Low-temperature properties of the orientational glass $KBr_{1-x}(CN)_x$

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The orientational glass $KBr_{1-x}(CN)_x$ has been studied at temperatures between 0.05 and 5 K and for $0.01 \leq x \leq 0.50$. The properties measured were specific heat, thermal expansion, thermal conductivity, and dielectric constant. With increasing x, the low-energy excitations associated with the orientational tunneling of interacting CN molecules closely approach in behavior the two-level states found in amorphous solids. As x increases from 0.10 to 0.50, the density of excitations decreases by a factor of 100 while the phonon mean free path remains constant for $T < 0.5$ K.

I. INTRODUCTION

We have measured several properties of $KBr_{1-x}(CN)_x$ at temperatures $\lesssim 1$ K to observe the behavior of the broad spectrum of low-energy excitations existing in this orientationally disordered material for $x < 0.57$. A phase diagram[1] for KBr:CN, shown in Fig. 1, is helpful in discussing the low-temperature behavior. The CN molecule is elongated along one axis, and thus neighboring CN molecules in KCN $(x = 1)$ interact via their elastic-strain fields. At a temperature T above 168 K the CN are thermally randomized in direction but, below 168 K, are locked into a ferroelastic phase.[2] However, the direction of a CN molecule, whether CN or NC, remains degenerate or disordered. The CN molecule does carry an electric dipole moment of roughly 0.3 D. At 83 K the electric dipolar interactions lift the CN,NC degeneracy and, at $T < 83$ K, KCN becomes antiferroelectrically ordered.
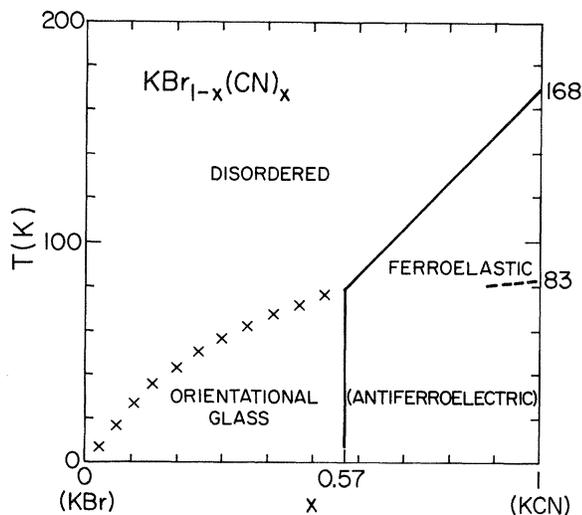
As KCN is diluted with KBr, the temperature at which the ferroelastic transition occurs is reduced until, near $KBr_{0.43}(CN)_{0.57}$, the transition ceases to occur. At lower CN concentrations the disorder of the paraelectric crystal "freezes in" with decreasing temperature as shown by the curve denoted by the X's of Fig. 1. The temperature T_F, at which freezing occurs, depends on the measurement frequency ω, T_F being lower for smaller ω. At sufficiently low temperatures, and at $x < 0.57$, the frozen, disordered crystal has become known as an orientational glass.

As the concentration of CN is further decreased to $x < 0.001$, the distance between CN molecules becomes sufficiently large that elastic and electric interactions essentially can be ignored. This regime has been studied previously.[3] The CN axis lies along the $\langle 111 \rangle$ crystallographic directions, but can tunnel quantum mechanically through the angular barriers between the eight $\langle 111 \rangle$ directions. The tunneling raises the degeneracy of the ground state, resulting in an energy splitting reported[4] to be ≈ 1.2 K.

Our efforts have been directed to the concentration range $0.01 < x < 0.57$ for which KBr:CN is an orientational glass at low temperatures. It has been suggested[5] that, near $x \approx 0.1$, the orientational glass should support a broad spectrum of low-energy excitations analogous to those found in ordinary oxide glasses or amorphous polymers.[6] At temperatures $\lesssim 1$ K, these excitations in amorphous solids give rise to a specific heat C roughly linear in T, a thermal conductivity κ roughly proportional to T^2, a frequency-dependent minimum in the temperature dependence of the dielectric constant ϵ, and unusual behavior in ultrasonic properties. A phenomenological model,[7,8] which has been quite successful, attributes this behavior to a broad spectrum of two-level states (TLS) in which the ground state and first excited state are well separated from excited states of yet higher energy. It is suggested that the TLS arise from some entity which tunnels between two neighboring potential-energy wells created by the atomic disorder of the glassy material. For TLS in KBr:CN, a tunneling entity is always present, namely the CN molecule. The broad energy spectrum of TLS would be produced by perturbation of the initial tunnel splitting of ≈ 1.2 K by strain (and electric) fields from neighboring

FIG. 1. Approximate phase diagram for $KBr_{1-x}(CN)_x$. The extent of the antiferroelectric phase is not known. The transition between disordered and orientational glass phases depends on probe frequency. This transition is referred to as the "freezing" temperature $T_F(x)$.

