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Shear elasticity and phase transitions in KCN_xBr_{1-x} and KCN_xCl_{1-x} mixed crystals

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The ultrasonic velocity of [100] transverse waves in KCN_xBr_{1-x} and KCN_xCl_{1-x} single crystals has been measured as a function of temperature at 1 atm and at pressures up to 3 kbar. Data were obtained in the cubic disordered phase for $x = 0.6$ and 0.8 (bromides), 0.75 and 0.85 (chlorides). Pressure has no effect on the extrapolated critical temperatures $T_c(x)$, which agree well with percolation theory. Surprisingly, the temperature variation of c_{44} (the "soft" mode) is the same for samples that undergo a weak first-order transition into a long-range-ordered orthorhombic phase and those that do not undergo a transition but exhibit only local ordering.

I. INTRODUCTION

At room temperature potassium cyanide has a pseudocubic rocksalt structure ($Fm3m$) in which the CN^- ions are predominately distributed at random along the various [111] directions.[1] On cooling below ~168 K, KCN crystals undergo an order-disorder transition into an orthorhombic structure ($Immm$)[2,3] with all the CN^- ions in a given domain aligned along one of the cubic [110] directions but still head-to-tail random. This transition is first order, but very distinct pretransitional effects are observed in the elastic properties over a wide temperature range.[4] In particular CN^- orientational modes are strongly coupled with TA lattice translational modes, and the c_{44} shear elastic constant softens dramatically. This mode extrapolates to zero at a critical temperature T_c that is ~14 K below the first-order transition temperature T_1.

Several theoretical models have been proposed to describe the orientational ordering in KCN and in the mixed crystals KCN_xBr_{1-x} and KCN_xCl_{1-x},[5-12] but a completely satisfactory description is still not available. In part, this is due to complications associated with the composition and pressure dependence of the ordering. On replacing CN^- with Br^- or Cl^- ions, the values of both $T_1(x)$ and $T_c(x)$ decrease until x falls below a critical CN^- concentration x_c. When $x < x_c$, no structural phase transition occurs and a "spin-glass" phase with local CN^- ordering at low temperatures has been proposed[10,12] but not yet established. In samples with $x < x_c$, c_{44} still shows a pronounced dip, going through a finite minimum value at progressively lower temperatures as x decreases.[10,11,13] Furthermore, a Brillouin scattering study of pure KCN has shown that the c_{44} values and T_c are independent of pressure but T_1 increases substantially with pressure.[5]

The present investigation involves measurements of the TA[100] acoustic velocity u in single crystals of $KCN_{0.8}Br_{0.2}$, $KCN_{0.6}Br_{0.4}$, $KCN_{0.85}Cl_{0.15}$, and $KCN_{0.75}Cl_{0.25}$ at 1 atm and at pressures up to ~3 kbar. The emphasis is on the low-frequency temperature dependence of this shear mode in the cubic phase for samples with $x > x_c$ and $x \approx x_c$. The 1-atm value of x_c is 0.58 for KCN_xBr_{1-x} crystals and 0.8 for KCN_xCl_{1-x} crystals.[13-16] The principal results of our work are: (1) pressure has no effect on the extrapolated T_c values in these mixed crystals but appears to shift T_1 to higher values; (2) the dependence of the T_c values on the mole fraction x agrees fairly well with percolation theory; (3) the dependence of the [100] shear velocity on $\Delta T = T - T_c$ in the disordered phase is very similar for KCN and all four mixed crystals, in spite of the fact that the $KCN_{0.75}Cl_{0.25}$ sample does not undergo a transition; and (4) the detailed behavior of mixed crystals as a function of composition and pressure is difficult to interpret in terms of current theory.

II. EXPERIMENTAL RESULTS

Single crystals of KCN_xBr_{1-x} and KCN_xCl_{1-x} were obtained from Professor F. Lüty and were grown from the melt at the Crystal Growth Laboratory of the University of Utah. The samples studied were thin slabs ($1 \times 1 \times 0.2$ cm^3) cleaved from a large boule, then polished and annealed. The crystals were free from any visible imperfections, but the materials are brittle and frequent trouble occurred with (100) cleavage cracks appearing at ~170 K on slow cooling. Possibly this was due to small composition inhomogeneities that are common in crystals grown from a melt. Such inhomogeneities could cause internal strains when local ordering began to occur. (Note that $T_1 \simeq 168$ K in pure KCN.)

