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Acoustic soft modes in KCN_xBr_{1-x} and KCN_xCl_{1-x} mixed crystals

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The ultrasonic velocity of [100] transverse waves has been measured as a function of temperature in KCN_xBr_{1-x} and KCN_xCl_{1-x} crystals with $x < x_c$, where x_c is the critical CN^- concentration required for a structural phase transition into an orientationally ordered phase. The shear stiffness c_{44} in these samples and in others with $x \simeq x_c$ and $x > x_c$ obeys an elastic Curie-Weiss law over a wide range of temperatures, with fitting parameters that agree with mean-field percolation theory. However, deviations from this Curie-Weiss behavior and also velocity dispersion are observed at low temperatures for samples with $x < x_c$. The realtionship between the c_{44} soft mode and orientational ordering is discussed.

I. INTRODUCTION

Potassium cyanide undergoes an order-disorder transition from a cubic $(Fm3m)$ structure with the CN^- ions distributed randomly along [111] directions to an orthorhombic $(Immm)$ structure with the CN^- ions aligned along one of the cubic [110] directions.[1] There are several theories in which this transition is associated with a soft-mode instability for the TA translational mode that is coupled to CN^- rotational modes.[2–6] Indeed, the shear elastic constant c_{44} is small in KCN and varies rapidly with temperature, extrapolating to zero at a critical temperature $T_c \simeq 153$ K that is close to the observed first-order transition temperature $T_1 = 167.7$ K.[7]

It is of interest to study the effect on this transition and on the elastic soft mode of replacing CN^- ions by bromide or chloride ions. In the mixed crystals KCN_xBr_{1-x} and KCN_xCl_{1-x}, no structural phase transition occurs when x is smaller than a critical CN^- concentration x_c and a "dipole-glass" phase with only local CN^- ordering has been proposed to occur.[8,9] The value of x_c is $\sim$0.58 for KCN_xBr_{1-x} crystals and $\sim$0.79 for KCN_xCl_{1-x} crystals.[10,11] TA[100] acoustic velocity measurements have been reported previously for samples with $x \approx x_c$ and $x > x_c$,[12] and the c_{44} variations in these samples are well characterized by elastic Curie-Weiss behavior. Pressure had no effect on the elastic constants of these mixed crystals but did shift T_1 to higher values, in agreement with behavior observed in pure KCN.[13]

The present work extends the measurements of c_{44} to mixed crystals with $x < x_c$: $KCN_{0.49}Br_{0.51}$, $KCN_{0.56}Cl_{0.44}$, $KCN_{0.41}Cl_{0.59}$. A mean-field elastic equation is still found to be a useful representation of the softening of this TA mode at high temperatures, but deviations from Curie-Weiss behavior are observed at low temperatures. A comparison of acoustic results at 10 MHz with available Brillouin and neutron data allows a discussion of dispersion effects. The relationship between the c_{44} soft-mode behavior and orientational ordering is also discussed.

II. RESULTS

The single crystals of KCN_xCl_{1-x} were obtained from the Crystal Growth Laboratory at the University of Utah, as were all the crystals studied in Ref. 12. Single crystals of $KCN_{0.49}Br_{0.51}$ were obtained from Dr. S. Susman at Argonne National Laboratory. Measurements were made on thin slabs ($\sim$0.2 cm thick) cleaved from a large single crystal, and then annealed and polished. Although the sample slabs were free from visible imperfections, residual strains could be seen in many of the samples under crossed polarizers and the crystals frequently developed (100) cleavage cracks on slow cooling. The data reported for $KCN_{0.56}Cl_{0.44}$ and $KCN_{0.41}Cl_{0.59}$ represent a composite of measurements made on two or three separate crystals over limited temperature ranges. The $KCN_{0.49}Br_{0.51}$ samples, which were very well annealed and homogeneous in composition, showed less strain and were subject to less serious cracking problems. Because the actual compositions may sometimes differ by significant amounts from their nominal values,[11] the samples used here and those used previously in Ref. 12 were analyzed gravimetrically for the halide content.

