

Dipolar Reorientation and Phase Transitions in Mixed Alkali-Halide-Alkali-Cyanide Crystals

James P. Sethna^(a)

Institute for Theoretical Physics, University of California, Santa Barbara, California 93106

and

Sidney R. Nagel

James Franck Institute and Department of Physics, University of Chicago, Chicago, Illinois 60637

and

T. V. Ramakrishnan

Department of Physics, Indian Institute of Science, Bangalore, 560012 India

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We show that the results of Lüty and Ortiz-Lopez relating the cyanide reorientation rates to the high-temperature phase diagrams of alkali-halide-alkali-cyanide mixed crystals can be understood within simple mean-field theory.

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Lüty and Ortiz-Lopez¹ studied the dielectric response in several cyanide-doped alkali-halide samples in which the cyanide replaces the halide at random. De Yoreo *et al.*² have shown that such disordered crystals possess most of the characteristic low-temperature features of glasses; the CN⁻ ions appear to form tunneling centers which dominate the specific heat and thermal transport below 10 K. However, the high-temperature behavior, in particular the existence of a spin-glass transition, is still controversial.³⁻⁷ Lüty and Ortiz-Lopez¹ presented two intriguing experimental observations relating the high-temperature phase diagrams to the CN⁻ reorientation rates.

In the pure alkali cyanides, there is a first-order ferroelastic phase transition, at temperature T_f , which ranges from 132 K for RbCN to 288 K for NaCN. This transition is associated with a freezing of the quadrupolar order in the cyanides where the orientation axis remains fixed but the molecule can still flip by 180°. Lüty and Ortiz-Lopez showed that the temperature dependence of this rate follows an Arrhenius form in every system. They extrapolate the Arrhenius expression to find the rate at T_f . Their first observation is that, within a factor of 2, this rate is 2×10^{10} rad sec⁻¹ *independent of material*. Moreover, weakly disordered samples also appear to have first-order transitions at lower temperatures. These samples have the same relaxation rate at the transition.

Three questions immediately arise. The existence of a critical relaxation rate suggests the possibility that the dynamics of quadrupole relaxation influences the static properties of the transition. Is

this the case? (We suggest below that it is not.) Why is the rate independent of material? Why is the rate so slow and in particular why is it 2×10^{10} sec⁻¹? (Debye frequencies are two orders of magnitude higher; the measured Arrhenius prefactors are four orders of magnitude higher.) Lüty and Ortiz-Lopez propose to answer the last two questions by associating this frequency with the weakly hindered quantum rotor frequency ($\hbar/4\pi I$) for the CN⁻ molecule, which is very close to 2×10^{10} sec⁻¹. We believe that this is a coincidence. The phase transition temperatures are high compared to $0.15 \text{ K} = \hbar(2 \times 10^{10})/k_B$; even if the rotor were weakly hindered, it would act classically at these temperatures.

We believe that the rate is independent of material because the barrier height, E_b , is primarily due to the same forces which drive the transition and determine T_f . In order for a CN⁻ ion to reorient 180°, it must pass through an energy barrier which in pure KCN is 160 meV.⁸ E_b is created partly from quadrupolar interaction forces and partly from the crystalline anisotropy. The latter is small; for dilute CN⁻ in KBr the barrier height (entirely due to crystal-field splitting) is 0.5 meV. To flip over, the CN⁻ ion must pass through orientations which are not aligned with the neighboring ions. The energy barrier to *dipolar* reorientations depends upon the *quadrupolar* interaction energies. Thus (if we neglect the small contribution of the crystalline anisotropy to the barrier height) both E_b and the phase transition temperature T_f are linearly proportional to the magnitude of the interaction force and thus proportional to each other. The rate at T_f

would thus be insensitive to composition since only the prefactor to the exponential will vary between materials. These solids are very similar and most characteristic phonon frequencies will vary only by about a factor of 2.

