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Angaben zur Veröffentlichung / Publication details:

Knorr, K., U. G. Volkmann, and Alois Loidl. 1986. “Low-frequency shear response of (KBr)1−x(KCN)x.” *Physical Review Letters* 57 (20): 2544–47.
https://doi.org/10.1103/physrevlett.57.2544.

Low-Frequency Shear Response of $(\mathrm{KBr})_{1-x}(\mathrm{KCN})_x$

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(Received 31 March 1986)

The elastic shear constant and the internal friction of three mixed crystals $(\mathrm{KBr})_{1-x}(\mathrm{KCN})_x$ have been determined from the resonance of a torsion pendulum in the 10^2-Hz range. Two glass-forming samples ($x=0.20,0.50$) and one sample ($x=0.75$) which orders ferroelastically have been investigated. Two regimes of loss have been observed; the primary one is related to domain-wall motion, the secondary one to dipolar reorientations.

PACS numbers: 62.20.Dc, 64.70.−p

$(\mathrm{KBr})_{1-x}(\mathrm{KCN})_x$ has attracted much interest since it is hoped that the study of the "orientational glass" state of this system might lead to a better understanding of the structural glasses. The system is cubic (NaCl) at room temperature and shows ferroelastic phases with long-range orientational order of the linear CN molecules for $x > x_c$, $x_c = 0.62$, and a glasslike low-temperature state for $x < x_c$ which is characterized by inhomogeneous shear strains and random CN orientations.[1,2] The elastic shear constant c_s softens and passes through a minimum at a characteristic temperature, called T_f or T_c, depending on whether the low-T state is glasslike or ordered.[1,3,4] The exact value of T_f depends on the measuring frequency[5] (megahertz in ultrasonics,[3,4] gigahertz in Brillouin scattering,[6] and terahertz in inelastic neutron scattering[1,7]). This suggests that the glass transition is a relaxational process.

We have determined the elastic shear constant and the internal friction from the resonance of a torsion pendulum in the 10^2-Hz range, five decades below the frequencies of the ultrasonic experiment. We will show that there are two loss peaks in the elastic response. The "primary" one will be interpreted in terms of ferroelastic domains; the "secondary" one coincides with the loss peak of the dielectric studies.

The single crystals ($x=0.75$, 0.50, and 0.20) have been obtained from S. Haussühl, Universität zu Köln. The pendulum consists of a crystal as the active element typically with a cross section of 3×3 mm^2 and a length l of 8 mm. The surfaces are $\{100\}$ cleavage planes. The sample is glued to a base plate; on the upper end it carries a crossbar with two plates, which in combination with four stationary plates form two pairs of diagonally opposed capacitors. To one pair an excitation voltage of 100 V rms and a frequency $\nu/2$ are applied. The other pair is biased to 100 V dc and detects the torsional amplitude a by means of a vector lock-in amplifier tuned to the frequency ν. A feedback loop holds the system in resonance, defined by the condition $\mathrm{Re}(a)=0$ for $\nu=\nu_0$. The quadrature signal is proportional to the resonance amplitude $a_0 = \mathrm{Im}[a(\nu_0)]$. Typical room-temperature values are 500 to 1000 Hz for ν_0, 2 Hz for the resonance width, and 10^{-4} deg for a_0.

The elastic shear constant c_s is given by $c_s = Al\nu_0^2$ where for long samples with circular cross section, $A = 8\pi\Theta r^{-4}$. Θ is the moment of inertia, r the radius. For short samples with a parallelepiped shape and the end cross sections fixed in shape by a glue no such simple formula exists. We have determined the factor A from reference measurements on a Cu sample and could then reproduce ultrasonic room-temperature data on the cy-

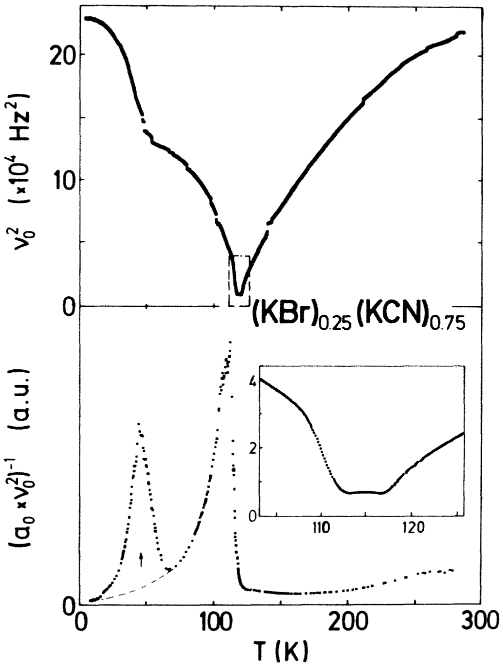

FIG. 1. The temperature dependence of the squared resonance frequency ν_0^2 (proportional to the elastic shear constant) of the pendulum and of the quantity $(\nu_0^2 a_0)^{-1}$ (proportional to the logarithmic decrement of the oscillation, the "internal friction"); a_0 is the resonance amplitude. Inset: $\nu_0^2(T)$ in the vicinity of the cubic-rhomobohedral-monoclinic phase transitions. The arrow indicates the maximum of the dielectric loss, obtained at comparable frequencies. The CN concentration x is 0.75.

