BR 85 10330

# ELECTRIC DIPOLE ORDERING IN ALKALI-CYANIDES: NaCN AND KCN*

Belita Koiller, Maria A. Davidovich, L.C. Scavarda do Carmo

Departamento de Física, Pontifícia Universidade Católica
Cx.P. 38071, Rio de Janeiro, RJ, Brasil

and

F. Lüty

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

June 1983

ABSTRACT. We present ∥ is presented 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 the calculated values for the local electric fields are in agreement with experimental results. A parametrization for the elastic potential confirms the plausibility of our model. (Author)

RESUMO. Apresenta-se um modelo simples para o ordenamento elétrico no estado fundamental do NaCN e KCN. O modelo considera efeitos de "vestimento" dos dípolos elétricos.os quais incluem deslocamentos de cations determinados experimentalmente. A estrutura encontrada para o estado fundamental e os valores obtidos para os campos elétricos locais, estão de acordo com resultados experimentais. Uma parametrização para o potencial elástico confirma a plausibilidade do nosso modelo. (Autor)

# 1. 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 involve 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 non-spherical 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 non-spherical 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 barry only a weak electric dipole moment (measured as p=0.07 eÅ in KCl hosts)[5]. It is 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 pseudo-cubic structure of the crystal. Due 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 for the KCN and NaCN case, which is different from that of the other cyanides and much better investigated.

## 2. ORDERING IN KCN AND NaCN

At a critical temperature $T_{c1}$ of 280 K and 168 K in NaCN and KCN respectively, the CN$^-$ elastic dipole tensors align in a parallel way close to the <110> orientation of the originally cubic crystal ("ferro-elastic 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 [-6% uniaxial ($E_g$) contraction and $-11^o$ $T_{2g}$ shear angle in KCN] are typical distortion amplitudes, as expected for the nearest neighbors around a <110> 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 K and 172 K respectively, in both cases at a temperature when the dipole reorientation rate reaches a value of ~5.10$^6$ sec$^{-1}$. The ordering effect shows up experimentally by a gradual decrease of the dielectric response, a specific heat anomaly, and a characteristic shift of the CN$^-$ stretching vibration observed in Raman or ir.

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. (a) represents parallel "ferroelectric" dipole alignment, (b) - (f) various possible configurations for anti-parallel---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] that indicated for the ground state the AFE$_4$ type of antiferroelectric structure (Fig.2(e)). 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.

For an isolated electric dipole, the $T_{1u}$ distortion field illustrated in Fig.1C is its natural "dressing". Neutron scattering measurements[13,16] confirm that the ground state structure involves the ordering of "dressed dipoles", i.e., dipoles accompained 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.

## 3. 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]:

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

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

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

where $\Delta U_{FE}(\vec{p})$ is a correction due to macroscopic polarization effects which exists 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 $(M^+CN^-)$ molecules is then given by:

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

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 $\Delta_0$ corresponds to the value of $\Delta$ which minimizes the total energy

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

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:

$$U_{ij} = \lambda \exp(-R_{ij}/p) . \tag{5}$$

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

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

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

## 4. RESULTS

In the calculations for NaCN and KCN we take $p=0.07e\text{Å}$ 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 ferro (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 $\Delta$.
For both NaCN and KCN the $AFE_4$ structure becomes the most
favorable electrostatically for $\Delta \gtrsim 0.01 \overset{\circ}{A}$ . 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 $\Delta$ 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 $\Delta$ slower than for the
$AFE_4$.

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

become relevant. As $\Delta$ increases further the macroscopic term dominates again causing the energy decrease.

For the experimentally observed values $\delta_0$ of the cationic distortions[16] in NaCN and in KCN given in Table II, the electrostatic energy of the $APE_4$ 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 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 $CN^-$ anharmonic vibrational stretching mode infrared absorption[10] shows good agreement (within 15%).

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 $\lambda$ and $\rho$ 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 $(CN)^-$.

In Fig.4 we present the superposition of electrostatic and repulsive energy versus cationic displacement for KCN and NaCN. The value of $\lambda$ is taken to be the same as for the corresponding bromide, while $\rho$ is calculated by fitting the minimum of the curve to the observed equilibrium distortion. The required values of $\rho$ 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 energy for the AFE$_4$ "dressed" dipolar structure which is higher than that for the AFE$_1$ structure by about a factor of 2.