We can make this more precise, and explain why the rate is so slow, by studying the mean-field theory of the transition.⁹ The interaction energies involving the site a are approximated by an effective field:

$$-\left[\sum_b R_{ijkl}(\vec{r}^a - \vec{r}^b) n_i^b n_j^b\right] n_k^a n_l^a \simeq -\bar{R}_{ijkl} Q_{ij} n_i^a n_j^a, \quad (1)$$

where \vec{r}^a and \hat{n}^a are the position and orientation direction, respectively, of the molecule at site a . $\bar{R}_{ijkl} = \sum R_{ijkl}(\vec{r})$, and in a crystal with cubic symmetry it has three independent components \bar{R}_{xxx} , \bar{R}_{xxy} , and \bar{R}_{xyx} . Q_{ij} is the average quadrupole moment $\langle n_i n_j \rangle_b - \frac{1}{3} \delta_{ij}$ (the trace of Q couples only to n^2 and adds a constant to the energy). The deviation from complete isotropy $\bar{R}_{xxx} - \bar{R}_{xxy} - \bar{R}_{xyx}$ determines the axis of ferroelastic order. It will not be important to include this for our purposes and would complicate our algebra; for simplicity we choose $\bar{R}_{xyx} = \bar{R}_{xxx} = R$ and $\bar{R}_{xxy} = 0$, so that the effective coupling to $n_i^a n_j^a$ is $R Q_{ij}$.

The mean-field solutions will be uniaxial; because we chose R to be isotropic, we can choose the axis to be \hat{z} :

$$Q_{ij} = 3\alpha \delta_{i3} \delta_{j3} - \alpha \delta_{ij}. \quad (2)$$

We can solve self-consistently for α .⁹ The results are shown in Fig. 1. The barrier E for the rotation of a molecule from \vec{z} to $-\vec{z}$ is $3\alpha R$. At low temperatures $E(T) \sim R - \frac{3}{2}kT$, which gives an effective Arrhenius law for the relaxation rate:

$$\Gamma = \omega e^{-E(T)/kT} \simeq (\omega e^{3/2}) e^{-R/kT} = \omega_0 e^{-R/kT}. \quad (3)$$

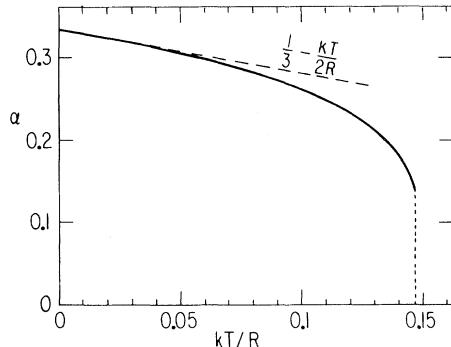


FIG. 1. Mean-field order parameter, α , as a function of temperature. The linear dependence of α on T at low temperatures leads to an effective Arrhenius law.

Thus the experimentally measured prefactor ω_0 will be $e^{3/2}$ times the microscopic attempt frequency ω .

There is a first-order transition at $kT_f = 0.1468R$. The extrapolated relaxation rate at T_f is thus $\omega_0 e^{-6.81} = 1.1 \times 10^{-3} \omega_0$ within mean-field theory. Fluctuation effects for the nearest-neighbor Ising model in an fcc lattice lower¹⁰ T_f by a factor of 0.82. If we assume that the same correction can be used in this Heisenberg quadrupole model, the rate at T_f is $2.4 \times 10^{-4} \omega_0$. The extrapolated rate is low at T_f because the transition temperature is substantially smaller than the low- T barrier height. Moreover the quadratic term in $E(T)$ is unimportant in the frequency range probed by experiments as shown in Fig. 2; a plot of $\log \Gamma$ vs R/kT shows excellent Arrhenius (or linear) behavior until quite near T_f . If we choose $\Gamma(T_f) = 2 \times 10^{10} \text{ sec}^{-1}$ in order to fit the experiment we find that $\omega_0 \simeq 8.4 \times 10^{13} \text{ sec}^{-1}$ ($\omega_0 = 1.8 \times 10^{13} \text{ sec}^{-1}$ in mean-field theory) for the experimentally observable prefactor and $\omega \simeq 1.9 \times 10^{13} \text{ sec}^{-1}$ for the microscopic attempt frequency. Not only does this value for ω_0 agree well with the experimental values¹ but the attempt frequency itself is physically reasonable.

