has been studied in simpler cases.[34] In our model there are, however, several complications: the scattering is not off static disorder, rather off a libration oscillator with internal degrees of freedom, and anharmonic interactions between the phonons could also affect localization. To the best of the authors' knowledge no rigorous treatment of the full problem exists. However, since the thermal conductivity results will turn out to be insensitive to the details, and, in fact, to the existence, of localization, a rather simple analysis will suffice; see Ref. 6 for details.

The scattering of the phonons from the libration modes is coherent; indeed, the coupled Hamiltonian is a quadratic form, and our perturbative calculations below are simply estimates of the mobility edge for the true normal modes of the system. (In principle, of course, we could diagonalize the random harmonic phonon-libration Hamiltonian and determine whether the true normal modes are extended or localized.) We assume that anharmonic effects are weak enough that they do not destroy localization.

In localization theory it is customary to use the diffusion coefficient which is related to the transport lifetime via $D(\omega)=\frac{1}{3}v^2\tau(\omega)$ in the dc limit; it is precisely this quantity that enters the thermal conductivity expression (3). Our earlier treatment of phonon scattering from local libration modes is valid in the Boltzmann regime, where $\omega\tau\gg1$. The renormalization of the diffusion coefficient, due to weak localization corrections, can be computed perturbatively in the parameter $(kl)^{-1}\equiv(\omega\tau)^{-1}$. Using the self-consistent approximation of Vollhardt and Wölfle[35] we can study this renormalization in the strong disorder regime. In keeping with the terminology of the rest of this paper, we write the result for the renormalized diffusion constant in terms of the corresponding lifetime. We find[6] that the self-consistent renormalized scattering rate is given by

$$\tau_{l,\rm ren}(\omega)^{-1}\simeq\frac{\tau_l(\omega)^{-1}}{1-[\alpha/\omega\tau_l(\omega)]^2}\ , \tag{17}$$

where α is a dimensionless constant of order unity, which determines the precise location of the mobility edges. Since our results are rather insensitive to this choice, we have (somewhat arbitrarily) chosen $\alpha=1$.

Given the peaked shape of the "bare" scattering rate off librations, we find (see Fig. 5) two mobility edges, one on either side of the maximum in $\tau_l(\omega)^{-1}$, where $\omega\tau_l(\omega)=1$. At each of the mobility edges, the renormalized scattering rate diverges, or the corresponding diffusion coefficient vanishes, i.e., the mobility edges enclose a rather narrow band of localized phonons.

Inclusion of the renormalized scattering rate (17), which explicitly takes into account phonon localization,

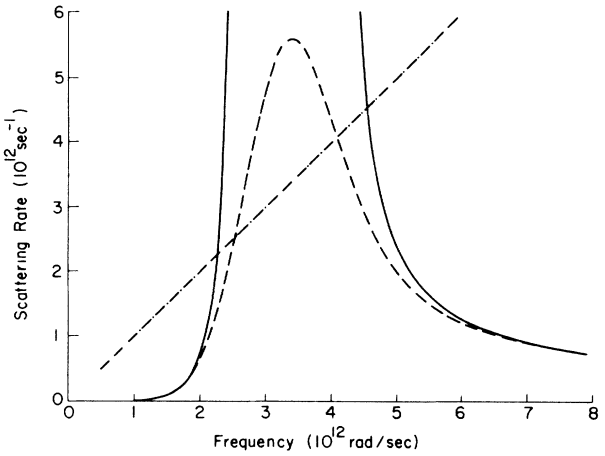

FIG. 5. Scattering rate from librations. The "bare" rate (of Fig. 3) obtained from lowest-order perturbation theory is given by the dashed curve. The renormalized rate incorporating the effects of phonon localization is given by the solid curve. The two mobility edges are marked by the divergence of the renormalized rate and correspond to the intersection of the bare rate with the $\tau^{-1}=\omega$ line. The phonons are localized in the interval enclosed by the two mobility edges.

in the thermal conductivity calculation does not substantially change the agreement with the data. Since the bare scattering rate itself was so large in the localized region, any further enhancement of this rate due to multiple scattering has no effect on the conductivity. In other words, what seems to matter, for thermal transport, is the very large amount of scattering that the libration modes provide, rather than the narrow band of localized phonons they give rise to. It should be emphasized that phonon localization is *not* the cause of the plateau and it is quite possible that in some glasses which show a plateau in Λ, there is no true localization, only strong resonant scattering.[36]

It is clear from the above considerations that thermal conductivity measurements are not, at least for KBr:KCN and probably for all glasses, a very useful way to probe phonon localization. This is in marked contrast to the electronic localization problem. The reason for this is simply that heat is carried by a broad Planck distribution of phonons as opposed to electrical transport by "monochromatic" electrons at the Fermi energy. However, monochromatic phonon propagation experiments in the plateau region in glasses, if feasible, could be used to study phonon localization.

