

Possible mechanism for thermal conductivity in $(\text{KBr})_{1-x}(\text{KCN})_x$

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Recent low-temperature experiments on $(\text{KBr})_{1-x}(\text{KCN})_x$ indicate that initially, as expected, the thermal conductivity κ decreases as x increases. However, for $x \geq 0.01$, κ increases with increasing x . We propose that this increase is a result of energy diffusion due to elastic interactions between the CN^- ions.

There has been considerable interest in glassy systems since Zeller and Pohl¹ found that the low-temperature specific heat depends linearly on temperature and that the thermal conductivity varies as T^2 . Theoretically these properties have been explained by invoking two-level systems (TLS).^{2,3} However, the microscopic nature of these objects remains a mystery. It has been suggested that some insight into glasses could be achieved by studying $(\text{KBr})_{1-x}(\text{KCN})_x$ in which the randomly distributed CN^- molecules are the analog of TLS.⁴ The CN^- axis lies along the $\langle 111 \rangle$ crystallographic directions and can tunnel quantum mechanically between the eight possible orientations.⁵ The barrier height is about 0.5 meV and the tunnel-split levels A_{1g} , T_{2u} , T_{2g} , and A_{2u} have separations of roughly 1.2 K. Recently, DeYoreo *et al.*⁶ and Moy, Dobbs, and Anderson⁷ have measured the low-temperature properties (≤ 1 K) of $(\text{KBr})_{1-x}(\text{KCN})_x$ for a variety of CN^- concentrations. They find that the thermal conductivity decreases and the specific heat increases as the CN^- concentration increases for $x \leq 0.01$. This behavior can be ascribed to noninteracting molecules which resonantly scatter phonons and which contribute to the entropy of the system. Indeed, structure in the thermal conductivity versus temperature curves has been identified as resonant absorption of phonons with energy equal to the tunnel splitting.⁸ The specific heat at low temperatures also reveals a broad Schottky peak when the T^3 phonon contribution is subtracted.⁹ As the concentration increases above $\sim 1\%$, however, these trends are reversed — the thermal conductivity *increases* and the specific heat *decreases* with increasing x . One possible explanation is that interaction between the CN^- ions causes most of them to freeze in their orientations at low temperatures. The few isolated ions which are not frozen contribute to the specific heat and thermal resistivity as before. This does not appear to be a tenable explanation for the following reasons. First of all, if one estimates the fraction of isolated CN^- molecules from the specific-heat data, e.g., the $x=0.25$ sample appears to have $x \sim 10^{-5}$ free ions, one would predict the associated thermal resistivity due to phonon scattering to be an order of magnitude smaller than what is observed. Secondly, freezing means that low-energy excitations are no longer accessible, i.e., that there is a hole in the density of states $n(E)$, where E is the tunnel splitting. Since the thermal conductivity $\kappa \propto n(E)^{-1}$ and the specific heat $C \propto n(E)$, one would expect κC to be independent of $n(E)$ and hence x . This is certainly not the case experimentally for $(\text{KBr})_{1-x}(\text{KCN})_x$, nor for glasses in general.

In this paper we propose that the mechanism for thermal transport is the transfer of energy from one CN^- molecule

to another which has nearly the same tunnel splitting. In other words, one CN^- flips from one energy level to another, which in turn causes another to flip, and so on down the line. Thus, energy diffusion occurs. Since each energy eigenfunction is a linear combination of different orientations, this should not be confused with flipping from one orientation to another. Before elaborating on the thermal conductivity, we note that the specific heat decreases as x increases above 1% because increasing interactions cause the density of states $n(E)$, as well as the Schottky peak, to broaden. Hence, the specific heat decreases.

