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History effects, domains, and glass formation in the mixed cyanides

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A mixed crystal of $(\mathrm{KBr})_{0.36}(\mathrm{KCN})_{0.64}$ has been cycled several times between 200 and 10 K and investigated by x-ray diffraction. A virgin sample undergoes a cubic-to-rhombohedral phase transition. After some cooling cycles a sequence of phases, cubic-rhombohedral-monoclinic, has been observed. In the last cooling cycles the orientational glass state could be stabilized at low temperatures. The results cast light on the formation of the glass state of the mixed cyanides. A qualitative interpretation is given in terms of the ferroelastic domain walls of the competing crystallographic phases.

INTRODUCTION

Due to the coupling between the orientational degrees of freedom[1] of the aspherical CN ion and the translational ones of the center-of-mass lattice, $(\mathrm{KBr})_{1-x}(\mathrm{KCN})_x$ shows a rich variety of structural states.[2] At room temperature the cubic NaCl structure is stabilized by rapid CN reorientations. For higher CN concentrations, $x > x_c$, $x_c = 0.6$, noncubic crystalline low-temperature phases, five in total, have been reported. Samples with x just above x_c pass through the sequence cubic-rhombohedral-monoclinic. Basically, the noncubic structures result from a ferroelastic shear deformation and a long-range orientational ordering. Below x_c a new low-temperature state, the orientational glass, is observed, characterized by inhomogeneous shear strains and short-range orientational order.[3]

So far, a detailed understanding of the structures and transformations has not been achieved, though it has been demonstrated theoretically that frustrated interactions do exist between the CN molecules[4] and that random strain fields presumably play an important role.[5]

Some unusual features observed above x_c can be viewed as first indications of the glass state for $x < x_c$: Besides the polymorphism of the crystalline state of the mixed cyanides,[2,6] which seems to be a necessary condition for the formation of a glass state, an extreme softening of the elastic shear constant,[7] extremely large mean-square displacements[7] and anomalous diffraction profiles have been reported.[8]

In this paper we will study the x-ray diffraction profiles of a mixed cyanide $(\mathrm{KBr})_{0.36}(\mathrm{KCN})_{0.64}$, which is the sample with the lowest CN concentration with crystalline low-temperature phases available to us. We will show that this sample can be trained by thermal cycling to show different low-temperature structures: rhombohedral, monoclinic, and glasslike. The results will be discussed in reference to domain formation. We recall that history-dependent effects, though less dramatic ones, have been known in pure KCN for a long time, in which crystals a monoclinic phase with a width of 7 K can be established by thermal cycling of small single crystals between the cubic and the orthorhombic phases.[9]

EXPERIMENTAL

The single crystal of $(\mathrm{KBr})_{0.36}(\mathrm{KCN})_{0.64}$ was supplied by S. Haussühl from the Universität Köln. Its room-temperature lattice constant is 6.552 Å. The concentration was derived from its macroscopic mass density. A powder and a small single crystal were prepared from adjacent parts of the specimen. The diffraction experiments were carried out on a conventional two-circle diffractometer using Cu$K\alpha$ radiation ($\lambda = 1.542$ Å) and a graphite monochromator in the primary beam. The powder patterns were recorded with a position-sensitive detector connected to a multichannel analyzer. 25.8 channels corresponded to 1° in the scattering angle 2θ. The powder was cooled down 8 times, from temperatures of the order of 150 to 200 K down to 10 K, and diffraction data were taken systematically for every cooling process. The single crystal was subjected to the same cycling. Here diffraction profiles were measured on the first ($n = 1$) and last ($n = 30$) cooling cycle.

