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Specific Heat of $(KBr)_{1-x}(KCN)_x$.

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Abstract. – Using adiabatic calorimetry, the specific heat of the mixed molecular system $(KBr)_{1-x}(KCN)_x$ was investigated for concentrations $0.5 \leqslant x \leqslant 1$ and temperatures $10\,K \leqslant T \leqslant 200\,K$. For concentrations above the critical concentration $x_c \simeq 0.6$, the crystals undergo transitions into elastically ordered low-temperature phases. The specific-heat anomalies which can be interpreted as a rough measure of the configurational entropy changes decrease continuously with decreasing CN^- concentrations. Phenomenologically, first-, second- and third-order transitions can be identified. For $x \leqslant x_c$, these systems undergo glass transitions and no specific-heat anomalies are detectable.

During the past decade, the mixed molecular system $(KBr)_{1-x}(KCN)_x$ has attracted much interest: for concentrations $x \geqslant 0.6$ these crystals are model systems for order-disorder phase transitions driven by a strong rotation-translation coupling [1-4]. At $T_s = 168\,K$ pure KCN undergoes a structural phase transition from a high-temperature cubic phase (plastic phase with dynamic disorder) into an elastically ordered state (quadrupolar order) followed by an antiferroelectric transition, which removes the head-to-tail disorder of the cyanide ions (dipolar order) at $T_N = 83\,K$ [5, 6]. For $x \leqslant 0.85$ the dipolar disorder is frozen-in [7] and finally, below a critical concentration $x_c \simeq 0.6$ a quadrupolar glass state occurs at low temperatures [8-11]. The structural phase transition is now replaced by a frequency-dependent glass transition. The quadrupolar freezing dynamics is dominated by strain interaction forces and characterized by cusps in the susceptibility similar to the freezing process as observed in spin glasses [11]. The glass state is characterized by low-temperature thermal, dielectric and elastic properties analogous to those found in canonical glasses and in amorphous materials [12].

Specific-heat measurements focusing on the phase and glass transition temperature anomalies have been performed by Suga *et al.* [5] and later on by Lüty and coworkers [13], Mertz and Loidl [14], Moriya *et al.* [15] and by Matsuo *et al.* [16]. The main findings of these experiments were

i) The structural phase transition in pure KCN is strongly of first order [5].

ii) The entropy changes at T_s disappear rapidly with decreasing concentration x [13].

iii) Below the critical concentration x_c and at the orientational glass transition temperature, no specific-heat anomalies can be detected [14].

iv) Relaxational heat capacities due to the head-to-tail disorder were detected in $(KBr)_{0.3}(KCN)_{0.7}$. The experimentally observed temperature-time curves followed a Kohlrausch-Williams-Watt behaviour [16].

In this letter we report a detailed calorimetric investigation of $(KBr)_{1-x}(KCN)_x$ for concentrations $0.5 \leqslant x \leqslant 1$ and for temperatures $10\,K \leqslant T \leqslant 200\,K$. In an impressive manner the data observed demonstrate the gradual disappearance of the specific-heat anomaly: classifying the anomalies according to Ehrenfest's scheme first-order ($0.8 \leqslant x \leqslant 1$) second-order ($0.7 \leqslant x \leqslant 0.8$), third-order ($0.6 \leqslant x \leqslant 0.7$) and higher-order (glass) transitions ($x \leqslant 0.6$) were observed.

For a qualitative interpretation of the experimental data arguments given for the concentration dependence of the specific-heat anomalies in randomly diluted Ising spin systems [17-19] are used. In addition, these specific-heat data combined with previously published X-ray data allow a representation of a complete phase diagram of KBr:CN mixtures.

$(KBr)_{1-x}(KCN)_x$ crystals with concentrations $x = 0.53$, 0.57, 0.65, 0.73, 0.84, 0.91, 0.93 and 1 were investigated. All the crystals were grown by Haussühl at the Institut für Kristallographie at the Universität zu Köln. Single crystals with a weight of approximately $(2 \div 5)$ g were used employing a standard adiabatic technique, where a known amount of heat is introduced into the sample and the subsequent temperature change is measured. An online microcomputer aided the acquisition and the processing of the specific-heat data.

