

Dipolar Reorientation and Order-Disorder Behavior of Pure and Mixed Alkali Cyanides

Fritz Lütty and Jaime Ortiz-Lopez^(a)

Physics Department, University of Utah, Salt Lake City, Utah 84112

(Received 8 December 1982)

A simple empirical relation connects the critical temperature of the order-disorder transition T_c to the dipolar reorientation rate $\tau^{-1}(T)$ of CN^- molecules by the concept of a critical reorientation rate $\tau_c^{-1}(T_c)$. This relation is derived from experimental data on four pure alkali cyanides, the dipole-diluted $(\text{KBr})_{1-x}:(\text{KCN})_x$ system, and the mixed alkali cyanides $(\text{KCN})_{1-x}:(\text{NaCN})_x$ and $(\text{RbCN})_{1-x}:(\text{KCN})_x$. The observed disappearance of the order-disorder transition at a certain x value occurs in all mixed systems, when the spread of relaxation rates exceeds a particular value.

PACS numbers: 64.70.Kb, 77.40.+i, 77.80.-e

The study of the reorientation and ordering behavior of diatomic molecules in ionic solids is a field of intense current interest. CN^- molecular ions have become phototypical model cases in these studies, because they can be incorporated—in connection with alkali and halide ions—into a variety of regular and irregular solid-state structures. The case of a regular CN^- sublattice—the pure alkali cyanides—is characterized at high temperatures by an orientationally disordered structure, which transforms by a first-order transition at T_c into a state of parallel (ferroelastic) order.¹ Dilution of the CN^- dipole concentration by halide substitution—in systems such as $(\text{KCN})_x:(\text{KBr})_{1-x}$ —shifts T_c gradually to lower temperatures, until at a critical CN^- concentration x_c all measurable indications of a long-range order disappear abruptly (observed first in mixed $\text{KCl}:\text{KCN}$).² It has been speculated that systems with $x < x_c$ freeze under cooling into a glasslike structure of dipolar disorder and electric and elastic spin-glass behavior.³ This spin-glass aspect has attracted recently a great deal of experimental and theoretical interest in these systems.^{4,5} We have extended these studies for the first time to a new class of disordered materials by producing continuous mixture between different alkali cyanides such as $(\text{KCN})_{1-x}:(\text{NaCN})_x$. In these mixed crystals, the CN^- sublattice is essentially preserved, but becomes interspaced (and strongly perturbed) by a disordered sublattice of large and small cations.

In all the above-mentioned systems, we have studied the order-disorder and reorientation behavior of CN^- ions with dielectric, Raman, calorimetric, and optical techniques. From this extended material, which will be published in detail, we present here selected results about two fundamental properties, (a) the dipolar reorientation

rate as a function of temperature, $\tau^{-1}(T)$, and (b) the critical temperature T_c of the ferroelastic order-disorder phase transition [measured by the discontinuity of both the dielectric constant $\epsilon(T)$ and the optical transmission of the sample].

In Fig. 1, we summarize for the *pure alkali cyanides* the measured electric dipole reorientation rate τ^{-1} , plotted logarithmically against the inverse temperature. The center part in the 10^2 – 10^6 -sec⁻¹ range is data from our dielectric measurements, in which $\tau^{-1}(T)$ has been obtained from the maxima of measured loss peaks $\epsilon''(\omega, T)$. (KCN and RbCN data—of lower accuracy

