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Alois Loidl, K. Knorr, R. Feile, J. K. Kjems

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## Inelastic Neutron Scattering Study of the Structural Glass Transition in a K(Br,CN) Mixed Crystal

A. Loidl and K. Knorr

*Institut für Physik, Johannes Gutenberg Universität, D-6500 Mainz, West Germany*

and

R. Feile and J. K. Kjems

*Risø National Laboratory, DK-4000 Roskilde, Denmark*

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The coupled rotational-translational excitations in  $(\text{KBr})_{0.992}(\text{KCN})_{0.008}$  were studied by inelastic neutron scattering. For the first time the  $A_{1g}$ - $T_{2g}$  tunneling transition and the  $A_{1g}$ - $E_g$  librational excitation were followed at the transition from the paraelastic to the structural glass state. The drastic reduction of the  $T_{2g}$  rotation-translation coupling suggests that the number of free-ion tunneling states is reduced in favor of cluster re-orientation modes which are effectively decoupled from the lattice.

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The present study was motivated by recent experimental<sup>1-5</sup> and theoretical<sup>6,7</sup> evidence that a structural glass state exists in the mixed crystals  $(\text{KBr})_{1-x}(\text{KCN})_x$ . It is characterized by a short-range order of the frozen-in CN orientations as suggested by the pattern of the quasielastic neutron scattering experiments.<sup>1,6</sup> The freezing temperature  $T_F$  is defined by cusps in the dipolar<sup>2,3,5</sup> and quadrupolar<sup>2,4</sup> susceptibilities which exhibit a strong frequency dependence demonstrating that the orientational glass state is a nonequilibrium phenomenon. However, a microscopic picture of the glass transition is still missing. The key for the understanding of the structural and dynamic properties of these crystals is the knowledge of the rotational excitations of the CN<sup>-</sup> ions and their coupling to the lattice. This was successfully demonstrated by inelastic neutron scattering experiments in the paraelastic phase<sup>8</sup> and has been pointed out in a heuristic model for structural glasses.<sup>7</sup> In this Letter we will pose the question of how these molecular excitations and their coupling to the lattice strains are affected by the onset of the glass state.

The inelastic neutron scattering experiments in  $(\text{KBr})_{0.992}(\text{KCN})_{0.008}$  were carried out on the spectrometers TAS6 and TAS7 located at the cold source of the reactor DR3 at the Risø National Laboratory. Previous ultrasonic<sup>4</sup> and dielectric<sup>5</sup> measurements on pieces of the same crystal yielded freezing temperatures  $T_F < 3$  K at 100 kHz and  $T_F = 4$  K in the megahertz range.

In the first set of experiments the freezing temperature in the terahertz range was determined from the temperature dependence of the quasielastic short-range-order scattering and of the

long-wavelength phonon frequencies in the  $[100]$   $T_y$  branch. Temperature scans at  $\vec{Q} = (2, 0, 1, 0)$  and  $\hbar\omega = 0$  showed that short-range-order scattering sets in at 9 K and saturates below 2.5 K with an extra intensity of about 15% above the incoherent background. Figure 1 demonstrates the behavior of the long-wavelength transverse-phonon frequencies in comparison with phonon frequencies which are obtained by extrapolating the ultrasonic results with the assumption of linear dispersion. For wave vectors  $q/q_{ZB} \geq 0.06$  a softening of the modes could not be detected. However, for wave vectors  $q/q_{ZB} \leq 0.04$  the phonon frequencies as a function of temperature pass through a minimum at about 10 K. At  $q/q_{ZB} = 0.03$  and low temperature one notes a splitting of the branch due to a hybridization with a low-lying molecular excitation. From Fig. 1 and the short-range-order scattering we determined the freezing temperature  $T_F = 10 \pm 1$  K at terahertz frequencies.

The main concern of the present work is the study of rotational excitations in the paraelastic and in the orientational glass state. Results in  $E_g$  symmetry are presented in Fig. 2. The constant- $\vec{Q}$  scans show the temperature dependence of the  $[110]$   $T_{xy}$  mode at the wave vector where the molecular excitation anticrosses the phonon branch. At first glance the data taken in the paraelastic phase (30 and 15 K) and in the glass state (4.8 and 2 K) look very similar. Evidently there are only minor effects in the energy and the line-width of the molecular excitation in passing the freezing temperature.

