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Shear elasticity of RbCN and related mixed crystals

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RbCN and the RbCN-rich solid solutions with KCN, RbBr, and KBr show a cubic-to-monoclinic structural phase transition. The real and imaginary parts of the macroscopic shear compliance—obtained with a torque-shear setup—have been measured across the transition on six such samples. For RbCN the ferroelastic hysteresis curve has been determined and the shape-memory effect has been demonstrated. [S0163-1829(97)07330-X]

I. INTRODUCTION

The characterization of ferromagnets and ferroelectrics by measurements of the appropriate susceptibility and of hysteresis curves, respectively, is well established in solid-state science. Analogous measurements on ferroelastic phases are rare,[1] in particular in nonmetallic, brittle samples. This is mainly because special nonstandard equipment is necessary for this purpose. We have recently developed a shear-torque apparatus and applied it successfully to the study of the shear elasticity of mixed alkali cyanides like $(\mathrm{KBr})_{1-x}(\mathrm{KCN})_x$ in context with the orientational glass state occurring in such systems.[2] In the present article we will report measurements on RbCN and related mixed crystals which all undergo a ferroelastic-type phase transition.

NaCN, KCN, and RbCN crystallize in the pseudocubic NaCl-type structure which is stabilized by rapid reorientations of the linear CN ions. Due to a bilinear coupling of the CN orientations and the T_{2g} lattice strains, a (first-order) phase transition occurs on cooling.[3] The low-T phase of NaCN and KCN is orthorhombic $Immm$. The low-T phase of RbCN is monoclinic Cc and actually not of the proper ferroelastic type;[4,5] it is rather due to the coupling of the shear mode at the zone center to a component of combined orientational and displacive character at the L point. This leads to a canted pattern of CN orientations in addition to the spontaneous deformation of the lattice (ferroelastic species $m3mF2/m$). Nevertheless, the transition is still preceded by the strong softening[6] of the elastic shear constant c_{44} which follows the same type of temperature dependence as that of the proper ferroelastics NaCN and KCN. The tensor of spontaneous deformation has been determined by diffraction.[4,5] Most important are the off-diagonal shear components. The uniaxial E_g-type deformation and volume change are of secondary importance, only. The spontaneous deformation can be visualized as changes of the three cell angles (by about 3.6°, 3.6° and 1.3°). This leads to 12 domain states. The orientational relation of these ferroelastic domains with respect to the cubic parent lattice has been determined for $(\mathrm{KBr})_{0.2}(\mathrm{KCN})_{0.8}$, which is isomorphous to RbCN, and explained in terms of strain matching.[7,8] We will assume that the low-T state of the mixed crystals of the present study is also monoclinic. This assumption is supported by the phase diagrams derived from optical transmission experiments,[9] ultrasonic measurements[10,11,12] of c_{44} in the cubic phase on series of $(\mathrm{KCN})_{1-x}(\mathrm{RbCN})_x$ and $(\mathrm{RbBr})_{1-x}(\mathrm{RbCN})_x$ mixed crystals and x-ray diffraction[13] on $(\mathrm{RbCN})_x(\mathrm{KCN})_{1-x}$.

The cubic-monoclinic transition leaves the dipolar head-tail degree of freedom of the CN ions disordered.[4] Whereas head-tail ordering is achieved in a second phase transition in the orthorhombic low-T state of KCN and NaCN ($Immm$ to $Pmnm$), there is no subsequent phase transition in the monoclinic case. Instead, a freezing process is observed both in dielectric[14] and heat capacity measurements[15] on RbCN. The relaxations obey an Arrhenius law for the temperature dependence and a Kohlrausch-Williams-Watts law for the time dependence. Since obviously the frozen-in state of RbCN lacks long-range dipolar order, the idea of a dipolar glass (on the background of a crystalline center-of-mass lattice and of an ordered quadrupolar system) has been propagated.[15]