The strong coupling between the orientation of the CN^- ions and the lattice gives rise to an effective quadrupole-quadrupole interaction which is mediated by phonons:¹⁰

$$H_{\text{eff}} = -\frac{1}{2} \sum_{i,j;\alpha\beta} Y_{\alpha}^{\dagger}(\Omega_i) J^{\alpha\beta}(\mathbf{R}_{ij}) Y_{\beta}(\Omega_j), \quad (1)$$

where i and j denote CN^- sites and Ω_i is the orientation of the CN^- ion at site i in terms of the polar angles (θ_i, ϕ_i) . The tensor operators Y_{α} transform under rotations as the following linear combinations of the $l=2$ spherical harmonics:

$$\begin{aligned} Y_1 &= Y_{2,0}, \\ Y_2 &= (3/2)^{1/2}(Y_{2,2} + Y_{2,-2}), \\ Y_3 &= i(Y_{2,2} - Y_{2,-2}), \\ Y_4 &= (Y_{2,1} - Y_{2,-1}), \\ Y_5 &= -i(Y_{2,1} + Y_{2,-1}). \end{aligned}$$

The first two Y_{α} have E_g symmetry and the last three have T_{2g} symmetry. Experiments have shown that it is excitations with these symmetries which are strongly coupled to phonons.¹¹ Thus, we will ignore excitations to other tunneling levels. The T_{2g} state is 0.28 meV above the A_{1g} ground state and the librational E_g state has an energy of 1.6 meV. Since we are interested in behavior below 1 K, we can ignore librational excitations. The coupling $J^{\alpha\beta}(\mathbf{R}_{ij})$ is proportional to R_{ij}^{-3} for large distances, i.e., for $(\pi R_{ij}/a) \gg 1$, where a is the lattice spacing.¹² The constant of proportionality, $B^{\alpha\beta}$, is on the order of $8 \times 10^3 \text{ K } \text{\AA}^3$.¹⁰ This is an order of magnitude larger than the direct electric dipole-dipole interaction. The CN^- dipole moment of $\mu \sim 0.3 \text{ D}$ gives $\mu^2 \sim 7 \times 10^2 \text{ K } \text{\AA}^3$.

We will now follow the approach that Continentino¹³ used for TLS to estimate the contribution to the thermal conductivity from the effective interaction given by (1). The E_g -type interactions [$\alpha, \beta \in (1, 2)$] are the analog of J_{ij}^{α} in

spin-spin interactions. They give rise to a distribution of tunnel splittings and a width in the density of states. The T_{2g} -type interactions [$\alpha, \beta \in (3, 4, 5)$] are associated with energy transfer between "like" quadrupoles in which one quadrupole is excited from the A_{1g} ground state to a T_{2g} state while the other is deexcited from a T_{2g} state to the ground state. For simplicity we are thinking in terms of single site A_{1g} - T_{2g} transitions. By "like" quadrupoles we mean those which satisfy the condition

$$|J^{\alpha\beta}(\mathbf{R}_{ij})| \geq |E_i^\alpha - E_j^\beta|, \quad (2)$$

where $Y_\alpha^\dagger(\Omega_i)$ induces transitions from the ground state to a state with energy E_i^α . Thermal transport occurs via diffusion of energy between like quadrupoles. The thermal conductivity κ is given by

$$\kappa = n\rho_l CD, \quad (3)$$

where ρ_l is the density of like quadrupoles and n is the number of channels of like quadrupoles which can transport energy. We will take $n\rho_l$ to be roughly equal to the density of CN^- ions, i.e., $x=0.01$ corresponds to $n\rho_l \sim 0.02 \text{ g/cm}^3$. C is the specific heat associated with noninteracting quadrupoles. Noting that the specific heat for $x=1.5 \times 10^{-4}$ at $T=0.1 \text{ K}$ is about 10 erg/gK ; we estimate C to be 10^{-2} Wsec/gK at $T=0.1 \text{ K}$. D is the diffusion constant which we can estimate in the same way that Bloembergen¹⁴ estimated spin diffusion:

