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Elastic behavior of $K_xNa_{1-x}CN$ quadrupolar glasses

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Ultrasonic measurements of c_{44} shear elastic constants are reported in $K_xNa_{1-x}CN$ mixed crystals. The data were analyzed quantitatively with a quenched–random-field model. Over the range $0.65 < x \le 1$ the c_{44} data are well represented by the model, and the fitting parameters are consistent with the general pattern of behavior in several other mixed cyanide crystals. For $0.13 \le x < 0.65$, the $c_{44}(T)$ data can be represented empirically by the model, but the fitting parameters deviated appreciably from those expected.

Following extensive study of diluted cyanide mixtures,[1-5] such as $K(CN)_xBr_{1-x}$, there is a growing interest in the behavior of undiluted cyanide mixed crystals $A_xB_{1-x}CN$, where A and B are alkali cations.[2,6-11] The phase diagram for $K_xNa_{1-x}CN$ mixtures is especially interesting.[2] Pure NaCN and KCN crystals both undergo a weakly first-order soft-mode phase transition from a disordered cubic phase into an orientationally ordered orthorhombic ferroelastic phase. However, such an orientationally ordered phase exists in $K_xNa_{1-x}CN$ mixed crystals only over a limited range of small $(0 \le x < 0.15)$ or large $(0.89 \le x \le 1)$ potassium concentrations. For a wide range of intermediate x values, $K_xNa_{1-x}CN$ crystals freeze into an orientational quadrupolar glass state upon cooling. Thus, the phase diagram is very similar to that of the dipolar glass system $Rb_{1-x}(NH_4)_xH_2PO_4$ [rubidium ammonium dihydrogen phosphate (RADP)].[12] However, there is a significant difference. In RADP the glassy state is caused by the frustration of competing ferroelectric [rubidium dihydrogen phosphate (RDP)] and antiferroelectric [ammonium dihydrogen phosphate (ADP)] interactions, whereas in $K_xNa_{1-x}CN$ the two pure compounds exhibit the same CN^- ordering. Recent experiments[6-9] suggest that the orientational glass state in $K_xNa_{1-x}CN$ may be caused by large random strain fields induced by different alkali-cationic sizes. Such strain fields interfere with the lattice-mediated CN^--CN^- coupling and frustrate long-range ordering.

In this paper, we report ultrasonic (10-MHz) measurements of the shear elastic constant c_{44} in $K_xNa_{1-x}CN$ mixed crystals for seven different potassium concentrations in the range $0.13 \le x \le 0.94$. These data are analyzed with a quenced random-strain field model[5,13,14] that has been successfully applied to $K_xRb_{1-x}CN$ (which exhibits low-temperature ordering for all x) (Ref. 8) and several diluted mixed cyanide systems.[4,5]

Single crystals of $K_xNa_{1-x}CN$ were obtained from the Crystal Growth Laboratory of the University of Utah. Standard atomic absorption spectroscopy was used to determine the sample compositions. The mass densities ρ were calculated from the room-temperature lattice constants of the crystals as determined by powder x-ray diffraction. The absolute ultrasonic velocity (u) for [100] transverse acoustic waves was measured at room temperature with the pulse-superposition technique.[15] Velocity changes as a function of temperature were measured using a modified MATEC MBS 8000 system.[16] The shear elastic constants c_{44} were then obtained from $c_{44}=\rho u^2$.

Figures 1 and 2 show the temperature dependence of c_{44} for crystals with various K^+ concentrations. The c_{44} data for $x=0$ and $x=1$ have been taken from Refs. 6 and 17, respectively. The data in Figs. 1 and 2 stop at a "lowest" temperature (T_l) where the ultrasonic signal was lost due to very high acoustic attenuation.[18] Measurements of the frequency and temperature dependence of the ultrasonic attenuation are in progress, and the dynamical aspects of this system will be presented elsewhere.

For both pure NaCN and KCN, c_{44} shows a very dramatic softening due to the strong bilinear lattice translational and CN^- rotational (TR) coupling.[13] For the mixtures studied, there are three distinct features in the c_{44} data. First, the temperature dependence of c_{44} varies significantly with x. In the middle of the composition range $(0.3 \le x \le 0.6)$, c_{44} varies rather slowly with temperature, in contrast to the rapid variation seen when $x \to 0$ or 1. Second, the shape of the $c_{44}(T)$ curve deviates slowly from that of KCN as x decreases on the KCN-rich side. In contrast, the $c_{44}(T)$ curves change dramatically from that of pure NaCN as x increases on the NaCN-rich side. This asymmetry is evident when data for $x=0.13$ and 0.30 are compared with those for $x=0.88$ and 0.73. Third, $c_{44}(T)$ curves for $x=0.73$, 0.88, and 0.94 show a point of inflection, whereas the c_{44} data for the other concentrations $(0.13 \le x \le 0.60)$ exhibit positive curvature at all temperatures.

