

Low-Energy Excitations in $(\text{KBr})_{1-x}(\text{KCN})_x$ in the Orientational Glass State

J. J. De Yoreo, M. Meissner,^(a) and R. O. Pohl

Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York 14853

and

J. M. Rowe and J. J. Rush

National Measurement Laboratory, National Bureau of Standards, Washington, D. C. 20234

and

S. Susman

Solid State Science Division, Argonne National Laboratory, Argonne, Illinois 60439

(Received 2 May 1983)

The thermal conductivity of single-crystal $(\text{KBr})_{1-x}(\text{KCN})_x$, $0.05 \leq x \leq 0.5$, in the temperature range 0.08–100 K shows behavior characteristic of amorphous solids. The low-temperature specific heats ($T < 2.5$ K), measured on long (~ 50 s) and on short (< 0.2 ms) time scales, also are identical to those found in amorphous solids. It is proposed that the KBr-KCN system provides a connecting link between the low-energy excitations in amorphous solids and in spin-glasses.

PACS numbers: 66.70.+f, 63.50.+x, 65.40.-f

In one of the first attempts to explain¹ the anomalous low-energy excitations observed in amorphous solids,² it was suggested that spin-glasses might have similar excitations. This connection has yet to be experimentally established. In this paper, we wish to report the existence of such anomalous excitations in a quadrupolar glass, i.e., in a crystalline system containing randomly distributed elastic dipoles, rather than spins. The measurements performed were neutron scattering, thermal conductivity, and specific heat.

CN^- ions substituting in small concentrations for Br^- ions in the KBr lattice are known to possess low-energy, quasirotational tunneling and librational states.³ At large concentrations (molar ratio $x > 0.01$), $(\text{KBr})_{1-x}(\text{KCN})_x$ has recently attracted much interest.⁴⁻⁹ Because of its perfect miscibility, this system has been used as a model for the study of interactions between randomly distributed ions. It has been concluded that for $x < 0.6$, the CN^- dumbbells gradually assume preferred arrangements in an orientationally disordered, glassy phase, as the temperature is lowered.^{4,5} The onset, called the freezing temperature, T_F , decreases with decreasing x . Dielectric measurements indicate little change in the dipolar relaxation rates associated with this glassy phase,⁶⁻⁹ but the unusual spread of relaxation rates in this concentration regime has been discussed in detail recently.⁹ The similarity to spin-glasses has been stressed.

The single crystals of $(\text{KBr})_{1-x}(\text{KCN})_x$ were those studied previously.⁴ The neutron-scattering line shapes for the $[100]\text{TA}$ branch of the phonon dispersion relation have been measured at high resolution for $x = 0.25$, Fig. 1. The results are similar to those reported earlier for the sample with $x = 0.5$.^{4,5} The frequency of the mode remeasured at $\frac{1}{10}$ of the way to the zone boundary first falls as the temperature is reduced, then increases below 50 K. At the same time, a peak centered at zero energy transfer with a resolution-limited width begins to appear at 150–200 K, then increases rapidly in intensity below 50 K, the same temperature at which the energy of the phonon reaches a minimum. These measurements indicate that this crystal begins to freeze into an orientational (quadrupolar) glass state at $T_F \approx 70$ K. Extrapolated dielectric measurements indicate a continuous slowing down of the electric dipolar reorientations in this temperature range.^{6,8,9} These results are not inconsistent with the measurements presented here, which are probing the onset of complex quadrupolar arrangements in an orientational glass. We now present independent macroscopic evidence for the existence of this glassy state.

Thermal conductivity was measured with the steady-state gradient method, and specific heat with the transient heat-pulse method as described by Raychaudhuri and Pohl¹⁰ and by Meissner and Spitzmann¹¹ for long and for short measuring times, respectively. The optically clear single-crystal samples are only slightly more brittle

