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Shear elasticity of mixed cyanide orientational glass

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Four mixed crystals of KBr:KCN and NaCN:KCN, complemented by KCN, have been investigated by torque-shear measurements. The real and imaginary parts of the shear compliance s_{44} at a measuring frequency of 2 Hz have been determined. Zero-field-cooling–field-cooling–remanent-shear-strain cycles have been performed. For $(\text{KBr})_{0.47}(\text{KCN})_{0.53}$ the creep after zero-field cooling and the elastic aftereffect after field cooling have been followed within a time window from 0.1 to 10^4 s. Results on the nonlinear part of the shear compliance have been obtained. It is shown that the field-cooled strain represents the static limit of the elastic response. The results are discussed in reference to pure KCN and to spin glasses.

INTRODUCTION

In some mixed crystals in which an aspherical molecular entity is partially substituted by a spherical species, a so-called orientational glass state has been observed.[1] The most prominent examples are para-ortho-H_2 (Ref. 2), Ar:N_2 (Refs. 3 and 4) and mixed alkali halide-cyanides such as KBr:KCN (Ref. 5). In this state the orientations of the aspherical molecules (ortho-H_2, N_2, CN-, respectively) are frozen randomly, i.e., without long-range orientational order. The orientational glass is reminiscent of the spin glass,[6] the molecular orientations playing the role of the spin. The relevant moment is the quadrupolar one. (CN- also carries a dipole moment which is, however, of secondary importance for the formation of the orientational glass.) The interaction between the quadrupoles may be mainly of the electrostatic quadrupole-quadrupole type, as for the hydrogens and for Ar:N_2, or of an indirect type mediated by the elastic deformations of the center-of-mass lattice (elastic dipole-dipole interaction). In both cases the sign of the interaction depends not only on the orientation of the quadrupole tensors with respect to each other but also with respect to the bond vector. This anisotropy leads to frustrated interactions which, in combination with the site disorder of the mixed crystal, generate a spin-glass-like frustrated state. Because of the different symmetries of dipoles and quadrupoles the transfer of concepts or even explicit theoretical results from spin glasses to orientational glasses is, however, problematic.

The three examples of orientational glasses mentioned above and the spin glasses share a common temperature-composition-phase diagram. At high temperatures the systems are in the para phase with dynamical orientational disorder. Above a threshold concentration of the active species, x_c, the systems undergo an orientational ordering transition at $T_c(x)$. Finally, for $x < x_c$ the systems freeze into the glasslike state at low T.

For the cyanides the high-T center-of-mass lattice has NaCl structure. For $(\text{KBr})_{1-x}(\text{KCN})_x$, $x_c = 0.60$, $T_c(x_c) = 95$ K, $T_c(x=1) = 163$ K, and the freezing temperature $T_F(x)$ roughly extrapolates the $T_c(x)$ boundary.[7] The most detailed information exists on samples around $x = 0.5$. In the present study samples with $x = 0.53$, 0.41, 0.23 (and KCN, i.e., $x = 1$) have been investigated. The investigation has been extended to one representative of the $(\text{NaCN})_{1-x}(\text{KCN})_x$ series, namely, $x = 0.85$. In this series the glasslike low-T state exists for $x_{c1} = 0.15 < x < x_{c2} = 0.90$ (Refs. 8 and 9).

In orientational glasses the bulk quadrupolar susceptibility, which is the counterpart of the magnetic susceptibility of the spin glasses, is not easily accessible in the experiment. In fact, no such data exist for the hydrogens or for Ar:N_2. In the cyanides, however, the CN orientations couple to the long-wavelength deformations of the center-of-mass lattice in a bilinear way,[10] the effects being strongest for the T_{2g} components. Therefore, there is a linear relation between the orientational and elastic susceptibility:[11]

$$s_{44} = 1/c_{44} = s_{44}^0 + b\chi , \tag{1}$$

where s_{44} and χ are the full elastic shear and orientational T_{2g} susceptibility of the coupled orientational-elastic system. s_{44}^0, is the background compliance if the orientational degrees of freedom were absent (as in an alkali halide like KBr). χ can be related to the local orientational susceptibility χ_0 via $\chi = \chi_0/(1-c\chi_0)$. The validity of Eq. (1) is well established for both the pure cyanides and for individual CN impurities in an alkali halide matrix. We will assume that Eq. (1) also holds for intermediate concentrations. On this basis we understand results on s_{44} as being analogous to data on the magnetic susceptibility in spin glasses.