## 5. DISCUSSIONS AND 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. In particular,

the absense of cationic diplacements may be attributed to the orientation of the CN⁻ elastic dipoles in the <111> direction of a nearly cubic structure, which gives zero electric field at the cation sites. Such a study will be presented in a shortcomming work.

## REFERENCES

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

2. H.B. Shore and L.M. Sander, Phys. Rev. B12, 1546 (1975).

3. A. Diaz-Gongora and F. Lüty, Phys. Stat. Solidi B86, 127(1978).

4. H.U. Beyeler, Phys. Rev.

5. M. Julian and F. Lüty, Int. Conf. On Low Lying Lattice Vibrational Modes, Puerto Rico (1975).

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

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

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

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

10. L.C. Scavarda do Carmo, D. Durand and F. Lüty (to be published).

11. T. Matsuo, H. Suga and S. Seki, Bull. Chem. Japan 41, 583(1968).

12. R.R. dos Santos, et al., J. Phys. C11, 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, "These de Doctorat D'Etat", Université Pierre et Marie Curie, Paris VI (1978).

17. C. Kittel, "Introduction to Solid State Physics", New York Willey, $3^{rd}$ ed., pg 91 (1967).

**FIGURE CAPTIONS**

Fig.1 - Elastic and electric dipole dressings for a <110> oriented defect.

Fig.2 - Ordered dipolar configurations: cationic displacements due to electric dipole dressing are indicated.

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 $\delta_0$ is indicated.

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 $\Delta_0$.

Table I

| | | | 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) | |
| | | | NaCN | KCN |
| Bare dipolar energy per $CN^-$ pair | (0,0,0) | FE | -3.97 | -3.49 |
| | (±1/a,0.±1/c) | AFE$_1$ | -3.51 | -2.55 |
| | (±1/a,±1/b,±1/c) | AFE$_2$ | -1.36 | -0.662 |
| | (±1/a,±1/b,0) | AFE$_3$ | -0.984 | -0.346 |
| | 2(±1/a,±1/b,±1/c) | AFE$_4$ | 0.781 | 0.322 |
| | (0,±1/b,±1/c) | AFE$_5$ | 3.87 | 2.79 |

[a] Taken from Ref 16.

Table II

| | | NaCN | KCN |
|---|---|---|---|
| Equilibrium displacement along b-axis: $\Delta_0$ (Å)[a] | | 0.15 | 0.073 |
| $E_{loc}$ (V/cm) | bare | $-1.11 \times 10^6$ | $-4.61 \times 10^5$ |
| | dressed | $1.97 \times 10^7$ | $1.36 \times 10^7$ |
| | experiment[b] | ~~$2.3 \times 10^7$~~ | ~~$1.5 \times 10^7$~~ |

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

Table III

| | NaBr[a] | KBr[a] | NaCN | KCN |
|---|---|---|---|---|
| $2\lambda$ (eV) | 5.54 | 9.6 | 5.54[b] | 9.6[b] |
| $\rho$ (Å) | 0.328 | 0.336 | 0.271[c] | 0.287[c] |

a- from M.P. Tosi, Solid State Physics 16, 1 (1964) as quoted in Ref 17
b- taken to be the same as the corresponding bromide
c- Fitted to give equilibrium distortion.
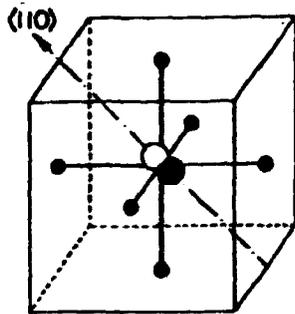
⟨110⟩ Oriented
Electric and Elastic Dipole
Defect

A) Without Lattice Distortions
("undressed")

