

Experimental Evidence for Quenched Random Strain Fields in Mixed Cyanide Crystals

J. O. Fossum and C. W. Garland

*Department of Chemistry and Center for Materials Science and Engineering,
Massachusetts Institute of Technology, Cambridge, Massachusetts 02139*

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Ultrasonic measurements of static c_{44} shear elastic constants in $\text{K}(\text{CN})_x\text{Cl}_{1-x}$, $\text{K}(\text{CN})_x\text{Br}_{1-x}$, and $\text{Rb}(\text{CN})_x\text{Br}_{1-x}$ mixed crystals are reported and analyzed with a recent mean-field theory including random strain fields. The good agreement between theoretical predictions and the present experiments clearly supports the suggestion that there exists a pretransitional temperature regime where the static shear elastic behavior can be understood in terms of competition between cyanide quadrupolar pseudospin lattice-mediated nonrandom interactions and quenched random strain fields.

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Mixed cyanide crystals are known to exhibit rich and interesting phase diagrams,^{1,2} and recently several investigations have focused upon the possible existence of structural (orientational) glass phases.^{1,3,4} Although the present Letter is concerned with so-called diluted cyanide mixtures of the type $A(\text{CN})_xX_{1-x}$ where A is an alkali-metal (K, Rb, Na, etc.) and X is a halogen ion (Br, Cl, etc.), much of what is said here also applies to nondiluted cyanide mixtures of the type $A_xB_{1-x}\text{CN}$ where both A and B are alkali metals. All of these mixed-crystal systems possess time-averaged cubic high-temperature phases in which the dumbbell-shaped cyanide ions jump rapidly between favorable orientational potential minima. The strong bilinear coupling between cyanide orientational and neighboring alkali-ion translational modes, both of quadrupolar symmetry, results in a strong effective lattice-mediated cyanide-cyanide quadrupolar orientational coupling and a dramatic softening of the shear elastic constant in these systems. In the pure cyanides (KCN, RbCN, and NaCN), these interactions trigger first-order elastic phase transitions where the quadrupolar modes mentioned above freeze out simultaneously, and there is a change in the lattice structure.^{5,6} There is experimental evidence for electric dipolar freezing at lower temperatures, both in pure^{1,7} and mixed crystals.^{3,8}

The pretransitional softening of the shear c_{44} elastic constant in pure cyanides is well described by a simple mean-field elastic Curie-Weiss law of the form^{5,6,9-11}

$$c_{44} = c_{44}^0(T - T_c)/(T - T_0), \quad (1)$$

where c_{44}^0 is the bare elastic constant one would observe in the absence of any bilinear coupling between quadrupolar translational and rotational (TR) modes, T_0 is an effective hypothetical temperature at which the cyanide pseudospins would obtain quadrupolar order in the absence of the TR coupling, and T_c is the second-order elastic transition temperature where c_{44} goes to zero and the elastic compliance $s_{44} \equiv 1/c_{44}$ diverges. It follows from mean-field theory that $T_c = T_0 + \gamma^2/ac_{44}^0$, where γ is

the TR-coupling strength and α is a constant.^{9,11} The parameters c_{44}^0 , T_0 , γ , and α may all be weakly temperature dependent.^{5,6} Because of the presence of third-order invariants, the elastic transition is actually first order and occurs at t_1 , where $t_1 > T_c$.^{1,2}

In $A(\text{CN})_xX_{1-x}$ mixed crystals it is found that below a certain critical cyanide composition x_c there is no elastic or orientational quadrupolar ordering. In these cases the crystals stay cubic down to the lowest temperatures¹² and an incomplete softening of the c_{44} elastic constant is observed.³ c_{44} exhibits a minimum at a temperature $T_f = T_f(x, \omega)$ which depends on the crystal composition and the measuring frequency ω .³ Experimental results have thus suggested the existence of pseudospin-glass phases in diluted cyanide mixtures.^{1,3} Theoretical models have been based on assumptions of quenched randomness of the quadrupolar interaction strength¹³ and more recently on assumptions of the existence of a quenched random strain field which couples linearly to the cyanide pseudospins.^{14,15} Both these approaches are found to represent experimental data at least qualitatively, i.e., give a minimum in c_{44} . Both kinds of quenched randomness (random interaction and random field) may be expressed in terms of the Edwards-Anderson order parameter $q = [\langle s_i \rangle^2]_{\text{av}}$, where $\langle \rangle_T$ denotes the thermal average for given random configuration and $[\]_{\text{av}}$ denotes the sample average.¹⁶ Random pseudospin-pseudospin ($s_i - s_j$) interaction can give rise to a spontaneous nonzero q below a pseudospin-glass transition, whereas a random field yields a nonzero q at all temperatures.^{16,17} It is found from a simple high-temperature expansion within mean-field theory with both types of randomness present that $q \approx \sigma^2/(kT)^2$, to leading order, where σ is the width of the random field distribution and k is Boltzmann's constant.^{14,15,17} Michel^{14,15} has included quenched random conjugate fields in a mean-field analysis of a microscopic model for diluted cyanide crystals and finds that Eq. (1) should be replaced with