The shear velocity u was measured at 10 MHz and

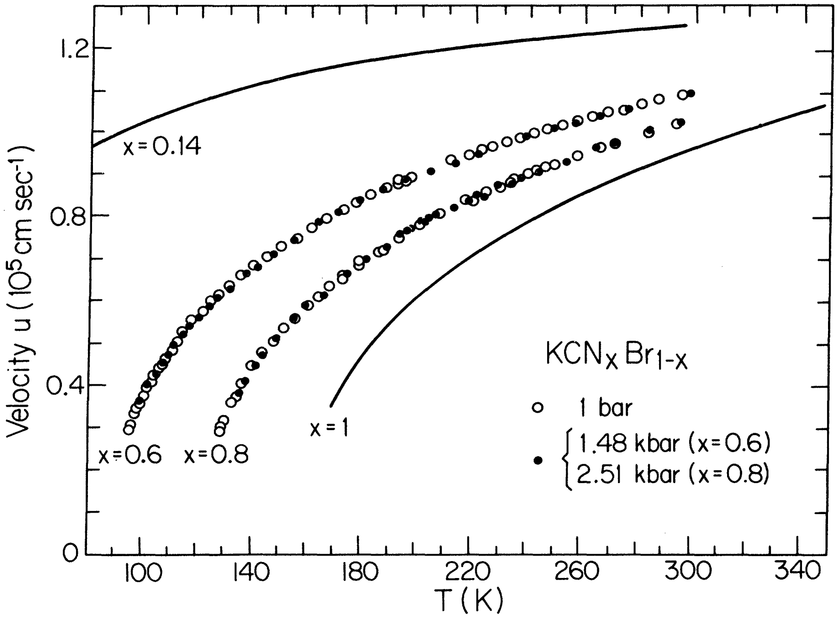

FIG. 1. Temperature dependence of [100] transverse-acoustic velocity in KCN_xBr_{1-x} mixed crystals. Curves for $x = 1$ and 0.14 are taken from Refs. 4 and 11, respectively.

the corresponding elastic constant c_{44} is given by $c_{44} = \rho u^2$, where ρ is the mass density. The ultrasonic techniques used in this work were the same as those described in Ref. 17. The effects of thermal expansion and compressibility were taken into account by interpolation between the known values for KCN and the pure potassium halides. The resulting *linear* thermal expansion coefficients [$10^5\ \alpha = 5.26$ K^{-1} ($KCN_{0.8}Br_{0.2}$), 4.85 K^{-1} ($KCN_{0.6}Br_{0.4}$), 5.32 K^{-1} ($KCN_{0.85}Cl_{0.15}$), 5.08 K^{-1} ($KCN_{0.75}Cl_{0.25}$)] were taken to be independent of temperature over the range of our measurements. The magnitude of the thermal expansion correction for u or c_{44} is only 0.9% at 95 K for the $KCN_{0.6}Br_{0.4}$ sample, and it is correspondingly less for other samples and higher temperatures. The bulk compressibility κ was taken to be independent