II. EXPERIMENT

For the experiment a single-crystalline column with (100) cleavage faces with typical dimension of $(2\times2\times7)\ \mathrm{mm}^3$ is glued to the cold plate of the cryostat. On the free end the crystal carries a small permanent magnet and a mirror, Fig. 1. Torque f is applied by means of a magnetic field. The resulting twist angle α (and a possible bending) of the sample is probed by means of a light pencil reflected from the mirror and falling onto a two-dimensional detector. Various modes of operation are possible: (i) subresonant drive with small-amplitude ac forces at fixed frequencies $[f=f_0\cos(2\pi\nu)]$. The frequencies ν have been varied over a range from 1 Hz to a few hundred Hz. Here the ratio of α to f_0 is proportional to the macroscopic elastic shear compliance, ignoring minor corrections which are expected for elastic bodies with noncircular or slightly nonuniform cross sections. In a cubic single-crystalline column with an axis of torque along [100], the macroscopic compliance is given by the component $s_{44}=1/c_{44}$ (in Voigt's notation). The phase delay between force and twist angle gives the loss angle. (ii) The same type of information is obtained from measurements of the fundamental torsional resonance which is for

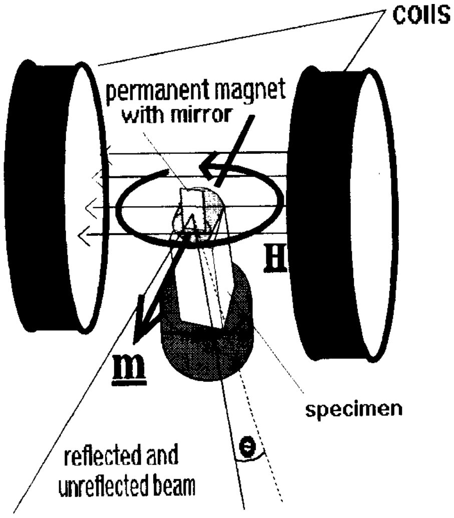

FIG. 1. Schematic view of the torque-shear setup.

our samples in the order of a few kHz: see Fig. 2 for resonance curves taken on $(\mathrm{RbCN})_{0.95}(\mathrm{RbBr})_{0.05}$ at a series of different temperatures. Here the inverse squared resonance frequency ν_0^{-2} is proportional to s_{44}. The loss is obtained from the width of the resonance or more easily from the amplitude at resonance a_0. Thus the measurements of types (i) and (ii) give access to the real and imaginary parts of the elastic compliance, even in regions of large elastic loss where ultrasonic echoes and Brillouin signals are usually lost. On the other hand, the present method cannot compete with these latter methods as far as the determination of absolute values is concerned. In fact, we did not try to convert the compliance data to an absolute scale. (iii) The equipment can also be used with dc torques of appreciable strength. This allows measurement of the macroscopic shear response under various temperature-torque histories. We have performed a few measurements of this type on RbCN. One has to keep in mind, however, that the strains and stresses of a twisted body are necessarily inhomogeneous. They vanish in the center of the sample along the neutral fiber and increase with distance from the neutral fiber, attaining a maximum value in the outer parts of the sample. For this reason there is no way to drive the sample into a ferroelastic monodomain state by application of an external torque. Hence one cannot expect that a measurement of the ferroelastic hysteresis is demonstrating ferroelastic switching in a clear-cut way. Furthermore, our samples have built-in considerable preexisting strains, as can be seen by inspection of the samples between crossed polarizers. It is not known how these strain fields compare and arrange with those induced by the external torque.

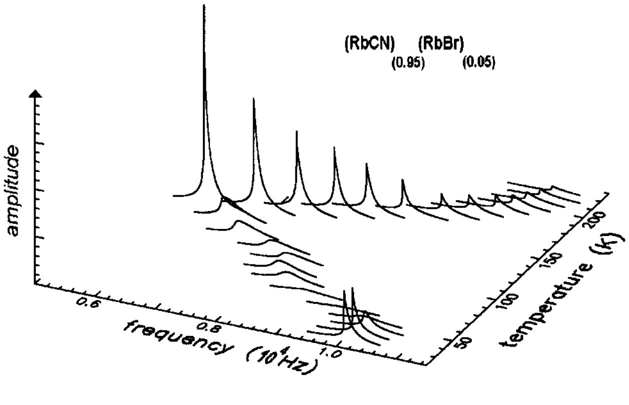

FIG. 2. Torsional resonance curves of $(\mathrm{RbCN})_{0.95}(\mathrm{RbBr})_{0.05}$, measured at different temperatures.