Representative results for $(KBr)_{1-x}(KCN)_x$ mixed crystals are shown in fig. 1. In pure KCN, a first-order phase transition at 168 K which indicates the transition from the cubic phase, where the CN^- orientations are dynamically disordered, into an elastically ordered orthorhombic state, is followed by a second-order phase transition, where electric (dipolar) order is established [5, 6]. The transition from elastic disorder to elastic order is more complicated for concentrations $x = 0.93$ and $x = 0.91$: here a sharp first-order cubic-to-monoclinic transition is followed by a rather complex c_P *vs.* T signal. It indicates the transition into a coexistence region of orthorhombic and monoclinic phases [7, 20]. Obviously, only in a very limited concentration range near $x = 1$ the orthorhombic phase is stable. We conclude that pure KCN is close to a triple point where cubic, orthorhombic and monoclinic phases coexist consistent with the observation that by continuous cycling treatment KCN can be forced into a monoclinic phase [5]. Within the coexistence region only the orthorhombic phase undergoes an antiferroelectric phase transition. The monoclinic phase exhibits frozen-in dipolar disorder down to the lowest temperatures [7]. For $x = 0.84$, the c_p *vs.* T curve indicates only one first-order transition into a monoclinic low-temperature state. No dipolar ordering occurs. $(KBr)_{0.27}(KCN)_{0.73}$ exhibits two succeeding quadrupolar phase transitions: the transition from the cubic to the rhombohedral state is very close to second-order, followed by a first-order transition into a monoclinic phase. These findings are consistent with recent diffraction and ultrasonic experiments [4]. It seems worthwhile mentioning that $(KBr)_{0.27}(KCN)_{0.73}$ is the first example, where the elastic shear constant c_{44} softens completely corresponding to the $m = 2$ universality class [4]. Here m denotes the dimension of subspace of reciprocal space which is covered by the fluctuations. The transition in KBr:CN leads to critical fluctuations of T_{2g} symmetry, the wave vectors of which are defined within cubic planes. Folk, Iro and Schwabl have treated these ferroelastic transitions with renormalization group theory and predicted logarithmic corrections to the specific-heat anomaly for $m = 2$ systems [21]. The present experimental results give no support to these theoretical predictions. However, a detailed and rigorous analysis is

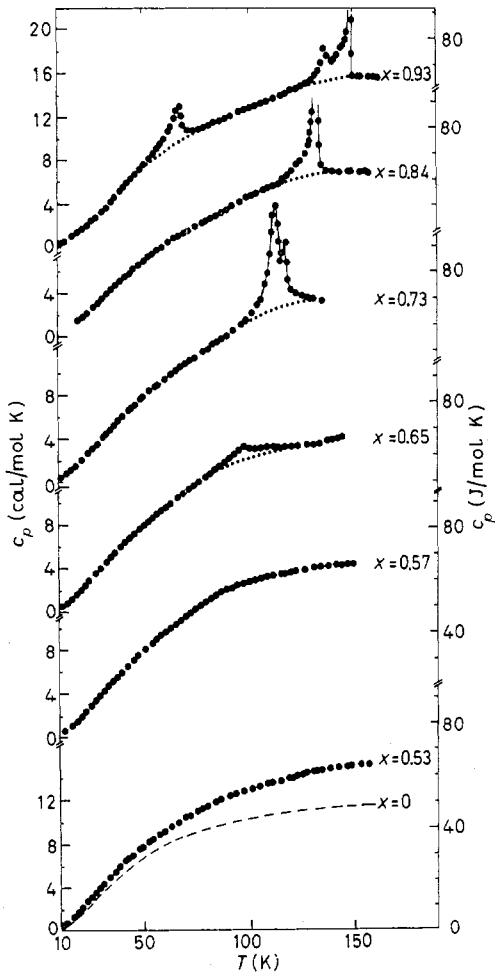

Fig. 1. – Adiabatic specific heat for the mixed molecular crystals $(KBr)_{1-x}(KCN)_x$ for concentrations $0.5 \leqslant x \leqslant 1$ and temperatures $10\,K \leqslant T \leqslant 200\,K$. The dotted line gives the estimated background specific heat; the dashed line c_p of pure KBr.

hampered by the onset of the second structural phase transition at somewhat lower temperatures. For $x = 0.65$ the specific-heat data only exhibit a change of slope at the cubic-to-rhombohedral transition temperature. Finally for $x \leqslant 0.60$ no specific-heat anomalies are detectable. All the c_p *vs.* T curves look smooth down to the lowest temperatures.

If we follow on a purely phenomenological basis, Ehrenfest's suggestion to characterize the elastic phase transitions in $(KBr)_{1-x}(KCN)_x$ mixed crystals by discontinuities in the derivatives of the Gibbs free energy, we can identify the following transitions:

First-order phase transitions: in the concentration range $0.8 \leqslant x \leqslant 1$ one observes latent heat which indicates a discontinuous change of slope in the free energy *vs.* temperature curve and a discontinuity in the first derivative, the entropy. This result is consistent with discontinuities in the lattice spacings at the cubic-to-orthorhombic or the cubic-to-monoclinic transitions as measured by X-ray scattering [20].

