

K. Gray (Plenum, New York, 1981), p. 1.

<sup>13</sup>P. Herth and O. Weiss, *Z. Angew. Phys.* **29**, 101 (1970).

<sup>14</sup>O. Weiss, *J. Phys. (Paris), Colloq.* **33**, C4-48 (1972).

<sup>15</sup>M. W. Cole, *Phys. Rev. Lett.* **28**, 1622 (1972).

<sup>16</sup>A detailed analysis of this problem will be presented

in a future publication.

<sup>17</sup>R. Elgin and D. Goodstein, *Phys. Rev. A* **9**, 2657 (1974).

<sup>18</sup>It is interesting to note that the calculation in Ref. 6 suggests that  $E > -\mu$  by 25%, in contrast to our observations.

## Frequency Dependence of the Orientational Freezing in $(\text{KBr})_{1-x}(\text{KCN})_x$

A. Loidl, R. Feile, and K. Knorr

*Institut für Physik der Universität Mainz, D-6500 Mainz, Federal Republic of Germany*

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Dielectric, ultrasonic, and neutron-scattering measurements in  $(\text{KBr})_{1-x}(\text{KCN})_x$  are reported for concentrations  $x$  ranging from 0.01 to 0.5. The dipolar and the quadrupolar susceptibilities exhibit frequency- and concentration-dependent cusps showing that the freezing process into an orientational glass state is a relaxational phenomenon.

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In KCN and the related compounds  $(\text{KBr})_{1-x}(\text{KCN})_x$  the aspherical dumbbell-shaped CN molecule resides in an octahedral Devonshire potential. The structural, elastic, and dynamic properties were explained by a coupling of the rotational excitations to the translational modes.<sup>1,2</sup> In the last two years there has been increasing experimental evidence that a glasslike phase exists for CN concentrations  $x$  less than 0.56.<sup>3,4</sup> The orientational glass state is characterized by a short-range order of the frozen-in CN molecules as suggested by the pattern of quasi-elastic diffuse intensity in neutron scattering experiments.<sup>3,5</sup> The temperatures of minimum sound velocities—determined from ultrasonic, Brillouin, and inelastic neutron scattering experiments—were regarded as freezing temperatures  $T_F(x)$ .<sup>4,5</sup> The occurrence of a glass state in these molecular systems was first predicted by Fischer and Klein.<sup>6</sup> It is thought to result from a frustration of the effective multipole interaction between CN pairs into which not only the orientations of the multipoles but also the bond vectors enter.

So far no attention has been paid to the question of whether the ordering in  $(\text{KBr})_{1-x}(\text{KCN})_x$  is strictly static or rather of a relaxational type. We therefore report measurements of the freezing temperatures over ten decades of frequency. In order to cover this wide frequency range we used three experimental methods: dielectric (87 Hz–100 kHz), ultrasonic (megahertz range),

and neutron-scattering (terahertz range) measurements. As above,  $T_F(x, \omega)$  is defined by the maximum of the appropriate susceptibility as a function of temperature.

The experiments were carried out on single crystals of  $(\text{KBr})_{1-x}(\text{KCN})_x$  which have been grown in the crystal growth laboratory of the University of Utah from zone-refined KBr and KCN materials. Single crystals with concentrations  $x = 0.01, 0.04, 0.14, 0.25$ , and  $0.5$  were investigated. (The concentrations 0.01, 0.25, and 0.50 refer to the composition of the melt; the figures 0.04 and 0.14 have been determined by chemical analysis. The composition of the melt in these cases was 5% and 20%, respectively.) Pieces of the same single crystals were used in the different experimental setups.

The dielectric constant  $\epsilon'$  measured at four frequencies is shown in Fig. 1 for  $x = 0.14$ . With decreasing temperature  $\epsilon'$  increases in a Curie-like fashion and for all concentrations  $x \geq 0.04$  passes through a maximum at temperatures  $T_F(x, \omega)$ . The maximum of the dielectric loss is always reached significantly below  $T_F$ .