RESULTS

On first cooling the powder and the single crystal show a structural phase transition from the cubic high T phase to a noncubic low T phase, the structure of which is readily identified as rhombohedral from the splitting of the Bragg reflections. The changes $\Delta\alpha, \Delta\beta, \Delta\gamma$ of the cell angles α, β, γ with respect to the cubic phase, $\Delta\alpha = \alpha - 90°$, etc., represent the shear components of the spontaneous strain order parameter.[10] For the rhombohedral phase the three components are equal, $\Delta\alpha = \Delta\beta = \Delta\gamma$, their T dependence is shown in Fig. 1. The transition temperature T_c is (93 ± 2) K. A more precise determination of T_c is prevented by the fact that the peak splitting evolves out of cubic reflections which have broadened considerably for $T \rightarrow T_c$.[2] As there is no detectable jump of the cell volume at T_c, the transition is

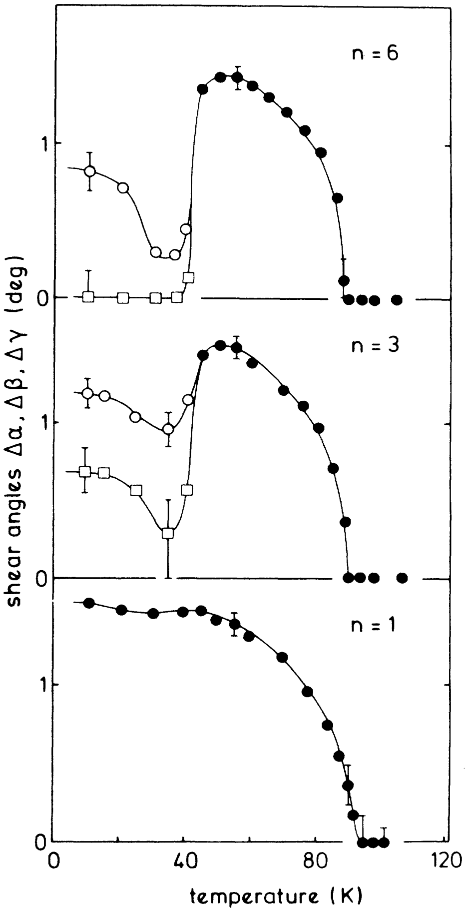

FIG. 1. The ferroelastic shear strain order parameter as a function of temperature. ●: $\Delta\alpha=\Delta\beta=\Delta\gamma$, rhombohedral and cubic phase, respectively; ○: $\Delta\alpha=\Delta\beta$; □: $\Delta\gamma$, monoclinic phase. n denotes the number of the cooling cycle.

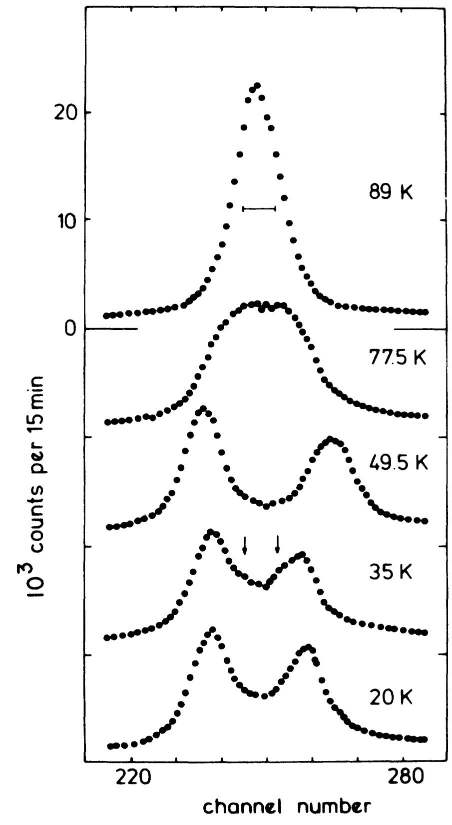

FIG. 2. (220)-powder profiles of the second cooling cycle. The horizontal bar gives the width of the peak at room temperature. The arrows direct attention to slight deviations from a purely rhombohedral profile. The channel number is a linear measure of the Bragg angle 2θ. 25.8 channels correspond to 1°.

continuous, or at least very close to it.

