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NEUTRON SCATTERING STUDIES in $(\text{NaCN})_{1-x}(\text{KCN})_x$

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Static and dynamic properties of $(\text{NaCN})_{1-x}(\text{KCN})_x$ mixed crystals were studied by neutron diffraction. By following the temperature dependence of the glass state order parameter the predictions of recent theories, which were developed in terms of random strain fields and using the concept of a non-ergodic instability, were tested.

Alkali cyanide-alkali halide mixtures are model systems for structural phase transitions [1, 2] and for orientational glass formation [3, 4]. In earlier theories the orientational glass state was interpreted as a consequence of frustration effects analogous to the concepts of spin glass systems [5]. At present static temperature independent random strain fields which couple to the orientational degrees of freedom are favoured to be responsible for the suppressed orientational order in mixed cyanides [6]. Recently Michel [7] modified his theories by the concept of a non-ergodic instability based on the theory of the Anderson localization.

$(\text{NaCN})_{1-x}(\text{KCN})_x$ mixed crystals exhibit a low temperature glass state over a wide concentration range [8, 9]. In this system random strain fields are implanted by the site disorder of different sized alkali ions while the CN^- sublattice is essentially preserved. Thus it is an ideal touchstone to test the role played by random strain fields in orientational glasses because frustration concepts due to the dilution of the orientational degrees of freedom are not applicable for this system.

A preliminary phase diagram of $(\text{NaCN})_{1-x}(\text{KCN})_x$ was constructed by dielectric and optical measurements [8]. Only close to the pure cyanides was an indication of structural phase transitions observed yielding two critical concentrations $x_{c1} \approx 0.15$ and $x_{c2} \approx 0.9$. The phase diagram was examined by neutron powder diffraction in more detail [10]. Preliminary results are shown in fig. 1. For concentrations

$x \geq x_{c2}$ different non-cubic low temperature structures were observed. The second order antiferroelectric phase transitions observed in pure KCN is suppressed even by a small amount of Na^+ ions randomly diluted in KCN. Thus for $x = 0.97$ and $x = 0.95$ the low temperature ground states are of bc-orthorhombic symmetry which is characterized by elastic order and by dipolar disorder. The tendency of decreasing orientational order with increasing cationic disorder is further manifested by the observations for $x = 0.89$: The rhombohedral phase coexists with the cubic phase down to the lowest temperatures. For NaCN rich mixed crystals with con-

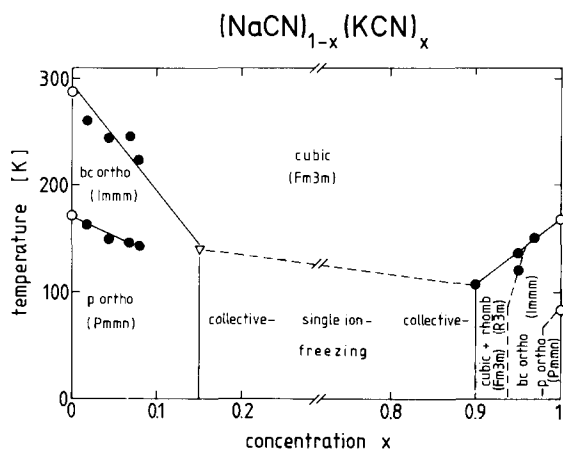


Fig. 1. Phase diagram of $(\text{NaCN})_{1-x}(\text{KCN})_x$. Transition temperatures for pure cyanides [11, 12] (\circ), $x \approx x_{c1}$ [8] (∇) and approximate transition temperatures for mixed crystals determined by neutron powder diffraction (\bullet). Dashed lines are chosen arbitrarily.

centrations $x < x_{c1}$ the subsequent phase transitions observed for pure NaCN are unaffected by the cationic disorder up to $x = 0.08$. It is conspicuous that increasing cationic disorder decreases the first order phase transition temperature from the cubic (Fm3m) to the bc-orthorhombic phase (Immm) more strongly than the second order phase transition temperature from bc- to the p-orthorhombic structure (Pmmn).

In the mixed cyanides the formation of a low temperature glass state with frozen-in long range orientational disorder is indicated by frequency dependent cusps in the quadrupolar susceptibility or equivalently by minima in the temperature dependence of the elastic properties [3]. The freezing-in of orientational disorder is accompanied by diffuse scattered intensities which appear around the cubic Bragg reflections [3, 14]. In inelastic neutron scattering experiments these diffuse scattered intensities are observed as a central line in addition to the phonon side bands. The intensity of the central peak can be interpreted as the glass state order parameter [3]. Fig. 2 shows a selection of typical constant Q scans for $x = 0.19$. The profiles clearly demonstrate the temperature dependent shift of phonon side bands, and for decreasing temperatures the increasing intensity of the central peak which indicates the transformation into an orientational glass state. The width of the central peak is resolution limited at all temperatures. For three different concentrations with $x_{c1} < x < x_{c2}$ the temperature dependence of the shear elastic constants, as determined by these inelastic neutron scattering results, is summarized in fig. 3. While for $x = 0.19$ and $x = 0.85$ well-defined minima in $c_{44}(T)$ are observed, for $x = 0.59$ the shear constant c_{44} is nearly temperature independent. The predictions of Michel's theory [7] for the glass state order parameter were tested by log-log plots of the observed diffuse intensities versus temperature (fig. 4). Figs. 3 and 4 demonstrate the delicate balance between strain-rotation (SRC) and translation-rotation coupling (TRC). As a common feature for $x = 0.89, 0.85$ and 0.19 , at high temperatures the slope of log-log plots is of comparable magnitude but the low temperature behaviour is quite different. For $x = 0.89$ a

