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Specific heat of $(KBr)_{1-x}(KCN)_x$ from 1 to 25 K

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The specific heat of $(KBr)_{1-x}(KCN)_x$ for $x=0.0$, 0.19, 0.41, and 0.60 has been measured from 1.5 to 25 K. The data are compared with the theory developed by Grannan, Randeria, and Sethna [Phys. Rev. Lett. **60**, 1402 (1988)] to describe the specific heat of $(KBr)_{1-x}(KCN)_x$ at intermediate temperatures through the librational motion of CN^- ions modeled as interacting elastic dipoles. Data are also presented on the specific heat of KI between 1.5 and 30 K. We review $(KBr)_{1-x}(KCN)_x$ elastic-constant data for c_{44} and c_{11} at 4.2 K and c_{12} at 300 K.

I. INTRODUCTION

Recently, much effort has gone towards characterizing and understanding the properties of $(KBr)_{1-x}(KCN)_x$, a mixed crystal with glasslike thermal properties in the concentration range $0.2<x<0.6$.[1-3] Sethna and coworkers have proposed that the tunneling centers responsible for the thermal properties below 1 K are associated with randomly distribute cyanide ions which reorient by 180°.[4] The present work is motivated by an extension of their study to intermediate temperatures to account for the hump in the specific heat above 1 K and the plateau in the thermal conductivity.[5,6] They postulate that the excitations responsible for both quantities are small-angle oscillations (librations) of interacting cyanides.

At the time of the Grannan *et al.*[6] study of $(KBr)_{0.5}(KCN)_{0.5}$, the data available from several investigations for KCN concentrations close to 50 mol % disagreed in the temperature region of overlap below 5 K (see Fig. 2 of Ref. 6). In this paper, we present new data between 1.5 and 25 K for samples with KCN concentrations of $x=0.19$, 0.41, and 0.60 in order to facilitate the comparison between theory and experiment.

II. EXPERIMENTAL MATTERS

The samples with 19 mol % and 60 mol % KCN were from the same boules as those studied previously;[1] the sample with 41 mol % KCN was grown recently at Cornell University. The KCN fractions listed in DeYoreo *et al.*[1] were the concentrations in the melt from which the samples were grown by seed pulling, since it was believed that these concentrations were close to those in the crystals. It has since been shown[7] that for $(KBr)_{1-x}(KCN)_x$ the mole fraction of KCN in the solid, x, is smaller than that in the melt and that the mass density of the mixed crystals varies in linear proportion with x. (A linear fit using the room-temperature cell volume versus concentration data shown in Fig. 2 of Ref. 7 gives $\rho=2.75-1.20x$ g cm^{-3}.) This allowed us to determine concentrations to ±3% by measuring sample densities gravimetrically using Archimedes' principle.

For density measurements, samples of roughly 50 mg were suspended from a balance using 0.075-mm copper wire. The difference between the sample weight measured in air and in paraffin oil[8] (density $=0.8635$ g cm^{-3}) determined the sample volume. Negligible differences were found between densities determined using paraffin oil straight from the bottle and oil which had been degassed first. When measuring the weight of the sample suspended in oil, we corrected for the effect of surface tension on the copper wire: the difference (~ 0.9 mg) between the weight of the copper wire in air and its weight when partially suspended in oil was subtracted from the weight of the sample suspended in oil. (With no surface tension effect, the weight of the wire in and out of oil would differ by only ~ 0.1 mg.) Table I lists the densities and mole fractions of KCN in the melts and in the crystals used here.

The specific heat was measured with the transient heat pulse technique and cryostat described by Swartz.[9] Samples were attached to a sapphire disk onto which a heater and thermometer were glued.[9,10] Due to the large difference in thermal expansion between $(KBr)_{1-x}(KCN)_x$ and sapphire, we found it useful to glue the sample to a second piece of sapphire using GE 7031 varnish and then to bond the two pieces of sapphire together with Apiezon-*N* grease. Mounted in this way, the sample and sapphire disk maintained good thermal contact as they were cooled. The calorimeter was suspended by 0.051-mm diameter Pt:W wires. The thermal link was through the two heater leads which were made of 2.54-cm-long, 0.127-mm-diameter brass wire. This length of wire gave a sample-to-bath thermal time constant on the order of 10 sec at 1.5 K, increasing to roughly 15 min at 30 K, long enough to ensure complete internal equilibration of the sample.