The shear velocity u of the TA[100] mode in the

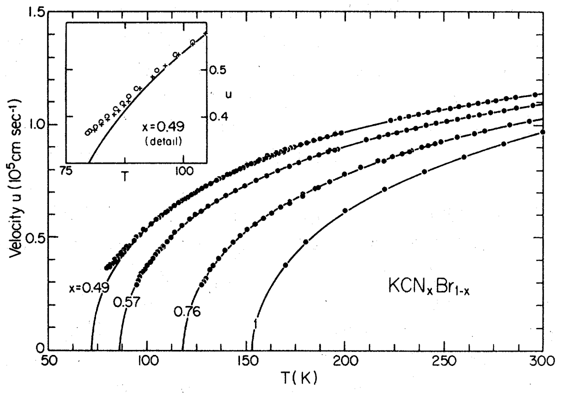

FIG. 1. Temperature dependence of the TA[100] velocity in KCN_xBr_{1-x} single crystals. The smooth curves represent the best fits to these data with Eq. (1). The inset shows that the small systematic deviation from Eq. (1) observed for $KCN_{0.49}Br_{0.51}$ at low temperatures is reproducible in runs on two different samples.

TABLE I. Smooth-curve values of c_{44}, in units of 10^{10} dyn $cm^{-2} = 10^9$ Pa, for single crystals of KCN_xBr_{1-x} and KCN_xCl_{1-x} with $x < x_c$.

T (K)	$KCN_{0.49}Br_{0.51}$	$KCN_{0.56}Cl_{0.44}$	$KCN_{0.41}Cl_{0.59}$
300	2.812	3.041	3.590
280	2.692	2.863	3.488
260	2.556	2.662	3.350
240	2.407	2.464	3.183
220	2.243	2.203	3.029
200	2.046	1.949	2.841
180	1.844	1.670	2.618
160	1.593	1.380	2.362
140	1.315	1.091	2.084
120	1.004	0.875	1.818
100	0.649	0.747	1.654
80	0.298	. . .	. . .

cubic phase was measured at 10 MHz using ultrasonic techniques described in Ref. 14. The results are shown in Figs. 1 and 2, where data from Ref. 12 are also shown for comparison. The corresponding smooth-curve values of $c_{44} = \rho u^2$ are listed in Table I. These values are based on room-temperature (293 K) densities of 1.745 gcm^{-3} ($KCN_{0.56}Cl_{0.44}$), 1.810 gcm^{-3} ($KCN_{0.41}Cl_{0.59}$), 2.163 gcm^{-3} ($KCN_{0.49}Br_{0.51}$), and on thermal expansion coefficients interpolated between the known values for KCN and the pure potassium halides.

Although no transition to an orientationally ordered phase occurs for these samples with $x < x_c$, the echo pattern disappeared at low temperatures. (This behavior was similar to that reported in Ref. 12 for samples with $x > x_c$, where an abrupt loss of the acoustic signal was presumably due to scattering from small ordered-phase domains.) In the case of $KCN_{0.49}Br_{0.51}$, an increase in attenuation and a deterioration of the echo pattern began on cooling below ~85 K and the echoes disappeared at 80 K. The corresponding temperatures were ~112 and 98 K for $KCN_{0.56}Cl_{0.44}$ and ~100 and 86 K for $KCN_{0.41}Cl_{0.59}$. The echo pattern did not reappear on further cooling of the samples to 65 K. However, on subsequent warming, the echoes reappeared at the same temperature at which they had disappeared. In the case of $KCN_{0.49}Br_{0.51}$, low-temperature measurements on two separate crystals were in very good agreement (see inset on Fig. 1). Such a loss of acoustic signal at low temperatures is an intrinsic effect, definitely not due to cleavage cracking or failure of the transducer bond; the same effect has also been observed in the very dilute mixed crystals $KCN_{0.14}Br_{0.86}$ and $KCN_{0.04}Br_{0.96}$.[15]

