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ANTIFERROELECTRIC PHASE TRANSITIONS IN $(NaCN)_{1-x}(KCN)_x$

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Abstract The antiferroelectric ordered groundstate in the molecular system $(NaCN)_{1-x}(KCN)_x$ has been studied by means of neutron powder diffraction for concentrations $x \leq x_{C1} \approx 0.16$. Cristallographic parameters have been determined by Rietveld refinement procedures in detail. From atomic positions, static cationic displacements have been deduced in accordance with theoretical predictions.

INTRODUCTION

The ionic molecular crystals KCN and NaCN exhibit two successive Landau-type of phase transitions, characterized by a definite group-subgroup relationship between parent and daughter phases.[1] On cooling from room-temperature they show a first order ferroelastic transition from a plastic high-temperature cubic phase (Fm3m) into an intermediate orthorhombic phase (Immm). The transitions are driven by a translation rotation coupling (TRC), different in strength for both systems as reflected by the critical temperatures T_C=288K for NaCN[2] and T_C=168K for KCN.[3] This intermediate phase is characterized by long range orientational order of the aspherical CN^- molecules, oriented along the crystallographic (110) direction of the previous cubic cell. A dynamic head to tail disorder of the CN^- dipols is achieved via 180deg flips which are still allowed in the ferro-elastically ordered phase.

Under further cooling the dipolar disorder is removed by a continuous transition into an antiferroelectric ordered ground state (Pmnm). The transition tempertures T_E=172K for NaCN and T_E=83K for KCN were first determined by specific heat experiments.[2,3] Indications of the antiferroelectric ordering (AFEO) were also observed by dielectric[4], ultra-sonic[5] , and torsion pendulum[6] techniques. A clear identification of the AFEO is supplied by a (010) super-lattice reflection observed in neutron powder diffraction studies.[7,8,9]

During the last decade, solid solutions of alkali cyanide and alkali halide systems gained an intense experimental and theoretical interest. The random substituton of either CN^-anions by halides or of alkali cations by alkali ions of different size yields a decrease of transition temperatures for increasing impurity concentration. The absence of elastic order at low temperatures leads to the concept of an orientational glass state, intermediate between disordered materials and the spin glasses. The low temperature properties of these mixtures are discussed in terms of random bond disorder in the case of CN^-diluted systems or in terms of random strains which are induced by the site disorder of different sized substituents. Since the CN^-sublattice remains undiluted, $(NaCN)_{1-x}(KCN)_x$ definetely refers to the type of random strain systems where random strain-rotation coupling (RSRC) and translation rotation coupling (TRC) operate as competing interactions. In order to test the role played by random strain fields on the polymorphic behaviour of mixed cyanides we performed detailed neutron powder diffraction studies in $(NaCN)_{1-x}(KCN)_x$. Here we want to concentrate on the antiferroelectric phase transition observed for concentrations $x \leq x_{c1} \approx 0.16$.

EXPERIMENTAL

Single crystals with x=0, 0.02, 0.06, 0.11, 0.13, 0.16 were supplied by J. Albers and A. Klöpperpieper from the University of Saarbrücken, FRG. The actual concentrations were determined from the room temperature lattice constants under the assumption that a linear Vegard's law holds. The absolute error of given concentrations should be less than 1%. Powder samples of approximately 2 cm^3in volume were prepared by grinding pieces of single crystals with mortar and pestle in a controlled inert gas atmosphere. To avoid hydrolisation of the extremely hygroscopic samples they were loaded into Va-cans of 6mm diameter under the same inert gas atmosphere. The neutron-powder diffraction measurements were performed on the high-resolution multicollimator diffractometer D1A located on a thermal neutron guide at the Institut Laue-Langevin, Grenoble. The incident wavelength was 1,909 Å and the scattering angle 2ϑ ranges from 20 to 130deg.

RESULTS AND ANALYSIS

Below the critical concentration x_{C1} antiferroelectric ordered ground states could be identified for all mixed crystals investigated. Figure1 shows representative results of neutron powder diffraction pattern, recorded at 5K for concentrations x=0.06, 0.11, and 0.16. The profiles for x=0.06 and 0.11 display pure orthorhombic line splitting in accordance to the spacegroup Pmnm. For both mixed crystals a (010) superlattice reflection was detected near $2\theta \approx 23^\circ$ as an anambigious fingerprint of the antiferroelectric ordered arrangement of CN^-dipols. In the case of AFEO the occurence of a superlattice reflection in neutron powder diffraction experiments results from the distinct contrast between C and N, arising from their different scattering length.

