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Electric-dipole ordering in alkali cyanides: NaCN and KCN

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We present a simple model for the low-temperature electrically ordered state of NaCN and KCN. The model takes into account electric-dipole dressing effects, which include cationic displacements determined experimentally. The ground-state structure and calculated values for the local electric fields are in fair agreement with experimental results. A parametrization for the elastic potential confirms the plausibility of our model.

I. INTRODUCTION

The study of reorientation and collective ordering processes of linear molecular ions $(XY)^-$ in ionic solids of the type $M^+(XY)^-$ is a field of intense current interest. Among the many compounds of this type, the pure alkali cyanides (NaCN, KCN, RbCN, and CsCN) are prototypical model cases which have been extensively investigated recently both experimentally and theoretically.

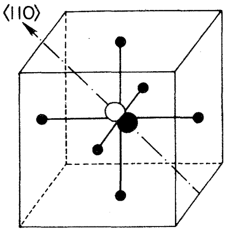
Reorientation and ordering in these compounds involves not only rotation of molecules within a rigid fixed lattice matrix, but involves sizeable deformations of the total (cationic and anionic) lattice due to the strong and anisotropic coupling of the molecular ion to its surrounding. This coupling effect has been extensively studied and clarified for the simpler case of diatomic molecular ions substituted in dilute form into cubic lattices like the alkali halides. It is useful to start considerations about the collective ordering of molecular sublattices from this *isolated molecular defect* case. The anisotropic properties of the molecular ion, replacing a spherical lattice ion, are of two types:

(a) An *"elastic dipole tensor"*[1] due to the nonspherical shape (elastic interaction) of the molecule.

(b) An *electric dipole vector,* due to the asymmetric head-and-tail charge distribution of the molecule.

(a) gives rise to a nonspherical gerade distortion around the defect; (b) gives rise to an ungerade distortion. Figure 1 illustrates this situation for the case of a ⟨110⟩-oriented molecular defect, substituted into a cubic lattice. The "bare dipolar defect" (A) becomes "dressed" with gerade (E_g+T_{2g}) distortions due to the elastic dipole properties (B), and with ungerade (T_{1u}) distortions due to its electric dipole property (C).[2] Under reorientation and alignment of the dipoles (which can be realized by elastic or electric fields at low temperatures), the E_g, T_{2g}, and T_{1u} distortions follow the dipole rotation and become aligned together with the dipoles. This strong "dressing effect" has profound influences on the tunneling and classical reorientational motion of molecular defects.[2]

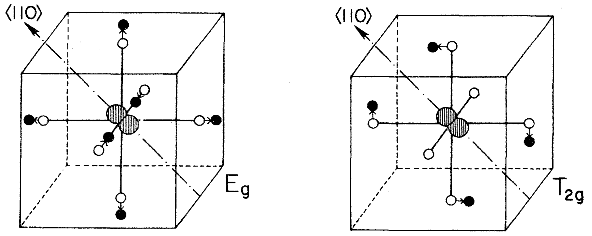
Isolated CN$^-$ defects are ⟨111⟩ oriented in potassium and rubidium halides, ⟨100⟩ oriented in sodium halides.[3] They are characterized by a strong elastic dipole moment (of pure T_{2g} or E_g symmetry for ⟨111⟩ or ⟨100⟩ orientation, respectively),[4] but carry only a weak electric dipole moment (measured as $p=0.07$ e Å in KCl hosts).[5] It is



⟨110⟩ Oriented Electric and Elastic Dipole Defect

(a) Without Lattice Distortions ("undressed")

(b) With Gerade Lattice Distortions ("Elastic Dipole Dressing")



(c) With Ungerade Lattice Distortions ("Electric Dipole Dressing")

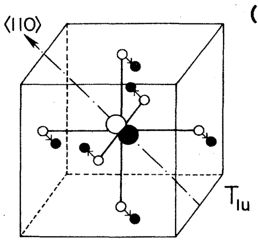


FIG. 1. Illustration of a ⟨110⟩ oriented molecular defect in a cubic lattice, in its "bare" state (a) and with elastic dipole (b) and electric dipole (c) dressing.

evident from the measured values that elastic interaction between CN$^-$ defects[6] should be much stronger than electric interaction.