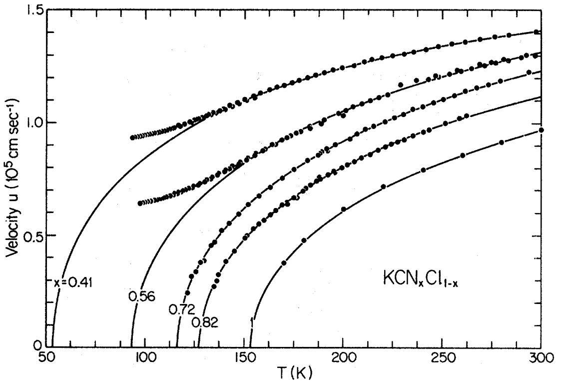

FIG. 2. Temperature dependence of the TA[100] velocity in KCN_xCl_{1-x} single crystals. The smooth curves represent fits to these data with Eq. (1).

III. DISCUSSION

The starting point in most theoretical treatments of the alkali halide-cyanide systems is a microscopic force model. The Hamiltonians derived from such models yield a coupling between the molecular orientational and translational degrees of freedom. In the treatment presented by Michel and co-workers,[2,3] the molecular orientations appear in the Hamiltonian in two ways—in a static bilinear coupling between translational and rotational degrees of freedom and in a crystal-field term that is purely rotational in character. The result of the bilinear coupling is an effective indirect orientational interaction between the CN^- ions which is equivalent to the interaction between elastic dipoles. This interaction leads to collective rotational behavior and to a rotational phase transition. When theoretical expressions are derived for the elastic constants of this model, it is found that c_{44} exhibits soft-mode behavior due to the effective coupling of the CN^- ions.

Similar results were obtained by Mokross and Pirc,[6] who treated the CN^- ions as elastic dipolar impurities in an ionic crystal. Again the result is an effective impurity-impurity coupling which is due to impurity-strain interactions and impurity-phonon interactions. The temperature dependence of the elastic constants reflects the collective behavior of the coupled impurity (CN^-) system.

In both models, the softening of the elastic constant c_{44} is driven by the divergence in the orientational susceptibility of the CN^- ions. The rigorous prediction is that the quantity $(s_{44}-s_{44}^0)$ is directly proportional to an orientational susceptibility χ_{44}, where $s_{44}\equiv 1/c_{44}$ and the superscript zero denotes the "bare" value that would be observed in the absence of rotational-translational coupling. When the behavior in the orientationally disordered phase is described within the mean-field approximation, the variation of c_{44} as a function of temperature can be written as[12]

$$\frac{1}{c_{44}}-\frac{1}{c_{44}^0}=\frac{B}{T-T_c}\ , \qquad (1)$$

where T_c is the critical temperature at which c_{44} extrapolates to zero and B is a constant to be discussed later.

A. Mean-field fits

The elastic Curie-Weiss expression given in Eq. (1) has proven to be a good description of the ultrasonic velocity in KCN_xCl_{1-x} and KCN_xBr_{1-x} crystals with large values of x.[12] The extension of ultrasonic velocity measurements to samples with x values less than x_c is of particular interest since the transition to the orientationally ordered phase is suppressed and the existence of a locally ordered glass phase has been postulated.[9]