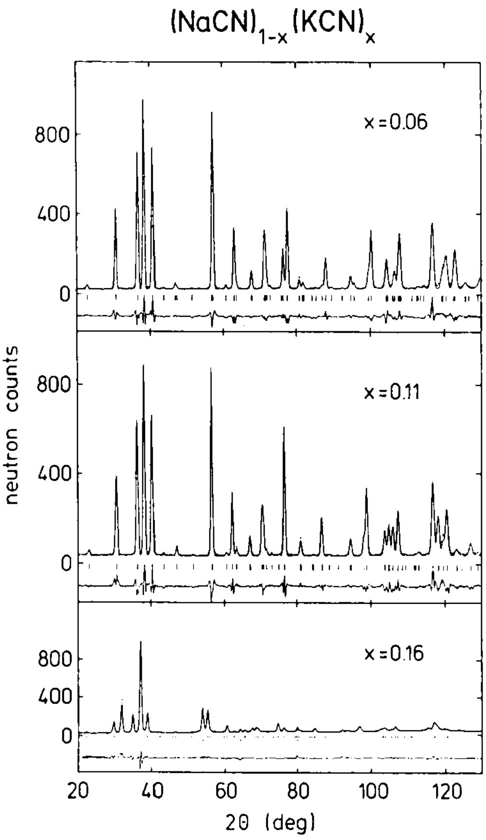

FIGURE 1 Powder diffraction data for $(NaCN)_{1-x}(KCN)_x$ with concentrations x=0.06, 0.11, and 0.16 recorded at 5K. Calculated data and deviations from observed data are presented by solid lines.

For x=0.16 (lower frame of Fig.1) the low temperature ground state is definetely not of pure orthorhombic symmetry. The powder lines could be indexed assuming a coexistence of cubic and orthorhombic phases. From the splitting of the (111) cubic Bragg reflection the ratio of both components is determined to 50% cubic (Fm3m) and 50% orthorhombic. The weak peak at lower scattering angles was identified as a (010) superlattice reflection indicating that the orthorhombic component establishes antiferroelectric order. In mixed cyanides, a coexistence of cubic and orthorhombic phases was observed for $(NaCl)_{1-x}(KCN)_x$[10], but antiferroelectric order could not be pointed out for the orthorhombic component.

For the continuous order-disorder transition (Immm-Pmnm) shifts of atomic positions along the b-axis should be expected from symmetry considerations.[1] Neglecting any shift, the y-component of the 2a-position of the Pmnm space group must be fixed to 0.25 and treated as a special position. On the base of this structural conditions, electrostatic energies were calculated for different electric ordered configurations of CN^-dipols.[11,12] Astonishingly, a ferro-electric arrangement is favoured from energy aspects for the low-T state of NaCN and KCN rather than an antiferroelectric configuration.[11,12] It was worked out that additional dipolar moments induced either by lattice vibrations[11] or by collective static cationic displacements[12] are essential for the experimentally observed formation of a AFE-ground state. Within the model of Koiller et al[12] the electrostatic energy of the observed configuration decreases stronger than the energy of alternative arrangements when induced dipolar moments are taken into account. Simultaneously, with increasing displacements a increasing term of a repulsive elastic energy arises. Thus the minimum of the displacement dependent superposition of both energies defines an equilibrium displacement δ_1. The existence of the appropriate sublattice shift was experimentally confirmed for the low-T ground state of pure NaCN[13] and was studied in detail for $(NaCN)_{0.98}(KCN)_{0.02}$.[9]