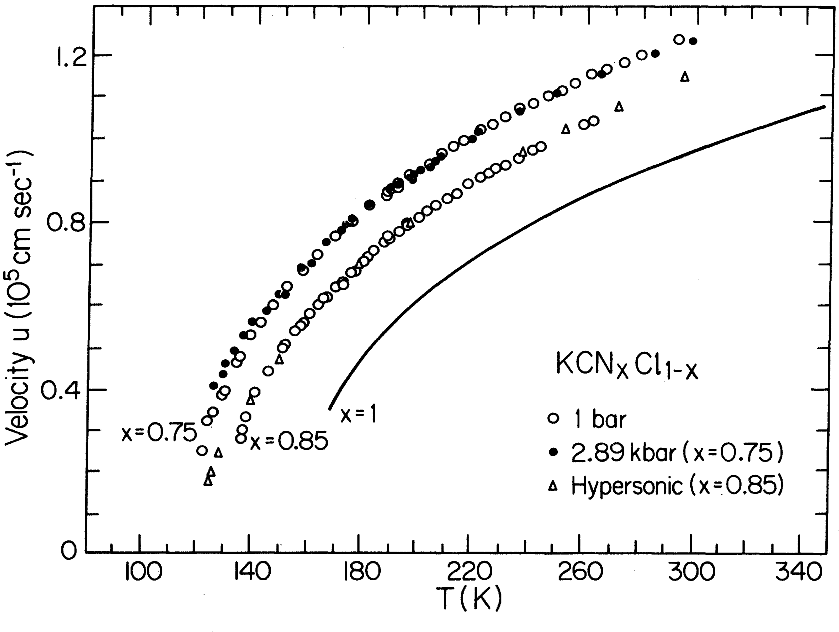

FIG. 2. Temperature dependence of [100] transverse-acoustic velocity in KCN_xCl_{1-x} mixed crystals. Brillouin results for $KCN_{0.85}Cl_{0.15}$ (Ref. 14) are given for comparison.

TABLE I. Smooth curve values of c_{44}, in units of 10^{10} dyn cm^{-2}, for single crystals of KCN_xBr_{1-x} and KCN_xCl_{1-x}. The c_{44} value obtained just before the acoustic signal disappeared on cooling is given on the last line. The KCN values are from Ref. 4.

T (K)	KCN	$KCN_{0.8}Br_{0.2}$	$KCN_{0.6}Br_{0.4}$	$KCN_{0.85}Cl_{0.15}$	$KCN_{0.75}Cl_{0.25}$
300	1.460	1.907	2.432		2.479
280	1.301	1.774	2.312		2.279
260	1.140	1.631	2.174	1.675	2.078
240	0.971	1.472	2.026	1.469	1.863
220	0.794	1.296	1.862	1.265	1.638
200	0.594	1.101	1.677	1.044	1.386
180	0.357	0.882	1.465	0.799	1.100
170	0.220	0.763	1.351	0.663	0.947
160		0.640	1.230	0.527	0.789
150		0.513	1.102	0.383	0.631
140		0.365	0.972	0.224	0.456
130		0.198	0.825		0.271
120			0.667		
110			0.478		
100			0.290		
	0.193	0.155	0.177	0.120	0.098

of temperature with values of $10^6\,\kappa = 7.21$ bar^{-1} ($KCN_{0.8}Br_{0.2}$), 7.06 bar^{-1} ($KCN_{0.6}Br_{0.4}$), 7.11 bar^{-1} ($KCN_{0.85}Cl_{0.15}$), and 6.95 bar^{-1} ($KCN_{0.75}Cl_{0.25}$). This correction only amounts to 0.7% at 2.9 kbar.

The velocity results are shown in Figs. 1 and 2, where the variation of u in pure KCN is given for comparison. Smooth-curve values of c_{44} in the disordered cubic phase of the mixed crystals are listed in Table I. These elastic constants were obtained using room-temperature (293 K) densities of 1.792 ($KCN_{0.8}Br_{0.2}$), 2.032 ($KCN_{0.6}Br_{0.4}$), 1.587 ($KCN_{0.85}Cl_{0.15}$), and 1.609 g cm^{-3} ($KCN_{0.75}Cl_{0.25}$).

In the case of KCN_xBr_{1-x} mixed crystals, ultrasonic velocities are also known for $x = 0.04$ and $x = 0.14$ samples,[11] and the $KCN_{0.14}Br_{0.86}$ results are included in Fig. 1. A general comparison with Brillouin scattering results on mixed crystals[13,14] suggests that no velocity dispersion occurs in the disordered cubic phase although comparison is complicated by different sample compositions and uncertain indices of refraction. Agreement in the case of $KCN_{0.85}Cl_{0.15}$ is indicated in Fig. 2.