Second-order phase transitions: for concentrations $0.8 \leqslant x \leqslant 0.7$ the c_p *vs.* T curves are characterized by a jump in c_p at the structural phase transition in agreement with continuous changes of the lattice spacings [20] and a complete softening of the elastic constant [4]. However, the λ-like anomaly is partly hidden by the onset of a second structural phase transition.

Third-order phase transitions: for $(KBr)_{0.35}(KCN)_{0.65}$ the specific-heat temperature curve is characterized by a change of slope. A discontinuity appears in dc_p/dT only.

Glass transitions: for concentrations $x < 0.6$ the $(KBr)_{1-x}(KCN)_x$ mixtures undergo no structural phase transitions. In these crystals, the sound velocities pass through a minimum corresponding to cusps in the quadrupolar susceptibility. The cusp maxima were interpreted as freezing temperatures T_F depending strongly on the measuring frequency [22]. Extrapolating the freezing temperatures to the time window of our specific-heat experiment we would expect $T_F \simeq 60$ K for the concentrations investigated. As can be seen from fig. 1 the specific-heat curves are smooth at all temperatures and even the first derivatives of the specific heat exhibit no anomalies.

We are aware that the Ehrenfest classification scheme is by no means complete or characterizes all transitions: *e.g.*, if the heat capacity increases logarithmically near T_s, as theoretically predicted for the $x = 0.73$ sample, all derivatives would diverge. However, we feel that it is still a useful scheme to characterize phase transitions.

Using the measured heat capacity data as presented in fig. 1 we calculated entropy, enthalpy and the derivative of the specific heat dc_p/dT. In table I we give the numerical values of ΔS, Δc_p and $\Delta c_p/\Delta T$ at the transition temperatures T_s for three representative samples with concentrations $x = 0.84$, 0.73 and 0.65. The values given in table I characterize the order of the transition as measured in these crystals.

TABLE I. – *Discontinuous steps in the entropy ΔS, in the specific heat Δc_p and in the temperature derivative of the specific heat as measured in $(KBr)_{1-x}(KCN)_x$ at the transition temperature T_s.*

x	T_s (K)	ΔS (J/mol K)	Δc_p (J/mol K)	$\Delta(\Delta c_p/\Delta T)$ (J/mol K^2)
0.84	132.5 ± 0.6	5.15		
0.73	117.5 ± 1.0		19.67	
0.65	97.0 ± 1.0			0.67

For a qualitative analysis of the specific-heat results and to get a microscopic understanding of the structural phase transitions and the glass transitions in $(KBr)_{1-x}(KCN)_x$, we use arguments as given for randomly diluted Ising spin systems [17-19]. We argue that our experimental results can be interpreted by assuming that the entropy changes, which are a measure of the orientational order, become smeared out in a wide temperature region with decreasing CN^- concentrations. Obviously, in glassy crystals the progressive freezing-in of local order takes place over a large temperature range so that the specific heat appears entirely smooth for all T. But even for concentrations $x \gtrsim x_c$, the establishment of local order sets in far above T_s. The additional entropy associated with the development of long-range order at the structural phase-transition temperature is negligible. It is this situation which is similar to the experimental and theoretical findings in randomly diluted Ising spin models with next nearest-neighbours interactions [17-19]. In

these systems already far above the percolation limit the specific heat appears entirely smooth. The additional entropy due to the development of long-range order is undetectably small except close to the fully concentrated systems.

We determined the entropy changes ΔS as defined by the area of the specific-heat anomalies which are a rough measure of the configurational entropy changes (in the case of double peak structures in c_p *vs.* T we integrated the area under both peaks; in addition large errors are also introduced due to the background subtraction of the pure translational phonon contributions. The dotted lines in fig. 1 show the estimated background. The dashed line gives the specific heat of pure KBr *vs.* temperature). Figure 2 shows $\Delta S/x$ *vs.* x for the elastic and the electric phase transition anomalies. Using this representation one expects a constant value of $\Delta S/x$ in clear disagreement with the experimental findings. Experimentally the configurational entropy decreases strongly with decreasing concentration for both transitions, the elastic and the electric transition, respectively. However, the cause of this behaviour is very different: the decreasing values of $\Delta S/x$ as determined for the elastic-order transition can be interpreted in two ways:

i) The elastically ordered phases exhibit orientational order in the complete volume of the crystal. Then the smearing out of entropy changes must cover a much wider temperature region as indicated in fig. 1 or

ii) With decreasing CN^- concentrations an increasing fraction of the crystals remains orientationally disordered yielding a coexistence region of glassy and crystalline states. Clearly, further diffraction experiments would help to clarify these questions.