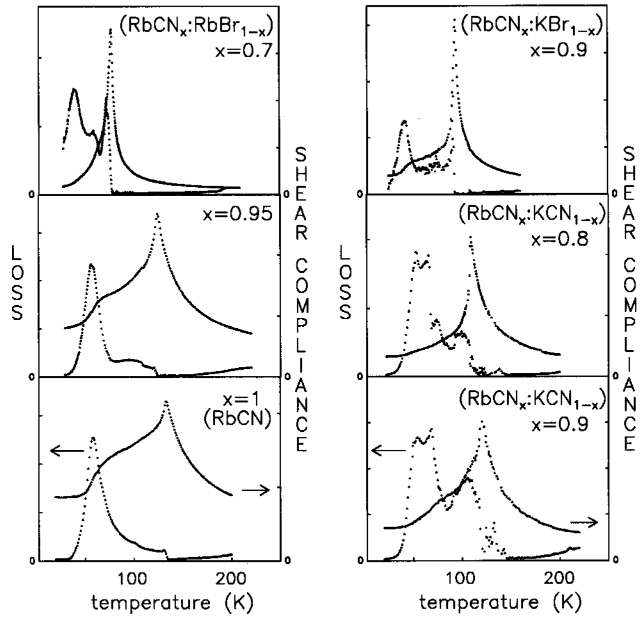

FIG. 3. Temperature dependence of the shear compliance and the corresponding loss, as obtained from the torsional resonance, of all samples investigated.

The single-crystalline samples of RbCN, $(\mathrm{RbCN})_x(\mathrm{RbBr})_{1-x}, x=0.95$ and 0.7, $(\mathrm{RbCN})_x(\mathrm{KCN})_{1-x}$, with $x=0.9$ and 0.8, and $(\mathrm{RbCN})_{0.9}(\mathrm{KBr})_{0.1}$ have been grown from the melt in the crystal growth laboratory of the University of Utah. The concentrations are the nominal concentrations of the melt. See Fossum and co-workers[10–12] for the deviation of these figures from the concentrations determined by atomic absorption spectroscopy. During the preparation of the samples and during the measurements, we noticed that the samples show different degrees of brittleness. Whereas RbCN and its solid solutions with RbBr survived several cooling cycles and the application of large torque, the others repeatedly broke on cooling and show discontinuities in the $s_{44}(T)$ curves, presumably due to the release of internal stresses, possibly via the generation of cracks.

III. RESULTS AND DISCUSSION

Figure 3 shows compliance and loss results as function of temperature on all samples investigated, as obtained with the resonance method on cooling. Clearly, there are features which are common to all samples.

A. Transition temperatures

The compliance data show a maximum at a temperature T_c independent of the measuring frequency. Hence we identify this temperature with the transition temperature T_c of the cubic-monoclinic phase transition. The values are given in Table I; they compare favorably with the figures reported in the literature, obtained from optical transmission and ultra-

TABLE I. Cubic-monoclinic transition temperatures T_c, the Curie-Weiss parameters T_0 and θ of the shear compliance of the paraelastic phase, and the Arrhenius parameters τ_0^{-1} and V of the secondary loss of the monoclinic phase.

		Curie-Weiss		Arrhenius	
	T_c (K)	T_0 (K)	Θ (K)	τ_0^{-1} (Hz)	V (meV)
RbCN	132.4±0.8	108.2±0.1	−97.3±3	8×10^{13}	114±3
$(RbCN)_{0.95}(RbBr)_{0.05}$	124.5±0.3	103.2±0.2	−138±3	2×10^{15}	128±3
$(RbCN)_{0.7}(RbBr)_{0.3}$	77.3±0.2	75.3±0.6	−111±20	1.5×10^{6} (10^{33})	32.3±0.6 (375±40)
$(RbCN)_{0.9}(KCN)_{0.1}$	121±0.5	104.2±0.3	−77±7	4×10^{13} (2×10^{16})	109±13 (163±13)
$(RbCN)_{0.8}(KCN)_{0.2}$	109.4±0.4	96.5±0.2	−297±20	8×10^{13} (2×10^{14})	107±15 (159±18)
$(RbCN)_{0.9}(KBr)_{0.1}$	93.5±0.5	88.9±0.1	27±3	1.6×10^{10}	71±2

sonic data.[9–12] For RbCN, heat capacity measurements[15] give a value of 132.3 K, which is identical within 0.1 K with the value (132.4±0.8) K of our measurement.