No attempt was made to carry out a systematic investigation of the acoustic attenuation, but a few qualitative observations are worth noting. In general the attenuation was significant (say 3–6 dB cm^{-1}) at 300 K and increased slowly on cooling to ~180 K. At temperatures below ~180 K, the echo pattern was often nonexponential with distorted pulse shapes (due possibly to local strains). Velocity measurements were made on cooling until the echo pattern completely disappeared. On subsequent warming of the sample, the echoes reappeared at about the same temperature at which they had disappeared. This confirms that the loss of signal was due to an intrinsic property of the sample rather than cleavage cracks or failure of the transducer-sample bond.

The loss of acoustic signal may be caused by scattering from small ordered-phase domains, as in the case of pure KCN (Ref. 4) or KH_2PO_4 near its ferroelectric transition,[18] or may possibly be due to dynamic coupling of the shear mode to the CN^- reorientations. If domain scattering is responsible, one obtains a fairly good measure of T_1. However, one must be careful since recent work[11] on $KCN_{0.14}Br_{0.86}$ and $KCN_{0.04}Br_{0.96}$ shows that the acoustic signal disappears at low temperatures even when no structural transition occurs. For all our mixed crystals except $KCN_{0.75}Cl_{0.25}$ (for which $x < x_c$), the lowest temperature at which velocity data could be measured was taken as the approximate value of T_1. It is hoped that these upper bounds are fairly close to the true first-order transition temperatures.

III. DISCUSSION

A. Pressure effects

It is clear from Fig. 1 that pressure has no effect on the c_{44} shear stiffness of KCN_xBr_{1-x} crystals and thus no effect on the T_c values corresponding to the point where c_{44} extrapolates to zero. In the case of the $KCN_{0.75}Cl_{0.25}$ crystal, pressure does have a small effect over a restricted temperature range (see Fig. 2); but this does not necessarily imply a pressure dependence for T_c. Over the range $45 < \Delta T < 180$ K, the data at 2.89 kbar follow those at 1 atm and extrapolate to zero at the same T_c value. The pressure independence of T_c and c_{44} observed[5] in KCN and in these mixed crystals is in agreement with an explicit prediction of the Mokross-Pirc model.[9]

In contrast to the insensitivity of T_c to changes in the applied pressure, the first-order transition temperature T_1 appears to increase substantially with pressure. Estimates of dT_1/dp based on the bromide mixed-crystal data yield ~3.1 K/kbar for $KCN_{0.8}Br_{0.2}$ and ~3.2 K/kbar for $KCN_{0.6}Br_{0.4}$. These mixed-crystal transition slopes are comparable to the various dT_1/dp values reported for pure KCN: 2.31,[16] 2.56,[19] and ~2.7 K/kbar.[5] This pressure dependence of T_1 suggests that anharmonic coupling between CN^- orientations and the volume needs to be taken into account.[9]

B. Temperature dependences at 1 atm

The character of the variation of the velocity u with the temperature difference $\Delta T = T - T_c$ is very similar in KCN and in the mixed crystals studied here. This is illustrated in Fig. 3, where a scaled velocity $u^* \equiv Fu$ is plotted versus ΔT. A temperature-independent scale factor F and the value of T_c have been adjusted for each mixture to provide the best agreement with $u(\Delta T)$ in KCN,[4] and the resulting parameters are given in Fig. 3. The superposition is excellent for the chloride samples and also quite good for the bromide samples. In the latter case there are, however, small but definite changes in the shape of $u^*(\Delta T)$ that are most clearly seen for the $KCN_{0.6}Br_{0.4}$ sample.

Having established that the shear elasticity of our mixed crystals is very similar to that in pure KCN, we have carried out fits to our data with two forms previously used to represent KCN:

$$c_{44}/\rho = u^2 = A \ln(T/T_c) \tag{1}$$

and

$$s_{44} - s_{44}^0 = \frac{B}{T - T_c} , \tag{2}$$

where $s_{44} \equiv 1/c_{44}$. The quantity $s_{44}^0 = 1/c_{44}^0$ represents the bare value in the absence of rotational-translational coupling. Equation (1) corresponds to the empirical expression first used by Haussühl,[4] except that we fit u^2 rather than c_{44}. Equation (2) is equivalent to the form

$$c_{44} = c_{44}^0 \frac{T - T_c}{T - T_0} \tag{3}$$

discussed in Refs. 7–9, where T_0 is a negative constant. The parameter B is identical to $(T_c - T_0)/c_{44}^0$. The form given in Eq. (2) has the advantage that

