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A NEUTRON DIFFRACTION STUDY OF THE GLASS TRANSITION IN $(KBr)_{0.47}(KCN)_{0.53}$

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The molecular crystal $(KBr)_{0.47}$ $(KCN)_{0.53}$ has been investigated by elastic neutron diffraction at the transition from the paraelastic to the orientational glass state. The freezing temperature is characterized by the onset of a momentum transfer dependent broadening of the diffraction lines indicating the transition from a crystalline to an amorphous state.

CURRENTLY CONSIDERABLE ATTENTION is being given to dipolar and quadrupolar glasses. The most prominent examples are $(KBr)_{1-x}(KCN)_x$ [1–10], $K_{1-x}Li_xTaO_3$ [11, 12], $Rb_{1-x}(NH_4)_xH_2PO_4$ [13, 14], mixtures of ortho- and para hydrogen [15] and $(N_2)_{1-x}Ar_x$ [16, 17] solid mixtures. At low temperatures they are characterized by frozen-in, frustrated multipoles with no long-range orientational order. The freezing process is indicated by frequency dependent cusps in the dipolar [2, 3, 11–13] and in the quadrupolar [2, 7, 12, 14] susceptibilities and shows striking similarities with the spin glass transition. In addition these molecular glasses exhibit low temperature thermodynamic properties which are anlogous to those found in canonical glasses and in amorphous solids [4, 5]. A very recent theoretical approach [6] shows that with increasing impurity concentration a broad distribution of low energy excitations develops from the interaction between tunneling states giving rise to a specific heat linear in T and a thermal conductivity proportional to T^2.

The phase diagram of alkali bromide-alkali cyanide mixtures can be divided in two regimes: for high CN^- concentrations ($x \gtrsim 0.6$) $(KBr)_{1-x}(KCN)_x$ crystals undergo structural phase transitions from a cubic high temperature phase, with a fast reorientational motion of the molecules, to a low temperature state, where the CN^- ions exhibit orientational order [18]. The concentration range $x < 0.6$ has recently received much attraction in view of the existence of a quadrupolar glass state. For this concentration range the ferroelastic transition disappears and the crystals remain cubic down to the lowest temperatures. In diffraction experiments this low temperature state can be characterized by an anisotropic pattern of quasielastic scattered intensitites centered around the Bragg peaks of the cubic lattice [1, 7] which was interpreted in the framework of an orientational glass state [8]. In a recent X-ray investigation [18] it has been demonstrated that for temperatures below the freezing temperature T_F the diffraction lines are broadened. This effect depends on the scattering angle. In addition it appears to be large in crystals near the crossover concentration $x_c = 0.6$. The motivation of the present work was to study this phenomenon and especially to investigate the temperature and the momentum transfer dependence of the line broadening in a $(KBr)_{(1-x)}(KCN)_x$ single crystal close to x_c. Our aim was to relate the increase of the linewidth of the Bragg reflection with a distribution of frozen-in lattice strains which would amount for the low temperature thermodynamic properties [6].

Elastic neutron scattering experiments on $(KBr)_{0.47}$ $(KCN)_{0.53}$ were carried out on the triple-axis spectrometer $D10$ located on a thermal neutron guide at the I.L.L. The sample was mounted on an Eulerian cradle to allow scanning along all reciprocal lattice directions. The vertically focussing (200) Cu monochromator gave a wavelength of 1.260 A. The pyrolytic graphite analyzer was set to the (004) reflection to give an energy resolution of approximately 1.5 meV and was set to zero energy transfer. A He-flow cryostat (Zeyen, Chagnon, Disdier and Morin, 1984) [19] allowed variation of the temperature from 10 K to 300 K with an accuracy of 0.05 K. The sample with a volume of 50 mm^3 was cut from the center of a large single crystal grown by Czochralski techniques by S. Haussül at the Institut für Kristallographie at the University of Cologne. The composition of melt was $x = 0.5$, while a gravimetric analysis yielded a concentration of $x = 0.53$.