We have analyzed the data using an extended mean-field model[8] that includes quenched random-strain fields and a nonideal $T_c(x)$ variation based on regular-solution theory. In this approach, the variation of c_{44} in the cubic phase can be described by

$$c_{44}=c_{44}^0\frac{T-T_c(1-q)}{T-T_0(1-q)}\ , \tag{1}$$

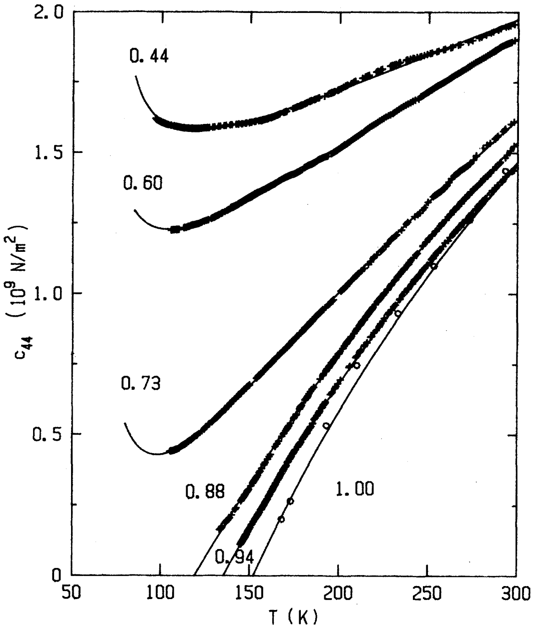

FIG. 1. The c_{44} shear elastic constant vs temperature for $K_xNa_{1-x}CN$ crystals with $x \geq 0.44$. Solid lines represent least-squares fits with Eq. (1).

where c^0_{44} is the bare elastic constant and q is an Edward-Anderson order parameter.[5,13] T_0 is an effective temperature at which the cyanide pseudospins would achieve quadrupolar order in the absence of bilinear TR coupling, while T_c is the second-order phase transition temperature in the absence of the random strain. From a high-temperature expansion, it is found that $q \simeq (\sigma/k_B T)^2$, where σ is the width of the quenched random-field distribution. For the random fields induced by the substitution of different size ions, σ^2 should be well approximated by[13]

$$\sigma^2/k_B^2 \equiv \Sigma = x(1-x)\Sigma_0 , \tag{2}$$

where Σ_0 is effectively independent of temperature and characterizes the amplitude of the random-field distribution widths. When $q=0$, Eq. (1) reduces to the well-known elastic Curie-Weiss equation, which provides a good representation of the c_{44} data for pure NaCN and KCN.[4,6]

Equation (1) with $q=\Sigma/T^2$ has been used to represent the mixed-crystal data. Because of correlations among the fitting parameters c^0_{44}, T_c, T_0, and Σ, it is necessary to introduce constraints to ensure convergence to a well-defined χ^2 minimum. We have been guided by earlier work[5,8] and have taken the c^0_{44} values to be linear interpolations between the values for NaCN and KCN. The least-squares-fitting parameters are listed in Table I, and c_{44} curves obtained with these parameters are shown in Figs. 1 and 2.

Although all the fit curves represent the data quite well, it is important to examine the behavior of the fitting parameters as a function of composition. For example, Fig. 3(a) shows Σ as a function of composition. The parabolic curve in this figure represents the behavior expected from Eq. (2), where $\Sigma_0 = 15\,400$ K^2 has been chosen to optimize the fit over the range $0.73 \leq x \leq 1$. Large systematic deviations of Σ from this curve are evident on the Na-rich side $(0.13 \leq x \leq 0.5)$. Values of Σ_0 reported in the literature for other mixed cyanide crystals[4,5,8] are plotted together with the present value in Fig. 4 as a function of the difference in the ionic radii of the substituted ions. These Σ_0 values fall onto two curves: one for the substitutions of cations with an undiluted sublattice of CN$^-$ ions, and one for diluted crystals where the CN$^-$ ions are partially replaced by a different anion. Empirically, the random-strain field parameter Σ_0 is more sensitive to $|\Delta r|$ in the diluted cyanide crystals than in the undiluted cyanide mixtures. This seems reasonable but needs theoretical justification along the lines of Michel's microscopic calculation.[13]