TABLE I. Computed parameters for KBr$_{1-x}$(CN)$_x$. Those above the dashed line were obtained from published data, those below the dashed line were obtained from the present data. The symbols are defined, and the computations explained, in the text. The heat capacities for the two samples having $x=2\times10^{-4}$ and 4×10^{-4} were reported in Ref. 12.

x	2×10^{-4}	4×10^{-4}	0.01	0.03	0.10	0.20	0.50
ρ (10³ kg/m³)	2.75	2.75	2.74	2.71	2.62	2.50	2.13
v_T (10³ m/sec)	1.36	1.36	1.35	1.31	1.19	1.01	
v_L (10³ m/sec)	3.85	3.85	3.67	3.58	3.47	3.45	
v_2 (10³ m/sec)	1.95	1.95	1.90	1.85	1.71	1.51	(≤1.55)[a]
v_3 (10³ m/sec)	1.84	1.84	1.81	1.76	1.61	1.40	(≤1.45)[a]
C_D/T^3 (J/m³ K⁴)	19.6	19.6	20.7	22.6	29.2	44.7	(≤40)[a]
κ/T^3l (10⁴ W/m² K⁴)	1.07	1.07	1.13	1.19	1.40	1.79	
N/N_{tot}	0.89	2.0	0.53	0.16	5.8×10^{-3}	4.7×10^{-4}	1.5×10^{-5}
$l_{0.1\,\text{K}}$ (10⁻⁵ m)			2.7	6.5	7.9	6.3	≤9
$(N/N_{\text{tot}})x$			5×10^{-3}	5×10^{-3}	6×10^{-4}	9×10^{-5}	8×10^{-6}

[a]Computed from Fig. 3, assuming all specific heat at $T>0.8$ K arises from phonons, and used only to estimate $l_{0.1\,\text{K}}$.

CN molecules.[5] In this view, the density $n(E)$ of TLS per unit energy interval, would not simply be proportional to CN concentration x. Higher concentrations would increase the interactions, resulting in a greater width to the spectrum $n(E)$.

To determine if TLS do exist in KBr$_{1-x}$(CN)$_x$ near $x=0.1$ we have measured for one or more of the concentrations $x=0.01$, 0.03, 0.10, 0.20, and 0.50 the specific heat, thermal expansion, thermal conductivity, and dielectric constant for temperatures in the range $0.05<T<5$ K. The results are presented in the following section.

II. EXPERIMENTAL RESULTS

Each measured property of the series of KBr$_{1-x}$(CN)$_x$ crystals[9] is discussed separately, and a general summary of qualitative results is given at the end of this section. Earlier data are included when available.

A listing of parameters for KBr:CN, as estimated from published data, is provided in Table I. The mass density ρ was obtained by interpolation between values for KBr and KCN. The longitudinal-phonon velocity v_L and transverse-phonon velocity v_T were estimated from ultrasonic data[1] for $x\leq0.2$, extrapolated to $T=0$ K and then interpolated graphically to obtain velocities for different values of x. The Debye specific heat C_D and thermal conductivity κ were computed from $C_D/T^3=12.2\times10^{10}v_3^{-3}$ and $\kappa/T^3l=4.08\times10^{10}v_2^{-2}$, where l is the phonon mean free path and