B. Paraelastic behavior

In the paraelastic cubic phase the shear compliance increases with decreasing T. This is a softening of the elastic shear constant c_{44}. The elastic loss is negligible in the cubic phase. The T dependence of the shear compliance follows the so-called Curie-Weiss law $s_{44} \propto (T-\theta)/(T-T_0)$. This law, well established in many alkali cyanides, is based on the linear coupling of the lattice strains and the orientations where the latter obey a Curie-Weiss type orientational susceptibility, with the Weiss temperature θ. T_0 is the extrapolated temperature where s_{44} would diverge, thus giving rise to a second-order proper ferroelastic phase transition. The parameters T_0 and θ are included in Table I. Fit curves are shown in Fig. 4. A direct comparison with the ultrasonic data of Fossum and co-workers[10,12] is possible for RbCN, $(RbCN)_{0.7}(RbBr)_{0.3}$, and $(RbCN)_{0.9}(KCN)_{0.1}$ where these authors report T_0 and θ values of 121 and −143, 71 and −123, and 103 and −168 K, respectively. Altogether there is an acceptable agreement (the most conspicuous difference occurring surprisingly for the T_0 value of RbCN). This suggests that in the paraelastic phase both techniques measure the same quantity, namely, the low-frequency–long-wavelength limit of the intrinsic elastic shear response function c_{44} and s_{44}, respectively. The divergence of the compliance is the more complete and the phase transition is the closer to second order the smaller the difference between the actual (first-order) transition temperature T_c and the extrapolated temperature T_0. In this respect $(RbCN)_{0.7}(RbBr)_{0.3}$ is outstanding. Here the difference between T_c and T_0 is 2 K, only, and the s_{44} increases by almost a factor of 30 between 270 K and T_c. Presumably the series $(RbCN)_x(RbBr)_{1-x}$ is similar to $(KCN)_x(KBr)_{1-x}$ in the sense that upon dilution the character of the phase transition changes towards second order, perhaps also with an intermediate rhombohedral phase and a coexistence between ordered and glassy regions in the low-T state, before eventually the transition is suppressed completely in favor of the orientational glass state.[16] Indications for such effects exist in optical transmission measurements,[9] already on a sample with a somewhat higher CN concentration, namely, $(RbCN)_{0.76}(RbBr)_{0.24}$.

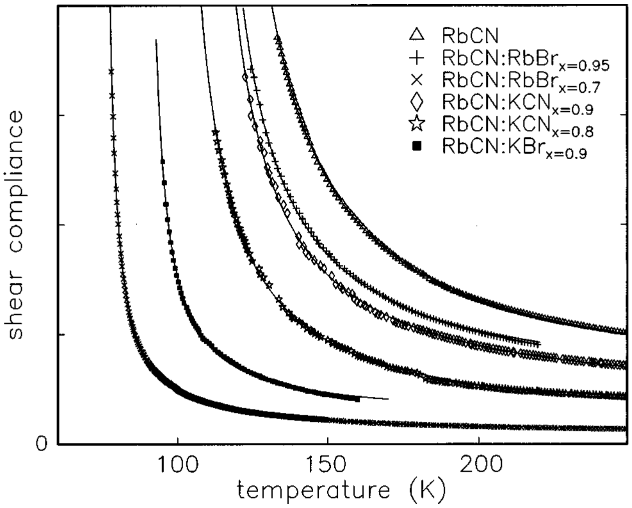

FIG. 4. Fits of the Curie-Weiss law to the shear compliance s_{44} of the paraelastic cubic phase.

Michel[17] has argued that in the mixed crystals the random occupation of the lattice sites by ions of different size gives rise to random local stress fields and derived a pertinent modification of the Curie-Weiss law. The condensation of the lattice strains in these random fields eventually leads to the suppression of long-range ordering of the CN quadrupoles and to the formation of the orientational glass state. Such effects should nevertheless also be present in the paraelastic phase of mixed crystals which—like the present ones—still undergo a conventional phase transition. Our experimental data do not give evidence for random field effects: $s_{44}(T)$ of the paraelastic phase is well described by fits to the Curie Weiss law, in agreement with the conclusions of Fossum and co-workers for ordering samples.[10,12]

C. Ordered regime

Needless to say that measurements in the ordered regime were only possible because the samples did not shatter upon crossing T_c. Obviously, they find a way to keep the transformation strains small by an appropriate matching of the cubic lattice to the monoclinic multidomain state.