We take these general ideas about isolated molecular defects and apply them to the case of a *molecular sublattice.* At high temperatures, the CN$^-$ dipoles in all four pure alkali cyanides are orientationally disordered and rapidly rotating. The microscopic distortions connected to the molecules are therefore disordered too, averaging out to a pseudocubic structure of the crystal. Owing to the strong elastic dipole character and interaction of CN$^-$ molecules (compared to the electric ones), the first ordering process under cooling in all four alkali cyanides is a purely elastic one. We discuss this—and the following—ordering processes first for the KCN and NaCN case, which is different from that of the other cyanides and much better investigated.

II. ORDERING IN KCN AND NaCN

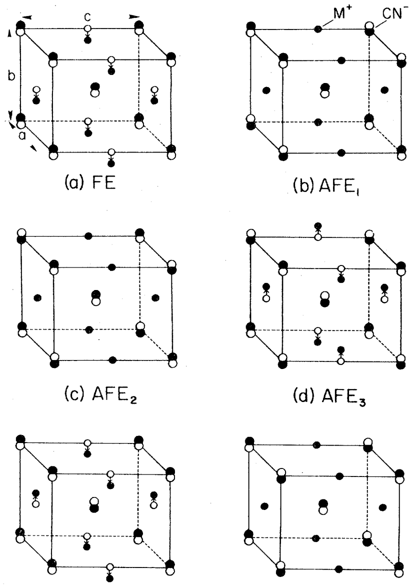
At a critical temperature T_{C1} of 288 and 168 K in NaCN and KCN, respectively, the CN$^-$ elastic dipole tensors align in a parallel way close to the $\langle 110 \rangle$ orientation of the originally cubic crystal *(ferroelastic ordering).* The accompanying alignment of the microscopic distortion fields of E_g and T_{2g} symmetry (Fig. 1) leads to macroscopic distortions of E_g and T_{2g} symmetry of the crystal, transforming it from a cubic into an orthorhombic structure. The size of the macroscopic crystal distortion [$\sim 6\%$ uniaxial (E_g) contraction and $\sim 11°$ T_{2g} shear angle in KCN] are typical distortion amplitudes, as expected for the nearest neighbors around a $\langle 110 \rangle$ oriented CN$^-$ molecular defect. These large macroscopic distortions are averaged out by the formation of a multidomain structure[7] at T_{C1}, such that the total crystal sample keeps its original shape, and—when averaged over all domain orientations—an effective macroscopic cubic character.

Within this elastically ordered state of orthorhombic domains, the electric dipoles are still free to execute reorientational motion between the two opposite dipole vector orientations. Under cooling the dipole reorientation rate slows down with a characteristic Arrhenius behavior.[8] The possible *ordering effects of the electric dipole system,* expected at some low temperatures, are the main subject of this paper.

For KCN and NaCN the onset of gradual electric ordering is observed at $T_{C2}=83$ and 172 K, respectively, in both cases at a temperature when the dipole reorientation rate reaches a value close to 10^6 sec^{-1}.[8] The ordering effect shows up experimentally by a gradual decrease of the dielectric susceptibility,[5] a specific-heat anomaly,[9] and a characteristic shift of the CN$^-$ stretching vibration observed in Raman or ir.[10]

Within the framework of the elastically ordered orthorhombic structure, a variety of periodic configurations for electric dipole ordering are possible in principle; Fig. 2 illustrates some of them. Figure 2(a) represents parallel "ferroelectric" dipole alignment, Figs. 2(b)—2(f) represent various possible configurations for antiparallel—antiferroelectric—dipole alignment.

Calculation of the electrostatic energy of the various electric dipole structures shown in Fig. 2 (neglecting any ion displacements)[11,12] yields the ferroelectric structure as the most favorable one. This result is in contradiction with neutron scattering results[13,14] which established for the ground state the AFE$_4$ type of antiferroelectric structure [Fig. 2(c)]. Recently Pirc and Vilfan[15] have shown that the inclusion of lattice displacements associated to dipolar ordering leads to the correct prediction for the ordered structure.