The heat capacity of the empty calorimeter was measured in a separate run. Constantan wires 1 cm in length and 0.127 mm in diameter were added between the cryostat and the brass heater leads so that thermal time constants (2.5 sec at 1.5 K to 90 sec at 35 K) were large enough to allow accurate measurement. The contribution of the mounting materials (GE 7031 varnish and the sapphire piece mentioned above) to the heat capacity of the full calorimeter and the contribution of the Constantan leads to the heat capacity of the empty calorimeter

TABLE I. Comparison of the concentration of KCN in the melt, x_{melt}, to that in the crystal, x, for samples used in this study. For $x=0.41$ and 0.60 the mole fraction of KCN in the crystal was determined from the mass densities measured at 300 K, as listed in column 2 (see text for details.) The value $x=0.19$ was determined using Ref. 7, Fig. 1 (mole fraction of KCN in the solid versus mole fraction of KCN in the melt).

Origin	$\rho_{300\ \text{K}}$ (g cm^{-3})	x_{melt} (mole fraction)	x (mole fraction)
Argonne (Ref. 1)		0.25	0.19
Cornell, boule 8704296W	2.26	0.50	0.41
Cornell, boule 8408154W (Ref. 1)	2.03	0.70	0.60

were calculated from their masses using specific-heat data.[11] Figure 1 (right ordinate) compares the heat capacity (divided by T^3) of KBr with that of all addenda[12] appropriate for that run. The relative contribution of the addenda to the heat capacity of KBr is also representative of that in the $(\text{KBr})_{1-x}(\text{KCN})_x$ mixed crystals; the addenda contribute less than 9% over the entire temperature range.

Four experiments were performed in order to test the experimental technique. The specific heats of KBr and KI were measured and the thermal conductivity of the Constantan in our heater leads was determined once from specific-heat measurements on a piece of YB_{66} studied previously[13] and once on the empty calorimeter.

For the specific-heat measurements on KBr and KI, sample masses were chosen so that the heat capacities were comparable to those of the $(\text{KBr})_{1-x}(\text{KCN})_x$ mixed crystals. According to the Debye model, the low-temperature specific heat of a pure, insulating crystalline solid should obey

$$C_{\text{Debye}} \equiv c_D T^3 = \left[\frac{234 n k_B}{\rho}\right]\left[\frac{T}{\theta_D}\right]^3 , \qquad (1)$$

where k_B is Boltzmann's constant, ρ the mass density, n the number of atoms per unit volume, and Θ_D the Debye temperature. From elastic constant data, $\Theta_D = 171$ K for KBr and 131 K for KI.[14,15] Our data (Fig. 1, solid symbols) agree very well with the Debye predictions (dashed lines) below 2 K and with published data[16] (open symbols) at higher temperatures.

For further tests, we determined the thermal conductivity of the Constantan portion of the heater leads which act as a thermal link between sample and bath. The conductivity was determined from the measured sample-to-bath time constant, $\tau = RC$, where R is the thermal resistance of the leads and C is the heat capacity of the sample and/or stage. We used heat-capacity data from the $\text{KBr}_{0.58}\text{KCN}_{0.41}$ experiment (with heater leads made of brass wire; no Constantan), the empty calorimeter (with heater leads made of constantan wire soldered to brass wire), and our heat-capacity data from a separate study on YB_{66} (same leads as for the empty calorimeter).[13] The excellent reproducibility of the results is taken as evidence of the reliability of our method. The data also agree quite well with published data (see Fig. 2 of Ref. 13).