Both the critical temperature $T_c(x)$ and the parameter

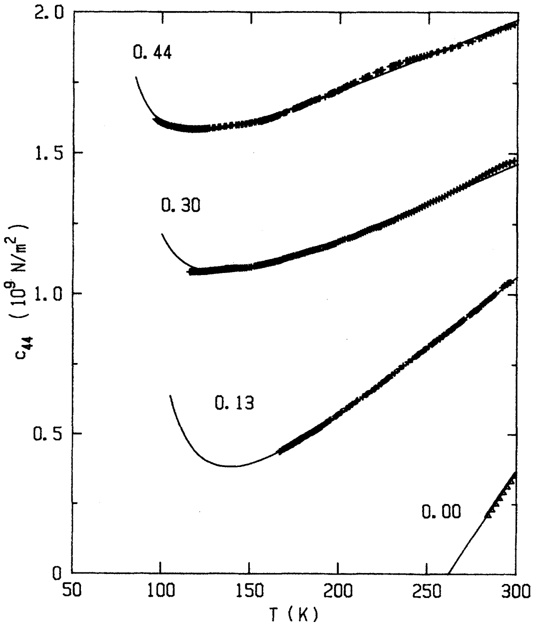

FIG. 2. The c_{44} shear elastic constant vs temperature for $K_xNa_{1-x}CN$ crystals with $x \leq 0.44$. Solid lines represent least-squares fits with Eq. (1).

TABLE I. Values of adjustable least-squares parameters T_c, T_0, and Σ for $K_xNa_{1-x}CN$ crystals. The chosen values of the bare stiffness c^0_{44} are given in units of 10^9 N/m^2. χ^2_ν represents the reduced chi-squared values. The parameters for NaCN and KCN are taken from Refs. 6 and 4, respectively.

x	c^0_{44}	T_c (K)	T_0 (K)	Σ (K^2)	χ^2_ν
0.0	9.50	262	−694	0	
0.13	8.94	150	−1132	6370	0.24
0.30	8.21	−83	−1944	5830	6.24
0.44	7.61	−230	−1792	4690	5.83
0.60	6.93	−50	−1006	3600	1.74
0.73	6.37	102	−512	3180	1.11
0.88	5.68	133	−312	1430	1.82
0.94	5.47	141	−299	730	1.25
1.00	5.21	152	−228	0	

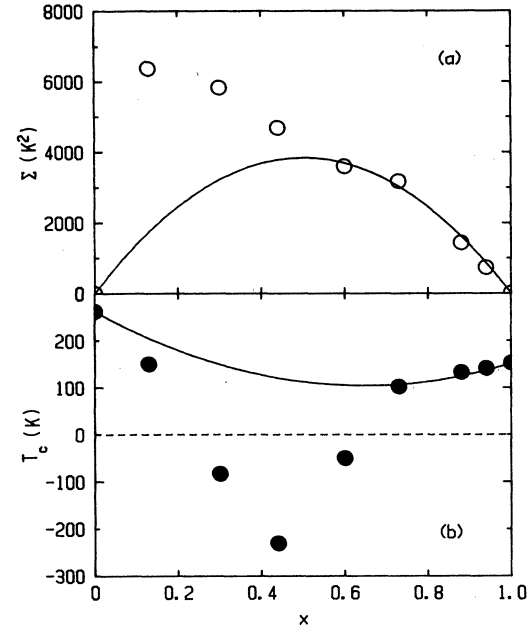

FIG. 3. (a) Composition dependence of the fitting parameter Σ. The parabolic line represents a fit with the form $\Sigma = x(1-x)\Sigma_0$ to data over the range $0.73 \leq x \leq 1$. (b) Composition dependence of the critical temperature T_c for quadrupolar ordering. The solid line is the best fit with Eq. (3) to data over the range $0.73 \leq x \leq 1$.

$T_0(x)$ exhibit pronounced dips centered roughly at $x \simeq 0.4$. As shown in Fig. 3(b), the T_c values become negative for fits to the $x = 0.30$, 0.44, and 0.60 data. This suggests the possibility that in the absence of quenched elastic strains some kind of antiferroelastic ordering might become dominant in the $0.2 < x < 0.65$ composition range; i.e., perpendicular CN^- alignments might occur rather than the ferroelastic parallel alignments. In view of the large difference in radii, it is also quite likely that K^+ and Na^+ positions are correlated over short distances rather than random in this composition range.