FIG. 2. Specific heat of KBr$_{(1-x)}$(CN)$_x$, divided by T^3 for (a) $x\leq10^{-2}$ and (b) $x>10^{-2}$. $\triangledown$, $x=0.01$; $\bigcirc$, $x=0.03$; $\times$, $x=0.10$; $\triangle$, $x=0.20$; solid line, $x=2\times10^{-4}$ (Ref. 12); dotted line, $x=4\times10^{-4}$ (Ref. 12); dashed lines, computed phonon contribution for x indicated. The $x=0.01$ and 0.03 samples have very nearly the same specific heats. (1 J/m³ K⁴ = 10 erg/cm³ K⁴.)
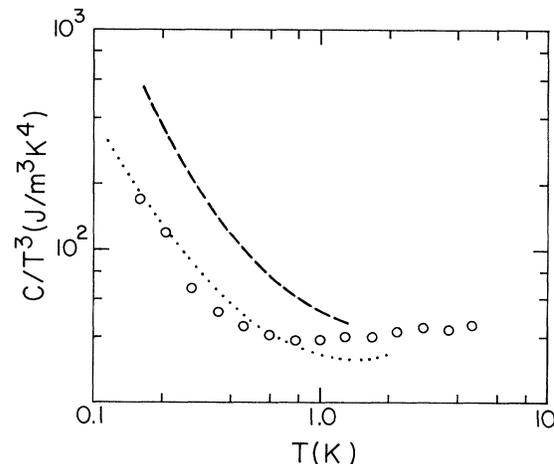
FIG. 3. Specific heat of KBr$_{1-x}$(CN)$_x$ divided by T^3. $\bigcirc$, $x=0.50$; dashed line, $x=0.20$ from Fig. 2(b) for reference; dotted line, amorphous epoxy (Ref. 25).
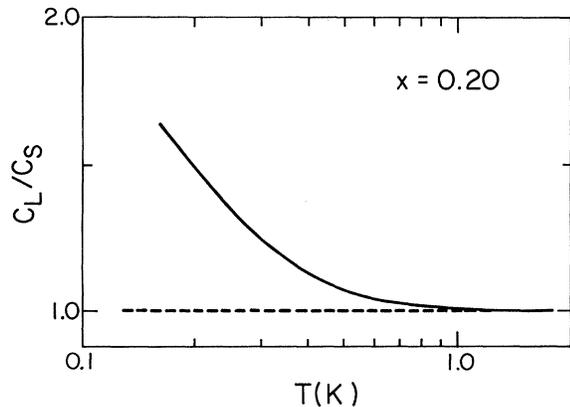
FIG 4. Ratios of specific heat C_L, measured during time interval 7—26 sec after application of heat pulse, to C_S, the specific heat measured during time interval 2—7 sec for $KBr_{0.8}(CN)_{0.2}$. Using the same technique, this effect is not observed in KBr:OH having a similar heat capacity (Ref. 21).

$v_3^{-3} = \frac{1}{3} (\sum_i \langle 1/v_i^3 \rangle)$ and $v_2^{-2} = \frac{1}{3} (\sum_i \langle 1/v_i^2 \rangle)$. The sum is over phonon mode and the arithmetic average is over crystalline directions $\langle 100 \rangle$, $\langle 110 \rangle$, and $\langle 111 \rangle$. Other parameters in Table I will be discussed below. The column under $x=0.50$ is partly vacant since the estimated C_D/T^3 was larger than the measured specific heat, indicating that a graphical extrapolation of elastic constants beyond $x=0.20$ failed to give a reasonable value for v_3.

A. Specific heat

The specific-heat data were obtained using a signal-averaging technique[10] and with dry sapphire plates[11] pro-
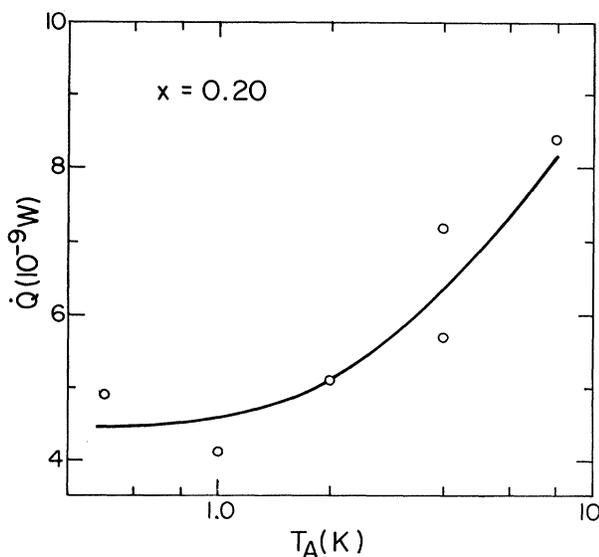
FIG 5. Heat flux $\dot{Q}$ appearing in sample of $KBr_{0.8}(CN)_{0.2}$ at 0.1 K immediately after cooling down from an "annealing" temperature T_A which had been maintained for a period of 10—30 h. Initially the sample had been held near 0.1 K until $\dot{Q}$ was reduced to a constant value dictated by vibration and other external sources. Only calibrated germanium resistance thermometers were used in this measurement.

viding thermal isolation for the sample. The results are shown in Figs. 2 and 3 where the specific heat C has been divided by T^3 to emphasize departure from T^3 Debye behavior contributed by thermal phonons at low temperatures. The Debye contribution, shown by the dashed lines in Figs. 2 and 3, changes with CN concentration as indicated in Table I.