III. LONG-WAVELENGTH PHONON CONTRIBUTION TO THE SPECIFIC HEAT; ELASTIC CONSTANTS AND DEBYE APPROXIMATION

We are interested in determining the effect of the CN^- on the specific heat of $\text{KBr}_{1-x}\text{KCN}_x$. For a pure, insu-

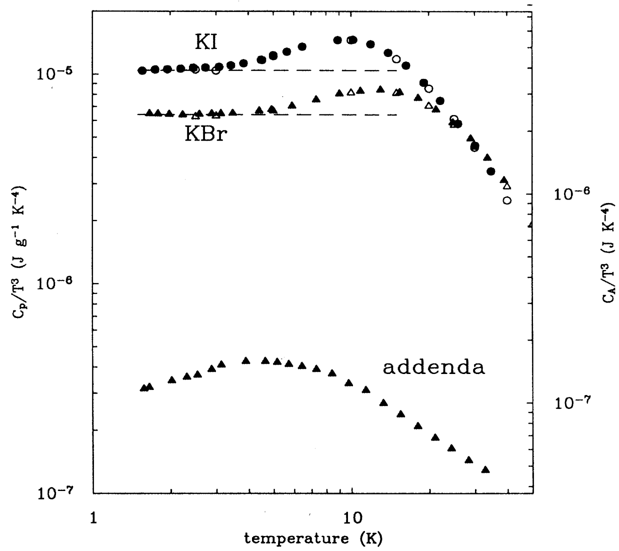

FIG. 1. Left ordinate: the specific heat C_p divided by T^3 of KBr (sample mass=0.373 g) and KI (sample mass=0.287 g) (solid symbols). Dashed lines represent the Debye predictions for KBr (listed in Table II of Ref. 14) and KI (Ref. 15); the agreement at low temperature illustrates the accuracy of the specific-heat measurements. Data at higher temperatures are in good agreement with published data (open symbols, Ref. 16). Right ordinate: the heat capacity C_A divided by T^3 of the KBr sample (without addenda) compared with that of the addenda. The latter is less than 9% of the total heat capacity over the entire temperature range studied.

lating crystalline solid, the specific heat for $T \leq 1$ K is entirely due to long-wavelength phonons and, from Eq. (1), is of the form $C_{\text{Debye}} = c_D T^3$. It is useful, therefore, to calculate that portion of the specific heat which is due to long-wavelength phonons for the mixed crystals.

In order to determine the T^3, long-wavelength phonon contribution to the specific heat (i.e., the Debye T^3 specific heat), it is necessary to know the elastic constants in the limit $T \rightarrow 0$. Given the elastic constants c_{44}, c_{11}, and c_{12}, the Debye T^3 specific heat can be computed by a variety of methods.[15] Betts' six-term extension of Houston's method was used in the present study; the method itself introduces a possible error of $\sim 1\%$ for materials which have anisotropy similar to that of $(KBr)_{1-x}(KCN)_x$.[17]

Figure 2 shows the elastic constants c_{44} and c_{11} at $T \leq 4.2$ K for $(KBr)_{1-x}(KCN)_x$ as a function of x, collected from several sources.[18-26] No data at 4.2 K are available for c_{12}; instead, we used c_{12} data at 300 K (room-temperature data are available for c_{44} and c_{11} as well; see Ref. 26). Fortunately, the Debye coefficient c_D depends most sensitively on c_{44} and c_{11} for $(KBr)_{1-x}(KCN)_x$ (c_D varies by $\sim 1\%$ when c_{44} is changed by 1%, by $\sim 0.6\%$ when c_{11} is changed by 1%, but only by $\sim 0.1\%$ when c_{12} is changed by 1%).