We can also gain a rough understanding of the effects of disorder using this approach.¹¹ In $(\text{KBr})_{1-x}(\text{KCN})_x$ the Br atoms have nearly the same volume as the CN^- molecules and act primarily to dilute the quadrupoles. Thus the strength

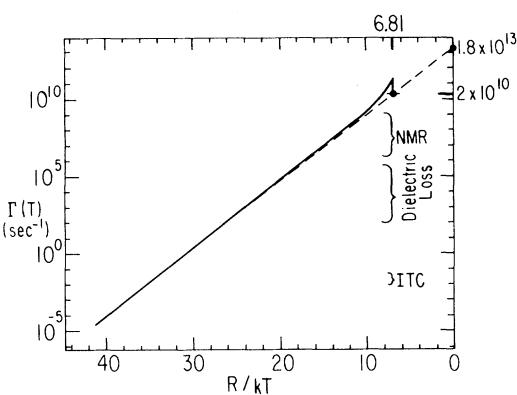


FIG. 2. Reorientation rate from mean-field theory. The CN^- dipolar reorientation rate is given [Eq. (3)] by the barrier height $E(T) = 3R\alpha(T)$, and thus is a direct measure of the magnitude $\alpha(T)$ of the quadrupolar order parameter (Fig. 1). Since the barrier height is temperature dependent, the rate is not strictly Arrhenius. However, since at low temperatures $E(T)$ is linear in T , there is an effective Arrhenius law over the entire range of experimental interest (dashed line). ω_0 in Eq. (3) was chosen to make the extrapolated value of $\Gamma(T_f) = 2 \times 10^{10} \text{ sec}^{-1}$. The frequency ranges where experiments have been performed are indicated.

of the mean-field coupling is reduced by a factor of x . This will not change the rate at T_f since both E_b and T_f are proportional to x in the diluted mean-field theory. This gives a good description of the KBr:KCN phase diagram (Fig. 2 of Ref. 1) as noted by Michel, Naudts, and De Raedt.⁹ In the systems with disorder in the alkali-metal sublattice [e.g., $(\text{KCN})_{1-x}(\text{NaCN})_x$], the environment of each CN^- is strongly perturbed. Presumably the cyanide will feel a strong random field, aligning it with its mixed alkali-metal neighbors. Although the random-field problem is not described with our mean-field theory, we are not surprised that the relationship between the apparent transition temperature and the barrier height persists.

Lüty and Ortiz-Lopez found that the samples with disorder in the alkali-metal sublattice have much larger values of ω_0 than do those where the disorder came from the dilution of the CN sublattice. This indicates that there may be a particularly strong temperature dependence to the barrier height below the transition for these samples. If $E_b(T)$ varies linearly with T , it is impossible to distinguish that dependence in the activation energy from an additional factor in the prefactor¹² (see above). Nevertheless the value of Γ extrapolated to the transition will be the same whether or not E_b varies linearly with T since $E_b(T = T_f)$ will still be proportional to the interaction strength and thus proportional to T_f .

This brings us to the second observation of Ref. 1. They find for weak disorder an apparent line of first-order phase transitions, which ends at a critical concentration. The width of the dielectric peak grows with disorder and reaches six orders of magnitude at each of the three critical concentrations where a first-order transition ends. There are several relevant issues we would like to discuss.

We note that, unlike a liquid-gas transition, the first-order line in this system cannot end inside the phase diagram.¹³ Since the ferroelastic phase has a broken symmetry, there must be a line separating it from the melted phase which denotes the restoration of the broken symmetry. There are three alternatives. First, there may be a transition line extending to zero temperature, separating the two phases. This is not supported experimentally, although it cannot be excluded. Second, disorder may destroy the ferroelastic phase immediately. This is not inconsistent with the experimental observation of a transition: For weak disorder, large clusters may align within a narrow band of temperatures and lead to a slightly broadened transition. Third, the disordered state may be metastable. It is

now thought that the equilibrium state of random-field Ising models in three dimensions has long-range order.¹⁴ On the other hand, it is known that in a large random field, the observed state found by cooling has clusters, and no long-range order; the domain state is reached first, and is metastable under further cooling on laboratory time scales even though long-range order is the equilibrium ground state. The existence of domains may be important for the ferroelastic state as well. In our system the random field is due to the locally distorted alkali-metal lattice and exists on cooling even without an externally applied field. The end of the critical line may correspond to where the internal relaxation times are too slow compared to the laboratory time scales for the system to find its true ground state. This would be consistent with measurements¹² on the distribution of times in $(\text{KBr})_{0.5}(\text{KCN})_{0.5}$ which show a temperature dependence of the width of the barrier distribution as well as possible T dependence to the average value of E_b .

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^(a)Permanent address: Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, N.Y. 14853.

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