Included in Fig. 2(a) are earlier data[12] for $x < 0.01$. At sufficiently small x in a crystal free of strain (and electric fields), the specific heat contributed by the CN should approach the temperature dependence of a Schottky peak. The data of Fig. 2(a), however, cannot be fitted to a Schottky peak suggesting that the energy splittings may be perturbed by residual strain fields within the samples.

Some of the scatter evident in Fig. 2(b) arises from a finite thermal relaxation time occurring within the samples. This means that some of the CN excitations couple only weakly to phonons, or thermally equilibrate very slowly. Hence the magnitude of the measured specific heat is a function of the time interval during which the measurement was made. For $x=0.01$ or 0.03 the measurement was made over a very long time $t=RC_{tot}$, where R is the thermal impedance between sample and refrigerator, and C_{tot} is the total heat capacity of the sample. Since C_{tot} is large for $x=0.01$ or 0.03 at $T<1$ K, t is also large, and an "infinite-time" specific heat may be extracted. The infinite-time specific heat records all contributions, even those having long equilibration times. However, for $x=0.20$, C_{tot} and t are a factor of ≈ 50 smaller, and an infinite-time specific heat is difficult to extract from the data. To illustrate this problem, Fig. 4 shows the ratio of specific heat deduced using data for the interval 2—7 sec (after application of the heat pulse) to that deduced from the interval 7—26 sec.

Additional evidence that a small fraction of CN excitations equilibrate with very long time constants (of order one day) was obtained from the observation that a portion of the residual heat flux $\dot{Q}$ arose from within the sample following initial cool down. Figure 5 indicates what happens if, after the sample had been held near 0.1 K for some days to reduce $\dot{Q}$ to a negligible magnitude, the sample was raised in temperature to T_A for 10—30 h then reduced again to 0.1 K. The internal heat flux was not reestablished unless $T_A \gtrsim 3$ K. Only for $T_A \gtrsim 3$ K do CN sites which contribute to $\dot{Q}$ repopulate thermally.

It has been suggested[13] that the presence of NCO in KBr samples may contribute to C/T^3 near 1—2 K. The NCO content of our samples was measured with a Fourier-transform infrared apparatus using both the 1297 and 2170 cm^{-1} lines. For the $x=0.10$ and 0.50 samples the NCO impurity densities were $\approx 2 \times 10^{18}$/cm^3 and $\approx 7 \times 10^{18}$/cm^3, respectively. However, when the specific heat of the $x=0.50$ sample is corrected for the presence of CNO, C/T^3 is reduced below that expected for phonons alone in KBr (i.e., at $x=0$ in Table I). Since this is unlikely, either the ir measurement has overestimated the NCO content or NCO does not contribute the specific heat suggested in Ref. 13.

From the measured specific heat it is possible to compute the entropy increase over the temperature range 0.1—1.0 K from the relation $\Delta S = \int_{0.1}^{1.0} (C/T)dT$. If we
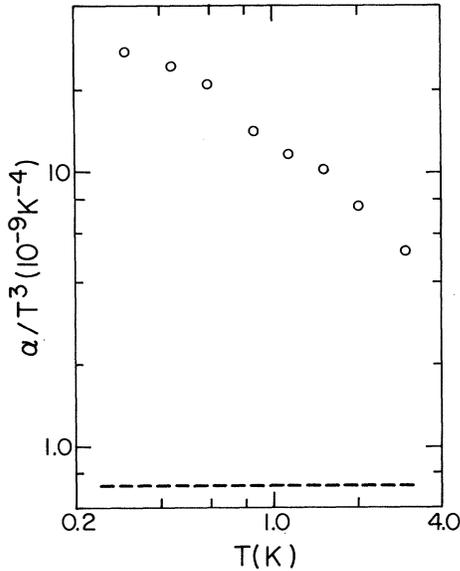
FIG. 6. Linear thermal-expansion of KBr$_{0.90}$(CN)$_{0.10}$ divided by T^3 to emphasize departure from a phonon contribution. The dashed line is the estimated phonon contribution.

further assume that only the ground state and one excited state are accessible to a CN ion at $T \lesssim 1$ K, the number N of CN molecules contributing to the entropy increase may be estimated from $\Delta S = Nk \ln 2$, where k is the Boltzmann constant. The fraction N/N_{tot} of participating CN is listed in Table I, where N_{tot} is the total number of CN ions quoted for the sample. The fraction ranges from $N/N_{tot} \approx 1$ for small x to $N/N_{tot} \approx 10^{-5}$ for $x = 0.50$. Hence, for $x \gtrsim 0.03$, the major fraction of CN ions contribute to the specific heat outside the range $0.1-1$ K.