In  $T_{2g}$  symmetry the only relevant interaction was found at 0.25 meV. At this frequency the

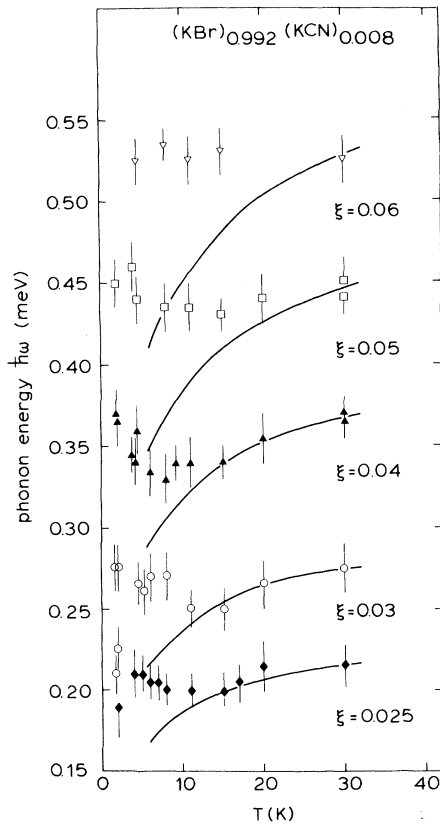


FIG. 1. Phonon energies along  $(2, \xi, 0)$  vs temperature compared to ultrasonic results (Ref. 4) (solid lines).

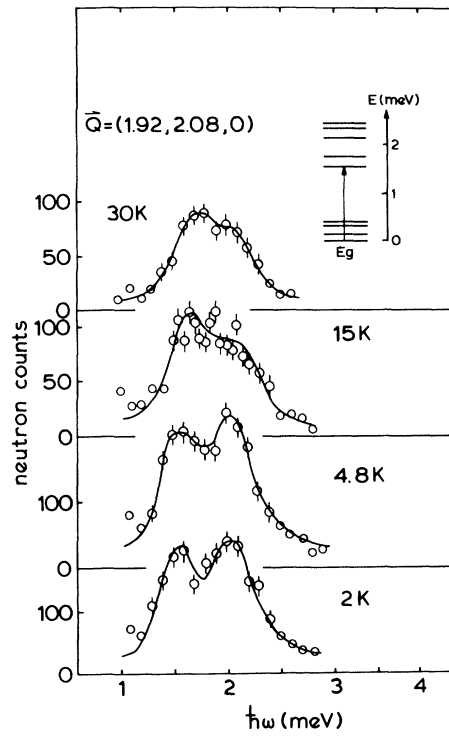


FIG. 2. Neutron scattering line shapes in  $E_g$  symmetry of the resonance frequency as a function of temperature. The inset shows an approximate energy-level spacing of a rigid dumbbell in an octahedral hindering potential (Ref. 10). The solid lines are theoretical results.

$[100]$  transverse phonons show the strongest coupling to a rotational excited state. The results at 2 K are shown in Fig. 3. Surprisingly these results are almost identical with those of Rowe *et al.*<sup>8</sup> on a crystal with a 20 times lower CN concentration. Figure 4 shows the temperature dependence of the neutron groups at the resonant frequency of the  $[100] T_y$  branch with the molecular excitation. With increasing temperatures the double-peak structure vanishes in favor of a broad single peak which narrows upon further heating. The behavior above 4 K is characteristic for phonons coupled to a purely relaxational channel.

The qualitative analysis of the data will be based on the pseudospin approach of Silverman.<sup>9</sup> The rotational susceptibility of a two-level system can be written as

$$\chi(\omega) = 2 \tanh\left(\frac{\hbar\Delta}{2k_B T}\right) \frac{\Delta^2 + \Gamma^2 + i\omega\Gamma}{\Delta(\Delta^2 + \Gamma^2 - \omega^2 + 2i\omega\Gamma)},$$

where  $\hbar\Delta$  is the energy and  $\Gamma$  is the linewidth of

the transition connecting the two levels. The phonon propagator of the coupled phonon-pseudospin system is given by

$$D(\vec{q}, \omega) = \frac{2\omega_0(\vec{q})}{\omega_0^2(\vec{q}) - \omega^2 - xG^2(\vec{q})\chi(\omega)}.$$

$\omega_0(\vec{q})$  is the bare phonon frequency and  $G^2(\vec{q})$  is the rotational-translational coupling constant. For small wave numbers we set  $G(\vec{q}) = \omega_0(\vec{q})g$ . Finally, the dynamic structure factor is proportional to the imaginary part of  $D(\vec{q}, \omega)$ . This formalism includes both a coupled-mode behavior for  $\Delta \gg \Gamma$  and a relaxational behavior for  $\Delta < \Gamma$ .