VII. CONCLUSIONS

In conclusion, we have given a detailed analysis of the thermal conductivity plateau (a universal glassy property) in the orientational glass KBr:KCN in terms of the CN libration modes. If this is to be an universal explanation, then what are the corresponding resonant modes in structural glasses? It is tempting to suggest that they are the small oscillation modes of the tunneling center double well, i.e., the "other levels" of the two level systems. Naively, this would seem unlikely; in typical glasses at 1 K there is only one active TLS per million atoms, while roughly one local mode per atom is seen. However, in KBr:KCN the TLS's have been explained[17] as the tail of a distribution of double-well CN^- potentials: the cyanide orientations are the common origin of the TLS and the local modes. Of course, this is not direct evidence for a common origin in general, since the cyanide orientations are the only glassy degrees of freedom in KBr:KCN.

We have recently used our model[7] of interacting defects as a phenomenological model to study thermal transport in structural glasses and have obtained encouraging results for vitreous silica. These results will be published separately.[37]

ACKNOWLEDGMENTS

We would like to thank R. O. Pohl, H. Fischer, A. M. de Göer, B. Golding, J. A. Krumhansl, S. R. Nagel, T. V. Ramakrishnan, and N. Trivedi for useful discussions and correspondence, and E. R. Grannan for a very fruitful collaboration. We would also like to thank A. C. Anderson for detailed comments on the manuscript. We gratefully acknowledge support from National Science Foundation (NSF) Grant No. DMR 8217227A-01, through the Materials Science Center at Cornell University; work at University of Illinois was supported by the John D. and Catherine T. McArthur Foundation Grant No. 0-6-40129 and NSF Grant No. DMR 86-12860.

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*Present address.

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[11]In KBr:KCN the only conceivable candidate for a correlation length, below which it may appear self-similar, is the percolation correlation length ξ for the CN molecules. For a sample with 50% CN, a crude estimate can be made as follows. We assume that scaling holds at $p=0.5$ and use $p_c \simeq 0.2$ for an fcc lattice, a correlation length exponent $\nu \simeq 0.8$ [D. Stauffer, Phys. Rep. **54**, 1 (1978)] and an amplitude of 5 Å, the CN near-neighbor distance. We obtain $\xi \simeq 13$ Å which is much too small to be relevant for the plateau.

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[16]For cyanides with very low barrier heights to reorientation, i.e., the tunneling centers, it is not valid to ignore interactions which lead to an asymmetry in the double well. See Ref. 17. This complication is, however, irrelevant for our present purposes.

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[19]In reality, each cyanide ion has *two* libration modes; however, the dielectric loss measurements give us no information about the higher-frequency one. Thus we shall ignore it here. We note that the numerical results of GRS (Ref. 7) show that the two modes have rather similar frequencies.

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[21]Simply translating a Gaussian distribution of barriers $P(V)$ into frequencies using $\Omega=(2V/I_{\rm eff})^{1/2}$ implies a *non*-Gaussian distribution $p(\hbar\Omega)\sim\Omega\exp[-C(\Omega^2-\Omega_0^2)^2]$. There is a broad shoulder in this distribution at very low frequencies which we believe is unphysical (see Ref. 6). In any case, this functional form for $p(\hbar\Omega)$ is strictly valid over a rather small range of frequencies since $P(V)$ itself is known over a restricted range of barriers V. For the sake of simplicity, we approximate $p(\hbar\Omega)$ by a Gaussian.

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[30]Stress dichronism experiments (H. Beyler, Ref. 20) on isolated CN^- molecules in a KBr host measure a shape factor $\lambda_s \simeq 0.2$. The coupling constant can then be shown to be given by $\lambda_0=2a_0^3\lambda_s\mu\simeq1.0$ eV, using a primitive cell volume $a_0^3=72$ Å^3 and a shear modulus $\mu\simeq5.6\times10^{10}$ dyn cm^{-2}. In Ref. 6 we had estimated the coupling to be too small by a factor of 2. We thank Eric Grannan for pointing out this error.

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[32]We acknowledge a very useful discussion with Brage Golding, and correspondence from A. M. de Göer on scattering mechanisms for low-frequency phonons in the plateau region.

[33]Note that one does not have to worry about a low-frequency divergence in (16) since the relaxation scattering rate ($=b\omega$), which dominates close to $\omega\simeq0$, leads to a finite integral.

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[36]It should be mentioned that the libration density of states obtained from the numerical simulation of GRS (Ref. 7) leads to a scattering rate which, though close, never reaches the Ioffe-Regel limit ($\omega\tau=1$); it does, however, give rise to a plateau.

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