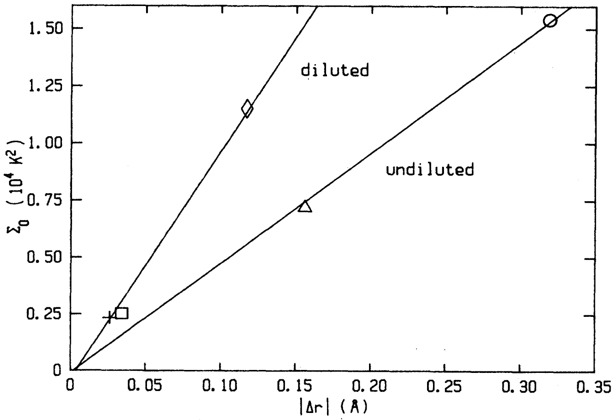

FIG. 4. Amplitude of the random-strain field parameter Σ_0 as a function of the difference in the ionic radii of the substituted ions for diluted cyanide crystals $Rb(CN)_xBr_{1-x}$ (+), $K(CN)_xBr_{1-x}$ (□), $K(CN)_xCl_{1-x}$ (◇), and undiluted cyanide crystals $K_xRb_{1-x}CN$ (△) and $K_xNa_{1-x}CN$ (○).

Nonideality in $T_c(x)$ can be described for $K_xRb_{1-x}CN$ mixed crystals with a regular-solution model:[8]

$$T_c(x) = xT_c^{AA} + (1-x)T_c^{BB} - 2x(1-x)\Delta T_c^{AB} , \qquad (3)$$

where ΔT_c^{AB} is an adjustable fitting parameter. A positive (negative) value of ΔT_c^{AB} means that the effective CN^--CN^- quadrupolar coupling is weakened (strengthened) relative to that associated with an ideal solution (linear interpolation). It is clear that Eq. (3) cannot describe the $T_c(x)$ variation for $K_xNa_{1-x}CN$ over the entire concentration range. We have, however, used Eq. (3) to fit $T_c(x)$ over the limited range $0.7 \leq x \leq 1$. Such a fit with T_c^{NaNa} and T_c^{KK} fixed at 262 and 152 K, respectively, yields $\Delta T_c^{\mathrm{KNa}} = 189$ K; the resulting $T_c(x)$ curve is shown in Fig. 3(b). The value of ΔT_c^{AB} is considerably larger here than for $K_xRb_{1-x}CN$(~40 K),[8] which is reasonable since $r_K / r_{Na} = 1.4$ while $r_{Rb} / r_K = 1.1$.

The form of Eq. (1) implies the existence of a critical composition x_c where the minimum in c_{44} as a function of T just equals zero.[5] Using Eqs. (1)–(3) and the parameter values $\Sigma_0 = 15\,400$ K² and $\Delta T_c^{\mathrm{KNa}} = 189$ K, one can calculate that $x_c = 0.31$ and 0.84; i.e., predict that an orientational glass should be observed over the range 0.31–0.84. The predicted upper x_c value is in quite good agreement with the experimental value of ~0.89, while the lower x_c value differs significantly from the experimental value of ~0.15, as expected since the empirical Σ and T_c values for small x do not fit the chosen parabolic $\Sigma(x)$ and $T_c(x)$ curves.

Thus, on the K-rich side of the $K_xNa_{1-x}CN$ phase diagram the shear elasticity can be well described in terms of an extended mean-field model that includes quenched random-strain fields and nonideal critical temperatures following regular-solution theory. Furthermore, the adjustable parameters Σ_0 and $\Delta T_c^{\mathrm{KNa}}$ have physically reasonable values that are consistent with those used to describe other mixed cyanide crystals.

The temperature dependence of $c_{44}(T)$ is markedly asymmetric when low-x and large-x data are compared. Furthermore, the values of the Σ, T_c, and T_0 parameters obtained on the Na-rich side of the phase diagram differ considerably from those expected, which casts doubt on the validity of Eq. (1) for such Na-rich mixtures. In the middle of the composition range ($\sim 0.25 \leq x \leq 0.65$), the data can be fitted with Eq. (1) only if the T_c values are negative. These failures of the model may be due to (1) charge redistribution in the CN^- ion (and thus a change in quadrupole moment) when large K^+ ions are substituted into the NaCN lattice, (2) noncubic local potentials in the middle of the composition range where CN^- may undergo single-particle relaxation rather than collective relaxations, and (3) possible changes in the form of the Edwards-Anderson order parameter as suggested by recent neutron scattering.[9]

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[18] For the sample with $x = 0.60$, the acoustic signal was recovered at ~ 63 K and data were obtained over the range 13–63 K. Attempts are being made to obtain low-temperature data on other samples but this is experimentally difficult. In any event, the present analysis, which is based on a high-temperature form for q, will not apply to data obtained below T_l; see Ref. 5 for a discussion of this point.