Least-squares fits to our data with Eq. (1) are represented by the smooth curves in Figs. 1 and 2 for both KCN_xBr_{1-x} and KCN_xCl_{1-x} mixed crystals with x values above and below x_c ($x_c \simeq 0.58$ for Br samples and $x_c \simeq 0.79$ for Cl samples). For $KCN_{0.76}Br_{0.24}$ and $KCN_{0.57}Br_{0.43}$ samples and the $KCN_{0.82}Cl_{0.18}$ sample, where the x values are close to or greater than the critical concentration, the elastic Curie-Weiss formula agrees very well with the observed velocities over the entire range of data. Since the forces between elastic dipoles are long ranged, it is not surprising that mean-field behavior is observed in these concentrated samples. The result that is somewhat surprising is the fact that Eq. (1) also provides a good fit for the $KCN_{0.72}Cl_{0.28}$ samples and almost all the data for the $KCN_{0.49}Br_{0.51}$ sample, where $x<x_c$. In the case of $KCN_{0.49}Br_{0.51}$, systematic deviations from Eq. (1) are quite small and only occur below 95 K (see inset on Fig. 1). Even the $KCN_{0.56}Cl_{0.44}$ and $KCN_{0.41}Cl_{0.59}$ samples display mean-field behavior from 300 K down to approximately 150 K, although the deviations from Eq. (1) at lower temperatures are substantial for these samples.

The least-squares fits with Eq. (1) were carried out with c_{44}^0, B, and T_c taken as freely adjustable parameters. The best-fit values of these parameters are listed in Table II, where the values for samples with $x>0.56$ are taken from Ref. 12 with a correction being made for a small error in the previously quoted B values for chloride mixed crystals. Both the nominal (composition of the initial melt from which the crystals were grown) and analytical composition values are given. Since it was not possible to obtain an

TABLE II. Values of the adjustable parameters T_c, B (in units of 10^{-10} dyn^{-1} cm^2 K), and c_{44}^0 (in units of 10^{10} dyn cm^{-2}) appearing in Eq. (1), together with the nominal and analytical values of the composition in mixed crystals of KCN_xBr_{1-x} and KCN_xCl_{1-x}.

Halide	x(nom)	x(anal)	T_c (K)	B	c_{44}^0
...	1	1	153.3	71.91	5.08
Br	0.8	0.76	118.2	56.69	4.66
Br	0.6	0.57	86.2	44.86	4.95
Br	0.5	0.49	71.8	38.78	5.40
Cl	0.85	0.82	127.3	56.30	6.00
Cl	0.75	(0.72)	116.2	47.06	7.18
Cl	0.6	0.56	93.2	39.2	7.1
Cl	0.5	0.41	53.3	27.3	6.0

analysis of the nominal $x = 0.75$ chloride sample, we have estimated $x \simeq 0.72$ on the basis of trends observed in similarly prepared samples. The T_c and B values in Table II are plotted as a function of composition in Figs. 3 and 4, respectively. The parameters for the $KCN_{0.56}Cl_{0.44}$ and $KCN_{0.41}Cl_{0.59}$ samples are rather uncertain since these fits are based on data obtained far from T_c.

The credibility of fits with Eq. (1) depends on reasonable trends in c_{44}^0, B and T_c as a function of x. This aspect will be considered on the basis of the theory presented by Mokross and Pirc,[6] where the effective CN^--CN^- coupling is due to both a CN^--strain interaction and a CN^--phonon interaction. The strength of the effective interaction is expressed in terms of the static coupling constants J and I, where J determines the overall CN^--CN^- coupling and J-I determines the impurity-strain coupling. The fit parameters B and T_c in Eq. (1) are related to the coupling constants by $T_c \propto xJ$ and $B \propto x(J-I)/c_{44}^0$. If one assumes that the magnitude of J does not depend upon concentration x, this leads to the mean-field percolation result $T_c(x) = xT_c(\mathrm{KCN})$. Figure 3 shows that the T_c values for all the samples agree quite well with this prediction. The observed variation in B values with x is also qualitatively reasonable. The solid line in Fig. 4 indicates the expected B variation if the quantity $(J-I)/c_{44}^0$ has the same value in all mixed crystals as in pure KCN. The small but systematic differences in the trend of B values for the bromide and chloride samples may reflect the fact that the c_{44}^0 value for KCl is slightly larger than for KBr (see Ref. 12).

The low-temperature deviations of the ultrasonic c_{44} values from mean-field behavior for samples with CN^- concentrations below the critical value x_c will be discussed in Sec. III C, but first let us consider the presence of velocity dispersion in such samples.