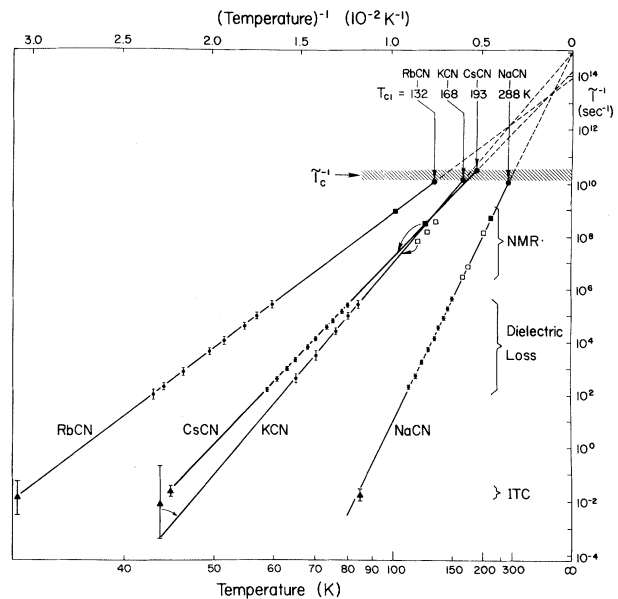


FIG. 1. Arrhenius plot of the dipole reorientation rate τ^{-1} of four pure alkali cyanides, measured with ITC, dielectric, and NMR techniques (open squares, Ref. 6; closed squares, Ref. 7).

cy—have been published previously by us.^{8,9)} The loss peaks are only slightly broader than ideal Debye curves; the bars in Fig. 1 indicate the small spread of relaxation rates. Extensions of these measurements to low temperatures with ionic thermal conductivity (ITC) techniques in our laboratory,¹⁰ and to high temperatures with NMR techniques^{6,7} extend the covered frequency range considerably. For each material the data can be fitted over a frequency range of eleven decades by a single Arrhenius expression yielding activation energy and attempt frequency for the dipole reorientation. An amazing empirical relation results from these data, as shown in Fig. 1. The extrapolated Arrhenius plots intersect for each material the critical temperature T_c at approximately the same relaxation rate (shaded area) within the experimental accuracy. Obviously each system changes under heating from the elastically ordered to the disordered structure, when the dipole relaxation rate reaches a critical value of $\tau_c^{-1} \approx 2 \times 10^{10} \text{ sec}^{-1}$.

Under dilution of the dipole concentration x from 1 to 0 in the $(\text{KBr})_{1-x}:(\text{KCN})_x$ system, the critical temperature T_c shifts continuously from 168 to ~ 80 K, until at x_c all physical manifestations¹¹ of the order-disorder transition disappear abruptly at $x_c \approx 0.60$ (Fig. 2) Parallel measurements of the dipolar reorientation with dielectric loss techniques yield Arrhenius behavior with activation energy and the attempt frequency val-

ues decreasing monotonically towards lower x .¹² Extrapolation of the determined Arrhenius expressions to the same critical reorientation rate, $\tau_c^{-1} \approx 2 \times 10^{10} \text{ sec}^{-1}$, as determined in Fig. 1, yields by our empirical relation "calculated" T_c values, as indicated by open circles in Fig. 2. They fit amazingly well the measured $T_c(x)$ behavior; however, they continue to "predict" T_c values below x_c where no ordering is observed any more.

With the same techniques and approach we have studied the new mixed systems $(\text{RbCN})_{1-x}:(\text{KCN})_x$ and $(\text{KCN})_{1-x}:(\text{NaCN})_x$. The results relevant to this paper are summarized in Fig. 3. In both mixtures a shift of T_c to low temperatures with increasing cationic disorder is observed. For the $(\text{RbCN})_{1-x}:(\text{KCN})_x$ system this shift is weaker, and a transition into an ordered state is observed under cooling throughout the whole mixture. For the $(\text{KCN})_{1-x}:(\text{NaCN})_x$ the shift of T_c to low temperatures is extremely strong, and a transition to an elastically ordered state is observed only close to the pure compounds at $0 \leq x < 0.1$ and $0.85 < x \leq 1$. Evidently, the elastic dipole interaction between CN^- ions becomes very effectively overpowered by the competing elastic interaction due to the interspaced disordered sublattice of large and small cations. Therefore, from a certain critical concentration of cationic disorder x_c , the molecular system can no longer achieve a state of collective

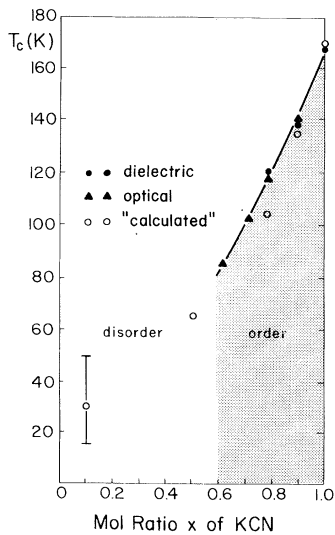


FIG. 2. Critical temperature T_c of ferroelastic phase transition in $(\text{KBr})_{1-x}:(\text{KCN})_x$, measured with dielectric and optical techniques and calculated from reorientation rate τ^{-1} .