$$D = Wd^2, \quad (4)$$

where d is the average distance between like quadrupoles and W is the "flip-flop" rate between like quadrupoles. W is proportional to the neutron scattering linewidth $\Gamma = \hbar T_2^{-1}$ which probes phonons that couple to T_{2g} transitions. It is phonons with this symmetry which mediate the flip-flop interaction. There are two primary contributions to the linewidth Γ . One is the E_g part of the Hamiltonian in Eq. (1) [$\alpha, \beta \in (1, 2)$], which changes the tunnel splittings but does not cause transitions to occur. It gives a width to the distribution of tunnel splittings. The second is the T_{2g} part of (1) [$\alpha, \beta \in (3, 4, 5)$], which induces transitions from the ground state to a T_{2g} state. This gives a finite width or lifetime to each tunnel splitting. These two effects are of comparable magnitude. It is when the total linewidth Γ becomes on the order of the bare tunnel splitting that there will be significant energy diffusion via quadrupoles. This smearing of the energy levels is consistent with the disappearance above $x \sim 0.01$ of the dip in the thermal conductivity versus temperature curves. This dip is due to the resonant absorption of phonons with energy equal to the tunnel splitting.⁸ Since the bare A_{1g} - T_{2g} splitting has an energy of 0.28 meV , we take T_2 to be 10^{-12} sec . This can be compared to neutron scattering linewidths which yield $T_2 \sim 2.6 \times 10^{-11} \text{ sec}$ for $x=0.008$ and $T=1.8 \text{ K}$, and $T_2 \sim 2.2 \times 10^{-13} \text{ sec}$ for $x=0.16$ and $T=10 \text{ K}$.¹¹ As we have just discussed, the strong concentration dependence arises from interaction effects, though our value for T_2 should be subjected to further experimental tests. In terms of T_2 the diffusion constant is given by¹⁴

$$D = \frac{d^2}{\lambda T_2}, \quad (5)$$

where λ^{-1} is proportionality constant, which relates the

linewidth to the flip-flop rate between like spins. For a Gaussian line shape it is proportional to \sqrt{f} if the CN^- ions are not too dilute.¹⁵ f is the fraction of CN^- ions which can exchange energy with one another, i.e., $f = \rho_l/\rho$. Thus, λ is roughly given by $10/\sqrt{f}$, where the numerator is basically a geometrical factor.¹⁵ To estimate f , we consider a certain tunnel splitting E_o^β at site o . The number $m_o^{\alpha\beta}$ of neighbors of o which satisfy $|J_o^{\alpha\beta}| \geq |E_j^\alpha - E_o^\beta|$ is given by

$$m_o^{\alpha\beta} = \sum_j \int_{\Delta_-}^{\Delta_+} dE^\alpha P(E^\alpha), \quad (6)$$

where $\Delta_\pm = E_o^\beta \pm \frac{1}{2}|J_o^{\alpha\beta}|$ and $P(E^\alpha)$ is the probability per site per unit energy that there is a state with symmetry α and energy E . It is normalized to unity. $P(E^\alpha)$ is related to the density of states $n(E)$ by $P(E^\alpha) = n(E)/\rho M$, where M is the number of levels per site. We will assume that $n(E)$ and $P(E^\alpha)$ are roughly constant in the interval of integration. The measured specific heat of 100 erg/gK for $x=0.005$ at $T=0.1 \text{ K}$ implies that $n(E) \sim 10^{35} \text{ erg cm}^3$ for $x=0.01$. Since the primary contribution to the specific heat at $T=0.1 \text{ K}$ comes from tunnel-split states, we take $M=8$. In principle we should sum $m_o^{\alpha\beta}$ over α to count all the neighbors m_o^β which can exchange energy with site o in state E_o^β , but this would also double count neighbors with more than one level which satisfy $|J_o^{\alpha\beta}| \geq |E_j^\alpha - E_o^\beta|$. Since $J_o^{\alpha\beta}$ is a strong short-range coupling, the latter will probably dominate the former and we will take $m_o^{\alpha\beta} \sim m_o^\beta$. Thus, we can write (6) in the form

$$m_o^\beta \sim \frac{n(E_o^\beta)}{\rho M} \sum_j |J_o^{\alpha\beta}|. \quad (7)$$