B. Thermal expansion

The linear thermal-expansion coefficient α of KBr$_{0.90}$(CN)$_{0.10}$ was measured using a superconducting quantum interference device (SQUID) dilatometer.[14] The data are shown in Fig. 6 and have been divided by T^3 to emphasize departure from the T^3 contribution expected
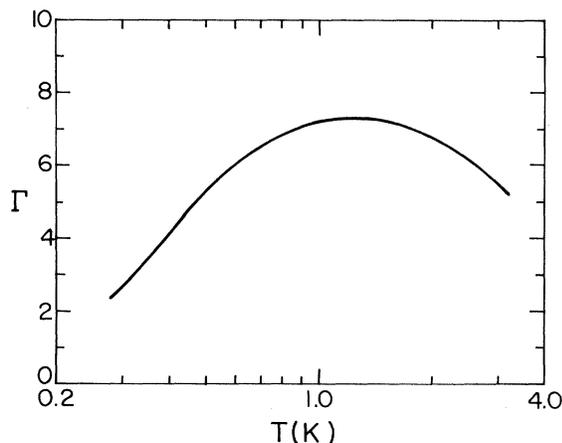
FIG 7. Grüneisen parameter of KBr$_{0.90}$(CN)$_{0.10}$.
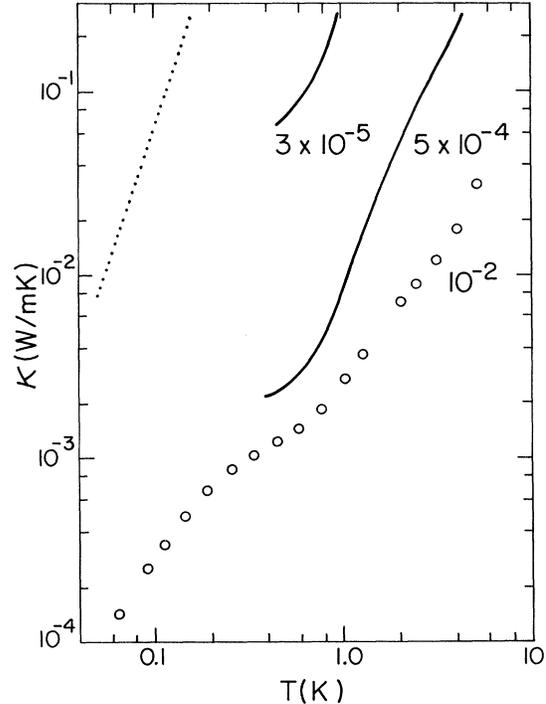
FIG. 8. Thermal conductivity of KBr$_{1-x}$(CN)$_x$ for concentrations x as indicated, showing the conductivity *decreasing* with increasing x. The solid lines are from Ref. 13, and the dotted line is the κ computed for $x=0$ and a sample having cross-sectional area of 0.26 cm^2, assuming only boundary scattering of phonons.

from thermal phonons at low temperatures. In a discussion of thermal expansion,[15] it is convenient to use the Grüneisen parameter Γ defined as $\Gamma = 3B\alpha/C$ where B is the elastic bulk modulus. For phonons $|\Gamma| \approx 2$, while, for impurities associated with tunneling states in alkali halides, $|\Gamma|$ as large as 300 have been reported.[16] The Grüneisen parameter for KBr$_{0.90}$(CN)$_{0.10}$ is shown in Fig. 7.

The thermal expansion of KBr$_{0.90}$(CN)$_{0.10}$ is very large compared to the value $\alpha/T^3 \approx 7 \times 10^{-10}$ K^{-4} expected from thermal phonons alone. Thus the CN excitations dominate α at all temperatures below 3 K. The Γ of Fig. 7 is seen to decrease with increasing temperature at $T > 1.5$ K. This decrease probably reflects the increasing contribution to phonons with increasing T, the phonons having $\Gamma \approx 2$. However, the decrease in Γ with decreasing temperature toward $T = 0.1$ K, where the CN dominate both C and α, can only mean that the effective coupling between CN and lattice is smaller for smaller CN excitation energy or level splitting.

C. Thermal conductivity

Since some samples were small, κ was measured using two heaters and one thermometer. The results are shown in Figs. 8 and 9, with earlier data[13] included in Fig. 8. In all samples the presence of CN greatly reduces the magnitude of the thermal conductivity. The dotted line in Fig. 8 indicates the κ expected in pure KBr if phonons were to scatter only from sample surfaces.