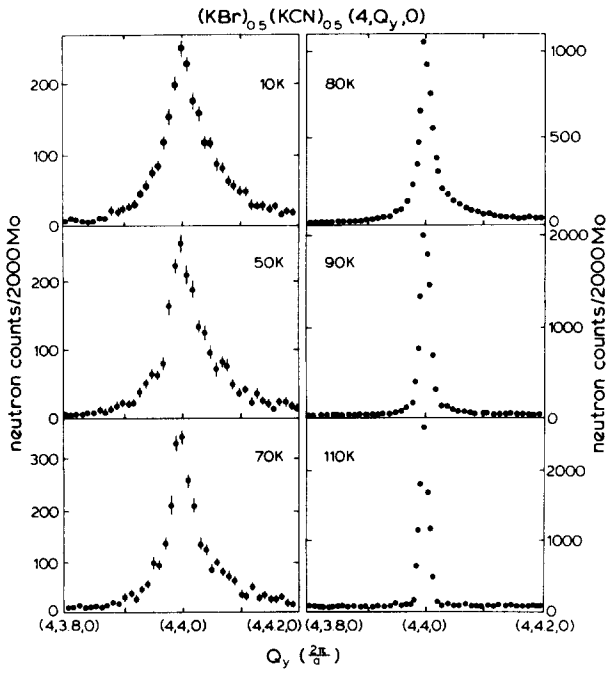

Fig. 1. $\mathbf{Q}_y$-scans at zero energy transfer in the (001)-plane through the (440) reciprocal lattice point at various temperatures

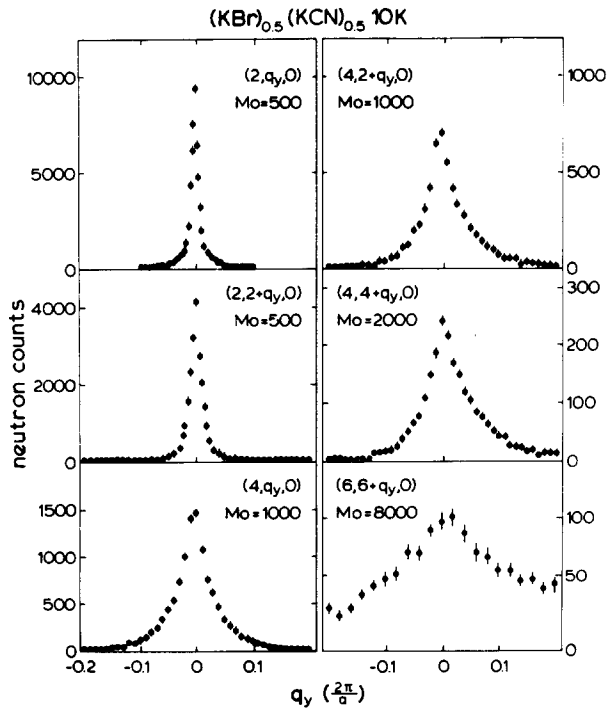

Fig. 2. $\mathbf{Q}_y$-scans at zero energy transfer in the (001)-plane through various reciprocal lattice points at 10 K.

Figure 1, showing scans through the (440)-Bragg reflection in the (001) plane at various temperatures,

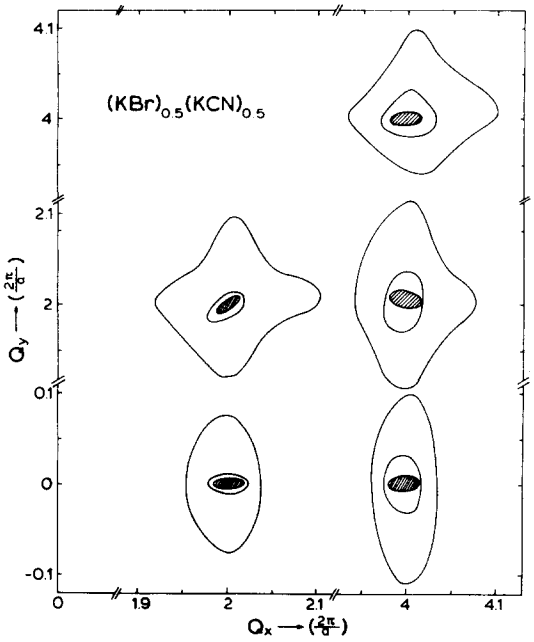

Fig. 3. Equal intensity contour map around different reciprocal lattice points in the (001)-plane. The shaded area gives the half widths of the Bragg peaks at high temperatures which are determined by the instrumental resolution only. The inner lines represent intensity contours at the wings of the Lorentzian peak at 10 K (depending on the maximum peak intensity we plotted 5% to 20% intensity contours).

gives a clear demonstration of the transition from the crystalline into the glassy state. At 110 K we find a Gaussian line shape with a width that is determined by the resolution of the spetrometer only. At 90 K the linewidth starts to increase with anomalous broad quasielastic intensities appearing in addition to the Gaussian contribution. For temperatures $T \leqq 80$ K the line shapes of the Bragg intensities clearly become Lorentzian with a dramatic drop of the intensity at the peak maximum and an equally dramatic increase in the linewidth.