The ultrasonic data were obtained in a conventional setup with a quartz transducer attached to the samples by using the pulse-echo-overlap method. Figure 2 shows the temperature dependence of the elastic constant  $c_{11}$  for  $x = 0, 0.01, 0.04, 0.14$ , and  $0.25$  at 10 MHz. All samples containing  $\text{CN}^-$  ions exhibit a minimum at a characteristic temperature  $T_F$ . For higher CN con-

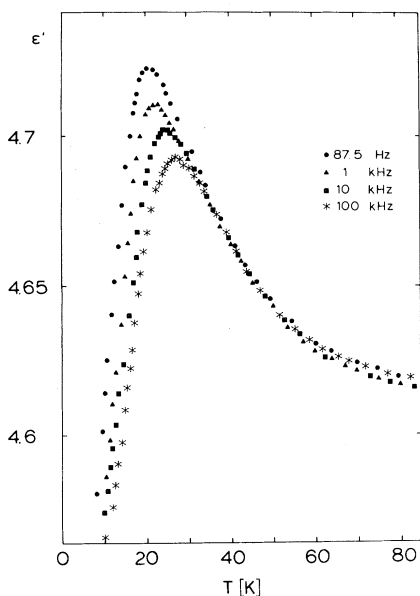


FIG. 1. The dielectric constant for  $x = 0.14$  measured at four frequencies: circles, 87.5 Hz; triangles, 1 kHz; squares, 10 kHz; and asterisks, 100 kHz.

centrations the echos were lost because of high attenuation in an intermediate temperature range below  $T_F$  but could be recovered again at low temperatures. At low CN concentrations ultrasonic experiments with overtone frequencies up to 90 MHz were successful. A clear dispersion and slight shifts of the minimum were observed (see inset of Fig. 2).

The elastic constants  $c_i$  are connected with the appropriate multipolar susceptibility  $\chi_i$  via<sup>4</sup>

$$\chi_i \propto 1 - c_i/c_i^0, \quad (1)$$

where  $c_i^0$  is the background elastic constant of the reference system KBr. Thus a minimum of  $c_{11}$  (which contains  $A_{1g}$  and  $E_g$  contributions) is connected with a maximum of the  $E_g$  quadrupolar susceptibility, since—as shown in our previous ultrasonic study for  $x = 0.04$ —the bulk modulus ( $A_{1g}$ ) is unaffected on crossing  $T_F$ .

Neutron-scattering studies were performed on the 14% and 25% samples. These data were collected on a triple-axis spectrometer located at a cold source of the reactor DR3 at Risø National Laboratory with an incident energy of 5 meV. We followed the temperature dependence of the [100] TA branch for  $0.075 \leq q/q_{ZB} \leq 0.15$  which is related to the elastic constant  $c_{44}$ . Qualitatively the results are similar to those reported by Rowe *et al.*<sup>3</sup> in a 50% sample. The phonon frequency as a function of temperature passes

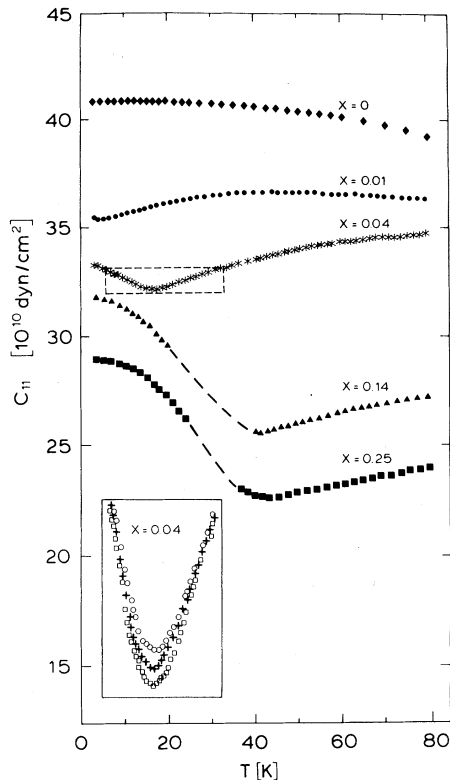


FIG. 2. The elastic constant  $c_{11}(T)$  measured at 10 MHz for five concentrations  $x$ . The broken lines at  $x = 0.14$  and  $0.25$  are guides to the eye in the region where the pulse echo was lost. Inset:  $c_{11}(T)$  for  $x = 0.04$  measured at 10 MHz (open squares), 30 MHz (pluses), and 50 MHz (open circles). The vertical axis is expanded by factor of 10.

through a minimum [ $T_F(x = 0.14) = 55$  K,  $T_F(x = 0.25) = 80$  K]. At the different  $q$  values we found no shift of  $T_F$  exceeding the experimental error. At all temperatures—above, at, and below  $T_F$ —well-defined neutron groups were observed. Quasielastic intensity with an energy width given by the instrumental resolution develops gradually above  $T_F$  and starts to grow strongly at  $T_F$ . The results in the 14% sample derived for  $c_{44}$  complemented with the respective ultrasonic data are shown in Fig. 3. The neutron experiment yields a minimum definitively above that observed in the megahertz region.