(a) FE (b) AFE$_1$

(c) AFE$_2$ (d) AFE$_3$

(e) AFE$_4$ (f) AFE$_5$

FIG. 2. Ordered dipolar configurations within orthorhombic structure; cationic displacements due to "electric dipole dressing" are indicated.

For an isolated electric dipole, the T_{1u} distortion field illustrated in Fig. 1(c) is its natural "dressing." Neutron scattering measurements[13,16] confirm that the ground-state structure involves the ordering of "dressed dipoles," i.e., dipoles accompanied by local ungerade lattice distortions, instead of the ordering of "bare dipoles" alone.

For a given bare dipolar configuration, the ungerade distortions of neighboring cells superimpose, and often cancel out. In Fig. 2 we indicate "collective" cation displacements compatible with the various ordered electric dipole configurations. In structures (b), (c), and (f) no such cation displacements along the b axis are allowed by symmetry.

III. THEORY

In the ground state of KCN and NaCN all CN$^-$ dipoles are known to be aligned along the b axis of the crystal. Their relative orientation may be specified by a $\vec{q}$ vector such that[12]

$$\vec{p}_j=\vec{p}_i\exp[i\vec{q}\cdot(\vec{r}_j-\vec{r}_i)] \ . \tag{1}$$

The bare dipolar interaction energy per CN$^-$ pair is given by a dipolar sum[12]

$$U_B(\vec{q})=p^2J(\vec{q})+\Delta U_{\mathrm{FE}}(\vec{p})\delta_{\vec{q},\vec{0}} \ , \tag{2}$$

where $\Delta U_{\mathrm{FE}}(\vec{p})$ is a correction due to macroscopic polarization effects which exist only in the ferroelectric structure.

Small cationic displacements give rise to local induced dipoles with moment $\vec{p}^*=e\vec{\Delta}$, where $\vec{\Delta}$ is the displacement vector, assumed to occur along the b-axis direction. Ungerade distortions generate an induced-dipole sublattice structure characterized by the same $\vec{q}$ vector as for the bare dipoles (see Fig. 2). The total electrostatic energy per pair of $(M^+\mathrm{CN}^-)$ molecules is then given by

$$U_D(\vec{q},\Delta)=p^2J(\vec{q})+2pp^*J^*(\vec{q})+p^{*2}J(\vec{q}) + \Delta U_{\mathrm{FE}}(\vec{p}+\vec{p}^*)\delta_{\vec{q},\vec{0}}\ , \qquad (3)$$

where the first term is the bare-bare, the second term is the induced-bare, and the third term is the induced-induced dipolar interaction, while the last term gives the macroscopic polarization effect.

In this model we do not consider anionic displacements because experimentally they are known to be negligible.[16] They could, however, be formally introduced by changing the value of p.

The equilibrium value of the cationic distortion Δ_0 corresponds to the value of Δ which minimizes the total energy

$$U_T(\vec{q},\Delta)=U_D(\vec{q},\Delta)+U_R(\Delta)\ , \qquad (4)$$

where $U_R(\Delta)$ is the repulsive elastic potential opposing the cationic displacements. We take for this potential a simple phenomenological form[17] such that the repulsive energy between nearest neighbors a distance R_{ij} apart is

$$U_{ij}=\lambda \exp\left[-\frac{R_{ij}}{\rho}\right]. \qquad (5)$$

The energy increase per $M^+\mathrm{CN}^-$ pair due to a collective distortion Δ in the b-axis direction is then

$$U_R=4\lambda\left[\exp\left[\frac{[(b-\Delta)^2+a^2]^{1/2}}{\rho}\right]-\exp\left[\frac{(a^2+b^2)^{1/2}}{\rho}\right]\right], \qquad (6)$$

where we assume for simplicity that only the two nearest-neighbor CN^- ions "react" to the cationic approach.