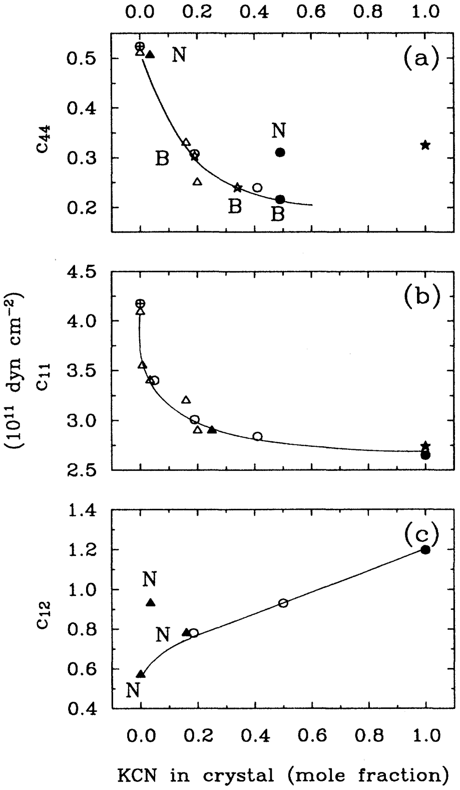

FIG. 2 . Elastic constants as a function of the mole fraction of KCN in the crystal. Solid lines reflect our critical review of this data. *N* and *B* denote data obtained by neutron (THz) and Brillouin (GHz) scattering experiments. All other data were obtained by ultrasound experiments (MHz). The Debye specific heat at 1 K is mainly due to phonons of frequency ~ 100 GHz. (Note that the c_{11} and c_{44} data points which we show at $x = 0.19$ and 0.41 were identified by their values in the melt as $x = 0.25$ and 0.50 in Ref. 1, resulting in different fits to the data.) (a) c_{44} for $T \leq 4.2$ K. Open circle with cross, Ref. 14; open triangles, Ref. 18; solid triangle, Ref. 19; open stars, Ref. 20; solid star, Ref. 21; open circles, Ref. 22; solid circle, Ref. 23. (b) c_{11}, for $T \leq 4.2$ K. Open circle with cross, Ref. 14; open triangles, Ref. 18; solid triangle, Ref. 24; open circles, Ref. 22; solid circle, Ref. 25; solid star, Ref. 21. (c) c_{12} at 300 K. Solid triangles, Ref. 19; open circles, Ref. 26; solid circle, Ref. 25.

For the mixed crystals in the glasslike concentration range, c_{44} and c_{11} are minimum at a temperature, T_g, which has been interpreted as a freezing temperature.[27,28] Loidl *et al.*[24] have found that at T_g, c_{44} and c_{11} depend upon the frequency of the measuring probe; the higher the frequency, the larger are c_{44} and c_{11} (the material is stiffer). Although, to our knowledge, no systematic study has been conducted, there is some evidence that even at temperatures much less than T_g (i.e., temperatures appropriate to this study), c_{44} and c_{11} are larger for higher probe frequencies.[19,23,29] Accordingly, in our figures we mark data points which were obtained by neutron (*N*, THz) and Brillouin (*B*, GHz) scattering experiments to alert the reader that some of the scatter in the data points may be due to the frequency dependence of the elastic constants. All other data points were obtained by ultrasound experiments (MHz). We note that the Debye specific heat at 1 K is mainly due to phonons of frequency ~ 100 GHz.

The scatter in the elastic constants, c_{44}, c_{11}, and c_{12}, around their average values indicated by the solid lines in Fig. 2 are ±6%, ±5%, and ±20%, respectively. As a result, the uncertainty in the Debye coefficient c_D is ±10% for all three mixed crystals. In Table II we display the elastic constant data and the values computed for the Debye temperatures Θ_D and the Debye coefficients c_D for the KCN concentrations relevant to the present work.

IV. EXPERIMENTAL RESULTS

Specific-heat data, plotted as $C/c_D T^3$ versus T/Θ_D for $x = 0.19$, 0.41, and 0.60, are shown in Fig. 3 along with data for $T/\Theta_D \leq 0.01$ from a previous study by our group.[1] Specific-heat and thermal conductivity measurements below 1 K have revealed that these three concentrations correspond to mixed crystals with glasslike excitations.[1] According to the work of Loidl *et al.* on the phase diagram for $(KBr)_{1-x}(KCN)_x$, the $x = 0.60$ sample is close to the phase boundary.[2,7] Although in Ref. 1 it was assumed that the $x = 0.60$ sample (therein referred to as "$x = 0.70$") possessed long-range order, it is no longer clear whether this is the case.

