DIPOLAR ENERGY OF CN^- IONS IN KCN

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Abstract. We have evaluated the dipolar energy of CN^- ions in KCN using a generalized Ewald theta function transformation. In addition to direct electrostatic dipole-dipole interaction, which favors ferroelectric ordering of dipoles, we consider the coupling between CN^- dipoles and vibrational displacements of CN^- and K^+ ions. It is argued that the resulting effective interaction has a maximum at the zone boundary, corresponding to antiferroelectric ordering of CN^- dipoles, in agreement with experimental observations.

INTRODUCTION

At room temperature, KCN crystals have a fcc structure with CN^- dipoles randomly distributed among the 8 possible $\langle 111 \rangle$ directions. At 168 K, the crystal undergoes a first order transition to an elastically distorted orthorhombic phase in which CN^- ions are aligned along [010] orthorhombic direction, but remain randomly oriented with respect to their heads (C) and tails (N). Finally, a second order transition to a fully ordered phase takes place at 83 K. From Raman[1] and neutron scattering[2] data it follows that the dipoles are ordered antiferroelectrically, however, no theoretical explanation of this arrangement has been given so far. If, for example, a direct electrostatic dipole-dipole interaction were responsible for the ordering, a ferroelectric ground state would exist, contrary to observation.[3] Obviously, additional interactions need to be taken into account in order to explain the actual ground state configuration. Elastic dipole-dipole interactions can be ruled out by symmetry arguments: namely, the energy of a CN^- dipole in a strain field is unchanged if the dipole is flipped by 180°.

In this work, we investigate an alternative mechanism involving the electrostatic forces between the dipoles and the displacements of K^+ and CN^- ions, which modifies the bare dipole-dipole interaction and is shown to lead to an antiferroelectric ground state configuration for KCN.

THE MODEL

Let $\vec{R}_i$ be the lattice vector of i-th cell, and $\vec{r}_\chi$ the basis vector within the cell. with $\chi = 0$ and $\vec{r}_\chi = 0$ for CN^-, and $\chi = 1$ and $\vec{r}_\chi = \vec{r}_1$ for K^+. The corresponding ionic charges are $Z(\chi)$, and the dipole moment of the i-th CN^- ion is $p_i = \pm p$, where p is the known permanent dipole moment, and the sign ± refers to up and down orientations. If the ion at site $(j\chi)$ is displaced by an amount $u_j^\alpha(\chi)$, $\alpha = x, y, z$, the α- component of the induced electric dipole moment is $Z(\chi)u_j^\alpha(\chi)$. This dipole interacts electrostatically with other induced dipoles as well as with all permanent dipoles. The total potential energy of the crystal is written as

$$V = -\frac{1}{2}\sum_{ij}{}' J_{ij}^{yy}(0\,0)\, p_i p_j - \frac{1}{2}\sum_{\substack{ij\\ \chi\alpha}}{}' J_{ij}^{y\alpha}(0\chi)\, p_i\, Z(\chi)\, u_j^\alpha(\chi) + \frac{1}{2}\sum_{\substack{ij\\ \alpha\beta\chi\chi'}} \phi_{ij}^{\alpha\beta}(\chi\chi')\, u_i^\alpha(\chi)\, u_j^\beta(\chi') \qquad (1)$$

where $\phi_{ij}^{\alpha\beta}(\chi\chi')$ is the force constant matrix including the Coulomb interaction between the displaced ions, and $J_{ij}^{\alpha\beta}(\chi\chi')$ the matrix of dipolar interaction:

$$J_{ij}^{\alpha\beta}(\chi\chi') = \frac{3\,(\vec{R}_{ij} + \vec{r}_{\chi\chi'})_\alpha\,(\vec{R}_{ij} + \vec{r}_{\chi\chi'})_\beta}{\left|\vec{R}_{ij} + \vec{r}_{\chi\chi'}\right|^5} - \frac{1}{\left|\vec{R}_{ij} + \vec{r}_{\chi\chi'}\right|^3} \qquad (2)$$

Here we have defined $\vec{R}_{ij} \equiv \vec{R}_i - \vec{R}_j$ and $\vec{r}_{\chi\chi'} \equiv \vec{r}_\chi - \vec{r}_{\chi'}$.