A series of (220) powder profiles for the second cooling cycle ($n=2$) is shown in Fig. 2. One notes that (i) the peak splitting at 35 K is slightly smaller than at 49.5 K and 20 K and that (ii) the 35-K profile is not the clear two-peak profile which is characteristic for the rhombohedral phase. These effects became more obvious in later cooling cycles. In the third cycle it was clear that the structure below 45 K is in fact monoclinic. A monoclinic distortion of the original cubic cell is characterized by the equality of two of the three shear components, say $\Delta\alpha$ and $\Delta\beta$.[10] As shown in Fig. 1, $\Delta\alpha$ and $\Delta\gamma$ are smaller in the low-T monoclinic than in the intermediate rhombohedral phase (45 $\text{K}<T<90$ K). In the monoclinic phase $\Delta\gamma$ is smaller than $\Delta\alpha$. The minimum values are observed around 40 K. In later cycles, represented by the sixth cycle in Fig. 1, the spontaneous shear strains of the low-T monoclinic phase are even smaller, $\Delta\gamma$ is now zero in the monoclinic phase, $\Delta\alpha$ almost vanishes around 40 K. The cubic-rhombohedral transition temperature T_c has stabilized in the last cycles at (85 ± 2) K. The maximum shear of the rhombohedral phase, reached at about 55 K, is independent of the sample history. Figure 3 demonstrates the radical effect of the cycling process on a diffraction line.

The profiles of rocking scans through the (400) reflection of the single crystal for the last cooling cycle ($n=30$) are shown in Fig. 4. For 85 $\text{K}>T>50$ K, a temperature range where one expects of the sample to be in the rhombohedral phase on the basis of the powder data, one indeed notes side peaks indicating that relatively well defined homogeneous shear deformations exist in this T range even after 30 cycles. These profiles can, however, not be explained by a single phase: Presumably they are due to a coexistence of rhombohedral, monoclinic, and perhaps even cubic components. Nevertheless the overall splitting and hence the values for the shear compare favorably with the powder results for 50 $\text{K}<T<85$ K. At low temperatures, however, the diffraction profiles consist of broadened cubic reflections, profiles which are indistinguishable from those of the glass state of the mixed crystals with slightly lower CN concentration.[2,3] Hence, we conclude that the single crystal has reached the orientational glass state after sufficient maltreatment. The

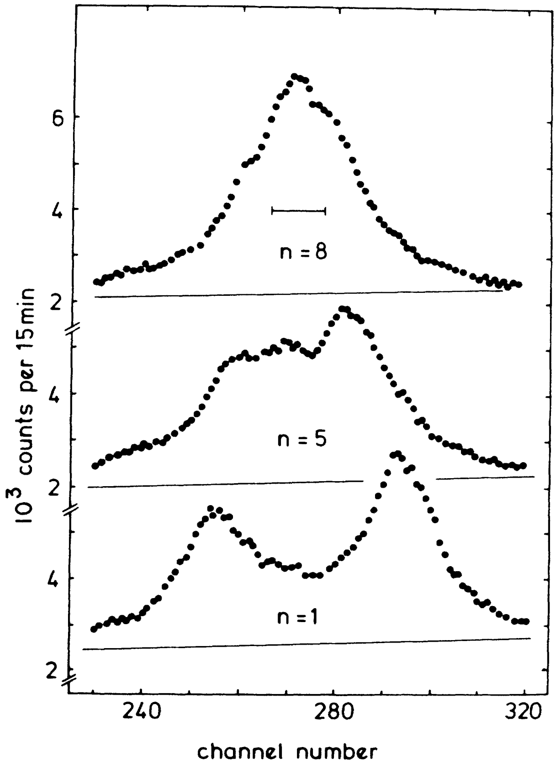

FIG. 3. (420)-powder profiles, measured at 35 K at different stages of the thermal cycling. n denotes the number of the cycle. The horizontal bar gives the peak width at room temperature. Solid lines are the background base line. 25.8 channels correspond to 1° in 2θ.

dependence of the structural state of the sample on the cycling process is shown in Fig. 5.

DISCUSSION

We will show that the role played by the thermal cycling can be understood in terms of domain formation at the two structural phase transitions from cubic to rhombohedral and to monoclinic, which in turn suggests that the glass state can be derived from the multidomain state of the ferroelastic phases. The discussion will start with some facts on the crystallographic phases involved and on the theoretical predictions on the domain walls.