The variation with x of the strength of the phonon scattering by CN excitations is not immediately evident in κ, as the phonon velocity also changes with x. We have therefore used the computed $\kappa/T^3 l$ of Table I and the measured κ at $T=0.1$ K to obtain an estimate of the mean free path $l_{0.1}$ for those phonons dominant in heat transport near 0.1 K. The results are included in Table I.

D. Dielectric constant

Typical dielectric constants ϵ, as measured with a three-terminal capacitance bridge,[17] are shown in Fig. 10. The dielectric constant ϵ_m of KBr is temperature dependent[18] above 10 K. This temperature dependence has been subtracted off so that Fig. 10 displays essentially only the temperature dependence of the contribution from CN. For $x=0.50$ the dielectric response of the CN appears to be paraelectric at temperatures down to ≈ 50 K. The ϵ then passes through a maximum[18-20] and decreases rapidly towards zero CN contribution as the CN "freeze out." That is, the CN no longer contributes an orientational response at a measuring frequency of 10^4 Hz. The position of this maximum decreases in temperature with either a decreasing measuring frequency or decreasing CN concentration.[18] The maximum in ϵ is the freezing temperature T_F for $x=0.50$ at a probe frequency of 10^4 Hz. The T_F of Fig. 1 were obtained at much higher frequencies.

For $x=0.01$ in Fig. 10, the maximum occurs at $T \lesssim 0.05$ K. Yet ϵ is frequency dependent already at ≈ 2 K as shown in Fig. 10. The temperature dependence near 0.3 K at 8×10^4 Hz (the dotted line) is unusual and generally indicates the freezing out of a fraction of the total population of electric dipoles. This could occur if the sample were inhomogeneous in CN concentration, but there is no other indication that the concentration is not macroscopically homogeneous. The unusual behavior might also be caused by a fraction of the CN having, statistically, closer CN neighbors than other CN. This

FIG. 9. Thermal conductivity of $KBr_{1-x}(CN)_x$ showing conductivity *increasing* with increasing x. $\triangledown$, $x=0.03$; $\circ$, $x=0.10$; $\times$, $x=0.20$; $\triangle$, $x=0.50$. The dashed line is for $x=0.01$ from Fig. 8, for comparison. The dotted line is for an amorphous epoxy (Ref. 25).

FIG. 10. Dielectric constant ϵ of $KBr_{1-x}(CN)_x$ for $x=0.01$ and $x=0.50$ divided by the dielectric constant $\epsilon_m=4.54$ of KBr at $T \lesssim 5$ K. The temperature dependence of ϵ_m at $T \gtrsim 10$ K has been subtracted to emphasize the contribution of CN to ϵ/ϵ_m. The solid lines were measured at 10^4 Hz, the dashed line at 10^3 Hz, and the dotted line at 8×10^4 Hz.

FIG. 11. Fractional change in dielectric constant ϵ, relative to the minimum near 0.1 K, for $KBr_{0.97}(CN)_{0.03}$ at measuring frequencies of 10^3 Hz ($\triangle$), 10^4 Hz ($\times$), and 8×10^4 Hz ($\circ$).
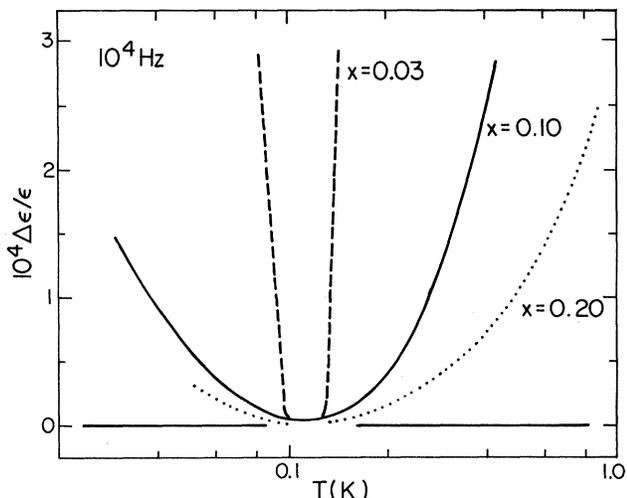
FIG. 12. Fractional change in smoothed dielectric constant ϵ, relative to the minimum near 0.1 K, for KBr$_{1-x}$(CN)$_x$ at a measuring frequency of 10^4 Hz.

behavior has been observed[21] in alkali halides containing OH.