$$c_{44} = c_{44}^0[T - T_c(1 - q)]/[T - T_0(1 - q)], \quad (2)$$

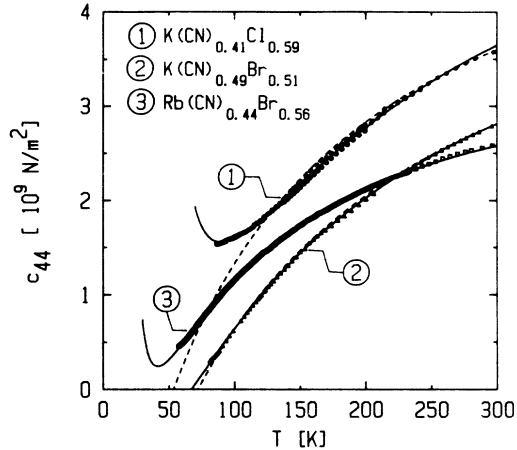


FIG. 1. c_{44} elastic constants as functions of temperature for three different mixed cyanide single crystals. The solid lines represent fits with Eq. (2); the dashed lines are previously reported Curie-Weiss fits with Eq. (1), which show systematic deviations at low temperature.

where c_{44}^0 , T_0 , T_c , and q all are functions of the composition variable x . Simple mean-field percolation arguments yield $T_0 \sim x$ and $T_c \sim x$. c_{44}^0 is expected to be only weakly x dependent. In the present case of mixed cyanide crystals, the quenched randomness is assumed to be due to the difference in ionic radii of the substitutional ions. Thus random site-dependent variations in the cyanide pseudospin local potentials are expected. Formally this is expressed in terms of a random conjugate field.^{14,15} One thus expects the random-field distribution width σ to have a maximum at $x=0.5$ and to be zero at $x=0$ and $x=1$, which in the simplest model^{14,15} yields $\sigma^2 \sim x(1-x)$. Corrections to Eq. (2) are expected for finite-frequency effects.¹⁵

In order to test these and other aspects of mixed cyanide systems specifically and random systems generally, we have recently performed a detailed study of the static and dynamic behavior of the shear elastic constant in mixed $\text{Rb}(\text{CN})_x\text{Br}_{1-x}$ single crystals for $x=0.064, 0.19, 0.25, 0.44, 0.53, 0.67, 0.79$, and 0.87 . Applying ultrasonic methods¹⁸ we have mainly focused our attention on the pretransitional high-temperature behavior, i.e., temperatures above T_1 in the case of first-order transitions or above the temperature where the elastic constant exhibits its minimum. For most x values several ultrasonic frequencies ranging from 8 to 77 MHz were used. In no case was any dispersion observed in the sound velocity, v , and in all cases the sound attenuation scaled as the frequency squared. The static elastic constants $c_{44} = \rho v^2$, where ρ is the mass density, were analyzed in terms of Eq. (2) with the high-temperature expansion form of q included, i.e., $q = \Sigma/T^2$ where Σ is a fitting parameter. This approach gives parameters c_{44}^0 , T_0 , T_c , and Σ whose x dependences are in remarkable agreement with the predictions summarized above.

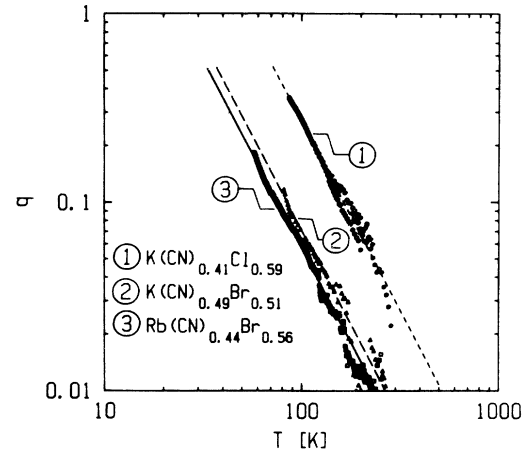


FIG. 2. Log-log plot showing the quenched-random-strain-induced Edwards-Anderson order parameter q calculated for the samples shown in Fig. 1 with parameters in Table I. The straight lines are drawn with slopes of -2 .