In  $E_g$  symmetry the analysis yields an energy-level separation  $\Delta = 1.8 \pm 0.2$  meV and a linewidth  $\Gamma = 0.3 \pm 0.05$  meV above and below the glass transition. However, the coupling constant—rewritten as  $T_s = xg^2$ —is reduced from  $1.1 \pm 0.1$  K in the paraelastic phase to  $0.9 \pm 0.1$  K in the glass state. The results of the analysis in  $T_{2g}$  symmetry are reproduced in Fig. 5. At the lowest temperatures we obtained  $\Delta = 0.25 \pm 0.01$  meV,  $\Gamma = 0.03 \pm 0.005$

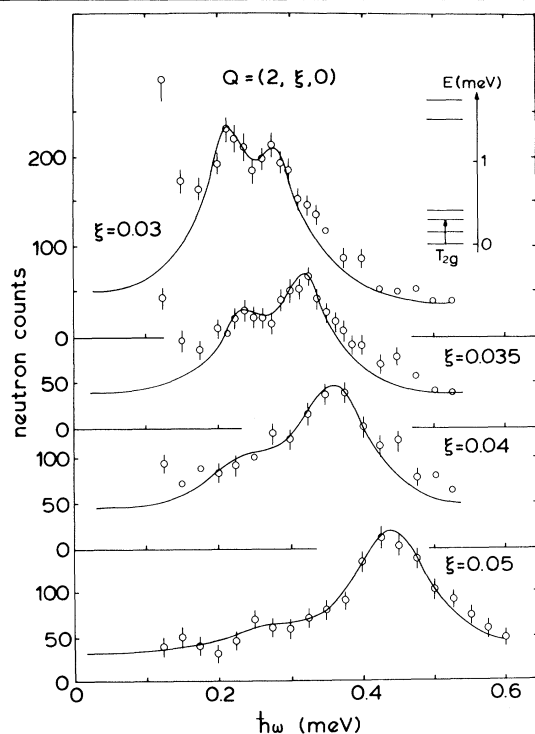


FIG. 3. Neutron scattering line shapes in  $T_{2g}$  symmetry at 2 K. The solid lines are the result of the Silverman model. The inset shows the approximate energy-level spacing after Beyeler (Ref. 10).

meV, and  $T_s = 0.18 \pm 0.02$  K. For higher temperatures a strong increase of  $\Gamma$  and  $T_s$  is noted. In the paraelastic phase we found a relaxational behavior with  $\Delta \lesssim \Gamma$  and a rotation-translation coupling constant  $T_s = 1.2 \pm 0.1$  K which is in agreement with ultrasonic results.<sup>4</sup>

The measurements yield information on two excitations of the molecular system: a  $T_{2g}$  transition at 0.25 meV and a  $E_g$  transition at 1.8 meV. Guided by the work of Beyeler<sup>10</sup> we identify the former one as a tunneling transition and the latter one as a libration around the  $\langle 111 \rangle$  easy directions of a Devonshire potential described by the potential strength  $K = 4$  meV and a mixing angle of  $\varphi = 225^\circ$  in the nomenclature of Beyeler.<sup>10</sup>

An explanation of all the experimental observations can now be obtained when the formation of the glass state is understood as a gradual blocking of the CN system into clusters with random patterns of locked  $\langle 111 \rangle$  orientations:

- (i) The cluster formation gives rise to quasi-static short-range-order scattering.
- (ii) The  $CN^-$  ions within the clusters can no longer respond to  $T_{2g}$  lattice strains by fast sin-

