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# Calorimetric measurements in the orientational glass $(\text{KBr})_{1-x}(\text{KCN})_x$

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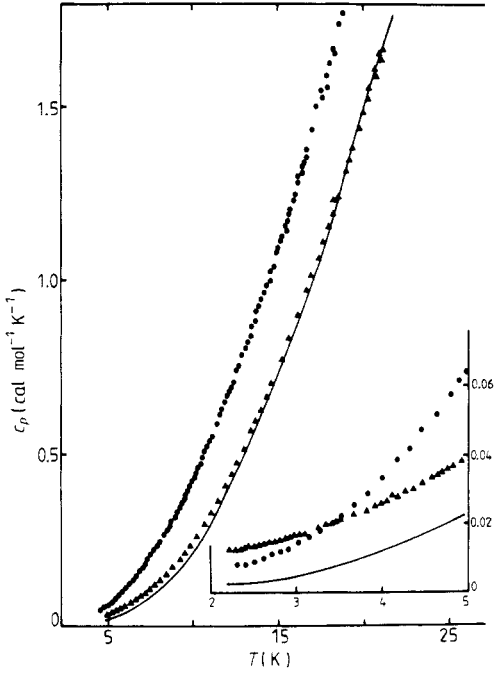
**Abstract.** The orientational glass  $(\text{KBr})_{1-x}(\text{KCN})_x$  has been studied by 'adiabatic' specific heat measurements at temperatures between 2 and 50 K. No specific heat anomaly was detectable. At low temperatures and in crystals with higher  $\text{CN}^-$  concentrations ( $x = 0.25$  and  $x = 0.53$ ) the molecular system is effectively frozen-in. Only a small fraction of  $\text{CN}^-$  molecules can equilibrate even on the timescale of these long-time measurements.

## 1. Introduction

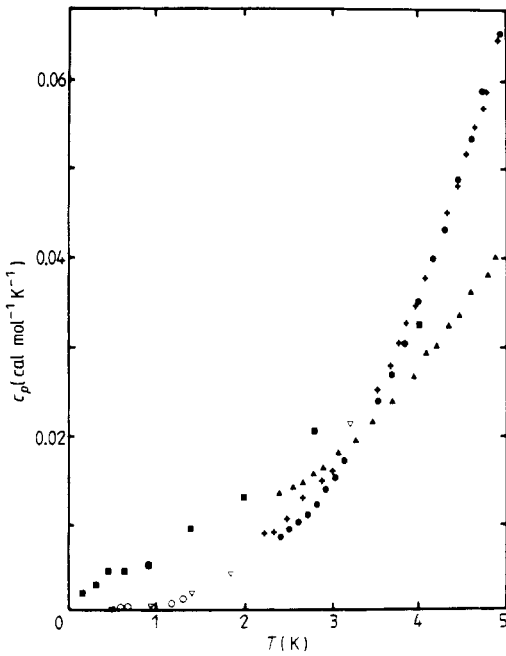
The molecular system  $(\text{KBr})_{1-x}(\text{KCN})_x$  has attracted much interest since it was found that for concentrations  $x < 0.60$  an orientational glass state occurs at low temperatures (Rowe *et al* 1979, Michel and Rowe 1980, Loidl *et al* 1981, 1983, De Yoreo *et al* 1983, Moy *et al* 1984). It is not yet clear whether this low-temperature state is a phase with an infinite correlation length (Michel and Rowe 1980, Loidl *et al* 1981, De Yoreo *et al* 1983) or a non-ergodic metastable state characterised by a cluster dynamic on a local scale (Loidl *et al* 1983). Previous calorimetric measurements at low temperatures ( $T \leq 4$  K) indicate a linear temperature-dependent term in the specific heat data similar to the results found in amorphous solids (De Yoreo *et al* 1983, Moy *et al* 1984). It was suggested that in  $(\text{KBr})_{1-x}(\text{KCN})_x$  the broad spectrum of two level energy splittings which was considered for the explanation of the linear specific heat in canonical glasses (Phillips 1972; Anderson *et al* 1972), is produced by the perturbation of the initial tunnelling transition energies by the strain fields from neighbouring  $\text{CN}^-$  ions (Moy *et al* 1984). We find that the tunnelling impurities which give rise to a Schottky-type anomaly in the low-temperature specific heat in the case of infinite dilution develops into a broad distribution of low-energy excitations at concentrations  $x \geq 0.008$ . This behaviour has been theoretically predicted by Klein (1984). For higher concentrations  $0.20 \leq x \leq 0.50$  and at low temperatures only a small fraction of  $\text{CN}^-$  ions can equilibrate on the timescales of these experiments ( $\sim 100$  s). In this concentration range the full rotational specific heat contributes at temperatures  $T \geq 20$  K.