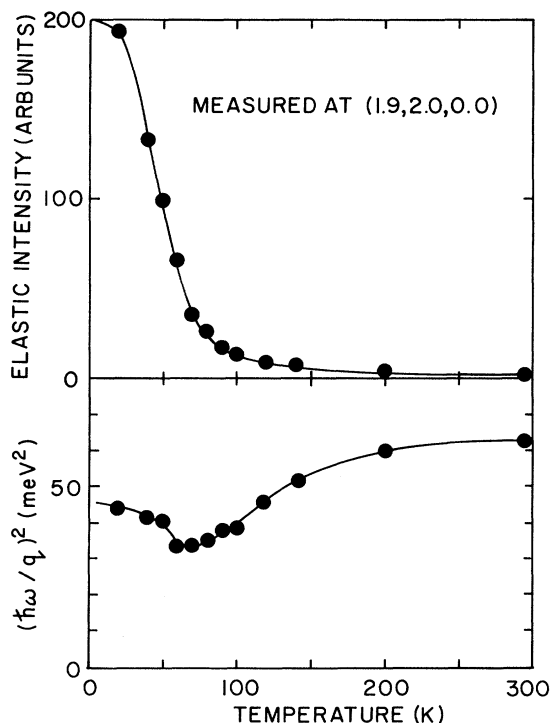


FIG. 1. Neutron-scattering results for $(\text{KBr})_{0.75}(\text{KCN})_{0.25}$. The upper half of this figure shows the temperature dependence of the intensity observed at zero energy transfer at a reduced wave vector $\frac{1}{10}$ of the way to the zone boundary about the (220) Bragg position. The energy width of this peak was resolution limited (< 0.10 meV) at all temperatures. The lower half of the figure shows the square of the energy of the discrete excitation observed at the wave vector (divided by the reduced wave vector). The errors in each case are of the order of the size of the plotted points. The solid lines are only a guide to the eye.

than pure KBr and were readily cleaved with a razor blade. They showed no sign of chemical inhomogeneity on length scales greater than 10 \AA , when inspected by small-angle neutron scattering.

As shown in Fig. 2, the thermal conductivity of pure KBr is strongly reduced in the presence of less than 1% CN^- in solid solution, through resonant scattering by the quasirotational states of the individual CN^- ions.³ However, as x increases beyond 0.01, the conductivity increases again, as shown for $x = 0.05, 0.25,$ and 0.5 . This indicates a disappearance of the tunneling states of the isolated CN^- ions. The striking similarity of the conductivity for the two largest- x samples to that of amorphous solids is brought out through a comparison with the conductivity of polymethylmethacrylate (Plexiglass) also shown in Fig. 2.

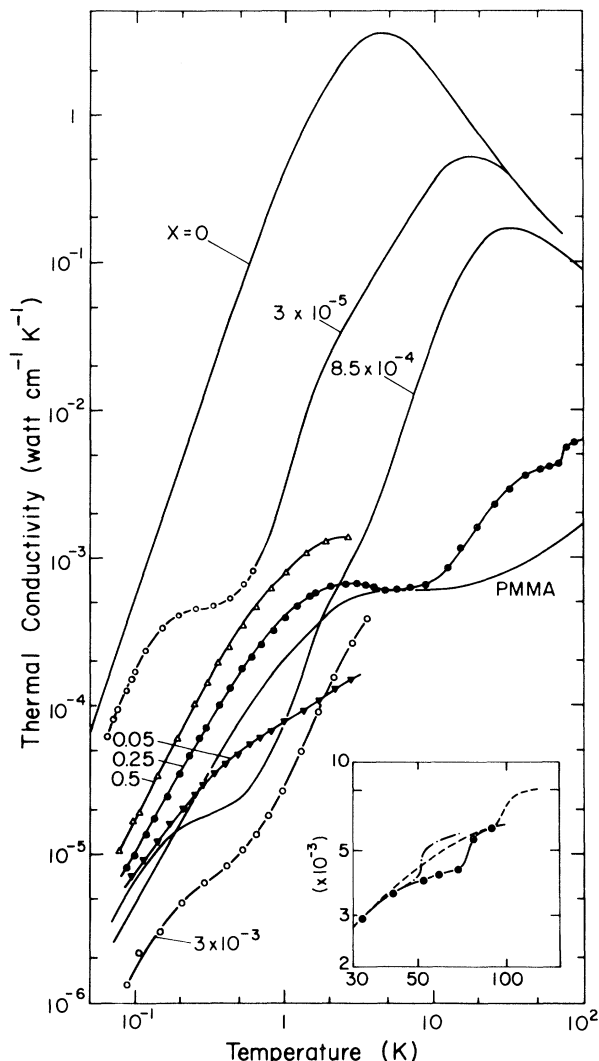


FIG. 2. Thermal conductivity of KBr containing different CN^- concentrations. Solid curves are for $x = 0, 3 \times 10^{-5}, 8.5 \times 10^{-4}$, after W. D. Seward and V. Narayanamurti, Phys. Rev. **148**, 463 (1966). Open circles show extension of the data for $x = 3 \times 10^{-5}$ to low temperatures, and data for $x = 3 \times 10^{-3}$ from this study. For $x = 0.25$ and 0.5 , the conductivity below 0.5 K varies as $T^{1.8}$ and $T^{2.0}$, respectively. A plateau occurs at ~ 10 K. These features are characteristic for amorphous solids. The thermal conductivity of polymethylmethacrylate (PMMA) is shown for comparison [R. B. Stephens, Phys. Rev. B **8**, 2896 (1973)]. The inset shows the abrupt jump of the thermal conductivity around 70 K. See text.