Figure 2 presents scans through various reciprocal lattice points in the (001) plane at 10 K. These data imply a strong increase of the intrinsic linewidth with momentum transfer $\mathbf{Q}$. An analysis of the data where we calculated the extra breath of the line width above the experimental resolution for a series of (hk0) reflections as measured in Q_y-scans yielded roughly $\Delta Q \propto Q^3$.

A closer inspection of Fig. 2 shows another interesting phenomenon. While the (400) diffraction peak shows a perfect symmetric Lorentzian line shape we find strongly asymmetric contributions in the (420), (440) and (660) diffraction line shapes. This distinct asymmetry is also visible in Fig. 1. It can be explained neither

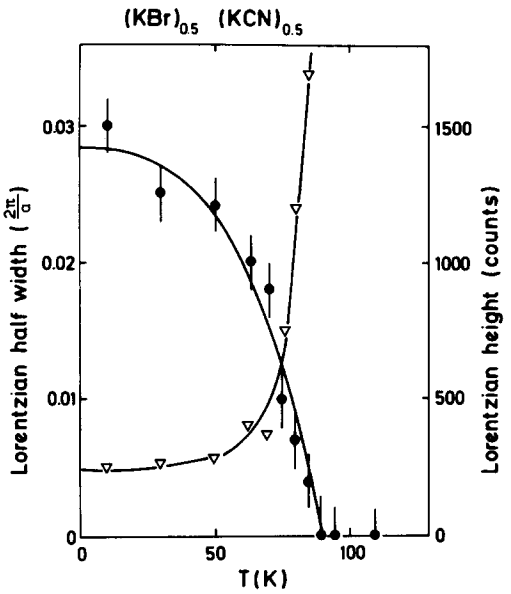

Fig. 4. Temperature dependence of the Lorentzian width (•) and the Lorentzian height (▽) as determined at the (440) reciprocal lattice point. The solid line is a result of the fit described in the text.

by the Lorentz factor nor by a Q^2-dependence of the scattering law.

In Fig. 3 we plotted equal intensity contours at 10 K. The shaded areas indicate the half widths of the Bragg peaks at high temperatures ($T \geqq 100$ K) which are solely determined by the resolution of the spectrometer. The inner contours represent the half widths of the Lorentzian line shapes at 10 K. Note, that there is a considerable broadening of the diffraction spots. This broadening is quite anisotropic and increases with increasing momentum transfer Q. The anisotropy becomes dominant if one takes equal intensity contours at 10 K at the Lorentzian wings which are shown by the outer lines in Fig. 3. These outer contour pattern can be described by a factor $(\mathbf{Q} \cdot \mathbf{e})^2$ where $\mathbf{e}$ is the polarisation vector of T_{2g} strains. It is important to note that these quasielastic intensities are not contributions due to thermal diffuse scattering processes since below 90 K these intensities increase with decreasing temperatures while the transverse sound velocities increase again [1, 2].

The temperature dependence of the half widths and the heights as determined around the (440) reciprocal lattice point along Q_y is shown in Fig. 4. Here we assumed that the line shape is Lorentzian, although theoretically [8] it should composed of a symmetric term $1/q^2$ and an asymmetric contribution $1/q$. For a fit of the half widths over the whole temperature region $T \leqq T_F$ we used a temperature dependence of the order parameter of the form $\psi = [1 - (T/T_F)^n]$. The best fit was obtained with $n = 3 \pm 0.5$. This gives a linear temperature dependence near $T_F = 89$ K and shows a saturation effect at low temperatures in good agreement with the experimental results.

Equal intensity contour lines around the (220) Bragg reflection have been reported previously by Rowe *et al.* [1]. Michel and Rowe [8] interpreted these experimental results by the onset of short range orientational order, where the coupling of translations and rotations explained the characteristic asymmetries of the equal intensity contours. They formulated a neutron scattering law, were in addition to the elastic Bragg lines quasielastic intensities appear, namely a symmetric contribution that follows a Q^2/q^2 dependence and, depending on the symmetry of the strain field, an asymmetric Q/q term. The quasielastic diffraction patterns of the Figs. 1 to 3 exhibit the symmetry as described in this theory by Michel and Rowe [8]. But the elastic cross section contains no δ-functions at the Bragg points. The experimentally observed Bragg scattering pattern is characterized by a line width dependence that can be described by $\Delta Q \propto Q^3$.