The second term in (1) can now be eliminated by minimizing V with respect to $u_j^\alpha(\chi)$. The inverse of the matrix $\phi_{ij}^{\alpha\beta}(\chi\,\chi')$ is expressed in terms of normal mode frequencies $\omega_{\vec{q}}(\lambda)$ and polarization vectors $e_{\vec{q}}^\alpha(\chi|\lambda)$, where $\vec{q}$ is the wave vector and λ the branch index.[4] The resulting effective dipole-dipole interaction is the sum of direct interaction given by the first term of (1), and an indirect interaction via dipole moments induced by lattice modes. The Fourier transform of the corresponding effective dipolar interaction matrix is given by

$$J_{\vec{q}}^{\mathrm{eff}} = J_{\vec{q}}^{yy}(0\,0) + \sum_\lambda \frac{1}{\omega_{\vec{q}}(\lambda)^2}\left|\sum_{\chi\alpha} \frac{Z(\chi)}{\sqrt{M_\chi}}\, J_{\vec{q}}^{y\alpha}(0\,\chi)\, e_{\vec{q}}^\alpha(\chi|\lambda)\right|^2 - C \qquad (3)$$

where M_χ are ionic masses and $J_{\vec{q}}^{y\alpha}(0\,\chi)$ is obtained by Fourier transforming

Expression (2):

$$J_{\vec{q}}^{\alpha\beta}(\kappa\kappa') = \sum_j J_{ij}^{\alpha\beta}(\kappa\kappa')\,(1 - \delta_{\kappa\kappa'}\delta_{ij})\, e^{i\vec{q}\cdot(\vec{R}_{ij} + \vec{r}_{\kappa\kappa'})} \qquad (4)$$

The constant C in (3) is determined by the condition $\sum_{\vec{q}} J_{\vec{q}}^{\text{eff}} = 0.$[5]

Knowing the effective interaction, one can calculate the thermodynamic average of the dipole moment $\langle p_i \rangle$ using mean field theory. In the ordered state, the dipolar configuration is described by the relation

$$\langle p_i \rangle = \langle p_j \rangle\, e^{i\vec{q}\cdot\vec{R}_{ij}} \qquad (5)$$

where $\vec{q} = 0$ for ferroelectric ordering, and $\vec{q}$ lies at the zone boundary if the ordering is antiferroelectric. The actual value of $\vec{q}$ is determined by the maximum of the effective interaction $J_{\vec{q}}^{\text{eff}}$.

RESULTS AND DISCUSSION

A method of evaluating lattice sums of the type (4) with $\kappa \neq \kappa'$ is described by De Wette and Nijboer[6] who expand $J_{ij}^{\alpha\beta}(\kappa\kappa')$ in spherical harmonics. We have applied a generalized Ewald theta function transformation which leads to two rapidly converging sums.[7] The result is:

$$\begin{aligned} J_{\vec{q}}^{\gamma\alpha}(\kappa\kappa') = \sum_i & \frac{3(\vec{R}_i + \vec{r}_{\kappa\kappa'})_\gamma (\vec{R}_i + \vec{r}_{\kappa\kappa'})_\alpha - |\vec{R}_i + \vec{r}_{\kappa\kappa'}|^2 \delta_{\gamma\alpha}}{|\vec{R}_i + \vec{r}_{\kappa\kappa'}|^5} \Bigg\{ \operatorname{erfc}\left[\sqrt{\pi\tau}\,|\vec{R}_i + \vec{r}_{\kappa\kappa'}|\right] \\ & + 2\sqrt{\tau}\,|\vec{R}_i + \vec{r}_{\kappa\kappa'}| \left[1 + \frac{2\pi\tau}{3}|\vec{R}_i + \vec{r}_{\kappa\kappa'}|^2\right] e^{-\pi\tau|\vec{R}_i + \vec{r}_{\kappa\kappa'}|^2} \Bigg\} e^{i\vec{q}\cdot(\vec{R}_i + \vec{r}_{\kappa\kappa'})} \qquad (6) \\ & - \frac{4\pi}{v_o} \sum_{\vec{g}} \left[\frac{(\vec{g} - \vec{q})_\gamma (\vec{g} - \vec{q})_\alpha}{|\vec{g} - \vec{q}|^2} - \frac{\delta_{\gamma\alpha}}{3} \right] e^{-|\vec{g} - \vec{q}|^2/(4\pi\tau)}\, e^{-i\vec{g}\cdot\vec{r}_{\kappa\kappa'}} \end{aligned}$$