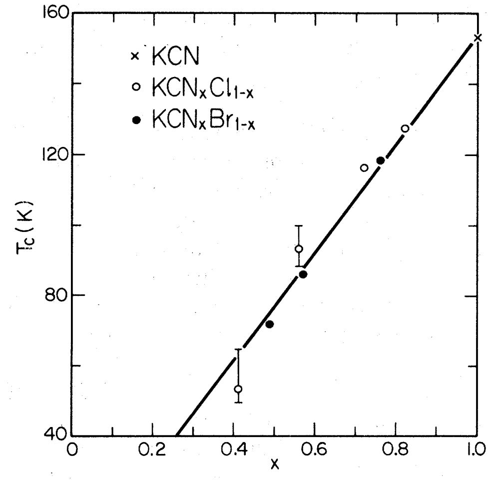

FIG. 3. Variation of T_c with the mole fraction of CN^-. The line represents the mean-field percolation result $T_c(x) = xT_c(\mathrm{KCN})$.

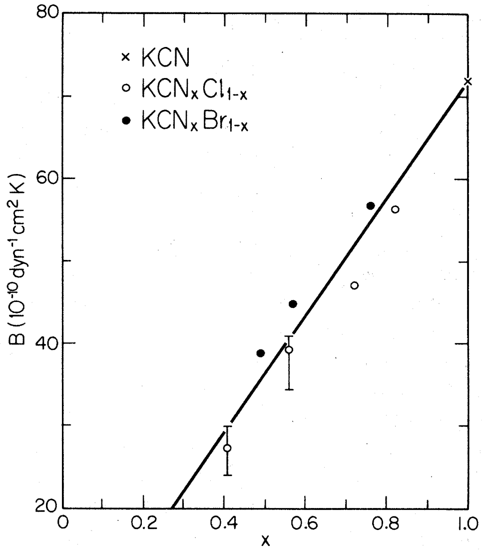

FIG. 4. Variation of the coupling strength B with the mole fraction of CN^-. The line represents the empirical variation $xB(\mathrm{KCN})$.

B. Velocity dispersion

It is known that the velocities of TA[100] phonons in the disordered phase of pure KCN are frequency independent up to frequencies in the range 100–200 GHz (neutron measurements at a wave vector $q = q_{BZ}/10$).[7,13,16,17] This is consistent with the very short rotational correlation time τ_2 for the CN^- ion in KCN determined recently from NMR studies[18]:

$$\tau_2 = 4.34 \times 10^{-14} \exp(392.6/T) \ ,$$

which yields $\tau_2 = 0.16$ psec at 300 K and 0.45 psec at 168 K.

For mixed crystals of KCN_xBr_{1-x} with $x < x_c$, neutron[8,19] and Brillouin[20] investigations of the TA[100] mode at fixed scattering vector show a decrease in phonon frequencies on cooling down to some characteristic temperature, followed by an increase on further cooling. This minimum in the high-frequency TA[100] velocity has been ascribed to (1) a crossover from fast orientational relaxation ($\omega\tau \ll 1$) to slow orientational relaxation ($\omega\tau \gg 1$) at low temperatures,[19,20] or (2) a finite cusp in the static orientational susceptibility on forming an elastic dipole glass.[9]

Thus it is of interest to compare ultrasonic (10 MHz) and hypersonic (1–5 GHz Brillouin and 70–200 GHz neutron) velocities and look for dispersion effects in various mixed crystals. Such a comparison is given in Figs. 5 and 6. In both figures, ultrasonic velocities are represented by the lines and smooth-curve values of Brillouin velocities are indicated by the solid points. Brillouin values for $KCN_{0.5}Br_{0.5}$ were obtained by interpolation of data given in Ref. 20 in order to provide a direct comparison with the neutron and ultrasonic values that are available for that composition. In the case of KCN_xCl_{1-x} crystals, where there are Brillouin data[21] for a sample with the nominal concentration $x = 0.5$, we have compared these values with an ultrasonic curve at $x = 0.5$ interpolated from our results at $x = 0.41$ and 0.56. It should be noted that all Brillouin frequency shifts were converted into velocities using the assumption that the index of refraction for mixed crystals is a linear average of that for pure KCN and that for the pure potassium halide.