Hitherto the behavior of the shear elastic constant, c_{44} has been studied experimentally by means of inelastic neutron[5,9,12] and Brillouin[13–15] scattering, by ultrasonic techniques,[16–21] and by a torsion pendulum,[22] and theoretically by molecular-dynamics simulations.[23,24] Clearly these experimental methods do not probe the static elastic response but that at the characteristic frequency of the method (MHz for ultrasonics, GHz for Brillouin, and THz for neutron scattering, about 100 Hz

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for the pendulum). c_{44} decreases with decreasing temperature down to the freezing temperature T_F' below which it stiffens again. This minimum of $c_{44}(T)$ is regarded as a counterpart of the cusp of the magnetic susceptibility at the spin-glass temperature. The value of T_F' and the response below T_F' are frequency dependent. Below T_F' there is elastic loss as is apparent from ultrasonic attenuation and damping of the torsion pendulum. The loss peaks at a temperature T_F'', $T_F'' < T_F'$. These are clear indications that the freezing is a relaxational process. It has been shown that the results are well described by a model[25] based on hierarchically constrained relaxations.[26]

Several experiments on quadrupolar glasses concentrate on quantities which might be connected to the static quadrupolar glass order parameter $q(T)$. It is agreed upon that the diffuse scattered, to a good degree static x-ray and neutron intensity ("central peak") of the mixed cyanides, which appears at low T close to the Bragg points in T_{2g} scattering geometry, represents frozen-in coupled shear-orientational displacement patterns.[27] Hence it is a measure of $q(T)$. Furthermore, there have been attempts to derive $q(T)$ from ultrasonic results on $c_{44}(T)$, Refs. 17–19, in spite on the fact that this experiment definitely does not probe the static response. Related problems occur in neutron scattering. The apparent width of the central peak is given by the frequency resolution of this experiment. Since the resolution is under the best circumstances of the order of GHz, one wonders whether this is a good approximation to the static case. One purpose of the present study is to characterize the relaxations in a sufficiently complete way in order to make the extrapolation to the static elastic response function $s_{44}(T)$ possible.

There is an ongoing debate whether $q(T)$ is due to "random bonds or interactions" or "random fields" or both. For the definition of these terms see Ref. 1. In spin glasses there is a clear distinction between random bonds and random fields which is, however, absent in quadrupolar systems. This is a consequence of the tensor property of the quadrupole moment. Thus, for a dilute lattice of quadrupoles, random interactions between the moments will automatically generate random-field-type contributions to the total free energy.[2] Furthermore, the size difference of substituents, such as CN and Br in the present compounds, set up random strain fields which can block the CN orientations.[28] Random fields of whatever origin lead to nonzero values of q at any finite temperature and thus smear out a possible phase-transition-like onset of the glass state at T_g.

The understanding of spin glasses has benefitted from experiments in which the magnetization is measured for different field-temperature histories, like, e.g., the application of the field after zero-field-cooling (ZFC) and the cooling in a constant field (FC).[6,29] A part of the present article will deal with analogous experiments.

In spin glasses the nonlinear part $\chi_{\rm nl}$ of the susceptibility is considered conjugate to the glass order parameter.[1,30] $\chi_{\rm nl}$ should diverge at the true glass transition temperature T_g. We will also report on measurements of the nonlinear part of s_{44}. Results of our elasticity measurements have been reported previously.[31,32]

EXPERIMENT

The composition of the samples has already been stated above. The samples have been grown from the melt. The mixed bromide with $x = 0.41$ has been bought from the crystal growth laboratory of the University of Utah, the others have been donated by Haussühl, Köln. The CN concentration x has been determined by gravimetry. The setup for the measurement of s_{44} is shown in Fig. 1. The samples, single-crystalline columns, typically $(6\times2\times2)$ mm^3, with $\{100\}$ faces, are glued to the cold plate of a closed-cycle refrigerator. On the free end they carry a permanent magnet and a mirror. Torque is applied via a magnetic field which is perpendicular to the magnetic dipole. The torque H is proportional to the magnetic field. The crystal responds to the torque by a twist which is determined from the deflection of a laser beam reflected from the mirror. The twist around [100] leads to a shear deformation M of the sample, which increases with the radial distance from neutral fiber. It has been verified that the twist angle is proportional to the magnetic field up to the maximum value of 5 kG of the field coils. The maximum twist angles which have been used in the experiments correspond to shear deformations at the surface of the sample of 0.005, in most cases lower values, around 0.001, have been used. These figures are estimated from the assumption of a cylindrical sample shape. (The calculation of shear strain distribution in twisted samples with a noncircular cross section is a nontrivial problem.) The ratio of the shear deformation M and the shear stress H is proportional to the T_{2g} shear compliance s_{44}. The time profile of H can be chosen freely. In some experiments with weak fields, H has been varied sinusoidally, up to frequencies of about 100 Hz, which is still well below the torsional eigenfrequency of the crystal loaded with the permanent magnet and the mirror. The amplitude of M and the retardation or loss angle δ with respect to H has been recorded with a vector lock-in amplifier or with a two-channel [for $H(t)$ and $M(t)$] digital storage oscilloscope, depending on whether the frequency ν is above or below 2 Hz. Attempts have been made to extract the 3ν component which is the proportional to the lowest-order component of the nonlinear part of s_{44}. In other experiments with stronger fields, the field has been switched on or off and M has been followed