Below T_c, s_{44} decreases and elastic loss appears. We will refer to this loss which sets in below T_c as ‘‘primary loss’’

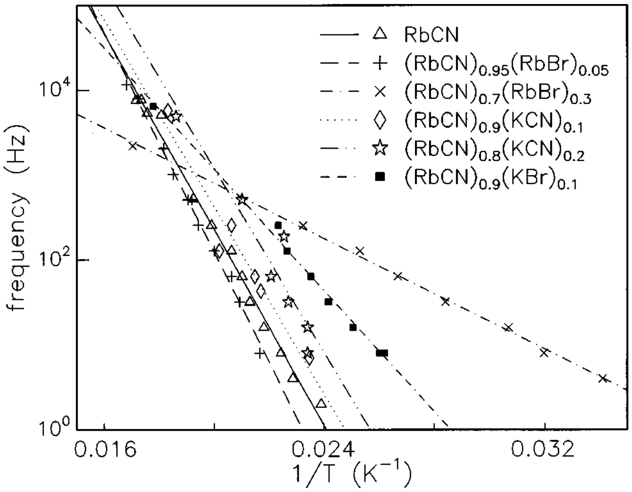

FIG. 5. Arrhenius plot of the maximum of the secondary loss of the low-T monoclinic phase.

and discriminate it from the "secondary loss" which gives rise to a strong loss peaks at temperatures in the 40–70 K range.

The secondary loss peak is the most conspicuous feature of the loss curves of all samples investigated. The maximum values of the loss angle are of the order of 5°–10°. The T value of the secondary loss peak and of the corresponding step in $s_{44}(T)$ shifts with the measuring frequency. This hints at a thermally activated relaxation process. The temperature of the maximum loss as function of measuring frequency follows Arrhenius laws, Fig. 5. The relevant parameters, the activation energy V and the attempt frequency τ_0^{-1}, are included in Table I. For the two $(\mathrm{RbCN})_x(\mathrm{KCN})_{1-x}$ mixed crystals, the secondary loss peak is split. Only the Arrhenius law of the low-T component is shown in the figure, but the table gives data sets for both components.

Secondary elastic loss has been observed in all cyanides investigated so far. In most cases—as in the present ones—the secondary relaxations are well separated from the primary ones on the T and ν scales. The secondary relaxations of the shear elasticity usually occur at temperatures and frequencies comparable to those observed in dielectric measurements. Therefore these relaxations should be related to the dipolar degrees of freedom, which can be in a local picture visualized as head-tail flips of the CN ions. For the present samples dielectric reference data[14] exist for RbCN. The Arrhenius parameters of this data are $V=0.107$ eV and $\tau_0^{-1}=4\times10^{13}$ Hz. These values are slightly outside of the error bars of the parameter values obtained from the present results. At 50 K, for example, the relaxation rate of the dielectric study is by a factor of 2 larger than that of the elasticity measurements. Nevertheless, we think that this comparison supports the idea that dielectric and elasticity relaxations have the same origin. The same statement should apply to those relaxation peaks of the mixed crystals which have Arrhenius parameters close to RbCN. We do not know of a model which accounts for the coupling of the CN dipole flips to the lattice. Within the elastic dipole approximation, the distortion field around a CN ion does not change upon a 180° flip. On the other hand, head and tail of the molecule are after all of slightly different size, a fact which is beyond this approximation. In any case, the dipolar freezing leads to a weak anomaly in the T dependence of the monoclinic cell angle,[5] i.e., in the spontaneous shear order parameter. It is therefore not surprising that strong effects can be seen in the corresponding compliance.

It is not clear whether the high-T component of the split loss peak of the $(\mathrm{RbCN})_x(\mathrm{KCN})_{1-x}$ samples is also due to this type of relaxation. Split loss peaks have been observed[18] in a dielectric study on $(\mathrm{NaCN})_{1-x}(\mathrm{KCN})_x$. We are reluctant to postulate that for these mixed crystals two different types of local CN sites exist, since there are no indications of structural phase coexistence or chemical segregation.

Finally, $(\mathrm{RbCN})_{0.70}(\mathrm{RbBr})_{0.30}$ appears to be a special case. There are two loss peaks in the ordered regime, a stronger one at low T with values of the Arrhenius parameters considerably lower than those of the secondary relaxations of the other samples and a weaker one at intermediate temperatures with Arrhenius parameters unphysically large for a local relaxation process (see Table I). As already pointed out above, the low-T structure of this sample is perhaps different. The loss at intermediate temperatures may be actually due to a second phase transition, and the loss at low T may be related to head-tail flips in a structure different from monoclinic.

