FERROELASTIC TRANSITION IN KBr:KCN STUDIED BY NEUTRONS, X-RAYS AND ULTRASONICS

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The ferroelastic phase transition of $(KBr)_{0.27}$ $(KNC)_{0.73}$ has been studied by X-ray diffraction, ultrasonics and inelastic neutron scattering. It is the first example of a cubic crystal where the elastic shear constant C_{44} softens completely corresponding to the $m = 2$ universality class. C_{44} and the Bragg intensities show a non-classical critical behaviour.

$(KBr)_{1-x}$ $(KCN)_x$ mixed crystals have been studied intensively in the last years because they are conceptually simple examples of systems with a coupling of the phonon modes to the rotational degrees of freedom, here of the dumb-bell shaped CN-ion. As a consequence of this coupling the CN-rich crystals ($x > 0.56$) show phase transitions from the cubic (NaCl) room temperature to non-cubic low temperature phases [1,2]. The low temperature state of the Br-rich crystals is regarded as glass-like with an average cubic lattice and frozen-in CN-orientations and a distribution of inhomogeneous strains [3,4]. The two types of low temperature states are announced by a softening of the elastic shear constant C_{44} of the cubic phase [5,6].

The structural phase transition of pure KCN at $T_s = 168$ K is of first order. As the CN-concentration x is reduced, $T_s(x)$ and the jump of the order parameter at $T_s(x)$ decrease [2]. For the present sample with $x = 0.73$ the X-ray powder patterns suggest a continuous transition cubic to rhombohedral at $T_s = (111.7 \pm 0.4)$ K followed by a second one to a monoclinic structure at 107 K.

Cowley [7] and Folk et al. [8] have treated the ferroelastic transitions with renormalization groups (RNG) and predict unusual properties for the universality class $m = 2$ for which the upper transition of the present crystal appears to be a first example: For $m = 2$, the order parameter is a spontaneous shear. The transition involves a softening of the elastic shear constant C_{44} and leads to diverging critical fluctuations of T_{2g} symmetry, the wave vectors of which lie in the cubic planes. The upper critical dimension for this class is three, hence one expects logarithmic corrections to the mean field behaviour in a three-dimensional crystal. A consequence of the softening of the T_{2g} phonons is the divergence of the mean square displacement $\langle u^2 \rangle$ at T_s. Thus the system should pass through a state of lost crystalline order when transforming from the high to the low temperature crystalline phase. Folk et al. [8] have noted a "conspicuous" absence of $m = 2$ systems in nature.

We will present X-ray, ultrasonic and inelastic neutron scattering results on the cubic phase. X-ray diffraction on the single crystal shows a dramatic decrease of the intensities of the Bragg reflections with decreasing T as shown in fig. 1 for the (620) reflection. At 114 K the Bragg peak has dropped to 3% of its high temperature intensity. When interpreted as a Debye–Waller factor this value corresponds to an rms-displacement of 11% of the next neighbour distance.

The ultrasonic experiments, carried out with 10 MHz transducers using the pulse echo overlap

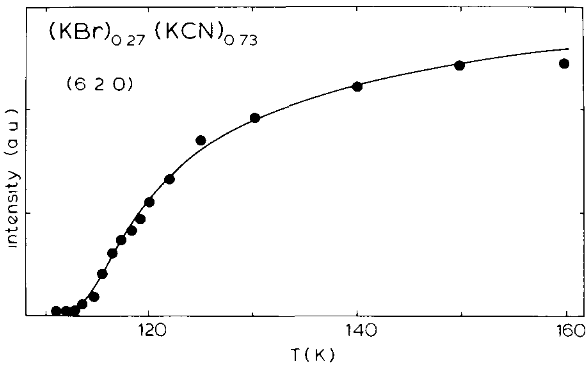

Fig. 1. The temperature dependence of the (620) Bragg intensity of X-ray experiment. The solid line is calculated from $C_{44}(T)$.

method, gave clear signals down to 135 K. At this temperature the last echo disappeared. $C_{44}(T)$ is shown in fig. 2. The usual mean field T-dependence of the form [5] $C_{44} = C_{44}^0\ (T - T_0)/(T - T_a)$ was fitted to the data, yielding $T_0 = 123$ K. $T_a = -130$ K and $C_{44}^0 = 5.4 \times 10^{10}$ dynes/cm (dashed line). Note that the extrapolated ordering temperature T_0 lies well above the actual transition temperature T_s.