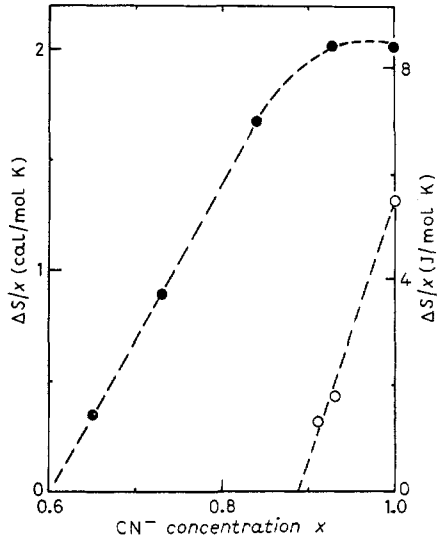

Fig. 2. – Configurational entropy changes $\Delta S/x$ at the elastic (●) and the electric (○) phase transition *vs.* CN^- concentration x for $(KBr)_{1-x}(KCN)_x$. The lines are drawn to guide the eye.

The decreasing values of $\Delta S/x$ for the antiferroelectric transition are a measure of the decreasing fraction of orthorhombic crystallites with decreasing x within the orthorhombic-monoclinic coexistence region. From neutron diffraction experiments it is known that only the orthorhombic structure exhibits electric order [7].

Characterized by amorphous low-temperature thermodynamic properties and by a spin glasslike freezing dynamics glassy crystals are thought to be a «missing link» between spin glasses and canonical glasses. The absence of any specific-heat anomaly in glassy crystals at the glass transition is similar to the findings in spin glasses where nothing happens at the freezing temperature [23]. Contrary, in canonical glasses and amorphous systems the glass transition temperature is characterized by a jump in the specific heat. In addition, a temperature can be defined where the extrapolated entropy of the liquid becomes less than that of the crystalline state. This Kauzmann paradox [24] is a well-known feature of canonical glasses [25] not displayed by $(KBr)_{1-x}(KCN)_x$ glassy crystals. Until now, we were unable to detect any well-defined relaxational heat-capacity anomaly indicative for the glass transition where the system falls out of thermodynamic equilibrium.

Finally, this calorimetric investigation in combination with previously published diffraction data [7, 20] define the complete phase diagram for $(KBr)_{1-x}(KCN)_x$. The result is shown in fig. 3 where we also included transition temperatures as measured by Lüty [13], Moriya *et al.* [15] and Matsuo *et al.* [16].

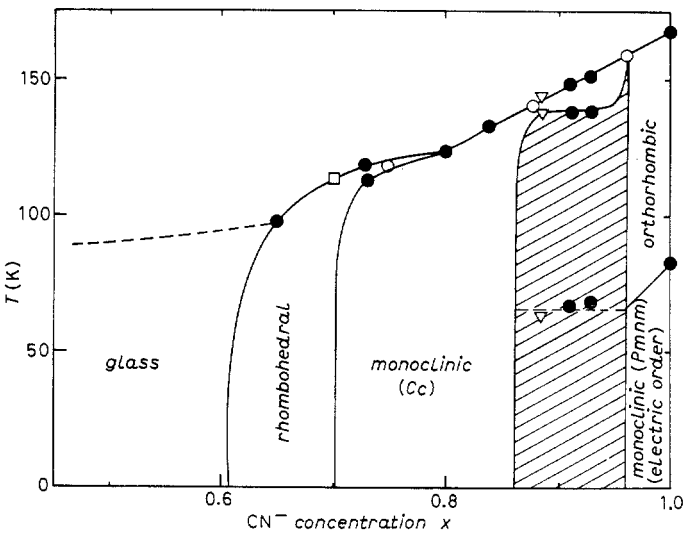

Fig. 3. – Phase diagram of $(KBr)_{1-x}(KCN)_x$ as determined from calorimetric investigations. The crystallographic structures of the phases were assigned using X-ray and neutron diffraction results (ref. [7] and [20]). ● present investigation, ○ ref. [13], ▽ ref. [15], □ ref. [16].

In conclusion, we presented a detailed specific-heat investigation of $(KBr)_{1-x}(KCN)_x$. The main findings were:

i) For concentration $x \geq 0.85$ a first-order ferroelastic phase transition is followed by a second-order antiferroelectric phase transition.

ii) For $0.85 \leq x \leq 0.6$ the ferroelastic transition changes from first to second and to third order; with decreasing concentration the configurational entropy changes are smeared out over a wide temperature range. The additional entropy due to the formation of long-range order at T_s becomes more and more negligible.

iii) For concentrations $x \leq 0.6$ the specific-heat curves are entirely smooth; the freezing-in of short-range order gives no thermodynamic anomaly.

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