Figure 3 also shows smoothed data for the pure crystals KBr and KCN which contains no glasslike excitations and which obey the Debye T^3 law at low temperature. For such crystals, C/C_{Debye} should approach 1 (dashed line in Fig. 3) at low temperature. (The data for KCN approach a value 10% less than 1, illustrating the uncertainty in $C_{\text{Debye}} = 103$ erg g^{-1} K^{-4} for KCN determined from specific-heat measurements between 90 mK

TABLE II. Low-temperature data on the elastic properties and Debye parameters for $(KBr)_{1-x}(KCN)_x$. The first column lists the mole fraction of KCN in the crystal. The values listed in column 2 are the densities of the crystals at 4.2 K determined from a linear extrapolation between the density of KBr (2.82 $g\,cm^{-3}$) and KCN (1.60 $g\,cm^{-3}$) at 4.2 K (Ref. 34). The number of atoms per unit volume, determined from the densities in column 2, is denoted by n; we count the CN^- ion as one atom (i.e., we ignore its rotational and internal degrees of freedom). Columns 4–6 list elastic constant values for our $x=0.19$, 0.41, and 0.60 samples determined from the curves shown in Fig. 2 for c_{44} and c_{11} at $T \leq 4.2$ K and c_{12} at 300 K; c_{ij} values (at 4.2 K) for $x=0.0$ are from Ref. 14. Debye temperatures in column 7 were calculated using Betts' six-term extension of Houston's method (Ref. 17). The Debye coefficients c_D listed in column 8 were calculated using Eq. (1).

x	n (10^{22} cm^{-3})	$\rho_{4.2\ K}$ ($g\,cm^{-3}$)	c_{44}	c_{11} (10^{11} $dyn\,cm^{-2}$)	c_{12}	θ_D (K)	c_D ($erg\,g^{-1}\,K^{-4}$)
0.0[a]	2.85	2.82	0.524	4.18	0.55	171	65.2
0.19	2.86	2.59	0.288	3.01	0.78	136	142
0.41	2.88	2.32	0.235	2.84	0.85	132	174
0.60	2.90	2.09	0.223	2.76	0.95	135	181

[a] Elastic constant data for $x=0.0$ from Ref. 18 give a value for Θ_D of 169 K which is smaller than that found from specific-heat data (172 K, this work; 174 K, Ref. 16; 172 K, Ref. 33).

and 1.5 K on the same sample in a different cryostat.[1,30]) A peak occurs at roughly the same reduced temperature of $T/\Theta_D=0.08$ for both the KBr and KCN data. For crystalline solids the origin of this peak is well understood. There is a sharp rise in the phonon density of states for wave vectors close to the Brillouin zone because of zone boundary dispersion. For specific-heat measurements, the rise in the density of states translates into a peak in C/C_{Debye} at intermediate temperatures. (Note that a harmonic excitation of frequency ω makes a maximum contribution to C/T^3 at a temperature $T \sim \hbar\omega/5k_B$. In other words, a peak in C/T^3 at $T \sim 15$ K, as for KBr, is mainly due to excitations of frequency $\hbar\omega/k_B = 75$ K.)