IV. RESULTS

In the calculations for NaCN and KCN we take $p=0.07\ e\,\text{Å}$ for the electric dipole moment of the CN^- ion,[5] and the values for the lattice parameters given in Table I. Results for the bare dipolar energy (2) for different structures are also given there. The slight discrepancy between the present results for KCN and those of Ref. 12 is due to the different values taken for the lattice parameters. Note that the experimentally observed structure, which corresponds to AFE_4 in Table I, is higher in energy than the ferroelectric (FE) and three other antiferroelectric structures (AFE_1, AFE_2, and AFE_3).

Cationic displacements are capable of drastically changing the ordering of energies above, as shown in Fig. 3, where electrostatic energies are presented for different dipolar arrangements (3) as a function of the displacement amplitude Δ. For both NaCN and KCN the AFE_4 structure becomes the most favorable electrostatically for $\Delta \gtrsim 0.01$ Å. This crossover value corresponds to less than 1% distortion in the b direction.

The AFE_4 energy decreases faster than it does for all other structures as Δ increases because it is the only ordered dipole configuration in which the ungerade distortions of the six surrounding cation neighbors of a single dipole is preserved. The resulting structure corresponds to a *constructive superposition of all the ungerade distortion fields around each permanent dipole.* In the AFE_3 structure there is partial destructive superposition, which causes its energy to decrease with Δ slower than for the AFE_4.

The behavior of the FE dipolar energy with Δ can be easily understood. For this structure the main contribution to U_D, for small Δ, comes from the macroscopic term $\Delta U_{\mathrm{FE}}(\vec{p}+\vec{p}^*)$, which is negative. Since $\vec{p}$ and $\vec{p}^*$ are antiparallel, the energy increases with Δ until $|\vec{p}^*|$ reaches $|\vec{p}|$, when local field effects become relevant. As Δ increases further, the macroscopic term dominates again causing the energy decrease.

For the experimentally observed values Δ_0 of the cationic distortions[16] in NaCN and in KCN given in Table II, the electrostatic energy of the AFE_4 structure is considerably lower than for any other structure. The calculated values of the local electric field at a CN^- site considering bare and dressed (total) dipolar contributions are also

TABLE I. Data for the low-temperature phase of NaCN and KCN.

			NaCN	KCN
Lattice parameters[a] (Å)		a	3.63	4.20
		b	4.85	5.27
		c	5.45	6.09
	$\vec{q}/\pi$	Structure	U_B (meV)	
Bare dipolar energy per CN^- pair	(0,0,0)	FE	−4.56	−4.01
	$(\pm 1/a, 0, \pm 1/c)$	AFE_1	−4.03	−2.93
	$(\pm 1/a, \pm 1/b, \pm 1/c)$	AFE_2	−1.56	−0.760
	$(\pm 1/a, \pm 1/b, 0)$	AFE_3	−1.13	−0.397
	$2(\pm 1/a, \pm 1/b, \pm 1/c)$	AFE_4	0.897	0.370
	$(0, \pm 1/b, \pm 1/c)$	AFE_5	4.44	3.20

[a] Taken from Ref. 16.