The characteristic temperatures  $T_F$  as derived with these different methods are given in Fig. 4 as a function of the logarithm of the measuring frequency. Clearly the direct comparison of the anomalies of the dipolar and the  $E_g$  and  $T_{2g}$  quadrupolar orientational susceptibilities needs some justification: The CN molecules are known to be oriented along one of the eight  $\langle 111 \rangle$  directions.<sup>7</sup>

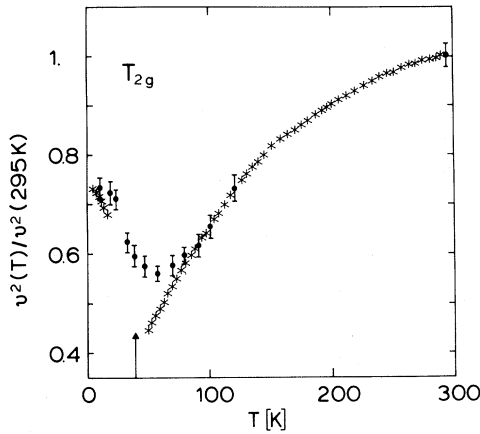


FIG. 3. The relative temperature dependence of the square of the sound velocity (proportional to  $c_{44}$ ) as determined from ultrasonic (asterisks) and neutron-scattering (solid circles) experiments. The arrow marks the minimum of  $c_{11}(T)$  measured at 10 MHz.

The dipole and the quadrupole moments are rigidly connected with the shape of the CN dumbbell. The hindering barriers are produced by the Born-Mayer potential generated by the neighboring  $K^+$  ions. Most reorientation processes, in particular the most likely one from a given  $[111]$  direction to a neighboring direction, e.g.,  $[11\bar{1}]$ , will affect the expectation values of all three—the dipole and the  $E_g$  and  $T_{2g}$  quadrupole moments. Thus any freezing of dipole moments should also block the motion of the two quadrupole moments and vice versa. The freezing temperature is expected to be mode independent, at least in this single-ion picture. In fact we showed recently for the 4% sample<sup>4</sup> that the  $T_{2g}$  and  $E_g$  modes yield identical freezing temperatures. Nevertheless one has to admit that in a quadrupolar glass phase the CN molecules could still fluctuate with respect to head and tail, although these direct  $180^\circ$  flips appear very unlikely. In any case, the quadrupolar freezing should at least significantly reduce the degrees of freedom for dipolar reorientations and should thus leave marks in the dipolar susceptibility.

The frequency dependence of  $T_F$  as shown in Fig. 4 clearly indicates that the freezing in  $(KBr)_{1-x}(KCN)_x$  is by no means a static process but rather a relaxational phenomenon. The  $T_F$  values determined from the Brillouin data of Satija and Wang<sup>8</sup> extrapolated to the concentrations of our work roughly fit into the general behavior of Fig. 4.

We evaluate the present results for a given CN

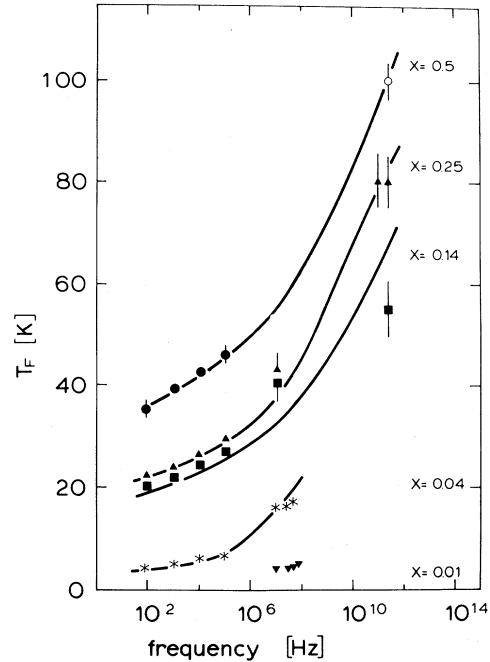


FIG. 4. The frequency dependence of the freezing temperatures at  $x = 0.01$  (inverse triangles), 0.04 (asterisks), 0.14 (squares), 0.25 (triangles), and 0.5 (solid circles). Results for a given concentration were obtained from pieces of the same single crystal. One datum point (open circle) is taken from Rowe *et al.* (Ref. 3) and refers to a 50% crystal. A comparison of the two 50% samples may suffer from differences in the actual concentration.