Using

$$\rho^{-1} \sum_j |J_o^{\alpha\beta}| \sim 4\pi B^{\alpha\beta} \ln|R/a| \sim 2 \times 10^{-34} \text{ erg cm}^3,$$

where R is the radius of a unit volume, we obtain $m_o^\beta \sim 3$, which implies that $f \sim 1$. It is not surprising that site o can exchange energy with several of its nearest neighbors since $J_{ij}^{\alpha\beta}$ is a strong short-range interaction. For $R_{ij} \sim 10 \text{ \AA}$, $|J_{ij}^{\alpha\beta}| \sim 8 \text{ K}$, which is larger than the bare tunnel splitting of $\sim 3 \text{ K}$ and is on the order of the renormalized tunnel splitting. We will take $\lambda \sim 10$ and d to be the average nearest-neighbor distance between CN^- ions, i.e., $d \sim 10 \text{ \AA}$ for $x=0.01$. Putting this all together, we find from (5) that $D \sim 10^{-3} \text{ cm}^2/\text{sec}$ and from (3) that $\kappa \sim 2 \times 10^{-7} \text{ W/cmK}$. To see that this is of the right order of magnitude, note that the minimum in the thermal conductivity with respect to x occurs between $\kappa(x=0.003) \sim 10^{-6}$ and $\kappa(x=0.05) \sim 7 \times 10^{-5} \text{ W/cmK}$.^{6,7} It is in the neighborhood of $x=0.01$ that thermal transport due to interacting quadrupoles begins to dominate over that due purely to phonons. These two contributions must be added in parallel. As x increases, so does resonant phonon scattering, and as a result the corresponding contribution to κ decreases. We shall show shortly that increasing x enhances the "flip-flop" mechanism for thermal transport. However, the energy barrier for reorientation also increases from 0.5 meV for isolated CN^- ions to 160 meV for pure KCN .⁴ As a result, the tunnel splitting decreases with increasing x , and in the limit of $x=1$ the phonons are solely responsible for thermal transport. The crossover from this flip-flop mechanism to phonons probably occurs in the region of $x \sim 0.10$. The onset of quadrupole-quadrupole interactions at $x \sim 0.01$ is

consistent with Luty's observation¹⁶ that the CN^- vibrational lifetime, which is constant for $x \leq 0.01$, dramatically decreases for $x > 0.01$. One might think that such a flip-flop mechanism between two-level systems would be important in the thermal conductivity of glasses. However, phonon-echo experiments¹⁷ indicate that T_2 is a few μsec , which implies that the corresponding contribution to κ is at least six orders of magnitude smaller than our estimate for $(\text{KBr})_{1-x}(\text{KCN})_x$. Indeed, Zaitlin and Anderson experimentally showed that phonons are responsible for thermal transport in glassy materials.¹⁸

We pause at this point to compare the flip-flop mechanism with the ordinary resonant scattering of phonons. Both involve the absorption and emission of phonons by tunneling centers. However, in the flip-flop mechanism the tunneling centers are interacting with one another, in such a way that the energy of the system of tunneling centers is approximately conserved. Heat transport occurs because one tunneling center emits a virtual phonon that is absorbed by another. On the other hand, in the standard model the tunneling centers are viewed either as interacting with other centers so strongly that they are frozen, or else as not interacting with one another and hence diminishing thermal transport by resonantly scattering phonons.

To determine the temperature dependence of κ , we note that neutron scattering experiments¹¹ performed between 1.8 and 8.0 K indicate that T_2^{-1} and hence D are proportional to T for $x \sim 0.01$. Since the specific heat C is linear in T , κ goes as T^2 according to (3). This is in rough agreement with experiment. However, experimentally T_2 is roughly temperature independent for $x=0.16$, though no measurements were made below 10 K.¹¹ If T_2 continues to be temperature independent at low temperatures, this would give a contribution to κ that is linear in T . Since the measured thermal conductivity goes as T^2 , this implies that phonons and resonant scattering are dominant for $x \geq 0.10$.