For $0.03 \leq x < 0.50$, and at temperatures below the maximum in ϵ, the temperature dependence of ϵ exhibits a minimum near 0.1 K. Figure 11 shows the frequency dependence of this minimum for $x=0.03$, while Fig. 12 indicates the temperature dependence near the minimum at 10^4 Hz as a function of CN concentration.[22] Similar minima occur in some alkali halides[21] containing OH.

E. Summary

The presence of CN in KBr has the following qualitative effects. The specific heat at $T \lesssim 1$ K increases with increasing x for $x \lesssim 0.02$, then decreases with increasing x for $x \gtrsim 0.02$. Some fraction of the excitations responsible for the specific heat have long thermal relaxation times. The thermal conductivity decreases with increasing x for $x \lesssim 0.02$, then increases for $x \gtrsim 0.02$. However, this dependence is very weak for $T \lesssim 0.2$ K when $x \geq 0.03$. The CN excitations contribute a large thermal-expansion coefficient which indicates an energy-dependent coupling between correlated CN motion and the lattice. The dielectric response freezes out at a temperature which is strongly x dependent and weakly frequency dependent (for the limited measurement range of 10^3–10^5 Hz). Well below the freeze-out temperature T_F, a minimum appears near 0.1 K in the temperature dependence of ϵ. The temperature of this minimum is essentially independent of x but weakly dependent on frequency. The width of this minimum is strongly dependent on x.

Finally, we note that the system KCl$_{1-x}$(CN)$_x$, though studied less extensively,[3,13,23] appears to have an orientational freezing behavior similar to that of KBr$_{1-x}$(CN)$_x$. Other alkali cyanides may also exhibit similar behavior.[24]

III. DISCUSSION

In the following discussion, it will be noted that several properties of the KBr$_{1-x}$(CN)$_x$ system approach those ob-

served in amorphous solids as x increases beyond ≈ 0.03. In light of this general similarity between KBr$_{1-x}$(CN)$_x$ and glasses for $x \gtrsim 0.03$, we will adopt the language applied to glasses and refer to the low-energy excitations of the interacting CN molecules as TLS.

As may be seen in Figs. 3 and 9 by comparison with the data for amorphous epoxy[25] represented by the dotted lines, the specific heat and thermal conductivity of KBr$_{0.50}$(CN)$_{0.50}$ are similar in magnitude and in temperature dependence to the universal behavior found in amorphous solids. The time-dependent specific heat of Fig. 4 and the minimum in the dielectric constant, Figs. 11 and 12, are additional "glassy" signatures. The thermal conductivity also appears to develop a plateau, a temperature-independent regime at $T > 1$ K, which is characteristic of glasses.[6]

Table I reveals a remarkable fact regarding the TLS. The concentration of TLS having an energy splitting lying in the range $0.1 - 1$ K is given roughly by $(N/N_{tot})x$. This concentration ranges from 5×10^{-3} for $x=0.03$ to 8×10^{-6} for $x=0.50$, a decrease of a factor of ≈ 600. Yet the phonon mean free path $l_{0.1 K}$ is nearly constant at $l_{0.1 K} \approx 7 \times 10^{-5}$ m. Thus the average coupling between phonons and TLS must increase drastically, by a factor of ≈ 600, as x increases from 3% to 50%. This observation will provide a stringent test of any model proposed to account for the properties of an orientational glass. It may also be an important factor in the formation of the ferroelastic phase at $x=0.57$.

A value for the coupling constant γ between phonons and TLS may be extracted by application of the phenomenological tunneling states model[7,8] developed for amorphous solids. Using the general approach of Ref. 26, we assume a density of TLS (per unit energy interval) $n(E) = n_0(E/kT_0)^m$ where n_0 and m are constants and $T_0 = 1$ K. In the original model $m=0$, but a finite positive m provides a better fit for amorphous solids. Table II lists the values of n_0 and m required to fit the magnitude and temperature dependence of the measured specific heat for $x=0.10$ and 0.20. The use of the one additional parameter γ^2 allows both the magnitude and temperature dependence of the thermal conductivity to be fitted for $T \lesssim 0.5$ K. With increasing CN concentration the value

TABLE II. Parameters obtained for KBr$_{1-x}$(CN)$_x$ assuming the phenomenological tunneling-states model is applicable. The symbols are defined in the text. The data for samples having $x=0.01$ and 0.03 could not be fitted with the model. Values for vitreous silica (SiO$_2$) and amorphous epoxy are included for comparison, from Refs. 26 and 25, respectively.

x	0.10	0.20	SiO$_2$	Epoxy
n_0 $(10^{46}/\mathrm{J\,m^3})^a$	21	4.2	1.0	1.6
m	+0.6	+0.2	+0.3	+0.3
γ (eV)^b	0.2	0.3	1.2	0.3

^{a}Details of the computation are available in D. Moy, Ph.D. thesis, University of Illinois, 1983.