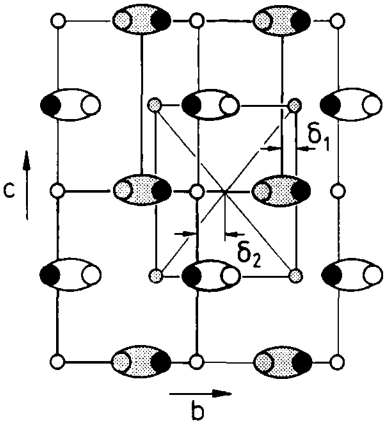

FIGURE 2 Schematic representation of atomic positions, projected down to a b-c plane. For the primitive orthorhombic cell (Pmnm) a setting with a<b<c was chosen for the lattice constants. Atoms indicated by shaded symbols are located in planes above or below the drawing plane, seperated by a distance of 0.5a. Alkali sites are represented by single open circles; CN^- dipols are shown as linked circles with the N atoms indexed as filled symbols. The sublattice shifts arising from static cationic displacements are marked by distances δ_1 and δ_2.

The observed AFE-arrangement is schematically illustrated in Figure 2 where atomic positions are projected down to the b-c plane of the orthorhombic lattice. Note that the CN^- molecules remain in their center position of the cell while strong off-center shifts δ_2 are displayed for the cationic sublattices. Displacements between the cationic and anionic sites are responsible for additonal induced dipol moments and are indexed with δ_1 .

From the low-T data of $(NaCN)_{1-x}(KCN)_x$ we determined atomic positions applying Rietveld refinement analysis. The y-component of the 2a-position was treated as a free variable, as required for a refinement in Pmnm. As expected from theory[12] collective static cationic displacements could be derived from atomic coordinates for all mixed crystals investigated. The displacement parameter $\delta_1 = 0.154$ Å obtained for $x=0$ is in excellent agreement with the value given for pure NaCN in Ref. 13. However for increasing substitutional disorder the parameter δ_1 decreases continuously. In Figure 3 the concentration dependence of δ_1 is depicted for Na-rich mixed crystals with $x \leq x_{C1} = 0.16$. $\delta_1(x)$ can be viewed as a concentration dependent order parameter and tends to zero when the critical concentration x_{C1} is reached. In particular at $x=0.16$ where the Pmnm structure is coexistent with a orientationally disordered cubic phase (Fm3m) the parameter $\delta_1 = 0.013$ is small but non-zero. This clearly demonstrates that, based on an orthorhombic structure, induced dipolar moments are essential to establish antiferroelectric ordered ground states in mixed cyanides.

For KCN-rich mixed crystals with concentrations $x > x_{C2}$ the AFEO was found to be rapidly suppressed by increasing substitutional disorder.[9,14] Smaller Na^+cations, randomly distributed on the alkali sites, lead to enhanced barrier hights and might act as trapping centers for CN^-orientations. However, pure KCN already exhibits a smaller displacement parameter $\delta_1 = 0.073$ Å, reduced approximately by a factor of 2 with respect to pure NaCN.[12] Therefore δ_1 rapidly reaches zero when it is decreased

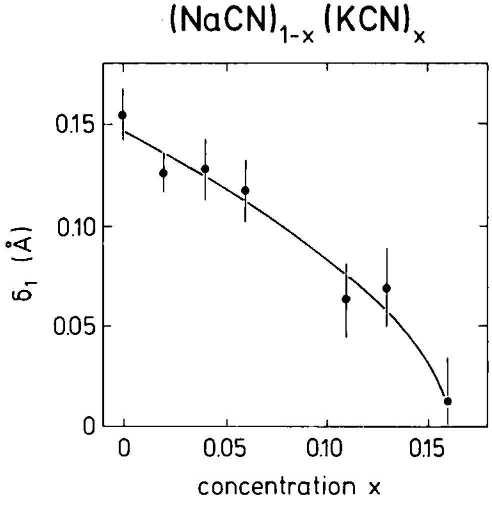

FIGURE 3 Concentration dependence of the displacement parameter δ_1 as determined from atomic positions obtained from Rietveld refinement procedures. The solid lines are drawn to guide the eye only.

by increasing cationic disorder in the case of KCN-rich mixed crystals in $(NaCN)_{1-x}(KCN)_x$. Obviously, even in pure cyanides δ_1 depends on the size of cations. Indeed for alkali cyanides the structural as well as the elastic behaviour is dependent on the ionic radii of alkali atoms. Thus due to larger size of cations AFEO is absent in RbCN and CsCN and even a orthorhombic low temperature state cannot be established.

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