Anisotropy of the Electrostatic Interactions and the Properties of Orientationally Disordered Cyanide Crystals

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Molecular-dynamics calculations have been used to investigate the role played by anisotropic electrostatic interactions in determining the structure and dynamics of the high-temperature phase of solid KCN. Good agreement with experimental Raman, NMR, and neutron data can be achieved if it is assumed that the charge distribution of $(CN)^-$ in the crystal corresponds to a quadrupole moment which is much smaller than that of the free ion.

This Letter draws attention to a previously unsuspected role played by the electrostatic charge distribution of the $(CN)^-$ ion in determining the structural and dynamic properties of alkali cyanide crystals. All previous theoretical work has ignored this effect, concentrating instead[1] on the short-range interactions between ions.

Most cyanide crystals exist in a high-temperature cubic structure (phase I) in which the $(CN)^-$ ions are undergoing rotational diffusion.[2] At lower temperatures, phase transitions occur to structures (phase II) in which the $(CN)^-$ ions align[3] (initially with dipoles disordered) along what was either the $\langle 110 \rangle$ direction (Na and K) or $\langle 111 \rangle$ direction (Rb) in the cubic phase I. At still lower temperatures, antiferroelectric ordering[4] may occur, but this effect will not concern us here. Various experimental techniques[2,5,6] have been used to obtain information on the orientational probability distribution $f(\vec{u})$ of the $(CN)^-$ ions in phase I, $\vec{u} = (x, y, z)$ being a unit vector directed along the C-N bond. Because of the cubic symmetry, $f(\vec{u})$ is conveniently expressed as an expansion[7] in the Kubic harmonics K_i of the form

$$f(\vec{u}) = (1 + c_4 K_4 + c_6 K_6 + \cdots)/4\pi.$$

The expansion coefficients c_i are ensemble averages of the K_i. In particular, $c_4 = \langle K_4 \rangle = \left(\frac{21}{16}\right)^{1/2} \times \langle 5(x^4 + y^4 + z^4) - 3 \rangle$. Neutron diffraction can be used to determine c_4 and to obtain an estimate of c_6, thereby giving information on the static structure of the crystal. On the other hand, polarized Raman spectra yield the Fourier transforms of time autocorrelations of the spherical harmonics $Y_2{}^m$ characterizing the orientation of the $(CN)^-$ ions. Thus the E_g and T_{2g} spectra[6] measure

$$R_{11}(t) = \sum \langle A_1(t) A_1^*(0) \rangle \quad (E_g),$$

$$R_{33}(t) = \sum \langle A_3(t) A_3^*(0) \rangle \quad (T_{2g}),$$

where $A_1 = Y_2{}^0$ and $A_3 = i(Y_2{}^2 - Y_2{}^{-2})$. In these definitions, the summations extend over all pairs of anions. However, since nearest-neighbor $(CN)^-$ ions are actually second neighbors in the crystal, it is common to consider only the contribution of the self terms.[6] The reorientation time τ_2 measured by NMR techniques[8] is then the normalized integral of the E_g component. The Raman spectra also yield values for $R_{11}(0)$ and $R_{33}(0)$ which are related to c_4 by simple numerical factors. The Raman experiments therefore complement the neutron work in probing the orientational order.

In view of the known structures of the low-temperature ordered phases, it might be expected that the experiments mentioned above would show that the $(CN)^-$ ions in phase I favor $\langle 110 \rangle$ orientations in NaCN and KCN and $\langle 111 \rangle$ in RbCn. However, it seems well established[2,5,6] that on cooling the crystals, $f(\vec{u})$ tends to peak more strongly in the $\langle 100 \rangle$ direction and that this tendency is greatest in NaCN, less in KCN, and least in RbCN. There is a similarly systematic trend in the shapes of the Raman spectra. Moreover, as the transition temperature is approached, a pronounced softening of the shear constant C_{44} has been observed,[9] with a concomitant anomalous dispersion[10] of the TA-phonon branch propagating along $\langle 100 \rangle$. This behavior has been interpreted[1,11] as arising from a coupling of the translational motion of the ions to the $(CN)^-$ reorientations.

Translation-rotation coupling also manifests it-self in the appearance of central peaks in the dynamical structure factor when the inverse of the reorientation time becomes comparable with the appropriate phonon frequency.[11] Detailed theories of the influence of translation-rotation coupling on the structure and dynamics have been presented,[1,11] formulated in terms of an indirect $(CN)^-$-$(CN)^-$ interaction, and shell models have been adapted to allow for such effects.[5] These phenomenological approaches have aided the interpretation of experimental data but, to date, no microscopic basis exists for determining the key parameters which enter the theory. Moreover, given the behavior of C_{44}, an explanation is required as to why it is the E_g Raman spectrum and not the T_{2g} which develops a central peak on cooling.[6] It must also be asked why $\langle 100 \rangle$ orientations are favored.[2,5] Steric effects presumably oppose the tendency[12] of isolated $(CN)^-$ ions to lie along $\langle 100 \rangle$.