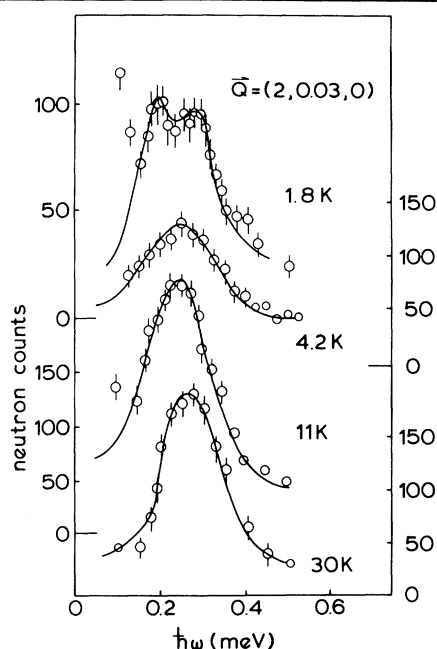


FIG. 4. Neutron scattering line shapes in  $T_{2g}$  symmetry of the resonance frequency as a function of temperature. The solid lines represent theoretical results.

gle-ion tunneling reorientations. Reorientations of this type are reserved to those molecules which are not yet firmly incorporated into the clusters. The reduced  $T_{2g}$  coupling constant  $T_s$  can be regarded as a direct measure of the fraction of the loose dumbbells. It is not surprising

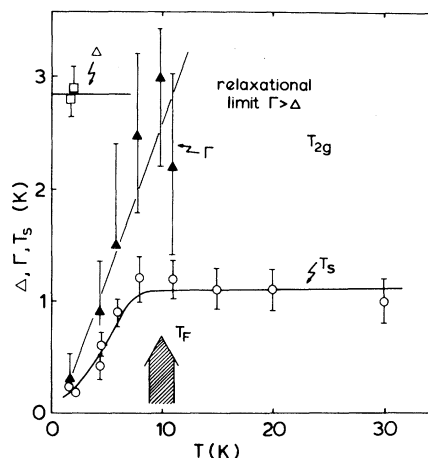


FIG. 5. Temperature dependence of the level separation  $\Delta$  (squares), the linewidth  $\Gamma$  (triangles), and the coupling constant  $T_s$  (circles) of the molecular susceptibility as measured in  $T_{2g}$  symmetry. The solid lines are a guide to the eye only.

that the loose  $\text{CN}^-$  ions in the present sample show the tunneling excitation at the same frequency  $\Delta$  as the isolated ions in the study of Rowe *et al.*<sup>8</sup> in a very dilute mixed crystal. The inverse lifetime  $\Gamma$  of the single-ion tunneling transition varies—within experimental error—linearly with temperature as one expects for a thermal modulation of the tunneling barrier rather than exponentially—Arrhenius-like—as would be the case when the lifetime of the single-ion tunneling states were limited by thermal activation across the barrier. The increase of  $\Gamma$  with  $T$  leads to a crossover from a slow to a fast relaxational behavior roughly, but presumably accidentally, at  $T_F$ . Of course, new collective reorientations will be possible within the clusters, but from the present results it is clear that these modes have either very low frequencies or are effectively decoupled from the lattice strains.

(iii) The  $E_g$  librations conserve the CN alignment along  $\langle 111 \rangle$ . Thus these modes are irrelevant for the formation of an orientational glass and there is no reason why these modes should not be still possible within the clusters perhaps somewhat reduced in their oscillator strength and possibly shifted and broadened in frequency because of various local environments. Indeed, the experiments show that the  $A_{1g}$ - $E_g$  librational excitation is only insignificantly affected by the freezing process.

These results give a clear understanding of the structural glass transition in  $(\text{KBr})_{1-x}(\text{KCN})_x$  and they are of importance to the physics of spin-glasses in general<sup>11</sup>: At temperatures  $T = T_F$  random strain fields divide the CN system into “fast” isolated  $\text{CN}^-$  ions and into “slow spins” blocked into clusters. The maximum in the quadrupolar susceptibility occurs through a competition between the setup of local order and the  $T^{-1}$  Curie law of the free ions. The cluster formation proc-

ess reduces the number of single-ion tunneling states which are strongly coupled to the lattice in favor of new only weakly coupled collective modes representing cluster reorientation processes. The different clusters give a broad distribution of low-energy excitations which have little direct effect on the ultrasonic properties and on the dynamic structure factor in an inelastic neutron scattering experiment, but they will contribute in calorimetric experiments depending on the time scale employed. Similar low-lying energy states are believed to be important in the low-temperature properties of “real” glasses as proposed by Anderson, Halperin, and Varma<sup>12</sup> and by Phillips.<sup>13</sup>

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