This is a rather unexpected result and at present we can give no theoretical explanation. However, referring to textbooks on X-ray and neutron diffraction, we can offer some simple arguments: the broadening of diffraction lines indicate an imperfect low temperature lattice. A linear increase of the line width ΔQ with momentum transfer Q can be due to a distribution of lattice parameters around an average pattern which is a characteristic property of diffraction lines scattered from non-uniformly strained crystals such as the work hardened states of metals. This was what we expected to find experimentally guided by the idea of a distribution of frozen-in lattice strains. According to fragmentation theories particle size effects give a Q-independent increase of the line width above the experimental resolution in a diffraction pattern. A combination of both effects may yield a more complex line width dependence. However, within these theories where the displacement fluctuations bear a defined relation to the former unit cell, there is no way to explain the experimentally observed Q^3 dependence of the Lorentzian width. We feel that this observation signals the breakdown of long range order and indicates the transition into an amorphous state. For a one dimensional chain with no long range order the scattering function displays a series of peaks of Lorentzian shape with a half width half maximum increasing with Q^2 [20]. To our knowledge there exists no analytic expression for the three dimensional state. We argue, that the experimental findings in $(KBr)_{0.47}(KCN)_{0.53}$ where the Lorentzian width increases with Q^3 is the three dimensional analogue and characterizes the loss of long range order in three dimensions. Of course this has to be proven theoretically.

In conculsion, we have performed a single crystal diffraction study in $(KBr)_{1-x}(KCN)_x$ near the crossover concentration $x_c = 0.6$. At low temperatures we found an increase of the line widths of the diffraction lines Q^3. For temperatures just below freezing these Lorentzian widths increase linearly with decreasing temperatures. We propose that the broadening of the diffraction lines indicates the transition from the crystalline into an amorphous state.

REFERENCES

1. J.M. Rowe, J.J. Rush, D.G. Hinks & S. Susman, *Phys. Rev. Lett.* **43**, 1158 (1979).
2. A. Loidl, R. Feile & K. Knorr, *Phys. Rev. Lett.* **48**, 1263 (1982).
3. S.Bhattacharya, S.R. Nagel, L. Fleishman & S. Susman, *Phys. Rev. Lett.* **48**, 1267 (1982).
4. J.J. De Yoreo, M. Meissner, B.O. Pohl, J.M. Rowe J.J. Rush & S. Susman, *Phys. Rev. Lett.* **51**, 1050 (1983).
5. D. Moy, J.N. Dobbs & A.C. Anderson, *Phys. Rev.* **B29**, 2160 (1984).
6. M.W. Klein, *Phys. Rev.* **B29**, 5825, 1984, B. Fischer & M.W. Klein *Phys. Rev. Lett.* **43**, 289 (1979).
7. A. Loidl, K. Knorr, R. Feile & J.K. Kjems, *Phys. Rev. Lett.* **51**, 1054 (1983), A. Loidl, R. Feile, K. Knorr & J.K. Kjems, *Phys. Rev.* **B29**, 6052 (1984).
8. K.H. Michel & J.M. Rowe, *Phys. Rev.* **B22**, 1417 (1980).
9. C.W. Garland, J.Z. Kwiecien & J.C. Damien, *Phys. Rev.* **B25**, 5818 (1982).
10. A. Loidl, R. Feile & K. Knorr, *Z. Phys.* **B42**, 143 (1981).
11. U.T. Höchli, *Phys. Rev. Lett.* **48**, 1494 (1982).
12. U.T. Höchli, H.E. Weibel & W. Rehwald, *J. Phys.* **C15**, 6129 (1982).
13. E. Courtens, *Phys. Rev. Lett.* **52**, 69 (1984).
14. E. Courtens. T.F. Rosenbaum, S.E. Nagler & P.M. Horn, *Phys. Rev.* **B29**, 515 (1984).
15. N.S. Sullivan, M. Devoret, B.P. Cowan & C. Urbina, *Phys. Rev.* **B17**, 5016 (1978).
16. D. Estève, W.S. Sullivan & M. Devoret *J. Phys. (Paris)* **43**, L793 (1982).
17. W. Press, B. Janik & H. Grimm *Z. Phys.* **B49**, 9 (1982).
18. K. Knorr & A. Loidl *Phys. Rev. B,* 1985 to be published.
19. C.M.E. Zeyen, R. Chagnon, F. Disdier & H. Morin, *Revue de Physique Appliquée*, 1984 to be published
20. I.U. Heilmann, J.D. Axe, J.M. Hastings, G. Shirane *Phys. Rev.* **B20**, 751 (1979).