Estimates of the thermal conductivity at higher CN^- concentrations and/or higher temperatures also have the right order of magnitude. For example, consider $x=0.25$ and $T=0.1$ K. Assuming that T_2 is roughly temperature and concentration independent for $x \geq 0.15$, we use the experimental value of $T_2(x=0.16, T=10 \text{ K}) \sim 2 \times 10^{-13}$ sec.¹¹ Taking $\rho = 0.5 \text{ g/cm}^3$, $n(E) \sim 2 \times 10^{33} \text{ erg cm}^3$, and our previous values for C and $\rho^{-1} \sum_j |J_{j\beta}^{\alpha\beta}|$, we find $f \sim 6 \times 10^{-2}$, $d \sim 20 \text{ \AA}$, and $\kappa \sim 2 \times 10^{-5} \text{ W/cm K}$, which compares favorably with the experimental value of $\kappa \sim 1 \times 10^{-5} \text{ W/cm K}$.^{6,7} As another example, consider $x=0.01$ and $T=1$ K. At this concentration $T_2 \propto T^{-1}$, which implies that $T_2 \sim 10^{-13}$ sec.¹¹ For $T=1$ K we estimate that the specific heat C of noninteracting quadrupoles is $\sim 8 \times 10^{-2} \text{ W sec/g K}$. Taking ρ , d , and α to be the same as for the case with $T=0.1$ K and $x=0.01$, we obtain $\kappa \sim 2 \times 10^{-5} \text{ W/cm K}$, which is of the same order of magnitude as the experimental value of $8 \times 10^{-6} \text{ W/cm K}$.^{6,7}

We now consider what experiments might be done to test our hypothesis. Such experiments should be able to differentiate between a flip-flop mechanism and a purely phonon mechanism of thermal transport. This is a bit tricky

since the quadrupole-quadrupole interaction is mediated by phonons. One possible test would be to dope samples of $(\text{KBr})_{1-x}(\text{KCN})_x$ with sodium ions in order to freeze out some of the cyanide dipoles. Sodium ions greatly increase the tunneling barrier height as can be seen in thermal-conductivity measurements below 1 K of $\text{NaCl}_{1-x}(\text{CN})_x$ with $x \sim 4 \times 10^{-3}$, which show no evidence of resonant scattering.⁸ Since the CN^- dipoles carry the heat in the flip-flop model, this will cause the thermal conductivity to decrease, while more traditional models, in which mobile cyanides increase thermal resistivity, predict κ will increase as sodium is added. Effects should be seen for sodium concentrations ≤ 0.01 . If the Na concentration is too high, both energy exchange via flip-flops and resonant phonon scattering would be inhibited, and the thermal conductivity would increase. In this regime of large sodium concentration the flip-flop model predicts that the specific heat and thermal conductivity should agree in much the same way as they did for very low CN^- concentrations ($x < 0.005$). If, on the other hand, the flip-flop mechanism is incorrect and the rise in κ for $x \geq 0.01$ is due to the "freezing out" of quadrupoles and reduced resonant scattering, then the thermal conductivity would continue to be considerably less than what one would predict by assuming that the specific heat was due entirely to free CN^- ions. Thus, a study of $\text{K}_{1-y}\text{Na}_y\text{Br}_{1-x}(\text{CN})_x$ with x and y in the neighborhood of 1% would be a good test of the flip-flop hypothesis. Other experimental tests that come to mind have difficulties. For example, aligning the CN^- ions with electric fields or applied stress is probably not experimentally feasible because of the very small electric dipole moment of the CN^- ion and because large stresses might introduce dislocations and cracking.^{5,8,19} Introducing heavier isotopes of CN^- could reduce the barrier height from, say, ~ 2 to ~ 0.5 K but $J_{j\beta}^{\alpha\beta}$ would still be large enough to satisfy condition (2) for nearest-neighbor quadrupole-quadrupole distances of $\sim 10 \text{ \AA}$. One might also consider doping the $(\text{KBr})_{1-x}(\text{KCN})_x$ samples with isotopes of potassium or with colloids²⁰⁻²² in such a way as to scatter phonons without greatly disturbing the elastic quadrupole-quadrupole interactions. However, below 1 K such phonon scattering goes as ω^4 and is negligible. Colloids which would be large enough to produce geometric scattering would have to have diameters of $\sim 10^3$ - 10^4 \AA . These large lumps would also introduce dislocations and stacking faults. The best bet seems to be doping $(\text{KBr})_{1-x}(\text{KCN})_x$ with sodium ions.

In summary, we have shown that it is plausible that low-temperature thermal transport in $(\text{KBr})_{1-x}(\text{KCN})_x$ occurs via energy diffusion due to elastic quadrupole-quadrupole interactions.

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