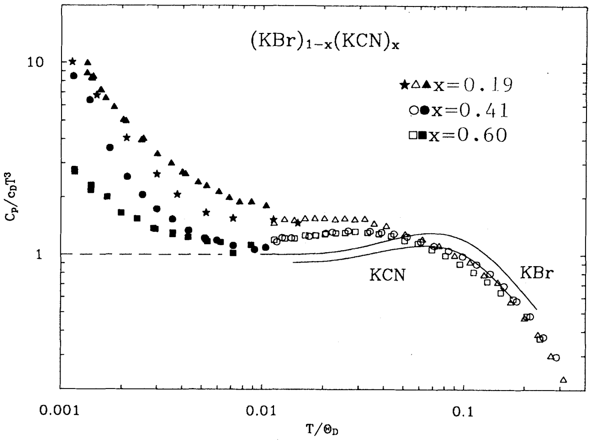

FIG. 3. The specific heat divided by $c_D T^3$ as a function of the reduced temperature (see Table II) for $x=0.19$, 0.41, and 0.60 (sample masses: 129.4, 126.1, and 141.7 mg, respectively). Data from a previous study by our group are plotted as solid symbols (Ref. 1). Stars represent data taken in Berlin (Ref. 1) on a sample from the same boule as the sample used for the data represented by the solid triangles; the discrepancy between the two low-temperature data sets for $x=0.19$ indicates the possible error in the data for $T/\Theta_D \leq 0.01$. Solid lines represent data for the pure crystals KBr and KCN. (The data for KCN approach a value 10% less than 1, illustrating the uncertainty in $C_{\mathrm{Debye}} = 103$ $erg\,g^{-1}\,K^{-4}$ for KCN determined from specific-heat measurements between 90 mK and 1.5 K on the same sample in a different cryostat, Ref. 1.) Values greater than 1 (dashed line) indicate contributions to the specific heat in excess of the T^3, long-wavelength phonon contribution.

The $C/c_D T^3$ data for the three mixed crystals in Fig. 3 are greater than 1 for $T/\Theta_D \geq 0.01$, indicating that there is a contribution to the specific heat in excess of the T^3, long-wavelength phonon contribution. Similar behavior is seen in many amorphous solids.[31] According to the theory of Grannan *et al.*[6] for the specific heat of $(KBr)_{1-x}(KCN)_x$ at intermediate temperatures, this excess specific heat is due to the small-angle librations of interacting cyanides. Figure 4 shows the good agreement between our data and this theory (dashed line) for

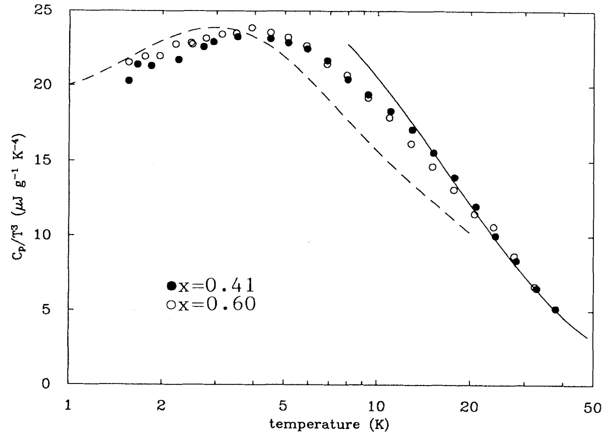

FIG. 4. Comparison of the specific-heat data from this study for $x=0.41$ and 0.60 to the calculation of Grannan *et al.* for $(KBr)_{0.5}(KCN)_{0.5}$ (dashed line, Ref. 6). The solid line represents smoothed data for $x=0.53$ above 8 K by Mertz and Loidl (Ref. 32, also shown in Ref. 6) showing the agreement with our data at higher temperatures; because of scatter, we omit their data below 8 K.

$(\mathrm{KBr})_{0.5}(\mathrm{KCN})_{0.5}$. We note, however, that in this calculation, the zone boundary dispersion of the lattice waves which is responsible for the humps in the C/C_{Debye} data for KBr and KCN was not included. (Due to the softening of the lattice in the mixed crystals, we would expect the hump from zone boundary dispersion to appear at even lower reduced temperatures than in the pure crystals.[31]) We also show smoothed data above 8 K for $x=0.53$ from Mertz *et al.*[32] (solid line) indicating the agreement with our data at higher temperature. Below 15 K, they report a specific heat that is larger than we see in any of our samples.

V. SUMMARY

We have measured the specific heat of $(\mathrm{KBr})_{1-x}(\mathrm{KCN})_x$ for concentrations $x=0.19$, 0.41, and 0.60 over the temperature range 1.5–25 K. The specific-heat data agree well with the theory of Grannan *et al.*[6] for $(\mathrm{KBr})_{0.5}(\mathrm{KCN})_{0.5}$ at intermediate temperatures and provide further evidence for the similarities between the low-temperature thermal properties of amorphous solids and certain mixed crystals with glasslike excitations.

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