^{b}The phonon coupling parameter γ is typically given in eV; 1 eV$=1.6 \times 10^{-19}$ J. The phonon mean free path l is proportional to $\rho v^3/\gamma^2$.

of the parameter n_0 approaches those found for vitreous silica or amorphous epoxy as shown in Table II. The magnitudes of m and γ are also similar.

Finding that $\gamma \approx 0.3$ eV poses a problem for KBr:CN, a problem which also occurs for amorphous solids.[27] A lattice coupling this large should normally produce a Grüneisen parameter Γ of order 10^4 near 1 K. This is much larger than the measured Γ of ≈ 7 at 1 K in Fig. 7. A proposed explanation[27] would not have a single or unique value for the coupling parameter between phonons and TLS, but rather a different coupling parameter at each TLS site. Assume, for convenience, a distribution in coupling parameters represented by a broad Gaussian centered near, but not on, zero. Thermal conductivity is proportional to $1/\gamma^2$ and indicates a large, root-mean-square value $(\gamma^2)^{1/2}$. On the other hand, the thermal expansion measures simply the arithmetic average of the coupling constants and indicates a small magnitude with a positive sign. Whether or not this explanation in terms of rms versus an arithmetic average is correct does not detract from the fact that the thermal-expansion measurements reveal an additional similarity between $KBr_{1-x}(CN)_x$ and amorphous solids.

In the theoretical model, the temperature T_{min} at the minimum in ϵ should vary[28] with measuring frequency ω as $(\omega)^{0.33}$. We find $T_{min} \propto (\omega)^{0.1}$ for $x=0.03$ and $T_{min} \propto (\omega)^{0.2}$ for $x=0.10$. Thus the frequency dependence is approaching that of a glass as x increases.

A free-volume model[29] of the glass transition suggests that $n(E)$ should be inversely proportional to the glass transition temperature T_g. Experimental evidence for the relationship $n(E) \propto 1/T_g$ was noted[30] in literature data for specific heat and thermal conductivity, and has found further support in recent measurements of specific heat[31] and ultrasonic properties.[32] In the orientational glass, T_g corresponds to T_F of Fig. 1. Thus T_g increases with increasing CN concentration x, and $n(E)$ should therefore decrease with increasing x. Indeed this is what happens, as may be seen in Table II. Thus the $KBr_{1-x}(CN)_x$ samples again seem to behave as amorphous materials, at least qualitatively. A quantitative comparison is not possible since T_F for $\omega \rightarrow 0$ is not known. In the free-volume

model, presumably the atomic diffusion of amorphous solids would have to be mapped into orientational diffusion of CN molecules.

Another orientationally disordered crystalline system which has been studied extensively at $T \lesssim 1$ K is OH^- in the alkali halides.[21] With decreasing tunnel splitting of the OH energy levels, and with increasing OH concentration, a glasslike behavior was observed to develop. The most glasslike example was KBr:OH. Since OH is not readily soluble in these alkali halides, the maximum OH content was $x \approx 10^{-3}$. It was argued that a "spin-glass" behavior (analogous to magnetic spin-glass or cluster-glass behavior in nonmetallic solids containing magnetic impurities) could not occur in KBr:OH since clusters consisting of more than two OH were statistically unlikely. It was suggested that a spin-glass transition was more likely to occur in a material such as KBr:CN having a smaller dipole interaction. It had earlier been suggested[33] that the rotational freezing in KBr:CN occuring at T_F (Fig. 1) was indeed analogous to spin-glass behavior. The present results make no additional contribution to this question.

In conclusion, it has been shown that several properties of $KBr_{1-x}(CN)_x$ approach those of amorphous solids as x increases beyond $x \approx 0.03$ toward $x \approx 0.57$, the concentration at which long-range orientational order occurs for the CN molecules. The broad spectrum of TLS excitations necessary for glassy behavior is, in KBr:CN, developed through elastic (and electric) interaction between CN molecules. Therefore the density of TLS, and other parameters, change significantly with changing CN concentration. The KBr:CN system will provide a rigorous test of any microscopic model developed to account for the behavior of an orientational glass.[34]

ACKNOWLEDGMENTS

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