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

$E_g$

$T_{2g}$
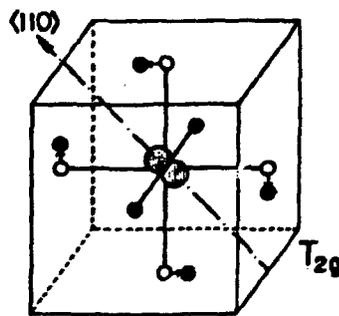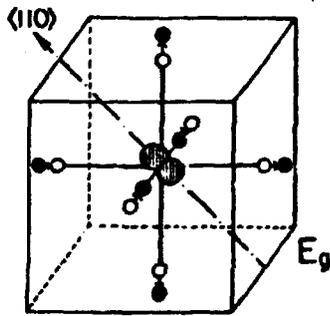
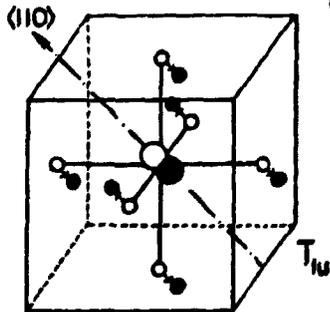C) With Ungerade Lattice Distortions
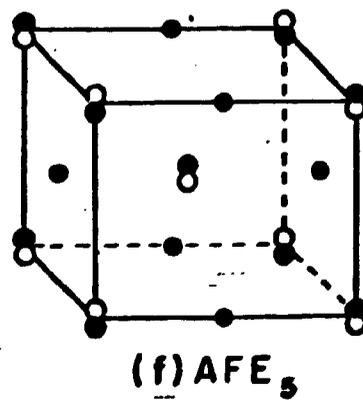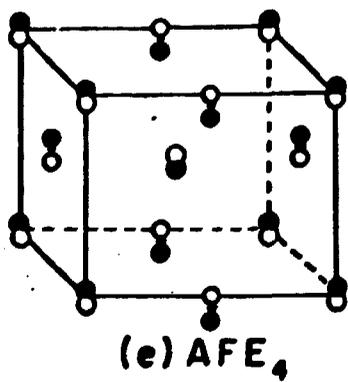("Electric Dipole Dressing")

$T_{1u}$
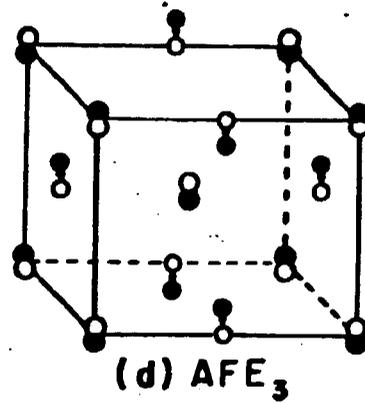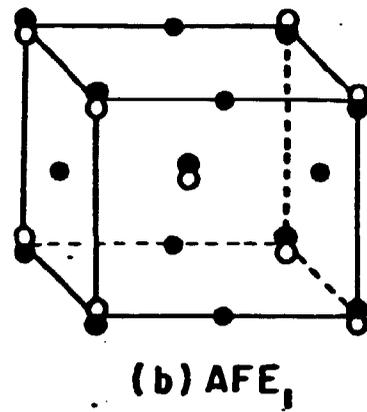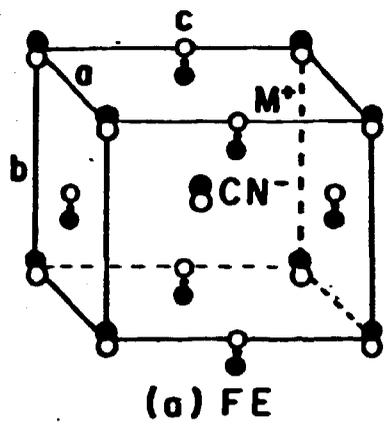
Figure 1

(a) FE       (b) AFE₁

(c) AFE₂       (d) AFE₃

(e) AFE₄       (f) AFE₅
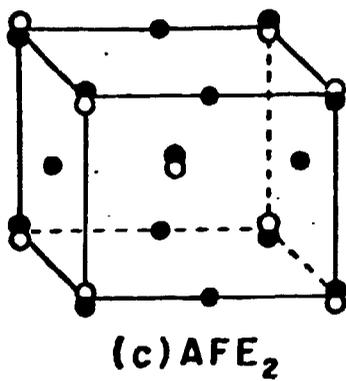
Figure 2

Figure 3

Figure 4