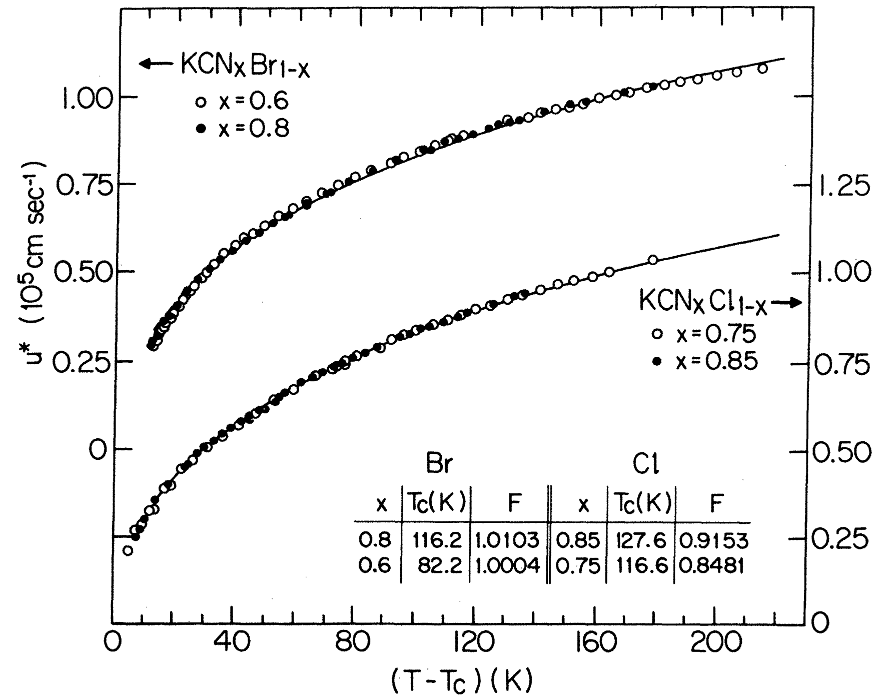

FIG. 3. Scaled velocity $u^* = Fu$ vs $T - T_c$ for bromide and chloride mixed crystals at 1 atm. F is a temperature-independent scale factor, and the smooth curve represents the variation for KCN ($F = 1$, $T_c = 153.9$ K).

TABLE II. Estimated first-order transition temperatures (upper bound on true value) and extrapolated T_c values obtained from two least-squares fits to shear elastic data. The values of other adjustable parameters in Eqs. (1) and (2) are also given.

		KCN	$KCN_{0.8}Br_{0.2}$	$KCN_{0.6}Br_{0.4}$	$KCN_{0.85}Cl_{0.15}$	$KCN_{0.75}Cl_{0.25}$
	T_1 (K)	167.7	127.8	94.7	135.1	. . .
Eq. (1)	A (10^{10} cm^{2}sec^{-2})	1.4055	1.141	0.969	1.469	1.622
	T_c (K)	153.9	117.9	86.6	128.5	(118.1)
Eq. (2)	T_c (K)	153.3	118.2	86.2	127.3	116.2
	B (10^{-10} dyn^{-1}cm^{2}K)	71.91	56.69	44.86	57.65	49.06
	c_{44}^0 (10^{10} dyn cm^{-2})	5.08	4.66	4.95	6.00	7.18

$(s_{44}-s_{44}^0)$ is directly proportional to the static orientational susceptibility χ_{44}.[6,9] Thus, Eq. (2) corresponds to a mean-field approximation for χ_{44}.