Figures 5 and 6 show that no dispersion is observed up to frequencies of a few gigahertz for samples with $x > x_c$ ($KCN_{0.75}Br_{0.25}$ and $KCN_{0.85}Cl_{0.15}$). However, for samples with $x = 0.5$, dispersion is definitely observed at temperatures below $T_{\min}$, the characteristic temperature where the phonon frequency is a minimum in the scattering experiments. Consider, in particular, the behavior of $KCN_{0.5}Br_{0.5}$, where velocity dispersion begins rather abruptly near $T_{\min}$. No dispersion is observed up to ~70 GHz at 100 K, whereas substantial dispersion is seen between the velocity values for 10 MHz (ultrasonic), ~1.5 GHz (Brillouin), and ~100 GHz (neutron) at 80 K. This behavior does not conform to expectations based on a relaxation mechanism unless there is an unusually broad spectrum of relaxation times near $T_{\min}$.

Chloride mixed crystals definitely exhibit larger velocity dispersion than bromide mixed crystals, as shown by the substantial dispersion in $KCN_{0.5}Cl_{0.5}$ below $T_{\min} \simeq 115$ K. However, it is not certain whether the apparent dispersion *above* $T_{\min}$ in this sample and in chloride samples with $x \simeq 0.7$ is a real effect or the result of some systematic error. Careful ultrasonic and Brillouin measurements on the same sample are needed to clarify the possible presence of weak dispersion above $T_{\min}$.

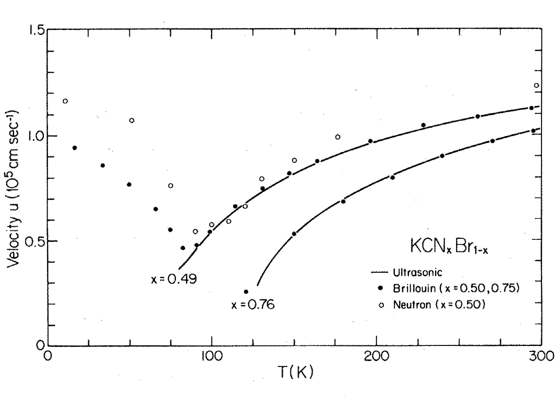

FIG. 5. Comparison of ultrasonic, Brillouin, and neutron results for the TA[100] velocities in various samples of KCN_xBr_{1-x}. The neutron and Brillouin velocities were obtained from Refs. 8 and 20, respectively.

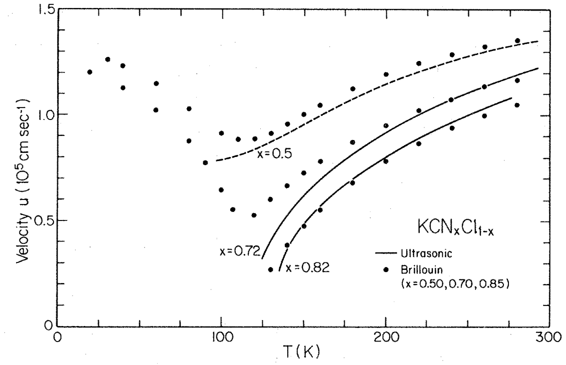

FIG. 6. Comparison of ultrasonic and Brillouin results for the TA[100] velocities in various samples of KCN_xCl_{1-x}. The dashed curve represents the interpolated ultrasonic velocity for a sample with $x = 0.5$. The Brillouin velocities were obtained from Ref. 21.

C. Concluding remarks

Although our understanding of orientational ordering in cyanide crystals has progressed substantially in recent years, there are still several unresolved difficulties with the theory for both concentrated and dilute samples.