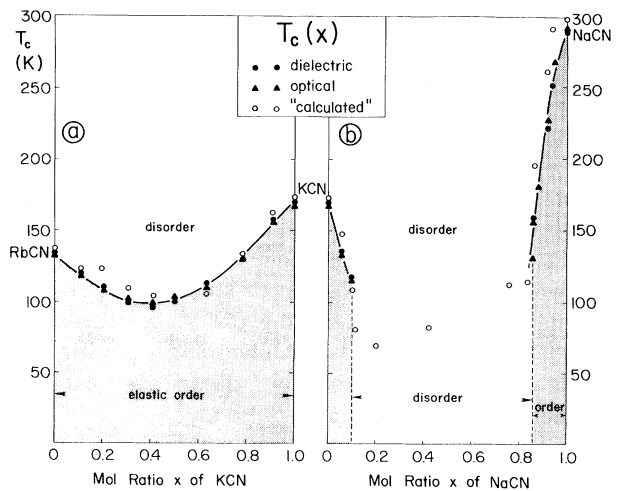


FIG. 3. Critical temperature T_c of ferroelastic phase transition for (a) $(\text{RbCN})_{1-x}:(\text{KCN})_x$ and (b) $(\text{KCN})_{1-x}:(\text{NaCN})_x$, measured with dielectric and optical techniques and calculated from dipole reorientation rate τ^{-1} .

long-range order, but will gradually freeze under cooling into an orientationally disordered state. For all mixed systems, displayed in Fig. 3, we have determined with dielectric loss measurements $\epsilon''(\omega, T)$, the Arrhenius reorientation rate $\tau^{-1}(T)$, and determined the mean activation energies $U(x)$ and attempt frequencies $\tau_0^{-1}(x)$. Extrapolation to our critical reorientation rate τ_c^{-1} yields again predicted T_c values according to

$$kT_c(x) = \frac{U(x)}{\ln\tau_0^{-1}(x) - \ln\tau_c^{-1}} \quad (1)$$

plotted as open circles in Fig. 3. The agreement with the measured $T_c(x)$ behavior of the $(\text{RbCN})_{1-x} : (\text{KCN})_x$ system is perfect. For the $(\text{KCN})_{1-x} : (\text{NaCN})_x$ case, the strong temperature shift T_c with increasing disorder is very well represented; however, we obtain (as in Fig. 2) "predicted" T_c values also in the regime of x where no transition is actually observed. It should be pointed out that the T_c variation [Eq. (1)] is produced for the systems in Figs. 1 and 2 mostly by variation in U ; for the systems in Fig. 3, however, it is produced mostly by a strong $\tau_0^{-1}(x)$ variation.¹⁰

Our empirical relation between dipole reorientation and ordering temperature should become questionable when the dipole reorientation rate becomes very nonuniform as it is indeed observed in all the mixed systems under increasing disorder: As Fig. 4 illustrates, the half-width of the dielectric loss $\epsilon''(\omega)$ increases from the Debye width (\sim one order of magnitude) for the pure crystals to very high values (up to eleven orders of magnitude), a behavior characteristic

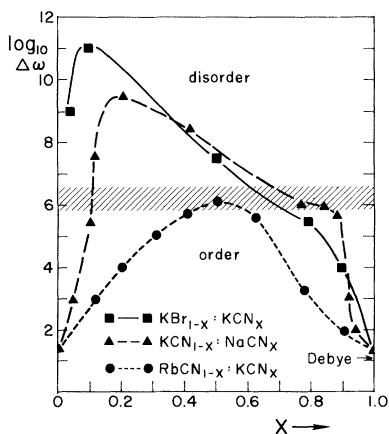


FIG. 4. Dielectric loss width (logarithmic) for three mixed cyanide systems as a function of mixture ratio x .

of spin-glasses. An empirical criterion for the necessary cutoff of the phase transitions at x_c is supplied by the data in Fig. 4, if we assume a critical width for the dielectric loss of about six orders of magnitude. For relaxation distribution width below this critical value, Eq. (1) can be applied and an order-disorder transition is present at T_c ; for widths above this value, no phase transition is observed. While $(\text{RbCN})_{1-x} : (\text{KCN})_x$ lies barely below this critical line and shows phase transitions over the whole mixture range, the $(\text{KBr})_{1-x} : (\text{KCN})_x$ and $(\text{KCN})_{1-x} : (\text{NaCN})_x$ systems cross the critical line (within the shaded range of accuracy) at the observed x_c values, dividing the mixture into a regime of collective ordering and orientational disorder, as observed.