## 2. Experiments and results

In this paper we report long-time calorimetric measurements in  $(\text{KBr})_{1-x}(\text{KCN})_x$  crystals for concentrations  $x = 0.008, 0.25, 0.53$  and  $0.92$  in the temperature range



**Figure 1.** Specific heat of  $(\text{KBr})_{0.992}(\text{KCN})_{0.008}$  ( $\blacktriangle$ ) and of  $(\text{KBr})_{0.47}(\text{KCN})_{0.53}$  ( $\bullet$ ) compared with the specific heat of an ultrapure KBr sample (full curve).



**Figure 2.** Low-temperature specific heat data of  $(\text{KBr})_{1-x}(\text{KCN})_x$ ; present experiments:  $x = 0.008$  ( $\blacktriangle$ ),  $x = 0.25$  (+),  $x = 0.53$  ( $\bullet$ ); Moy *et al* (1984):  $x = 0.01$  ( $\blacksquare$ ); De Yoreo *et al* (1983):  $x = 0.25$  ( $\nabla$ ),  $x = 0.50$  ( $\circ$ ).

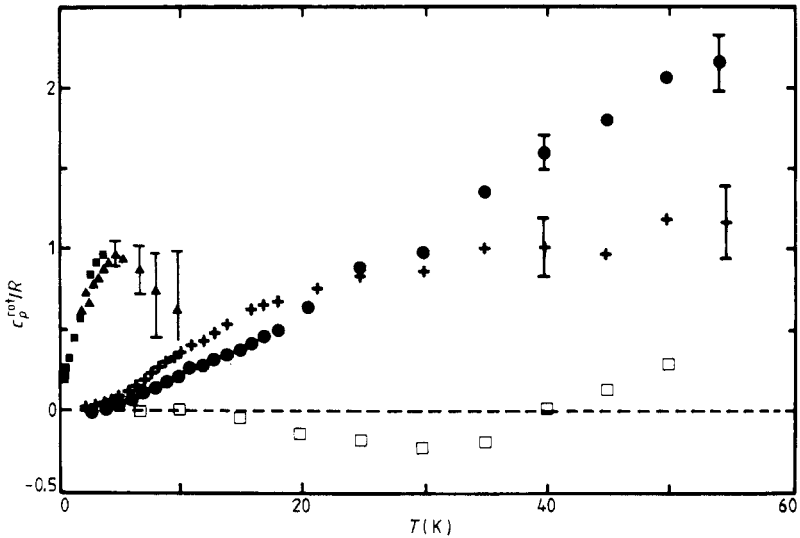
$2 \text{ K} \leq T \leq 50 \text{ K}$ . The crystals investigated were grown at the Crystal Growth Laboratory at the University of Utah and by S Haussühl at the Institute für Kristallographie at the Universität zu Köln. For these calorimetric investigations we used large single crystals with a weight of approximately 10 g. The measurements were performed employing a standard adiabatic technique, where a known amount of heat is introduced into the sample and the subsequent temperature change of the crystal is measured. The heating wire was wound directly around the crystal and secured with GE varnish, giving a better thermal contact. The temperature of the sample was reported using a Ge resistor. Heat pulses with a duration in the range of 5–30 s were applied while the preheat and postheat intervals had to be chosen to be 30 s at the lowest and 10 min at the highest temperatures. The preheat and postheat drift rates were then extrapolated to the midpoint of the heating period to determine the change in the temperature. At equilibrium conditions the temperature drift rates were of the order of  $10^{-5} \text{ K s}^{-1}$  at all temperatures. An on-line microcomputer aided the acquisition and the processing of the specific heat data.

Some representative experimental results for mixed crystals with  $\text{CN}^-$  concentrations  $x = 0.008$  and  $x = 0.53$  are shown in figure 1 where the full curve is the interpolated specific heat data from an ultrapure KBr sample. All the data are corrected for contributions due to the apparatus such as the heating wire and the Ge resistor. Figure 1 demonstrates the dramatically different behaviour of the rotational specific heat  $c_p^{\text{rot}}$  of the  $x = 0.008$  and  $x = 0.53$  samples.  $c_p^{\text{rot}}$  is the specific heat relative to the lattice specific heat, which in the first approximation is characterised by the pure KBr data. While for  $(\text{KBr})_{0.992}(\text{KCN})_{0.008}$  a contribution of approximately  $0.01 \text{ cal mol}^{-1} \text{ K}^{-1}$  was found for  $c_p^{\text{rot}}$  at low temperatures, which merges at approximately 15 K with the pure KBr data, the rotational specific heat in the 53% sample is lower at the lowest temperatures although the concentration of  $\text{CN}^-$  ions is now 60 times higher. However, in the latter sample the rotational specific heat is continuously increasing with increasing temperature.