For a closer inspection of the elastic response neutron experiments have been carried out with the triple-axis spectrometer TAS7 at Risø using a fixed outgoing neutron energy of 2.5 meV, Be-filters before and after the sample and an overall collimation of 60′. The energy resolution was 40 μeV at zero energy transfer. Series of constant-Q-scans, $Q = (1, 1, 1) + (\rho, 0, 0)$, $0.03 \leq \rho \leq 0.10$, have been performed at several temperatures between 171 K and 122.3 K. In the energy range chosen this scattering geometry measures the T_{2g} transverse acoustic phonons with sound velocity proportional to C_{44}. As T_s is approached, the phonon frequencies decrease and central peak grows (fig. 3). At the lowest temperature, 112.3 K, the scan profiles at all ρ investigated consist of a single peak at zero energy.

The elastic constant C_{44} has been determined from the frequencies of the phonon side bands and is included in fig. 2.

The deviations from the mean field T-dependence of C_{44} and the Bragg intensity are clearly apparent in figs. 1 and 2. This unusual behaviour is well accounted for by the RNG predictions [8] (solid lines in these figures): $C_{44} \sim \tilde{\tau}$ and $\langle u^2 \rangle \sim$

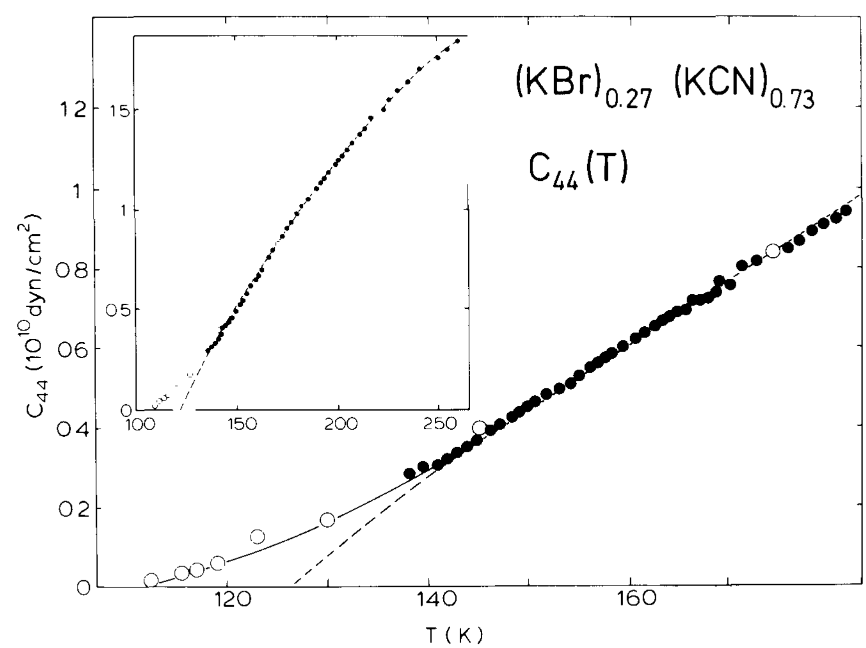

Fig. 2. The temperature dependence of the elastic shear constant C_{44} (ultrasonics ●, inelastic neutron scattering ○). The dashed line is best fit to an overall mean field behaviour, the solid shows the RNG-prediction.