The rhombohedral phase is derived from the cubic phase by a homogeneous shear deformation (ferroelastic species $m3mF\bar{3}m$ following Ref. 10). Note however that in the present system the cubic cell is squeezed rather than stretched along [111] (Ref. 2), $\Delta\alpha > 0$, contrary to $(\mathrm{NaCl})_{1-x}(\mathrm{NaCN})_x$ (Ref. 6) and CsCN (Ref. 11). Squeezing is much less effective than stretching in reducing the orientational entropy of the CN molecules since it implies residual orientational disorder within the (111) plane perpendicular to the axis of contraction. (Thinking in terms of discrete ⟨111⟩ orientations, squeezing along [111] reduces the original 8 degrees of freedom to 6, stretching to 2.) A further transition to a structure with more complete order is likely. However, the monoclinic phase also has residual entropy. The absence of head-tail ordering of the CN molecules in this phase has been established by neutron diffraction for $x = 0.90$.[12] Nevertheless the sequence cubic-rhombohedral-monoclinic with a stepwise reduction of orientational degrees of freedom, from 8 to 6 to 2 for a ⟨111⟩ model, connected with an increase of the spontaneous shear deformation seems reasonable. Actually this situation has been observed at a slightly higher CN concentration, $x = 0.75$, Fig. 6. There is hope that this behavior could be eventually reproduced by a mean field theory which is based on the bilinear coupling of CN orientations and lattice shear within the "virtual-crystal" approximation.

The present sample behaves differently: in all but the

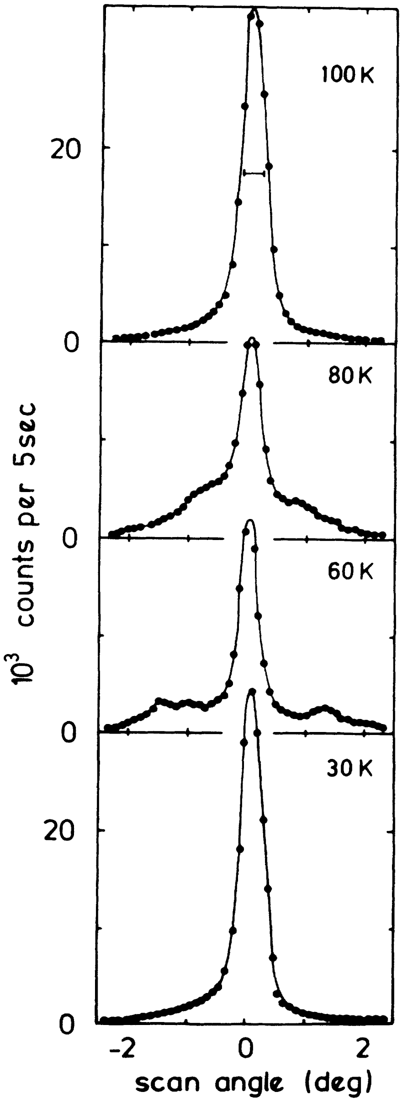

FIG. 4. Mosaic scans through the (400) reflection of a single crystal cycled 30 times. The horizontal bar gives the width at room temperature.

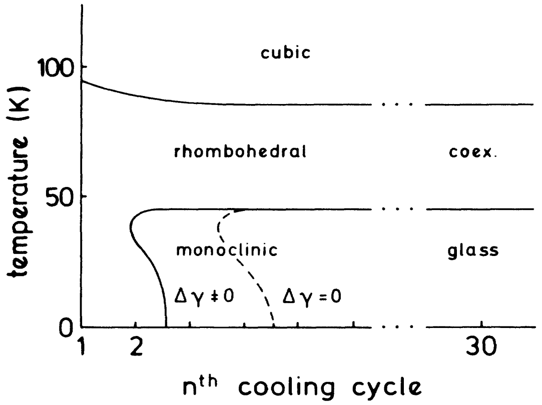

FIG. 5. Scheme of the structural states obtained after *n*-cooling cycles. "coex." denotes a state which definitely contains crystalline ferroelastic components, but which is not purely rhombohedral or monoclinic.