In figure 2 we present the low-temperature data for the concentrations  $x = 0.008$ , 0.25 and 0.53 and compare these results with the data published by De Yoreo *et al* (1983) and Moy *et al* (1984) on crystals with similar concentrations. The results agree reasonably well and document that at the lowest temperatures the  $\text{CN}^-$  ions for 25% and 53% crystals are frozen-in even on the timescale of these long-time measurements.

### 3. Discussion

For a correct analysis of the rotational specific heat it is necessary to subtract off the lattice specific heat. However, at this point a number of problems arise in  $(\text{KBr})_{1-x}(\text{KCN})_x$  which cannot be solved with the existing theoretical models: these crystals are characterised by a bilinear coupling of rotations and translations (Michel and Rowe 1980). In the excitation spectrum there always exists a mixed term combining a rotational and a translational coordinate. The coupling is extremely strong for low-energy excitations which dominate the specific heat at the temperatures investigated. For this reason alone it seems impossible to divide the measured specific heat properly into a translational and a rotational contribution. Furthermore, the elastic properties exhibit an anomalous temperature variation depending sensitively on the measuring frequency (Feile *et al* 1982) which hampers the calculation of the lattice specific heat in a simple lattice dynamical model. The calculation of the translational specific heat of pure KCN based on a breathing shell model (Bill 1976, Bill *et al* 1976) using bare,



**Figure 3.** The rotational specific heat of  $(\text{KBr})_{1-x}(\text{KCN})_x$ ; present experiments:  $x = 0.008$  ( $\blacktriangle$ ),  $x = 0.25$  ( $+$ ),  $x = 0.53$  ( $\bullet$ ),  $x = 0.93$  ( $\square$ ); Moy *et al* (1984):  $x = 0.01$  ( $\blacksquare$ ).

undisturbed phonon frequencies resembles the results obtained in KBr with a slightly higher Debye temperature. This model uses a number of uncertain input parameters and neglects the rotation translation coupling and the anomalous phonon dispersion. We believe that at present the most reliable procedure is to subtract off the pure KBr data as a rough estimate of the lattice specific heat. The resulting rotational specific heat for all the samples investigated is shown in figure 3, including published data for  $x = 0.01$  (Moy *et al* 1984). In the 0.8% sample we find an increase of  $c_p^{\text{rot}}$  up to 6 K where the data exhibit a specific heat maximum. Above 10 K the difference is taken between nearly equal large numbers and the calculated rotational specific heat is inside the estimated errors. For  $(\text{KBr})_{0.75}(\text{KCN})_{0.25}$  and  $(\text{KBr})_{0.47}(\text{KCN})_{0.53}$  only a small fraction of  $\text{CN}^-$  molecules equilibrate with the time constant of the present experiments at low temperatures. With increasing temperatures the fraction of quasi-free  $\text{CN}^-$  ions increases, saturating at approximately 30 K for the 25% sample while for the sample with a concentration of  $x = 0.53$  the increase of rotational degrees of freedom continues up to 50 K.

In these crystals freezing temperatures  $T_F$  at different measuring frequencies have been published previously, where  $T_F$  has been determined from the cusps in the dipolar and quadrupolar susceptibilities. They are listed in table 1. Assuming an Arrhenius-like behaviour of the freezing process we estimated the freezing temperatures at a measuring frequency of  $10^{-2}$  Hz which should be appropriate for the present investigation. Comparing these calculated temperatures with the experimental data of  $c_p^{\text{rot}}$  of figure 3 it seems that they roughly mark the region of the strongest increase in the rotational specific heat. From these results one can conclude that the specific heat in  $(\text{KBr})_{1-x}(\text{KCN})_x$  exhibits no anomaly at  $T_F$ , a behaviour that is similar to that found in spin glasses, where the most sensitive present-day experiments reveal that nothing happens at  $T_F$  (Mydosh and Nieuwenhuys 1980). Usually in spin glasses a broad Schottky-type maximum develop in  $c_p^{\text{mag}}$  at temperatures above  $T_F$  with a linear temperature dependence for  $T \rightarrow 0$  and  $1/T$  fall-off at very high temperatures, a finding that closely resembles the findings in  $(\text{KBr})_{0.992}(\text{KCN})_{0.008}$  (figure 3).

**Table 1.** Frequency dependence of the freezing temperatures as determined from the cusps in the dipolar ( $T_F^{\text{dip}}$ ) and quadrupolar ( $T_F^{\text{quad}}$ ) susceptibilities. These experimental values have been extrapolated to  $10^{-2}$  Hz using an Arrhenius law ( $T_F^{\text{calc}}$ ). (nd stands for not determined.)