We have also reanalyzed previously reported ultrasonic measurements of c_{44} elastic constants in $\text{K}(\text{CN})_x\text{Br}_{1-x}$ and $\text{K}(\text{CN})_x\text{Cl}_{1-x}$ mixtures.^{19,20} These data were previously analyzed in terms of the simple elastic Curie-Weiss law, Eq. (1). However, systematic deviations from this behavior were found at low temperatures, qualitatively suggesting Eq. (2) as a better data representation. Reanalyzing these data, we find as in the case of our recent $\text{Rb}(\text{CN})_x\text{Br}_{1-x}$ experiments good agreement with the quenched-random-field theory.

Figure 1 shows a plot of static c_{44} elastic constants for $\text{K}(\text{CN})_{0.41}\text{Cl}_{0.59}$, $\text{K}(\text{CN})_{0.49}\text{Br}_{0.51}$, and $\text{Rb}(\text{CN})_{0.44}\text{Br}_{0.56}$ versus temperature. In Fig. 2 we have plotted the Edwards-Anderson order parameter q for these three samples as calculated from Eq. (2), showing that $q \sim 1/T^2$ is a good representation in all three cases. Figure 3 shows the critical temperature T_c versus composition for fifteen $\text{A}(\text{CN})_x\text{X}_{1-x}$ samples. The agreement with mean-field percolation theory is good, except for several of the $\text{K}(\text{CN})_x\text{Cl}_{1-x}$ mixtures, possibly because of nonrandom Cl^- distribution. Writing $\Sigma = \Sigma_0 x(1-x)$ we have calculated the amplitudes Σ_0 of the random-field distribution widths for the three mixed cyanide systems.

TABLE I. Values of adjustable parameters c_{44}^0 (in units of 10^9 N/m^2 or 10^{10} dyn/cm^2), T_c , T_0 , and Σ appearing in Eq. (2) when the simple form $q = \Sigma/T^2$ is used. For the $\text{Rb}(\text{CN})_{0.44}\text{Br}_{0.56}$ sample, a weakly temperature dependent c_{44}^0 was used. Reported here is the room-temperature value.

	c_{44}^0	T_c (K)	T_0 (K)	Σ (K ²)
$\text{K}(\text{CN})_{0.41}\text{Cl}_{0.59}$	1.45	74.3	-134.5	2697
$\text{K}(\text{CN})_{0.49}\text{Br}_{0.51}$	1.82	79.6	-132.4	718
$\text{Rb}(\text{CN})_{0.44}\text{Br}_{0.56}$	3.99	54.1	-77.0	573

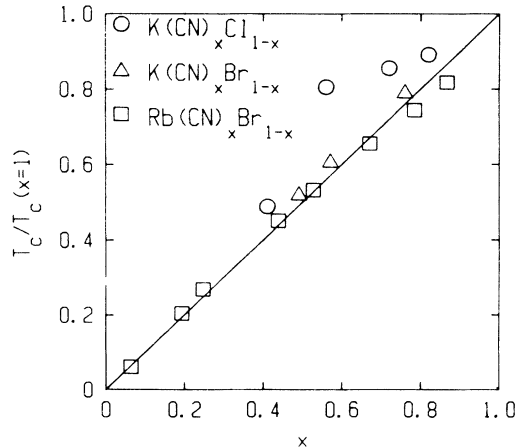


FIG. 3. Normalized critical temperature $T_c/T_c(x=1)$ vs composition x . $T_c(x=1)$ has been determined from a fitting of Eq. (1) to c_{44} elastic-constant data for pure KCN and RbCN (Ref.10).

Our results given in Table II are in quite satisfactory agreement with theoretical estimates by Michel.¹⁵

Since the data shown in Figs. 1 and 2 are in a temperature range where the high-temperature expansion parameter $\sigma^2/(kT)^2 \ll 1$, our interpretation is self-consistent. Although Eq. (2) with $q = \Sigma/T^2$ yields a minimum in c_{44} for two of the samples shown in Fig. 1, extrapolation of Eq. (2) in this form to lower temperatures is unjustified since Σ/T^2 becomes larger than 1 as shown in Fig. 2. Because of the possibility of quenched random pseudospin interactions in these systems, there could be an additional spontaneous nonzero component in q below a pseudospin-glass transition. The data in Figs. 1 and 2 alone cannot provide an answer to the question of whether the quadrupolar glass phases in mixed cyanides are of random-field nature, random-interaction nature, or both.