This Letter reports the main results of a series of molecular-dynamics (MD) simulations for models of KCN, taken as a representative cyanide crystal, which have been carried out in an attempt to cast light on the problems outlined above. The purpose of the work thus far has not been to perfect a model for KCN, but to consider certain general properties of a class of model interionic potentials. For this reason, we have used the rigid-ion approximation, notwithstanding its known limitations in the study of ionic crystals. Each of the MD runs was started from a NaCl-like structure of appropriate lattice constant,[9] with the $(CN)^-$ ions given initial random $\langle 111 \rangle$ orientations. The motion of the ions was then followed for several thousand time steps of 0.006 ps. Short-range interactions between the ions were represented by atom-atom Born-Mayer potentials constructed from parameters in the literature[13] and the charge distribution of $(CN)^-$ was modelled by fractional negative charges placed on the C and N atoms and a further charge at the center of mass such that the total charge was $-|e|$. Calculation of the electrostatic energies and forces was handled by the Ewald method and essentially the same results were obtained for systems of both 64 and 216 ions.

MD calculations were made for various anion charge distributions having electrostatic quadrupole moments (measured with respect to the center of mass) ranging from the free-ion value[14] of $\theta_0 = -4.63$ D Å to zero; the dipole moment was small, being 0.3 D or less. Runs were also car-

TABLE I. Kubic harmonic expansion coefficients and NMR reorientation times for phase-I KCN. $\theta_0 = -4.63$ D Å (Ref. 14). Figures in parentheses are the experimental uncertainties.

θ/θ_0	T (K)	c_4	c_6	c_8	τ_2 (ps)
0.91	295	-0.44	0.05	0.12	0.06
	185	-0.68	0.25	0.22	0.07
0.65	305	-0.31	0.02	0.10	0.06
	177	-0.49	0.09	0.16	0.07
0.37	315	0.03	-0.04	0.05	0.16
	186	0.19	-0.04	0.05	0.45
Expt.[a]	295	$-0.13(2)$	0.23(18)	$\cdots$	0.15
	180	$-0.02(2)$	0.22(14)	$\cdots$	0.38
$\langle 100 \rangle$ order		2.29	1.27	2.96	
$\langle 110 \rangle$ order		-0.57	-2.07	1.67	
$\langle 111 \rangle$ order		-1.53	2.27	0.88	

[a]Ref. 2.

ried out to explore the effect of changing the C-N bond length from 1.15 to 1.19 Å and of making modest changes in the coefficients of the atom-atom potentials. Within the context of the class of model we have studied, our main conclusion is that θ is the most important single parameter determining the structure and dynamics of the disordered phase.

The temperature dependence of the coefficients c_i which characterize the distribution $f(\vec{u})$ is shown for three particular models in Table I, together with the corresponding NMR reorientation times τ_2. The main structural information is contained in c_4, for which the model results display a clear trend towards $\langle 111 \rangle$ order as $\theta \to \theta_0$ and towards $\langle 100 \rangle$ order as $\theta \to 0$. Figure 1 shows the E_g and T_{2g} Raman spectra for the same three models at temperatures of approximately 300 K. When $\theta/\theta_0 \sim 1$, the spectra resemble in their qualitative features those observed[4] for RbCN. However, as θ decreases from its free-ion value, the E_g spectrum becomes less structured and the T_{2g} more so. By interpolation, a reasonable correspondence with the experimental curve for KCN would occur for $\theta/\theta_0 \sim 0.5$. The same conclusion regarding the magnitude of the effective quadrupole moment can be drawn from consideration of the behavior of the Kubic harmonic coefficients and NMR correlation times given in Table I. The growth in c_4 and pronounced lengthening of τ_2 which accompany a reduction in θ/θ_0 both greatly improve the agreement with experiment. The results for c_6 are less convincing but in this case the experi-
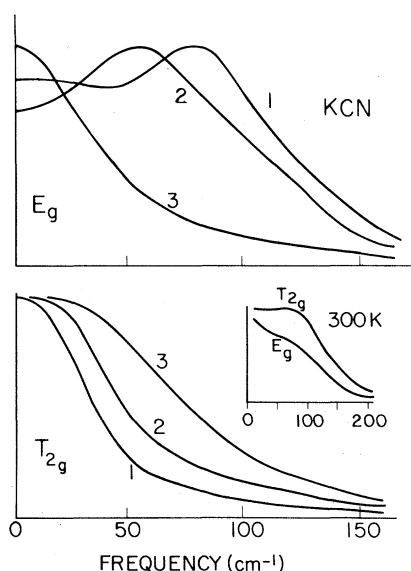
FIG. 1. Self contribution to the Raman scattering from phase-I KCN as a function of θ, the quadrupole moment of the $(CN)^-$ ion. The curves labeled 1, 2, and 3 correspond, respectively, to $\theta/\theta_0 = 0.91$, 0.65, and 0.37, where θ_0 is the free-ion value. For clarity the spectra are shown with equal peak heights. The inset shows the experimental spectra from Ref. 6.