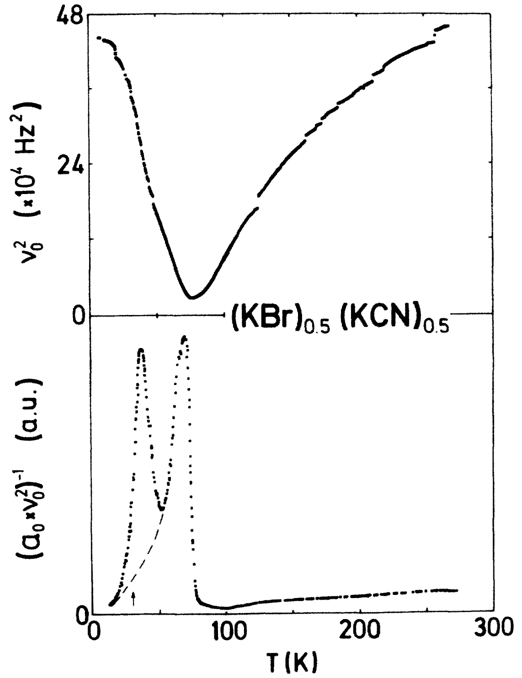

FIG. 2. Same as Fig. 1 but for $x = 0.50$.

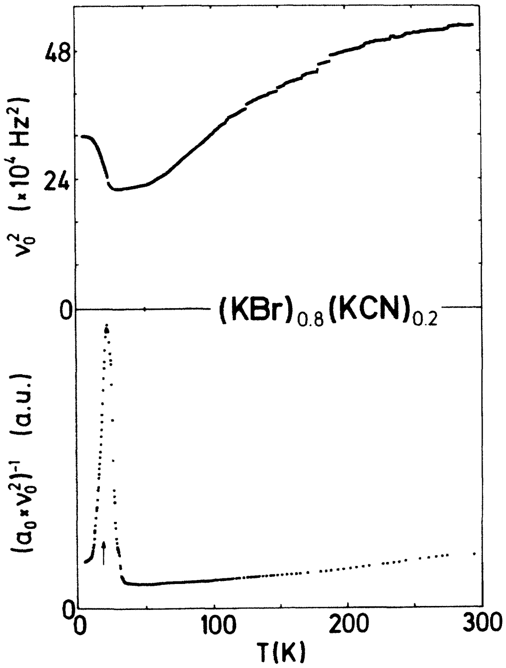

FIG. 3. Same as Fig. 1 but for $x = 0.20$.

anides within a factor of 1.5. The internal friction will be given in terms of $(v_0^2 a_0)^{-1}$, a quantity which is proportional to the logarithmic decrement of the oscillation.

The method has several problems. The most annoying one was that the crystal broke under the slightest mechanical shocks. The pendulum suffered from numerous parasitic eigenmodes. The stronger ones could be detected directly by sweeping of the frequency; the weaker ones were only visible via their hybridization with the torsional mode. They occur in particular at those T ranges where the damping is low. They show up as steps on the $v_0^2(T)$ curves. At the anticrossing points the resonance amplitude decreases dramatically. These effects have been filtered out in the curves of the internal friction.

Figures 1–3 show the T dependence of v_0^2 (proportional to c_s) and of the internal friction. The sample with $x = 0.75$ represents the CN-rich crystals which undergo structural phase transitions into noncubic low-temperature phases. One notes a deep minimum of c_s at $T_{c1} = 117 \pm 1$ K and $T_{c2} = 113 \pm 1$ K. Here c_s is as low as 2% to 5% of the room-temperature values. The two temperatures T_{c1} and T_{c2} compare favorably with the cubic-rhombohedral and the rhombohedral-monoclinic transition temperatures,[2] observed by complementary x-ray diffraction measurements on the same sample. The internal friction is low in the cubic phase, and rises below T_{c1} to a first maximum at about 110 K. A second loss maximum, centered at 45 K, is superimposed on the low-T wing of the first maximum which extends down to lowest T. A kinklike anomaly, related to this loss peak, can be seen in $v_0^2(T)$.

The sample with $x = 0.50$ represents the glass-forming cyanides with x slightly below x_c. The elastic behavior closely resembles that of $x = 0.75$. The deep minimum of c_s occurs at $T_f = 75$ K. The loss rises below T_f and peaks at 70 and 37 K. The sample with $x = 0.20$ represents the crystals with low x where the freezing of the orientational degrees of freedom loses its collective character and approaches the single-particle limit.[8] Here c_s passes through a shallow minimum around $T_f = 30$ K. A single loss peak with a maximum at 22 K develops below T_f.