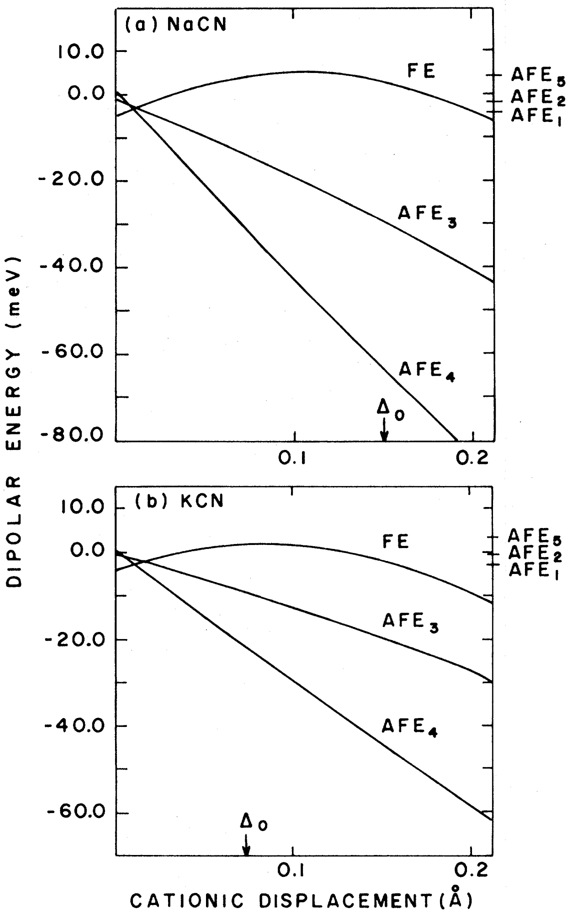


FIG. 3. Electrostatic dipolar energies as a function of the displacement amplitude for the ordered dipolar configurations shown in Fig. 2. Energies of the structures for which no collective cationic displacements occur are given in the right-hand side. The equilibrium displacement Δ_0 is indicated.

given in Table II. Note that lattice distortions "flip" the calculated local field towards the energetically favorable direction, as indicated by the sign change between the bare and dressed values for E_{loc} in Table II. Comparison of the calculated total field with those obtained experimentally by the CN^- stretching mode infrared absorption[10] shows fair agreement.

In order to test the plausibility of our model, the phenomenological elastic energy (6) must be added to the electrostatic energy. In Table III we give values of λ and ρ fitted[17] for the bromides NaBr and KBr. The Br^- ionic radius is, among the halides, the one which is closer to the average radius of the $(CN)^-$.

TABLE II. Cationic displacements and local electric fields at a $(CN)^-$ site.

		NaCN	KCN
Equilibrium displacement along b axis: Δ_0 (Å)[a]		0.15	0.073
E_{loc} (V/cm)	bare	-1.27×10^6	-5.29×10^5
	dressed	4.79×10^7	1.56×10^7
	experiment[b]	2.30×10^7	1.50×10^7

[a] From Ref. 16.
[b] From Ref. 10.

TABLE III. Parameters of the phenomenological repulsive energy U_R.

	NaBr[a]	KBr[a]	NaCN	KCN
2λ (eV)	5.54	9.6	5.54[b]	9.6[b]
ρ (Å)	0.328	0.336	0.275[c]	0.291[c]

[a] From M. P. Tosi, in *Solid State Physics*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1964), Vol. 16, p. 1, as quoted in Ref. 17.
[b] Taken to be the same as the corresponding bromide.
[c] Fitted to give equilibrium distortion.

In Fig. 4 we present the superposition of electrostatic and repulsive energy versus cationic displacement for KCN and NaCN. The value of λ is taken to be the same as for the corresponding bromide, while ρ is calculated by fitting the minimum of the curve to the observed equilibrium distortion. The required values of ρ are also given in Table III; they agree with the corresponding values for the bromides within 20%, which may be considered acceptable. The equilibrium energy value, however, should not be taken to be accurate, since it is based on a very simplified model. For KCN in particular it would predict an