FIG. 2. The variation of the Kubic-harmonic expansion coefficient c_4 for phase-I KCN with θ, the quadrupole moment of the $(CN)^-$ ion. The open circles labeled 1, 2, and 3 correspond, respectively, to $\theta/\theta_0 = 0.91$, 0.65, and 0.37, where θ_0 is the free-ion value. The solid circles explore the effect of changing the parameters in the atom-atom potentials and/or the $(CN)^-$ bond length. Both open and solid circles are for $T \approx 300$ K. The effect of cooling from approximately 300 to 180 K is indicated by the arrows. The curve is a guide to the eye.

mental uncertainties are large. The variation of c_4 with θ/θ_0 is shown in more detail in Fig. 2. From the graph, there appears to be a critical value of θ/θ_0 below which cooling takes the $(CN)^-$ ions out of $\langle 111 \rangle$ pockets into $\langle 100 \rangle$ directions. Again, therefore, it is only when $\theta/\theta_0 \gtrsim 0.5$ that the model behaves in a fashion resembling that of real KCN (see Table I). Finally, the effects of changes in the atom-atom potentials are minor in comparison with those brought about by changes in θ.

In summary, we have found that the polarized Raman spectra, NMR correlation times, and neutron structural data for phase-I KCN can be understood qualitatively on the basis of the type of model used in the MD simulations, provided that the quadrupole moment of $(CN)^-$ in the crystal is considerably reduced with respect to its free-ion value. This finding is not without precedent. It has been recognized for some time[15] that in ionic solids the crystal potential causes a shrinkage in the size (and polarizability) of anions. This would necessarily cause a reduction in the effective quadrupole moment of the ion. The subtle differences in behavior between the cyanides of Rb, K, and Na must ultimately
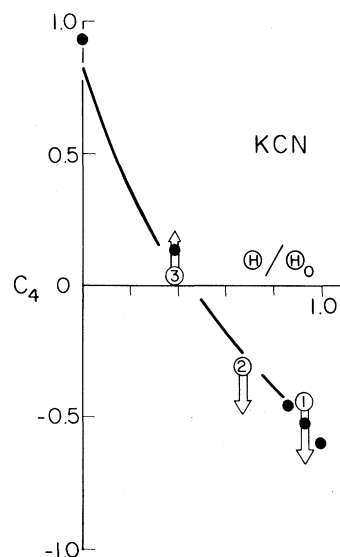
depend on the details of the interionic potentials. In this regard, it should be noted that the cell volume available to $(CN)^-$ decreases with the size of the cation, so that the anion shrinkage effect referred to above will be greatest for NaCN and least for RbCN. We therefore have a possible mechanism for explaining the observed systematic trends in the properties of the various cyanides. In any event, it is clear that no theory of the orientational order in cyanide crystals can be considered complete if it fails to take account of the effect of the crystal field on the charge distribution of the cyanide ion.

In future work, we plan to extend the scope of the MD calculations to include the dynamical structure factor,[10] diffuse scattering,[16] and properties of the low-temperature phases.[4]

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[12]We have found in self-consistent-field calculations on (CN)⁻ ions in an octahedral cage of positive charges that, with respect to the free ion, orientation along $\langle 100 \rangle$ results in an increase and orientation along $\langle 110 \rangle$ or $\langle 111 \rangle$ to a decrease in the dipole and quadrupole moments.

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Commensurate-Incommensurate Transitions in Two Dimensions: Discrete Models and Square Symmetric Substrates

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The phase diagram and the critical behavior of a discrete two-dimensional model of the commensurate-incommensurate transition is determined with use of an approximate mapping onto the six-vertex model. For an uniaxial substrate the critical behavior is that of the continuum case. For a square substrate either a single first-order transition or a second-order transition followed by a first-order transition is found.

In adsorbed gas monolayers phase transitions between commensurate (C) and incommensurate (IC) structures have been observed,[1-6] both of first and second order. Current theories of these transitions are either restricted to $T = 0$[7-9] or assume a substrate potential periodic only in one of two space directions,[9-11] and use a continuum approximation for the layer. Near the C-IC transition the IC state consists of large C regions separated by domain walls. The critical behavior of the transition is dominated by the walls. In the continuum models the walls can move freely; however, if the discrete nature of the layers is taken into account a periodic potential acts on the walls. At $T = 0$ this leads to the appearance of infinitely many C phases, the so-called devil's staircase.[12] In this paper discrete models of the C-IC transition at $T \neq 0$ are treated