The only difference, a rather sudden jump of the conductivity in a narrow temperature range, occurs around 70 K. This is shown enlarged for clarity in the inset. The temperature of the jump, however, was found to shift when the same $(\text{KBr})_{0.75}(\text{KCN})_{0.25}$ sample was remounted

in the cryostat. Thermal cycling did not affect it. We are positive that this jump is not the result of an experimental problem.¹² Additional work is clearly needed. At this time, it suffices to note that a jump of the conductivity occurs in the same range in which the onset of freezing is observed in Fig. 1.

The disappearance of the tunneling states of the the isolated CN^- ions is also observed in specific-heat measurements, Fig. 3. In the sample with $x = 0.25$, the specific heat below 0.5 K is smaller than that observed in KBr containing only 150 ppm CN^- ¹³ ($x = 1.5 \times 10^{-4}$). The specific heat of the $x = 0.25$ sample, which is almost identical to that of PMMA, can be written as

$$C_v = 38.4T^{1.08} + 100T^3 + C_D \text{ (erg g}^{-1} \text{ K}^{-1}\text{)}. \quad (1)$$

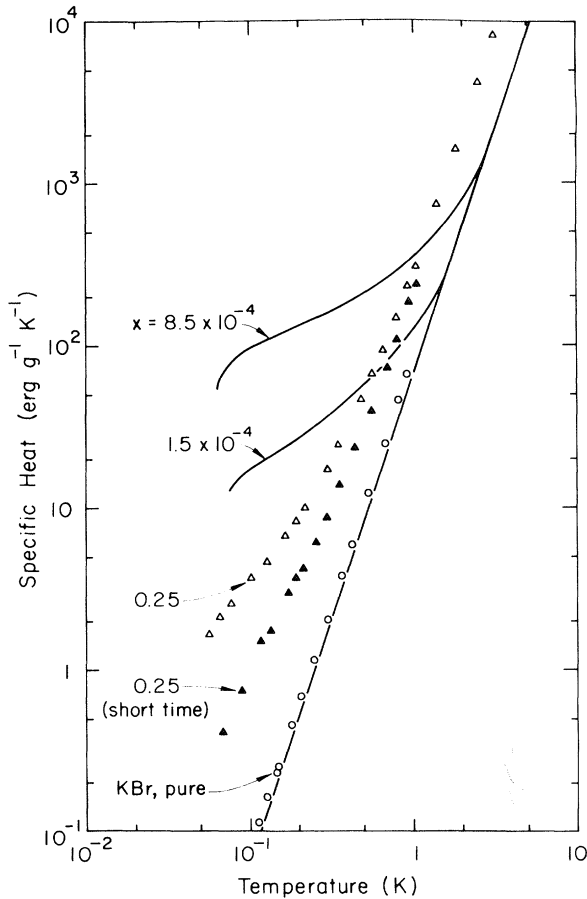


FIG. 3. Specific heat of KBr, with the theoretical Debye specific heat ($\theta = 172$ K) shown for comparison. Data for $x = 1.5 \times 10^{-4}$ and 8.5×10^{-4} are after Ref. 13. For $x = 0.25$, specific heat was measured on three time scales: upper curve, 50 msec and 50 sec; lower curve, < 1 msec. For this specific sample, $n_{\text{NCO}^-} = 15$ ppm.