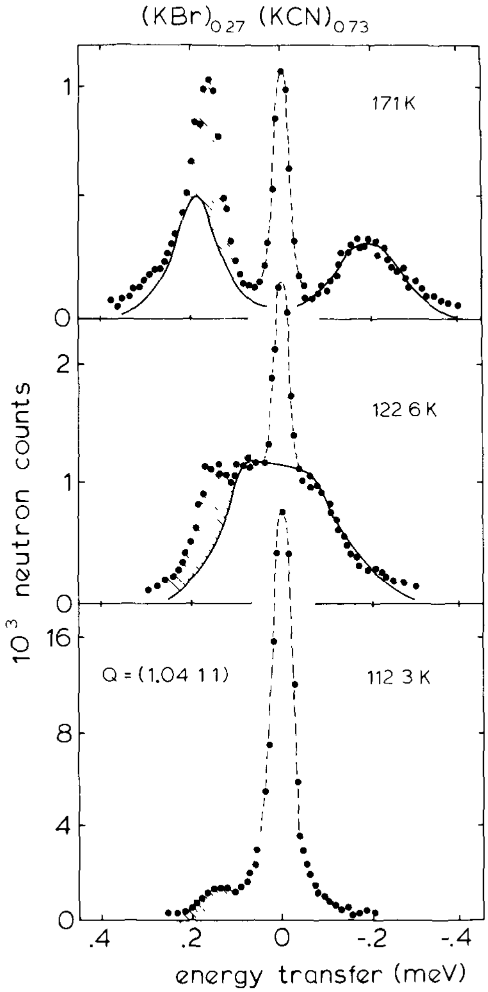

Fig. 3. Profiles of constant-Q-scans of the inelastic neutron scattering experiment. The hatched excess intensity is picked up from the (111) Bragg peak due to the finite resolution.

$\tilde{\tau}^{-1}$ with $\tilde{\tau} = \tau/|\ln \tau|^{1/3}$, $\tau = T/T_s - 1$. (In the calculation of the Bragg intensities it turns out that the effect of the small T-dependence of the other elastic constants, C_{11} and C_{12}, is negligible.)

As mentioned in the Introduction, the critical behaviour of a $m = 2$ system should eventually lead – when some threshold for $\langle u^2 \rangle$ is reached – to a breakdown of the concept of a crystal lattice with one-phonon modes as dominant excitations. In fact, there is experimental evidence that at temperatures close to T_s the present system is on the verge of "melting" and behaves to some degree like a system at the lower critical dimension: The rms-displacements fulfill the Lindemann criterion for melting. Within the experimental resolution the elastic shear constant vanishes. In addition to the soft phonon modes quasistatic disorder scattering, the central peak is observed which we interpret as the manifestation of random strain fields, i.e. its intensity is a measure of what extent the crystalline order is violated. We note that the existence of random strain fields in the mixed cyanides is a consequence of the effective strain mediated CN–CN interaction [3]. From the experimental data one cannot decide whether the central peak or the soft phonon response diverges at T_s, but from the mere fact that the sample finally transforms into a crystalline low temperature phase we conclude that the transition is ultimately driven by soft lattice modes in the presence of non-critical random strains. In the mixed crystals with low CN-concentrations ($x < 0.56$), which show a quasicubic low temperature glass state, the random strains block the evolution of the softening of the lattice modes.

Summarizing, we have found that the cubic-rhombohedral ferroelastic transition in $(KBr)_{0.27}$ $(KCN)_{0.73}$ appears to be continuous and that it involves a complete softening of the C_{44} elastic constant. This implies that the system belongs to the $m = 2$ universality class for ferroelastic transitions, and it represents the first example of this kind.

The observed T-dependence with its characteristic logarithmic corrections of the elastic constant and of the mean square displacement is consistent with the RNG prediction although these theories have not yet been developed to include the effects of the random strains implied by the non-stoichiometric nature of the present system.

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