concentration by a relaxational susceptibility

$$\chi(\omega, T) = \frac{1}{k_B T} \frac{1}{1 - i\omega\tau} \quad (2)$$

with a characteristic relaxation time  $\tau$ . This form implies that reorientation processes which are much slower than the measuring time  $1/\tau$  no longer contribute to the response. In the simplest model the temperature dependence of  $\tau$  follows the Arrhenius law

$$\tau = \tau_0 \exp(E_0/k_B T), \quad (3)$$

where  $\tau_0$  is the time between two consecutive attempts for passing the energy barrier  $E_0$ . In the low-concentration limit  $E_0$  can be visualized as the saddle point of the hindering potential between two neighboring  $[111]$  directions.  $E_0$  and  $\tau_0$  which describe the frequency dependence of  $T_F$  best are listed in Table I. The results of the  $T_F(\omega)$  calculation with these values are shown as solid lines in Fig. 4. Both  $E_0$  and the attempt frequency  $1/\tau_0$  increase strongly with the con-

TABLE I. Concentration dependence of the energy barrier  $E_0$  and the attempt frequency  $\tau_0$  in  $(\text{KBr})_{1-x}(\text{KCN})_x$ .

$x$	$E$ (K)	$\tau_0$ (s)
0.04	57	$1.2 \times 10^{-9}$
0.14	550	$1.0 \times 10^{-16}$
0.25	600	$1.0 \times 10^{-15}$
0.50	1160	$1.2 \times 10^{-17}$

centration  $x$ .

It must be clearly stated that the susceptibility of Eq. (2) describes the single-ion case. Collective effects which become more and more important for higher concentrations enter artificially into the free parameters  $E_0$  and  $\tau_0$ . For  $x=0.5$ , for example, the fit yields an unrealistic value for the barrier height of more than 1000 K.

The gross features of the present results propose that the dipolar and quadrupolar susceptibilities probe the same relaxation process. Expressed in an alternative way this means that the different type susceptibilities would yield a common  $T_F$  if they were measured at identical frequencies. Following our discussion from above this finding is quite plausible for low CN concentrations where the single-ion model is a reasonable approximation. The situation at higher concentrations is certainly more complex. It is only because of the continuity of our data when increasing  $x$  from 0.01 up to 0.5 that we hesitate to abandon the assumption of common relaxation times for the different modes. Of course, eventually the modes will gradually decouple and lead

to successive transitions. Two anomalies due to phase transitions are shown by the measurements of Julian and Lüty<sup>9</sup> for  $x=0.8, 0.9$ , and 1.

A closer inspection shows that even at lower concentrations there are deviations from the simple model proposed. One notes that for  $x=0.04$  the increase of  $T_F$  within the ultrasonic frequencies is by far not as drastic as predicted from the overall Arrhenius law. Secondly, a finite energy width of the quasielastic scattering should have been present somewhat below  $T_F$  in the neutron experiment.

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<sup>1</sup>J. M. Rowe, J. J. Rush, N. J. Chesser, K. H. Michel, and J. Naudts, Phys. Rev. Lett. **40**, 455 (1978); K. H. Michel, J. Naudts, and B. De Raedt, Phys. Rev. B **18**, 648 (1978).

<sup>2</sup>A. Loidl, K. Knorr, J. Daubert, W. Dultz, and W. J. F. Fitzgerald, Z. Phys. B **38**, 153 (1980).

<sup>3</sup>J. M. Rowe, J. J. Rush, D. G. Hinks, and S. Susman, Phys. Rev. Lett. **43**, 1158 (1979).

<sup>4</sup>A. Loidl, R. Feile, and K. Knorr, Z. Phys. **42**, 143 (1981).

<sup>5</sup>K. H. Michel and J. M. Rowe, Phys. Rev. B **22**, 1417 (1980).

<sup>6</sup>B. Fischer and M. W. Klein, Phys. Rev. Lett. **43**, 289 (1979).

<sup>7</sup>H. U. Beyeler, Phys. Rev. B **11**, 3078 (1975).

<sup>8</sup>S. K. Satija and C. H. Wang, Solid State Commun. **28**, 617 (1978).

<sup>9</sup>M. Julian and F. Lüty, Ferroelectrics **16**, 201 (1977).