The frequency width W at half maximum of the dielectric loss of RbCN is 1.32 decades, which is only slightly broader than 1.14 decades of the Debye case.[14] The frequency range of our measurements is not wide enough to allow the direct determination of W. Instead, we have replotted the secondary loss peak from the T scale to a ν scale by referring to the T-ν relation given by the experimentally determined Arrhenius law. The resulting width W is 2.8 decades for the secondary elastic loss of RbCN, 3.9 decades for $(\mathrm{RbCN})_{0.95}(\mathrm{RbBr})_{0.05}$, and 3.2 decades for $(\mathrm{RbCN})_{0.9}(\mathrm{KBr})_{0.1}$. Although this procedure is questionable for non-Debye-like cases, it shows that W increases upon substitution and that the elastic relaxation rates have a broader distribution than the dipolar ones, suggesting that the dielectric experiment probes flips of CN ions in a well-defined environment, whereas in the elasticity experiment the coupling to strain fields comes into play which obviously varies strongly across the sample. For RbCN this must be due to lattice faults, whereas the enhanced width of the mixed crystals may arise from that type of fields suggested by Michel.[17]

The primary relaxations occur below T_c and extend down into the T range of the secondary ones. Typical values of the loss angle in this regime are about 2°. It is natural to relate the primary relaxations to those degrees of freedom which condense at the transition, namely, the lattice strains coupled to the orientations of the CN quadrupole moments. The experiment probes not so much the elastic response of individual domains—though this will also contribute to the signal—but that of the multidomain state, which reacts to the external torque by domain wall motion and perhaps mechanical twinning. Clearly, such effects are influenced by imperfections of the samples (mosaic grain boundaries, dislocations, concentration gradients), and hence it is not surprising that in the regime from T_c down to where strong secondary relaxations set in the elastic behavior differs from sample to sample. Nevertheless, we think that there exist some typical features. We discuss mainly RbCN, which is

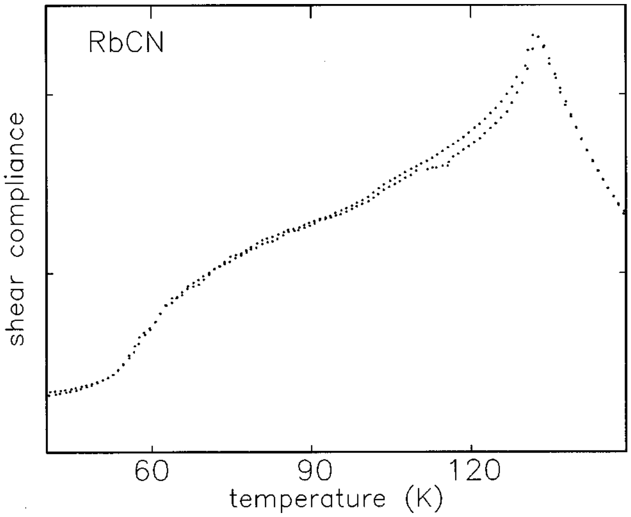

FIG. 6. Shear compliance of RbCN with (lower curve) and without (upper curve) a bias torque.

the clearest case. It is apparent from the data in this T regime that the primary loss is connected with relatively high values of the shear compliance. For a mean-field behavior, one would expect a decrease of the intrinsic shear compliance of a single monoclinic domain steeper below T_c than above T_c. This proposes that the softness of the sample just below T_c is due to stress induced changes of the domain pattern. Analogous to experiments in ferroelectrics[19,20] and ferromagnets, one then expects that the macroscopic susceptibility can be lowered by a bias field, preferentially one being strong enough to drive the sample into saturation. We applied a bias torque and used the resonance technique for the measurement of s_{44}. The result is shown in Fig. 6. The bias torque led to a twist angle of 10°, which translates into a shear angle of 2°—that is, about 2/3 of the spontaneous crystallographic shear—in the outer parts of the sample. In fact, the value of the macroscopic shear constant is slightly lowered by the bias field in the T range from T_c to about 100 K. Guided by interpretations of such effects in ferroelectrics,[19,20] we suggest that the response is this regime is partly due to thermally activated domain wall motion which eventually freezes in at the ‘‘domain wall freezing temperature,’’ here 100 K. On this basis we also relate the small loss peak at 100 K to this freezing process. Finally, we comment on another feature in the loss of RbCN: The small loss peak directly below T_c is presumably characteristic of a relatively narrow regime of cubic-monoclinic phase coexistence. Here the stress-induced dissipative motion of the cubic-monoclinic phase boundaries may contribute to the loss. The results on $(RbCN)_{0.95}(RbBr)_{0.05}$ are similar to those on RbCN. It is likely that domain wall freezing is also responsible for some loss peaks observed in the other samples, though—generally speaking—the decrease of the shear compliance below T_c is stronger in the mixed crystals, suggesting that here the domain wall mobility is reduced by the random stresses introduced by the chemical substitution.