The most unexpected feature of the present study is the appearance of two elastic loss peaks where the one at lower T occurs at the same temperatures as the dielectric loss. The temperatures of maximum dielectric loss, as measured at comparable frequencies,[8–11] are marked by arrows in the figures. Obviously the same relaxational process which leads to the dielectrical loss gives rise to strong "secondary" elastic loss for $x = 0.50$ and 0.75 and contributes to the single elastic loss peak for $x = 0.20$. It is agreed upon that the dielectric loss is due to 180° flips of the CN molecules in a locally noncubic environment. As the electric dipole moment and the head-tail shape asymmetry of the molecules are small, these flips are not believed to change the local strain field. Elastic waves may of course be emitted during the flip, but since the flips are rare at the temperatures of interest,[8] these effects should be small, too. The microscopic theory arrives at the same conclusion for the cubic phase of the pure cyanides.[12] It is furthermore known that the quadrupolar freezing does not lead to anomalous dielectric behavior. Even the ferroelastic phase transitions have only little effect on the dielectric constant.[9] We thus note that the dipolar and quadrupolar modes are effectively decoupled in the crystalline phases but that there is a surprisingly strong mixing in the glass state.

The elastic loss has been studied recently by Brillouin experiments.[13] The appearance of just one peak in the T dependence of the linewidth of the acoustic phonons found in that work is not in contradiction to the present results. In Ref. 8 it was shown that the dipolar and the quadrupolar loss peaks coincided at Brillouin frequencies. One wonders, however, how much of this single peak observed in Brillouin scattering is due to dipolar effects. The coupling of dipolar modes to the acoustic phonons is believed to increase more rapidly with frequency than that of quadrupolar modes.[12]

The primary elastic loss is the most direct evidence for the structural relaxations which lead to the formation of the quadrupolar glass. The internal friction of the elastic shear modes in the present samples plays a role directly comparable to that of the viscosity at the glass formation of supercooled liquids. It is remarkable that the elastic behavior of the glass-forming cyanide with $x=0.50$ closely resembles that of the ordering sample with $x=0.75$. Thus there is hope that an understanding of the elastic response of the ordering sample can contribute to an understanding of the quadrupolar glass state.

For the ordering sample one notes that there is hardly any loss in the cubic phase; the loss starts to increase at the upper ferroelastic transition, and reaches a maximum well in the monoclinic phase. Hence, the loss is not connected with critical effects, but is rather a property of the ferroelastic multidomain state. Gash[14] has worked out the martensitic aspect of the phase transitions of the pure cyanides on the basis of direct observation of the ferroelastic domains. We further note that the elastic response of the $x=0.75$ cyanide resembles that of martensitic metal alloys. In particular $\mathrm{In}_{1-x}\mathrm{Tl}_x$ is a useful example since this alloy undergoes an almost continuous martensitic transformation.[15,16] From the metallic alloys we adopt the interpretation of the low-frequency elastic response in terms of domain-wall motion[15]: The loss sets in at T_{c1} where the domains are formed. If we follow the general considerations of Sapriel,[17] the domain walls of the rhombohedral phase are all of the "permissible" (i.e., low-energy) type, parallel to $\{100\}$ and $\{110\}$. These walls are expected to be highly mobile, leading to a viscous-type elastic behavior with a low shear constant and a finite, but still relatively low internal friction. The rhombohedral phase can be regarded as a domain-wall fluid. At T_{c2} the rhombohedral domain pattern with four different domain states breaks up into a finer monoclinic pattern with twelve different domain states. In addition to the high-indexed walls there are now low-indexed walls and even pairs of domain states between which permissible walls do not exist. The stress-induced motion of these unfavorable walls is presumably highly dissipative and is most likely just below T_{c2} where the spontaneous strain order parameter is still small. A large elastic loss peaking slightly below T_{c2} therefore appears plausible.

The great similarity of the elastic response for $x=0.75$ and 0.50 strongly suggests that similar processes occur below x_c. Of course, the concept of domains as regions of well-defined ferroelastic strains with symmetry relations between the domain states does not hold in the glass state in a strict sense. Nevertheless we think that "domains," regions of almost constant strain, develop below T_f and that their motion under stress leads to the primary loss.

It has been shown that T_f is frequency dependent, following an Arrhenius law.[13] In the present context this means that a thermally activated process couples to the domain-wall motion. It is obvious to visualize this process as the collective reorientation of all the CN molecules across which the domain wall is swept under the external stress. This view explains the high activation energies observed for x close to x_c.[8] At lower x the number of molecules involved decreases; in addition the walls may become less sharp. Ultimately the reorientations reduce to single-ion processes, a situation where the barriers for dipolar and quadrupolar reorientation are expected to be identical. The two loss peaks should then overlap, as observed for $x=0.20$. Note that the loss peak for that concentration is sharp and symmetric, suggesting a unique relaxation time.

The two main results of the present study are as follows: (i) The elastic response of the glass-forming cyanides with higher x closely resembles that of the ordering cyanides. Hence a common interpretation in terms of elastic domains seems appropriate. (ii) The cyanides show—very much like structural glasses—a secondary structural loss peak. The secondary loss is due to strongly coupled dipolar-quadrupolar modes.

We are grateful to S. Haussühl who supplied the samples. We thank R. O. Pohl and D. Cahill for useful discussions.

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