Here v_o is the primitive cell volume. The convergency factor τ is chosen such that the sum over $\vec{R}_l$ and the sum over reciprocal lattice vectors $\vec{g}$ converge equally rapidly. The value of $J^{y\alpha}_{\vec{q}}(\kappa\kappa')$ is independent of the choice of τ. With τ properly chosen it is enough to sum over 3 or 4 lattice vectors.

Additional simplifications arise when $\vec{q}$ is parallel to one of the crystal axes. In such a case, only the diagonal element $J^{yy}_{\vec{q}}(\kappa\kappa')$ is different from zero.

The sums in (6) have been calculated numerically for several representative values of $\vec{q}$ using the lattice parameters of KCN. The results for $J^{yy}_{\vec{q}}(0\,0)$ and $J^{yy}_{\vec{q}}(0\,1)$ are shown in Table 1. The first term, $J^{yy}_{\vec{q}}(0\,0)$, which represents the contribution of direct dipole-dipole interactions, has maximum value at $\vec{q} = 0$ and is in agreement with the values given in Ref. 3 which were obtained by a slowly convergent direct summation over several lattice vectors. Clearly, if direct interactions alone were responsible for dipolar ordering, the structure would be ferroelectric.

TABLE I

Dipolar lattice sums $J^{yy}_{\vec{q}}(0\,0)$ and $J^{yy}_{\vec{q}}(0\,1)$ for the low temperature phase of KCN.

$\vec{q}$	$J^{yy}_{\vec{q}}(0\,0)$ Å^{-3}	$J^{yy}_{\vec{q}}(0\,1)$ Å^{-3}
$0,\ 0,\ 0$	0.05607	0.06871
$0,\ 0,\ \frac{\pi}{2c}$	0.04888	0.07971
$0,\ 0,\ \frac{\pi}{c}$	0.03054	0.10721
$0,\ \frac{\pi}{2b},\ 0$	- 0.12159	- 0.08636
$0,\ \frac{\pi}{b},\ 0$	- 0.08020	0
$0,\ \frac{2\pi}{b},\ 0$	0.00205	0.14858
$0,\ \frac{\pi}{2b},\ \frac{\pi}{2c}$	- 0.05257	- 0.02294
$0,\ \frac{\pi}{b},\ \frac{\pi}{c}$	- 0.04745	0

In contrast, the second term, $J^{yy}_{\vec{q}}(0\,1)$, has its maximum at $\vec{q} = (0, 2\pi/b, 0)$, that is, at the zone boundary. To calculate the additional contribution to $J^{\text{eff}}_{\vec{q}}$ in Eq. (3) we must know the normal mode frequencies and polarization vectors as well as the ionic charges $Z(\kappa)$. Preliminary results indicate that for KCN the maximum of $J^{\text{eff}}_{\vec{q}}$ also lies at $\vec{q} = (0, 2\pi/b, 0)$. According to Eq. (5), the corresponding dipolar configuration in the ordered phase is then antiferroelectric, the dipole at the center of the orthorhombic unit cell being antiparallel to the dipoles at the corners. This configuration has indeed been observed in KCN by Raman and neutron scattering experiments.[1,2] We conclude that the coupling between CN^- dipoles and induced dipole moments due to ionic displacements is responsible for antiferroelectric ordering in KCN, and possibly in other alkali cyanides.

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