D. Hysteresis and shape memory effect

We performed additional measurements with static external fields on RbCN. Figure 7 shows an attempt to measure a hysteresis cycle in the low-T phase, 5 K below T_c. The maximum torque applied is comparable to that of the previous section. Thus the sample as a whole is far from being driven into saturation. The loop is displaced from the starting point, suggesting that either there were preexisting strains in the sample which relaxed in the course of the loop or that extra strains have been introduced by the first application of the external torque which could be removed by torque reversal. In spite of these limitations, the experiments shows that ferroelastic switching is possible in the monoclinic phase of RbCN.

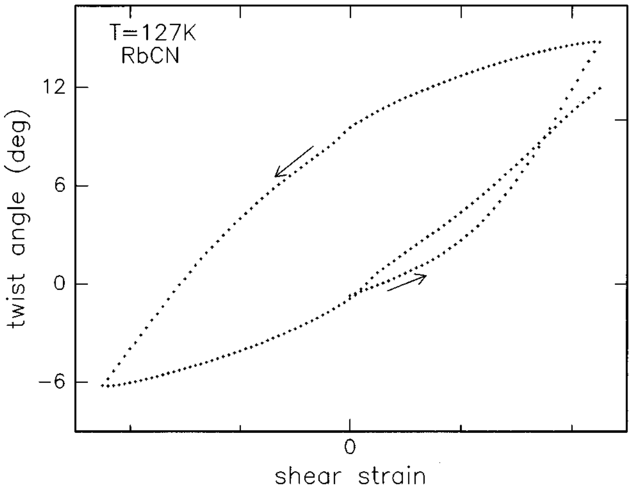

FIG. 7. Ferroelastic hysteresis (twist angle vs torque) of RbCN at 127 K.

In another experiment (Fig. 8), the sample was cooled across T_c in zero torque, and subsequently torque was applied in the low-T phase, at 115 K, for 30 min. After torque removal the sample was heated back into the cubic phase. The experiment shows that there is a spontaneous macroscopic twist of the sample at T_c even when no external torque has been applied. Usually, one expects for macro-

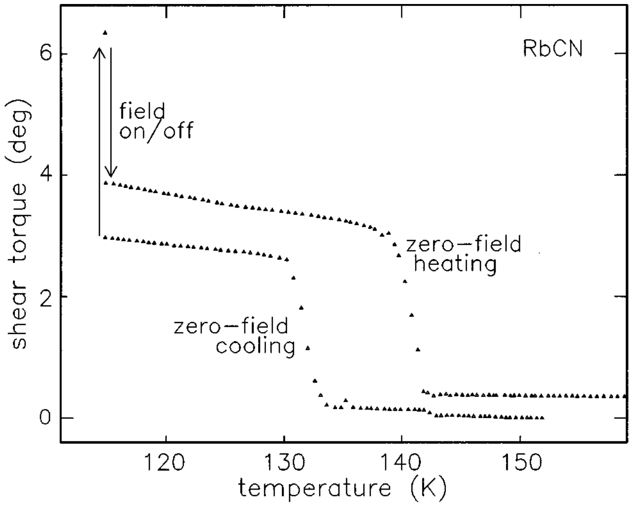

FIG. 8. Demonstration of the shape memory effect in a single crystal of RbCN. The sample is cooled with no torque applied through the transition. Torque is applied for 30 min in the monoclinic phase. Finally, the sample is heated back into the cubic phase in zero field.