Associated with the minimum in the c_{44} elastic constant, there is a maximum in the sound attenuation in mixed cyanides.⁸ In our recent experiments on $\text{Rb}(\text{CN})_x\text{Br}_{1-x}$ systems, we were able to recover the acoustic signal at low temperatures for one composition, $x=0.19$. The static c_{44} elastic constant for $\text{Rb}(\text{CN})_{0.19}\text{Br}_{0.81}$ is included (as an inset) in Fig. 4, which presents the corresponding Edwards-Anderson

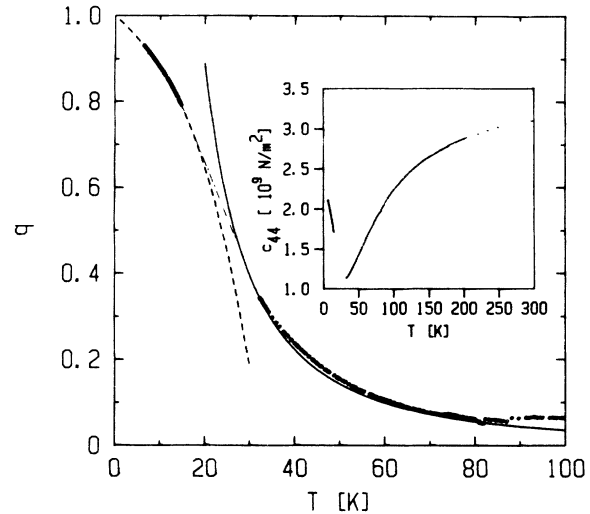


FIG. 4. The quenched-random-strain-induced Edwards-Anderson order parameter q in $\text{Rb}(\text{CN})_{0.19}\text{Br}_{0.81}$. Inset: c_{44} static elastic constant data. The solid and dashed lines are explained in the text. The dash-dotted line, which is merely a guide to the eye, represents a smooth interpolation between the high- and low-temperature data sets.

order parameter q . These q values have been calculated from the c_{44} data with parameters determined by our fitting the data above the temperature "gap" by Eq. (2) with $q = \Sigma/T^2$. The resulting parameters are $c_{44}^0 = 3.82 \times 10^9 \text{ N/m}^2$ (at room temperature), $T_c = 24.5 \text{ K}$, and $T_0 = -35.6 \text{ K}$. Extrapolation of the high-temperature fit $q = 355/T^2$ (solid line) to low temperatures clearly does not work well, since Σ/T^2 becomes larger than 1, invalidating the high-temperature expansion approximation.^{14,17} Figure 4 shows, however, that q is headed towards 1 as T goes to zero, as it should. Assuming that random-interaction effects and possible quantum corrections can be neglected, one can expand q in powers of kT/σ , where σ is the random-field distribution width as before. One finds $q = 1 - AT/\Sigma^{1/2} - BT^3/\Sigma^{3/2} +$ (higher-order terms), where A and B are constants of order of magnitude 1 for Ising systems.²¹ The dashed line in Fig. 4 represents a low-temperature expansion fit to q with Σ fixed to the value determined from the high-temperature fit; the resulting values of A and B are $A=0.19$ and $B=0.13$. Thus, both A and B are somewhat smaller than expected, or in other words q is slightly larger than one might expect from the high-temperature parameters. This could be taken as an indication of a small spontaneous component in q , i.e., a pseudospin-glass transition. However, in fitting the low-temperature data we have used the value of Σ determined at high temperatures and neglected the possibility that the width of the random-field distribution could be temperature dependent as suggested by previous experiments.^{3,22} For the latter reason and also because no theoretical estimates of A and B exist, we conclude that both high- and low-temperature c_{44}

TABLE II. Strength, Σ_0 , of the quenched-random-strain-distribution width, determined from fits by Eq. (2) with $q = \Sigma_0 x(1-x)/T^2$, where x is the CN^- concentration. Σ_0^M represent theoretically predicted estimates (Ref. 15).

	Σ_0 (K ²)	Σ_0^M (K ²)
$\text{K}(\text{CN})_x\text{Cl}_{1-x}$	11 000	11 500–15 000
$\text{K}(\text{CN})_x\text{Br}_{1-x}$	2500	1280–1670
$\text{Rb}(\text{CN})_x\text{Br}_{1-x}$	2300	...

static-elastic-constant data can be explained in terms of a simple mean-field model which include quenched random conjugate fields as the only random ingredient, at least for this one sample.

In summary, data are consistent with the idea that the glassy phases in mixed cyanide crystals are of random-field nature rather than random-interaction nature.^{8,14,15} It would be very interesting to test these ideas also in other structural-glass systems²³ and in connection with possible imperfection-induced pretransitional behavior at second-order or weakly first-order structural phase transitions in crystals.²⁴

A detailed discussion of the possibilities outlined here together with complete accounts of experiments and analyses of static and dynamic elastic behavior in the present $A(\text{CN})X_{1-x}$ mixtures will be presented elsewhere.

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