The mixed-crystal data can be fairly well described by Eq. (1) over the entire temperature range of our data. The best fit was obtained for $KCN_{0.6}Br_{0.4}$ ($\chi_\nu^2=0.90$ with a random distribution of deviations), and similar fits were found for $KCN_{0.8}Br_{0.2}$ ($\chi_\nu^2=1.56$) and $KCN_{0.85}Cl_{0.15}$ ($\chi_\nu^2=2.03$). The only poor fit was for the $KCN_{0.75}Cl_{0.25}$ sample ($\chi_\nu^2=10.4$ with a systematic pattern to the derivations). In view of Fig. 3, it seems likely that this reflects a breakdown in the empirical $\ln T$ fitting form rather than any systematic change in the behavior of u. The least-squares values of the parameters T_c and A are given in Table II.

Figure 4 shows that the elastic data on all four mixed crystals can be well described by the mean-field relaxation form given in Eq. (2). The least-squares values of the fitting parameters are given in Table II, and the reduced χ-squared values were $\chi_\nu^2=1.24$ ($KCN_{0.8}Br_{0.2}$), 0.99 ($KCN_{0.6}Br_{0.4}$), 2.17 ($KCN_{0.85}Cl_{0.15}$), and 2.16 ($KCN_{0.75}Cl_{0.25}$). These χ_ν^2 values and those cited for the fits with Eq. (1) are based on standard deviations in u that range from 500 cm sec^{-1} (~0.5%) at 300 K to 300 cm sec^{-1} (~1%) at 100 K. The fits with Eq. (2) are good in the sense that the deviations are small and randomly distributed over the entire temperature range for all four samples. There is, however, a difficulty with the resulting least-squares values of the bare stiffness c_{44}^0. For a rigid-ion model, the quantity a^4c_{44}, where a is the lattice constant, has a constant value for all univalent crystals with the rocksalt structure; and this is still a good approximation according to simple shell models.[20] Using the value of a^4c_{44} obtained from data on pure KBr and KCl, one can predict the expected c^0 values for KCN and the mixed crystals. These values are 5.3 (KCN), 5.25 ($KCN_{0.8}Br_{0.2}$), 5.2 ($KCN_{0.6}Br_{0.4}$), 5.45 ($KCN_{0.85}Cl_{0.15}$), and 5.55 ($KCN_{0.75}Cl_{0.25}$) in units of 10^{10} dyn cm^{-2}. As indicated in Table II, the least-squares values of c^0 for KCN and the bromide mixed crystals are fairly close to these values, but those for the chloride mixed crystals seem unreasonably large.

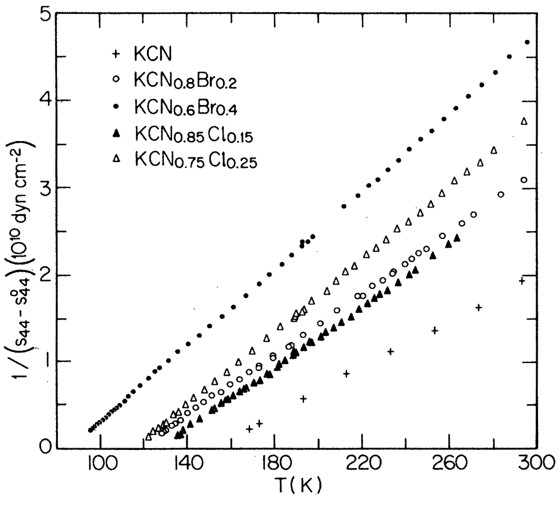

FIG. 4. Least-squares fit of elastic data using Eq. (2). The values of the adjustable parameters are listed in Table II. The KCN points are tabulated values given in Ref. 4.

A final fit to the elastic data was attempted with a more general form of Eq. (2) in which mean-field behavior was not assumed. In this case the *single-ion* susceptibility was taken to have the form y/T predicted by Michel and Naudts, where y is a known weak function of temperature.[6] Using this expression in the general equation of Mokross and Pirc [Eq. (47) of Ref. 9], one obtains

$$s_{44}-s_{44}^0=\frac{ay}{T-by}\ , \tag{4}$$

where a and b are constants. These fits are not as satisfactory as those with Eq. (2): the χ_ν^2 values are approximately twice as large, the deviations have a systematic pattern, and the c_{44}^0 values are ~1×10^{10} dyn cm^{-2} lower than those obtained with Eq. (2). Another version of Eq. (4) involves only two fitting parameters since $a = s_{44}^{0}b$.[6] However, this form provides an even poorer fit to the data and the resulting c^0 values have unattractively low values of $\sim 2.5 \times 10^{10}$ dyn cm^{-2}.