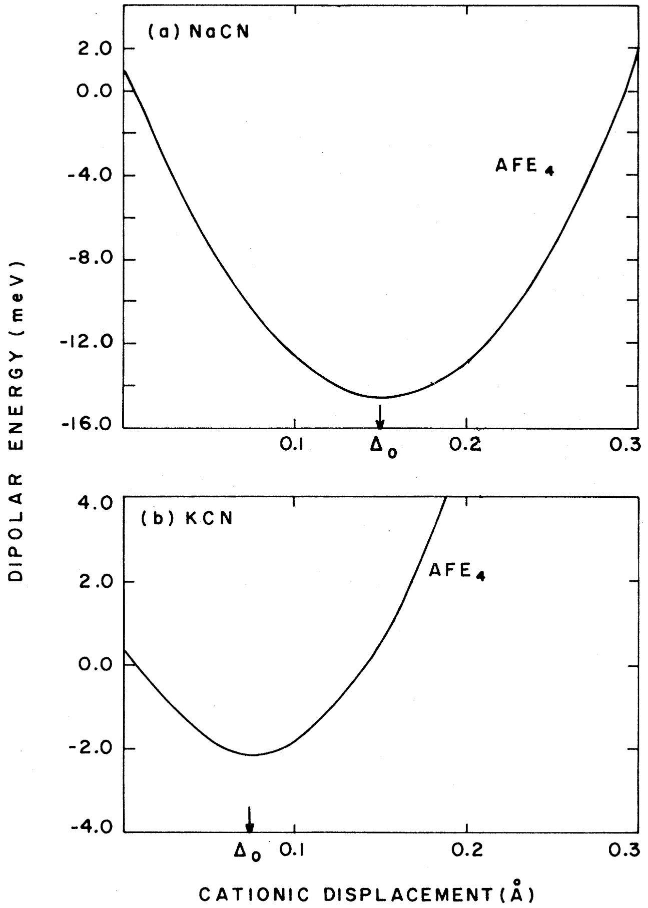


FIG. 4. Superposition of electrostatic dipolar and repulsive energy as a function of the displacement amplitude for the AFE_4 structure. The repulsive energy exponential parameter is fitted to give the minimum at the experimentally observed value Δ_0.

energy for the AFE_4 dressed dipolar structure which is higher than that for the AFE_1 structure by about a factor of 2.

V. CONCLUSIONS

We have presented a simple and plausible model for electric dipole ordering in NaCN and KCN which predicts the experimentally observed structure as the ground state for these cyanides. The only previous calculation which was capable of justifying the observed ground state is in the work by Pirc and Vilfan.[15] Their calculation is based on a dynamic model which includes a cross interaction between permanent CN^- dipoles and dipoles induced by lattice vibrations. Their values for $J(\vec{q})$ and $J^*(\vec{q})$ agree with ours; however their calculation gives no quantitative account for the experimentally measured cation displacements, and the effective dipolar interactions are determined in terms of an unknown self-interaction term.

We believe our intuitive model contains the relevant ingredients responsible for the ordering in NaCN and in KCN. Although our elastic potential parametrization should be taken only as a qualitative plausibility argument, the calculated values for the local electric fields can be considered as fair estimates for these quantities.

The absence of electric dipole ordering in RbCN and in CsCN may also be understood through simple models constructed from experimental observations in these cyanides. A planned study of these systems awaits results from an accurate determination of their low-temperature structure by neutron diffraction, presently under way.[18]

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[1] A. S. Nowick and W. R. Heller, Adv. Phys. 12, 251 (1963).

[2] H. B. Shore and L. M. Sander, Phys. Rev. B 12, 1546 (1975).

[3] A. Diaz-Gongora and F. Lüty, Phys. Status Solidi B 86, 127 (1978).

[4] H. U. Beyeler, Phys. Rev. B 11, 3677 (1975).

[5] M. Julian and F. Lüty, Ferroelectrics 16, 201 (1977).

[6] R. T. Shuey and H. U. Beyeler, J. Appl. Math. Phys. 12, 278 (1968).

[7] A. Cimino and G. S. Parry, Nuovo Cimento 19, 971 (1961).

[8] J. Ortiz-Lopez and F. Lüty, Phys. Rev. Lett. 50, 1289 (1983).

[9] H. Suga, T. Matsuo, and S. Seki, Bull. Chem. Soc. Jpn. 38, 1115 (1965).

[10] L. C. Scavarda do Carmo, D. Durand, and F. Lüty (unpublished).

[11] T. Matsuo, H. Suga and S. Seki, Bull. Chem. Soc. Jpn. 41, 583 (1968).

[12] R. R. Dos Santos *et al.*, J. Phys. C 11, 4557 (1978).

[13] D. Fontaine, C. R. Acad. Sci. Paris 281, B443 (1975).

[14] J. M. Rowe, J. J. Rush, and E. Prince, J. Chem. Phys. 66, 5147 (1977).

[15] R. Pirc and I. Vilfan, Solid State Commun. 39, 181 (1981).

[16] D. Fontaine, thèse de Doctorat D'Etat, Université Pierre et Marie Curie, Paris VI (1978) (unpublished).

[17] C. Kittel, *Introduction to Solid State Physics,* 3rd ed. (Wiley, New York, 1967), p. 91.

[18] J. M. Rowe, J. J. Rush and F. Lüty (unpublished).