$x$	$T_F^{\text{dip}}$ (K)		$T_F^{\text{quad}}$ (K)		$T_F^{\text{calc}}$ (K)
	87.5 Hz	10 kHz	1 MHz	1 THz	$10^{-2}$ Hz
0.008	nd	2.5 <sup>(a)</sup>	4 <sup>(c)</sup>	10 <sup>(c)</sup>	1
0.20	22.5 <sup>(b)</sup>	26 <sup>(b)</sup>	42 <sup>(d)</sup>	75 <sup>(d)</sup>	16
0.50	35.5 <sup>(b)</sup>	42.5 <sup>(b)</sup>	nd	90 <sup>(c)</sup>	30

<sup>(a)</sup> Loidl (1982).

<sup>(b)</sup> Knorr and Loidl (1982).

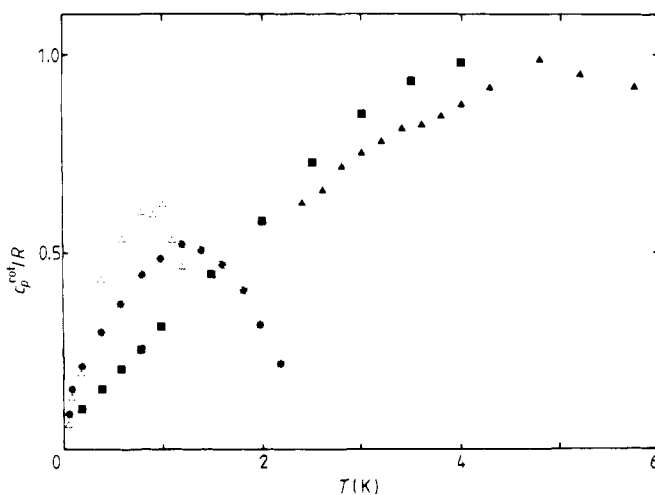
<sup>(c)</sup> Loidl *et al* (1982).

<sup>(d)</sup> Loidl *et al* (1983).

<sup>(e)</sup> Rowe *et al* (1979).

To compare the rotational specific heat of the glassy crystals with that of an orientationally long-range ordered system figure 3 contains the specific heat data of  $(\text{KBr})_{0.08}(\text{KCN})_{0.92}$ . This crystal exhibits quadrupolar long-range order where a monoclinic and an orthorhombic structure coexist. In addition, the orthorhombic regions undergo an antiferroelectric phase transition (Rowe *et al* 1983). The rotational specific heat in this crystal behaves very differently from  $c_p^{\text{rot}}$  measured in the orientational glasses. Because of the elastic and electric phase transition, the  $\text{CN}^-$  ions are caught in deep hindering potentials allowing only high-frequency oscillation.  $(\text{KBr})_{0.08}(\text{KCN})_{0.92}$  behaves like a 'quasi-harmonic' crystal with a somewhat higher Debye temperature than KBr, a behaviour which shows up as a negative rotational specific heat. The increase in the specific heat at temperatures above 40 K could be due to the onset of the lambda-shaped specific heat anomaly at the electric order phase transition.

In figure 4 we compare specific heat data of very diluted KBr : KCN mixtures (Peres-



**Figure 4.** The low-temperature rotational specific heat of  $(\text{KBr})_{1-x}(\text{KCN})_x$  crystals with low  $\text{CN}^-$  doping levels; present experiments:  $x = 0.008$  ( $\blacktriangle$ ); Peressini (1973):  $x = 0.00015$  ( $\triangle$ ),  $x = 0.00085$  (\*); Moy *et al* (1984):  $x = 0.01$  ( $\blacksquare$ ).

sini 1973), where the  $\text{CN}^-$  molecules are believed to behave like isolated single ions with the present data of the 0.8% crystal and the data of Moy *et al* (1984) measured in a sample with a concentration of  $x = 0.01$ . While the very diluted crystals exhibit a specific heat peak near 1 K which can be explained as a Schottky-type anomaly due to the tunnelling-split  $\langle 111 \rangle$  ground state of the  $\text{CN}^-$  ions, the results in the  $x = 0.008$  and  $x = 0.01$  crystals demonstrate the strong influence of strain-mediated interactions. Obviously at 1 K a large fraction of  $\text{CN}^-$  molecules are frozen-in.

In conclusion, the specific heat data of the present investigation reveal that for  $(\text{KBr})_{1-x}(\text{KCN})_x$  crystals with concentrations of  $x = 0.008, 0.25$  and  $0.53$ , the freezing process of the  $\text{CN}^-$  system is a highly collective phenomenon with a gradual freezing-in of the rotational degrees of freedom and that no specific heat anomaly is detectable. However, these results are not conclusive in characterising the glass transition in  $(\text{KBr})_{1-x}(\text{KCN})_x$  as a static or a dynamic phenomenon. Even at a transition to a thermodynamically stable glass phase the specific heat anomaly might be too weak to be detected experimentally.

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