first cycle the low-T state (monoclinic or glass) has smaller shear strains than the intermediate rhombohedral phase. A behavior of this type is not likely to be reproduced by a conventional model, based on an "internal" free energy only. Additional effects have to be considered. The theoretical works of De Raedt *et al.*[13] and Sapriel[14] suggest that the domain patterns are of importance. De Raedt *et al.* have shown that the structure of the low-temperature phase of the cyanides actually depends on the shape of a monodomain sample. Sapriel derives the orientations of "permissible" domain walls of ferroelastics from elasticity theory. (Permissible walls contain all directions for which the length changes introduced by the ferroelastic strain are the same in the two adjacent domains.)

The ferroelastic domains of the pure cyanides have been studied by direct microscopic observation.[15] In the mixed cyanides the loss of optical transparency below the transition temperature T_c has been taken as an indication for the formation of domains.[16]

Applying Sapriel's results to the rhombohedral and the monoclinic phase one arrives at the following conclusions: For all pairwise combinations of the four domain states of the rhombohedral phase prominent permissible walls exist with $\{110\}$ and $\{100\}$ orientations. These walls are expected to move easily under external stress, explaining the low elastic shear constant of the rhombohedral phase as observed for $x = 0.75$ (Fig. 6). The prominent walls leave the crystallographic coherence between the adjacent domains intact, they do not require the formation of lattice faults. It is therefore plausible that the cubic-rhombohedral transition is highly reversible.

The domain pattern of the monoclinic phase is more complex. There are now twelve domain states, three for each of the four rhombohedral ones. Hence the two subsequent phase transitions cubic-rhombohedral and rhombohedral-monoclinic will lead to unusually small domains. For 44 out of the 66 pair combinations possible, permissible walls can be found, some being again prominent $\{100\}$ and $\{110\}$ walls, the orientations of the others actually depending on the strain elements via equations of the form $\Delta\alpha z + \Delta\gamma y = 0$. Thus the evolution of the monoclinic phase with $\Delta\gamma = 0$ out of the rhombohedral phase ($\Delta\alpha = \Delta\gamma$) requires the rotation of these lattice walls from $\{110\}$ to $\{100\}$. It is likely that these rotations and the resulting changes of the domain shapes are an irreversible process. In this context we note that the internal friction for $x = 0.75$ increases below the rhombohedral-monoclinic transition temperature until $\Delta\gamma$ vanishes (Fig. 6). One might also think that the persistence of the rhombohedral phase in the virgin samples with $x = 0.64$ is due to a pinning of the domain walls in the $\{110\}$ orientations.

For the 22 pair combinations remaining, permissible walls are not predicted. If any of these do happen to be adjacent, an appreciable amount of crystalline mismatch is introduced at the boundary. In the present case these boundaries are low-angle grain boundaries which can be