For pure KCN and mixed crystals with $x > x_c$, we wish to note two problems. First, the predicted effect of pressure is inconsistent with experiment. In the theoretical model, pressure increases the strength of the single-particle potential, which leads to an increase in both the critical temperature T_c and the first-order transition temperature T_1.[3] Experimentally, T_1 increases with pressure but T_c is independent of pressure.[12,13] It seems likely that some type of coupling between CN^- orientations and a compressional strain needs to be taken into account. It should be noted that there is an appreciable contraction (~5%) along the c axis when pure KCN transforms into the orthorhombic ordered phase.[22] Thus the structural phase transition in KCN does not correspond to a pure shear, and c-axis contraction may play an important role in stabilizing the ordered phase.

The second problem involves the structure of the ordered phase. The single-particle potential inferred from the [111] CN^- orientations in the disordered phase does not explain the orthorhombic CN^- ordering along [110] in KCN.[3] Furthermore, it has recently been discovered[23] that the ordered phase of $KCN_{0.8}Br_{0.2}$ is not orthorhombic but may be similar to the metastable monoclinic phase[22] obtained on thermally cycling pure KCN near T_1. Since the ultrasonic shear velocity exhibits the same type of mean-field behavior for all x values between 1 and x_c, the soft mode does not provide a predictive indication of the character of the ordering that occurs at low temperatures.[24]

For mixed crystals with $x < x_c$, one must explain the deviations from mean-field behavior and the abrupt onset of velocity dispersion near $T_{\min}$. A promising model for such samples involves an orientational glass state proposed by Michael and Rowe[9] by analogy with the spin-glass state observed in dilute magnetic crystals. In the orientational glass phase, there is no long-range CN^- order but only a local ordering of CN^- orientations, which leads to the freezing in of local lattice strains. The main feature of this model is a static orientational susceptibility χ_{44} that exhibits a finite cusp rather than a divergence. Thus one should observe a minimum in the acoustic velocity at a temperature T_f, corresponding to the onset of the glass state. It should be noted that although the existence of such a glass phase would qualitatively account for the observed behavior of the c_{44} data at high frequencies, this phase is an *ad hoc* feature rather than a direct consequence of the microscopic force model.

At this point, a realistic theory is needed that provides a quantitative expression for the dynamical susceptibility $\chi_{44}(\omega)$ as a function of frequency, temperature, and composition in both bromide and chloride mixed crystals. The approximate form $\chi_{44} = (C - \Psi)/T$ given in Ref. 9, where C is a constant and Ψ is the order parameter characterizing an elastic dipole glass, is not adequate to represent our low-frequency velocity data. In particular, the high-temperature form for χ_{44} must be $C/(T - T_c)$, where T_c has a mean-field percolation value, and the static χ_{44} must have a rounded maximum rather than a sharp cusp. Furthermore, the differences between ultrasonic, Brillouin, and neutron velocities needs to be accounted for. Since the velocity dispersion effects near $T_{\min}$ are greater for chloride mixed crystals than for bromides, it is reasonable to assume that inhomogeneous local strains play a role. It seems plausible that the disappearance of the acoustic signal on cooling samples with $x < x_c$ is due to scattering from local clusters with dimensions comparable to ultrasonic wavelengths. Note that the acoustic signal in $KCN_{0.49}Br_{0.51}$ crystals is lost ~8.2 K above the T_c value used in the fit with Eq. (1); this is quite comparable to the signal loss at $T_1 = T_c + 8.5$ K in $KCN_{0.57}Br_{0.43}$ and $T_1 = T_c + 9.6$ K in $KCN_{0.76}Br_{0.24}$.[12]

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[24] This conclusion is strengthened by a comparison of the elastic behavior in KCN and in RbCN [S. Hussühl, Solid State Commun. 32, 181 (1979)]. The shear constant c_{44} shows the same soft-mode behavior in the disordered phase of both crystals, but RbCN exhibits long-range [111] orientational ordering at low temperatures in contrast to the [110] ordering observed in KCN.