scopic samples that the domains have about the same statistical weight and that consequently the transition does not lead to a change of the sample shape. This is not the case here. Obviously, there are preexisting stresses in the sample which favor some domains more than others. By the application of torque below T_c, the domain pattern is changed, and the size of domains favorably oriented with respect to the external field increased. After torque removal some remanence is observed, which, however, decreases on subsequent heating. The reverse crossing of the transition finally brings the sample back almost into its original shape. This is a demonstration of the so-called shape memory effect, which ultimately requires that the coherence of the lattice be maintained across the transition. The reverse transition is shifted to higher temperatures by about 10 K. A thermal hysteresis of similar size has been observed[21] for the cubic-orthorhombic transition of NaCN. Optical transition measurements on RbCN and other mixed cyanides show no noticeable thermal hysteresis of the cubic-monoclinic transition.[9]

IV. SUMMARY

With the shear-torque technique, it was possible to study the complex shear compliance of RbCN and related mixed crystals across the first-order cubic-monoclinic phase transition. In the paraelastic phase the results are in agreement with ultrasonic data, suggesting that the present macroscopic measurement probes the intrinsic compliance $s_{44}=1/c_{44}$. In the ordered phase the strongest feature is a loss peak and a related dispersion step of the compliance which is—as suggested by the comparison to dielectric relaxation data on RbCN—related to the coupling of the torque induced shear strains to the head-tail flips of the CN ions. The strength of this effect is surprising and calls for theoretical efforts. In the temperature range below T_c, evidence for mobile domain walls has been produced by measurements of the primary loss, by demonstrating the effect of a bias field, and by a hysteresis loop. In RbCN there is evidence that the domain walls freeze in at about 30 K below T_c.

The T dependence of the compliance in the paraelastic regime of the mixed crystals follows a Curie-Weiss law rather than modifications of this law due to random fields introduced by chemical substitution, as was suggested by theory. Thus there are no indications for random field effects in the paraelastic behavior. In the ordered phase random fields might be responsible for the broadening of the secondary loss peak and for the reduction of the domain wall mobility in the mixed crystals.

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[1] E. K. H. Salje, *Phase Transitions in Ferroelastic and Co-elastic Crystals* (Cambridge University Press, Cambridge, England, 1990).

[2] J. Hessinger and K. Knorr, Phys. Rev. B **47**, 14 813 (1993).

[3] K. H. Michel and T. Theuns, Phys. Rev. B **40**, 5761 (1989).

[4] J. M. Rowe, J. J. Rush, and F. Luty, Phys. Rev. B **29**, 2168 (1984).

[5] P. Bourson, A. Ndtoungou, J. Bouillot, J. L. Soubeyroux, and D. Durand, Physica B **180**, 351 (1992).

[6] S. Haussühl, Solid State Commun. **32**, 181 (1979).

[7] K. Knorr, Phys. Rev. B **41**, 3158 (1990).

[8] Yu. Vitali and K. Knorr, Ferroelectrics **184**, 99 (1996).

[9] J. Ortiz-Lopez and F. Luty, Phys. Rev. B **37**, 5452 (1988); **37**, 5461 (1988); **41**, 11 422 (1990).

[10] J. O. Fossum, A. Wells, and C. W. Garland, Phys. Rev. B **38**, 412 (1988).

[11] J. O. Fossum and C. W. Garland, Phys. Rev. Lett. **60**, 592 (1988).

[12] C. W. Garland, J. O. Fossum, and A. Wells, Phys. Rev. B **38**, 5640 (1988).

[13] P. Bourson, J. Bouillot, J. L. Soubeyroux, and D. Durand, Ferroelectrics **106**, 163 (1990).

[14] F. Luty and J. Ortiz-Lopez, Phys. Rev. Lett. **50**, 1289 (1983).

[15] T. Shimada, T. Matsuo, H. Suga, and F. Luty, J. Chem. Phys. **85**, 3530 (1986).

[16] K. Knorr and A. Loidl, Phys. Rev. B **31**, 5387 (1985).

[17] K. H. Michel, Phys. Rev. Lett. **57**, 2188 (1986).

[18] J. Ortiz-Lopez, Ph.D. thesis, University of Utah, Salt Lake City, 1983.

[19] E. Nakamura and K. Kuramoto, J. Phys. Soc. Jpn. **57**, 2182 (1988).

[20] M. Fally, P. Kubinec, A. Fuith, H. Warhanek, and C. Filipic, J. Phys., Condens. Matter. **7**, 2195 (1995).

[21] L. Gruber and K. Knorr, Z. Phys. B **79**, 185 (1990).