C. Composition dependence

Figure 5 shows that c_{44} is a smooth function of CN$^-$ mole fraction in KCN$_x$Br$_{1-x}$ over the entire range from $x = 0$ to 1. At no temperature in the 100–300-K range does the shear elasticity in the cubic phase give any indication that there is a difference in behavior for samples with $x > x_c$ and those with $x < x_c$. This is consistent with the view that such differences in the $u(T)$ behavior can only be seen at low temperatures (near and below the temperature where u goes through its minimum value for samples with $x < x_c$). Indeed, even the c_{44} values for the dilute crystals KCN$_{0.14}$Br$_{0.86}$ and KCN$_{0.04}$Br$_{0.96}$ can be very well represented by Eq. (2) down to 50 and 25 K, respectively.[11,21] The effective T_c and B values for these samples were 2 K and 17.1×10^{-10} cm^2 dyn^{-1} for $x = 0.14$ and 4 K and 2.8×10^{-10} cm^2 dyn^{-1} for $x = 0.04$. Fits of almost the same quality can be obtained with both T_c values fixed at 0 K, corresponding to a Curie-law susceptibility for these dilute systems where CN$^-$ ion interactions are expected to be negligible.

The critical temperatures T_c given in Table II are plotted as a function of composition in Fig. 6 together with a few other available T_c values. It is clear that these values are in reasonable agreement with percolation theory, although the data do not allow one to decide whether there are deviations from mean-field behavior.[22] In the theory of Mokross and Pirc $T_c \sim xJ$ and $B \sim x(J - I)/c_{44}^{0}$, where J is the effective CN$^-$-CN$^-$ coupling constant due to both CN$^-$-strain interaction and CN$^-$-phonon interaction and $(J - I)$ is the strain contribution alone. The behavior of T_c indicates that $J \approx 153$ K is insensitive to composition over the range studied here. If $(J - I) \approx 365$ K were also independent of x, one would expect that $(c_{44}^{0}B) = x(c_{44}^{0}B)_{\mathrm{KCN}}$. This relation is roughly obeyed for the bromide mixed crystals but not for the chloride samples. The failure in the latter case seems to be connected with the suspiciously large c_{44}^{0} values.

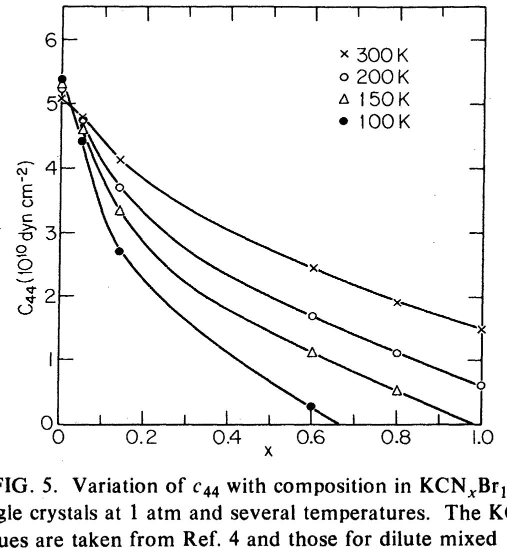

FIG. 5. Variation of c_{44} with composition in KCN$_x$Br$_{1-x}$ single crystals at 1 atm and several temperatures. The KCN values are taken from Ref. 4 and those for dilute mixed crystals ($x = 0.04$ and 0.14) are taken from Ref. 11.