The question for the physical origin and significance of the two empirical "critical" relations remains essentially unanswered at this stage. The constancy of τ_c^{-1} under host-material variation, observed in seven pure and mixed systems with widely varying physical properties, suggests a relation of τ_c^{-1} to a CN^- molecular property. We note that its value $\tau_c^{-1} \approx 2 \times 10^{10} \text{ sec}^{-1}$ lies very close to the rotational constant $B = \hbar^2 / (4\pi I)$ (I is the moment of inertia) of the CN^- molecule. (The analysis of the hindered rotational motion of CN^- defects in alkali halides with the Devonshire model^{13,14} yielded an effective value of $B = 3.0 \times 10^{10} \text{ sec}^{-1}$, somewhat lower than the free-molecule value.) This close coincidence of τ_c^{-1} and B indicates—purely phenomenologically—that the order-disorder transition occurs when the lifetime broadening (due to rapid reorientation) of the CN^- orientational states is comparable to the lowest-energy splitting of the quantized CN^- rotor.

In summary, we have shown that a provocatively simple two-parameter model can describe the complex order-disorder $T_c(x)$ properties of CN^- molecules in a large variety of regular and irregular lattices with amazing precision. It remains as a challenging task to the theory to find a foundation and interpretation for this empirical model, and to the experiment, to test its validity in other materials with molecular reorientation and order-disorder properties.

This work was supported by the National Science Foundation under Grant No. 81-05332, and was also partially supported by the Consejo Nacional de Ciencia y Tecnologia de México.

(a) On leave from Escuela Superior de Física y Ma-

temáticas, Instituto Politécnico Nacional, Mexico City, Mexico.

¹H. Suga, T. Matsuo, and S. Seki, *Bull. Chem. Soc. Jpn.* **38**, 1115 (1965).

²D. Durand and F. Lüty, *Ferroelectrics* **6**, 205 (1977).

³K. H. Michel and J. M. Rowe, *Phys. Rev. B* **22**, 1417 (1980).

⁴S. Bhattacharya, S. R. Nagel, L. Fleishman, and S. Susman, *Phys. Rev. Lett.* **48**, 1267 (1982).

⁵A. Loidl, R. Feile, and K. Knorr, *Phys. Rev. Lett.* **48**, 1263 (1982).

⁶H. T. Stokes, T. A. Case, and D. C. Ailion, *Bull. Magn. Reson.* **2**, 231 (1981).

⁷W. Buchheit, S. Elschner, H. D. Maier, J. Petersson, and E. Schneider, *Solid State Commun.* **38**, 665 (1981), and private communications.

⁸M. Julian and F. Lüty, *Ferroelectrics* **16**, 201 (1977).

⁹Y. Kondo, D. Schoemaker, and F. Lüty, *Phys. Rev.* **19**, 4210 (1979).

¹⁰J. Ortiz-Lopez, M. Siu Li, and F. Lüty, to be published.

¹¹S. K. Satija and C. H. Wang, *Solid State Commun.* **28**, 617 (1978).

¹²Dielectric data on the $(\text{KBr})_{1-x}:(\text{KCN})_x$ system were first reported by us at the Proceedings of the International Conference on Defects in Insulating Crystals, Riga, 1981 and published in *Defects in Insulating Crystals*, edited by V. M. Turkevich and K. K. Shvarts (Springer-Verlag, Berlin, 1981), pp. 69–89. Similar data (for certain x values) were reported later in Refs. 4 and 5.

¹³V. Narayanamurti and R. O. Pohl, *Rev. Mod. Phys.* **42**, 201 (1970).

¹⁴H. U. Beyeler, *Phys. Rev. B* **11**, 3078 (1975).