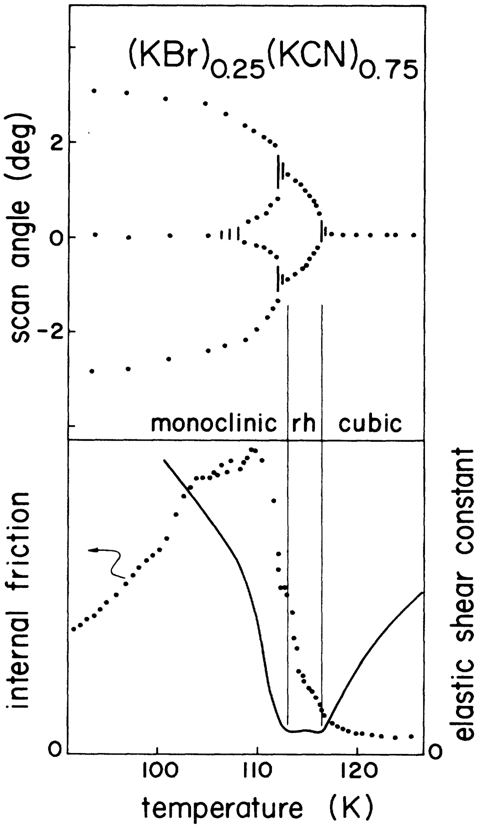

FIG. 6. The elastic response and the splitting of a diffraction peak in $(KBr)_{0.25}(KCN)_{0.75}$. The upper part shows the splitting of the (400) reflection as observed by rocking scans within the (001) scattering plane, indicating to successive transitions from the cubic (one peak) to the intermediate rhombohedral (two peaks) and to the monoclinic (four and three peaks, respectively) phase. Monoclinic three-peak profiles signal that one of the shear angles (say $\Delta\gamma$) has settled at zero value. The lower part shows the elastic shear constant C_{44} and the corresponding internal friction as determined from torsional oscillations in the 10^2 Hz range (from Ref. 17).

understood as patterns of dislocations. These boundaries introduce irreversible damage to the sample which cannot be removed at annealing temperatures of 150–200 K. A great number of such defects is accumulated during the cycling process. The inhomogeneous strain fields which are introduced by the defects are presumably very effective in lowering the local free energy, thus suppressing the need for ferroelastic ordering in large parts of the sample. Eventually, the ferroelastic strains become negligible compared to the inhomogeneous strains. It is this situation which is called the glass state of the cyanides.

FINAL REMARKS

Following these ideas the glass state of the cyanides is understood as an extremely fine pattern of ferroelastic domains[18] which are subject to inhomogeneous strains. The extreme proliferation of the domain walls is the result of the two successive ferroelastic transitions. The inhomogeneous strain fields ("random fields") are due to the incompatibility of the two ferroelastic phases which manifests itself in nonpermissible domain walls. Note that this view does not conceive the glass state as an arrangement of independent microcrystallites, since the dominant fraction of the walls is of the coherent type.

We propose that the glass state of $(\mathrm{KBr})_{1-x}(\mathrm{KCN})_x$ is a natural consequence of the polymorphism of that compound and that even a plausible mechanism for the formation of its glass state can be described. The main problem remaining is the understanding of the polymorphism, which clearly is a difficult problem since the crystallographic structures of the various phases are not independent of the domain pattern. Hence the theoretical models should explicitly take into account the multidomain state of the low-temperature phases by introducing strain gradient terms as demonstrated by Barsch and Krumhansl[19] for a cubic-tetragonal ferroelastic transition. The effects of the chemical substitution should not be ignored either. In fact, the volume mismatch of the substituents Br and CN has been considered in the recent theory by Michel[5] in terms of "random fields" and in molecular dynamics simulations by Lewis and Klein.[20] We suggest that the size mismatch is not the only source of random fields, but that additional inhomogeneous fields come into play when the transitions are approached.

The conclusions of this investigation can be generalized by stating that the competition of three phases, the cubic parent phase, and two ferroelastic low-temperature phases, is needed for the glass state to form in $(\mathrm{KBr})_{1-x}(\mathrm{KCN})_x$. The same criterion of three competing phases is met in $(\mathrm{NaCl})_{1-x}(\mathrm{NaCN})_x$.[6] [In the other glass forming cyanides $(\mathrm{KCl})_{1-x}(\mathrm{KCN})_x$ and $(\mathrm{NaCN})_{1-x}(\mathrm{KCN})_x$ the ferroelastic phases have not been studied yet in sufficient detail.] The idea of a polymorphism of the low-temperature phases as a favorable condition for a glass transition is not new. Recently it has been reformulated for vitreous silica, for example.[21] The present system has the great advantage that a detailed mechanism for the glass formation can be proposed. In that sense $(\mathrm{KBr})_{1-x}(\mathrm{KCN})_x$ has proven once more its usefulness as a model for glasses though on the other hand the present results underline the limitations of the analogy between the cyanide glass state and the structural glasses: History dependent effects rely on the high-temperature state to be a solid, they are unknown in structural glasses. The random-field concept seems to be more adequate to the cyanides than the glass concept. We do not see how the picture of ferroelastic microdomains could be reconciled with that of a continuous random network.

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