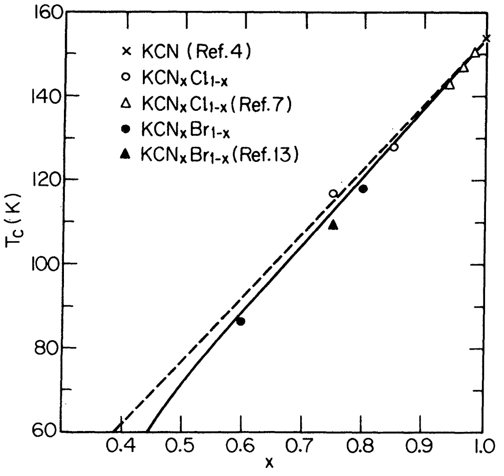

Fig. 6. Variation of $T_c(x)$ with mole fraction x of CN$^-$ in KCN$_x$Br$_{1-x}$ and KCN$_x$Cl$_{1-x}$. The dashed straight line represents the mean-field prediction $T_c(x) = xT_c(\mathrm{KCN})$, and the solid curve with a limiting slope $dT_c/dx = 1.06T_c(\mathrm{KCN})$ represents the percolation prediction for a three-dimensional Ising model (Ref. 22).

IV. SUMMARY AND CONCLUSION

In KCN$_x$Br$_{1-x}$ samples that undergo a weakly first-order transition to a phase with long-range [110] CN$^-$ order, pressure has no effect on c_{44} or the extrapolated critical temperature T_c but does increase T_1 appreciably. Furthermore, there is no observed difference in the character of the c_{44} temperature dependence for samples with $x > x_c$ and those with $x \lesssim x_c$. In the case of KCN$_{0.6}$Br$_{0.4}$, this sample is reported to undergo a transition at 1 atm but not at 1.5 kbar.[16] However, the c_{44} values observed over the range $100 < T < 300$ K at 1.5 kbar are identical to those at 1 atm. In the case of KCN$_{0.75}$Cl$_{25}$, where $x < x_c$ at 1 atm, there seem to be no systematic deviations from Eq. (2) associated with the absence of a transition at least down to $\Delta T \simeq 5$ K.

Thus any theory that explains the transition solely in terms of a soft shear mode instability is incomplete. It is necessary to explain (1) why the transition into the orthorhombic phase is always first order and occurs at a pressure dependent T_1; (2) why no transition occurs when $x < x_c$ in spite of the fact that the c_{44} behavior in all four samples is the same down to the quite small value $\sim 0.15 \times 10^{10}$ dyn cm^{-2}; and (3) why x_c is so different for chloride and bromide mixed crystals.

There are two competing directions for the development of a theory that would explain the behavior of samples over the entire composition range. One can start from the dilute limit ($x \rightarrow 0$) and treat the orientational susceptibility χ_{44} as due to uncoupled CN$^-$ ions. In the model of Loidl *et al.*[11] it is assumed that independent CN$^-$ ions are distributed over three well-defined rotational levels. Transitions between these levels are coupled to the TA phonons, and the c_{44} behavior in $KCN_{0.04}B_{0.96}$ and $KCN_{0.14}Br_{0.86}$ has been fitted with an expression involving five adjustable parameters. The model of Michel and Rowe[12] also treats the CN$^-$ ions as uncorrelated at high temperatures (i.e., $\chi \sim 1/T$ above T_f) but assumes a "spin-glass" state with local ordering in clusters below a characteristic temperature T_f. Neither of these models can lead to a transition into the orthorhombic phase since the effective coupling between CN$^-$ ions has not been taken into account. The second approach is to start from the concentrated limit ($x = 1$)[6–8,23] and treat the mixed crystals as a percolation problem. This is done in a mean-field approximation in the model of Michel, Naudts, and deRaedt[6] and that of Mokross and Pirc.[9] The difficulties with this approach are not associated with the mean-field treatment of percolation but rather with the disappearance of the transition at quite large x_c values. In the Mokross-Pirc model, tunneling provides a mechanism for the disappearance of the transition but the critical CN$^-$ concentration associated with tunneling is much too small to explain the observed x_c values.

An ultrasonic study of $KCN_{0.5}Br_{0.5}$ is currently in progress to establish the static elastic behavior in a sample where x is further below x_c and to explore possible velocity dispersion. A comparison of ultrasonic and neutron velocity data will allow a test of the suggestion of crossover from fast to slow relaxation regimes as an explanation of the neutron results in this sample.[10,12]

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