$C_D = 170T^3$ as calculated from the measured speed of sound.⁷ (For pure KBr, $C_{D, \text{KBr}} = 65T^3$.) Both the linear anomaly and the excess T^3 contribution are characteristic of glasses.²

The anomalous states in every amorphous solid have a wide range of relaxation times to the lattice. This has been directly observed through time-dependent specific-heat measurements.^{11,14} We have observed a similar time dependence. From the temperature rise observed as soon as the $x = 0.25$ sample was heated uniformly (after a time which varied from 0.2 ms at 60 mK to 1 ms at 2 K), the lower specific-heat data in Fig. 3 were obtained. On short time scales, the linear specific-heat contribution [the first term in Eq. (1)] is greatly reduced relative to the T^3 parts. After < 50 ms, thermal equilibrium had been reached at all temperatures. The upper data, obtained on that time scale, agreed with those obtained on the 50-sec time scale. All of these observations agree with those observed in amorphous solids.^{11,14}

Having thus established that the low-temperature thermal properties of $(\text{KBr})_{1-x}(\text{KCN})_x$ are indeed identical to those of amorphous solids, we now turn to the question of what we may learn about the physical nature of the excitations in either case.

Following the line of reasoning which has been employed in the tunneling model for amorphous solids,^{2,15} one would assume that in the high-concentration samples all but a small fraction of the CN^- ions will be frozen in at low temperatures. As a result of random stresses this small fraction has a wide range of tunnel splittings. These states give rise to the (long-time) specific-heat anomaly. The phonon scattering arises from the most rapidly relaxing fraction of these states (contained in the lower curve for $x = 0.25$ in Fig. 3). This fraction must have a constant density of states in order to explain the quadratic temperature dependence of the thermal conductivity below ~ 0.5 K, according to the tunneling model. A comparison of the specific heat of the dilute tunneling defects with the short-time specific heat of the $x = 0.25$ sample shows that the latter cannot contain more than $x \sim 10^{-5}$ of residual, isolated CN^- ions satisfying this condition. The effect on the thermal conductivity of such a small fraction of isolated CN^- tunneling ions (10 ppm) can be seen by extrapolation of the results in Fig. 2 to be at least one order of magnitude smaller than is observed for the $x = 0.25$ sample. It follows that the residual CN^- tunneling states

in the higher-concentration samples would have to be coupled more strongly to the phonons than are those in the low-concentration limit. This apparent increase in the interaction strength is yet to be explained.

On the basis of the earlier experimental work,⁴⁻⁹ the motional states of the high-concentration $(\text{KBr})_{1-x}(\text{KCN})_x$ can be described as follows: For $x > 0.6$, $(\text{KBr})_{1-x}(\text{KCN})_x$ undergoes a phase transition to a monoclinic phase where the quadrupole moments of the CN^- ions become aligned.¹⁵ Below $x = 0.6$ no such phase transition occurs and we believe that this system enters into a quadrupolar glass phase analogous to the spin-glass phase of some magnetic materials. At T_F , the orientational arrangements of the CN^- ions begin to freeze out collectively as in the case of spin-glasses. This onset is seen as the jump in the thermal conductivity which is similar in appearance to the jump observed at the glass transition temperature, T_g , in amorphous solids.¹⁶

For $T \ll T_F$, we propose that the excitations of this quadrupole glass are similar to those described by Anderson, Halperin, and Varma¹ and by Mydosh¹⁷ for spin-glasses. The interaction energy between the elastic CN^- dipoles, estimated by Narayanamurti and Pohl (Ref. 3, Table I) to be $1 k_B \cdot \text{K}$ for $x = 3 \times 10^{-3}$ and increasing as x^2 , is large and completely dominates the tunnel splitting ($\sim 1 k_B \cdot \text{K}$) in the orientational glass samples. The collective quadrupole system, however, will have a number of nearly degenerate states corresponding to local energy minima in configuration space. As long as the barrier to reorientation is sufficiently small, the system can make a transition from one minimum to another. This motion gives rise to the low-energy excitations seen in specific heat and thermal conductivity.

It is tempting, though premature, to apply the picture developed above to amorphous solids. We may think, for example, of elastic interactions between regions of the glassy structure. The objective for future study, however, seems clear from the observations reported here. In

the $(\text{KBr})_{1-x}(\text{KCN})_x$ system we can control the puzzling low-temperature excitations by varying x , and we have hence a much better chance of understanding their nature. This, in turn, may lead to a better understanding of the glassy state.

The thermal measurements reported here were supported by the National Science Foundation through Grant No. DMR-8207079. We thank J. P. Sethna for stimulating comments. One of us (M.M.) acknowledges the receipt of a fellowship from the Deutsche Forschungsgemeinschaft.

^(a)On leave from Institut für Festkörperphysik, Technische Universität, D-1000 Berlin 12, Federal Republic of Germany.

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