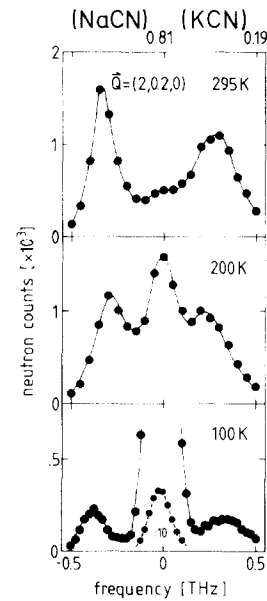


Fig. 2. Typical energy scans determined by inelastic neutron scattering at the reciprocal lattice point $Q = (2, 0.2, 0)$ for $x = 0.19$.

weak SRC allows a structural phase transition driven by a strong TRC. This is indicated by the sudden decrease of the diffuse scattered intensities below 110 K. For $x = 0.85$ a non-ergodic instability causes a sudden increase of the central peak intensities at a temperature which corresponds to the minimum in $c_{44}(T)$. At temperatures where c_{44} is soft, shear fluctuations are

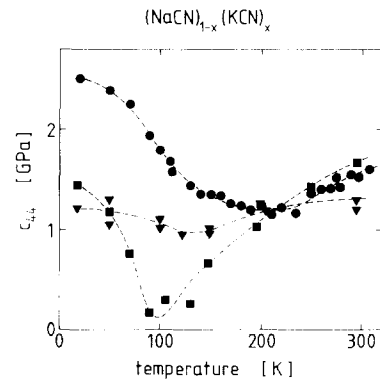


Fig. 3. Temperature dependence of elastic shear constant c_{44} for three different concentrations with $x_{c1} < x < x_{c2}$ determined by inelastic neutron scattering following the acoustic shear mode in T_{2g} symmetry at $Q = (1.1, 1, 1)$ for $x = 0.59$ (∇), 0.85 (\blacksquare) and at $Q = (2, 0.1, 0)$ for $x = 0.19$ (\bullet).

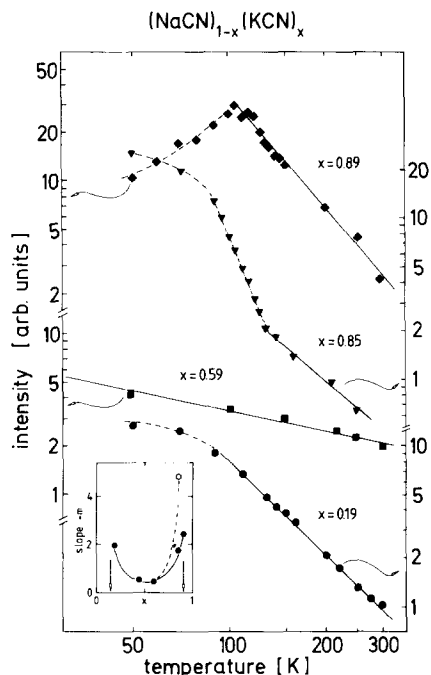


Fig. 4. Log-log plot of diffuse scattered intensities versus temperature for concentrations $x_{c1} < x \leq x_{c2}$. The insert summarizes the concentration dependence of slope for high temperatures (●) and in the case of $x = 0.85$ (○) for temperatures below the glass transition.

frozen in by the coupling to the weak random strain fields and prevent at the last moment the crystal from undergoing a structural phase transition. The discontinuity in the order parameter marks the non-ergodic instability at T_G . For $x = 0.19$, in the T -dependence of the central line no discontinuity could be observed. In this case the SRC coupling is strong enough to prevent a complete softening of c_{44} which is required when a non-ergodic instability should take place. For $x = 0.59$ the increase of quasielastic intensities is smooth and exhibits a constant slope down to the lowest temperatures. Due to a large cationic disorder the behaviour of this mixed crystal is completely governed by strong random strain

fields yielding a non-collective but single ion freezing of CN^- orientations. Quite similar results were obtained for a mixed crystal with $x = 0.44$ which is characterized by large cationic disorder too. The informations which are available for mixed crystals with $x_{c1} < x \leq x_{c2}$ are summarized in the insert of fig. 4. For high temperatures the $1/T^2$ dependence of the glass state order parameters predicted by Michel is only verified for concentrations close to the critical concentrations x_{c1} and x_{c2} where we determined slopes in the order of -2 . Below the non-ergodic instability for $x = 0.85$ the slope is approximately -4.9 . Obviously, below T_G an additional order parameter is responsible for this discontinuity [7]. For $x = 0.44$ and $x = 0.59$ we determined the slope $m = -0.5$ for all temperatures. It seems that in the case of large cationic disorder, i.e. extremely strong random fields, the $1/T^2$ prediction is not valid.

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