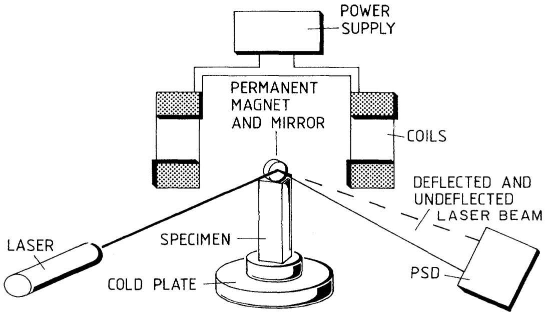

FIG. 1. Schematic view of the experimental setup. PSD represents position-sensitive detector.

with time after switching. Such transients are known as creep and elastic aftereffect. In this version of the experiment the accessible time window is between 0.1 and 10 000 s. The lower limit is given by the time constant of the field coils and the power supply, the upper one by the mechanical long-time stability of the rack to which the setup is mounted.

The sensitivity of the present experiment on s_{44} is much lower than that of the ultrasonic method, but it has two decisive advantages: (i) it can cope with large elastic loss and (ii) it gives direct access to the shear strain induced by an external stress. Needless to say that long-time relaxations put experimenter's patience on test. Many heating-cooling cycles and transients had to be stopped before completion because of failures of the crystals such as sudden cracks or because of external shocks to the equipment which offset the M scale.

MEASUREMENTS OF $s_{44}(T)$

Figure 2 shows the T dependence of s_{44} and the loss angle δ of all five samples investigated, ν is 0.05 Hz for KCN, and 2 Hz for the other samples. The T dependence of s_{44} is in agreement with what is known from previous measurements on $c_{44}(T)$. In the paraelastic phase $s_{44}(T)$ increases with decreasing T. The T dependence roughly follows a Curie-Weiss law $s_{44}=s_{44}^0+b'/(T-\Theta)$. After passing through a cusplike maximum, s_{44} decreases towards lower T, the decrease is accompanied by the appearance of elastic loss. In KCN the abrupt decrease of s_{44} around 160 K is due to the first-order ferroelastic-ferroquadrupolar phase transition from the cubic into the low-T orthorhombic *Immm* phase.[33] The finite loss just below T_c is presumably due to dissipative rearrangements of the ferroelastic domains. A second small step in $s_{44}(T)$ and a second maximum of the loss, around 60 K, are connected with antiferroelectric transition[34] *Immm* to *Pmnm* of the CN dipole moments. It is known from diffraction measurements (on the isomorphic crystal NaCN) that the antiferroelectric order parameter couples to homogeneous lattice deformations.[35] Thus, effects on the elastic compliance are to be expected. In the mixed crystals, which are known to remain cubic down to lowest T, the maximum of s_{44} and of the loss, which define the freezing temperatures T_F' and T_F'', signals a slowing down that is the freezing in of the CN orientations on a time scale set by the frequency of the experiment. Note that the temperatures of maximum s_{44} and of maximum loss are slightly different as expected for a relaxational process. In fact, the present low-frequency values of T_F are lower than previous values obtained with higher-frequency methods. The largest number of reference data exists for KBr:KCN with x about 0.5, here 0.53. $T_F'=95$ K in THz inelastic-neutron-scattering data,[5] 85 K in GHz Brillouin scattering,[14] about 80 K in ultrasonic measurements,[16,17] 75 K in the torsion pendulum experiment,[22] and 72.5 K in the present 2 Hz investigation. It is evident from Fig. 2 that the peak of $s_{44}(T)$ and of $\delta(T)$ are relatively sharp for the bromides with $x=0.41$ and 0.53, almost reminiscent of a ferroelastic phase transition (see KNC), but significantly broader for $x=0.23$ and for the NaCN:KCN sample. The behavior of the bromides suggests that the maxima sharpen for $x \rightarrow x_c$, on the other hand, the composition of the Na sample is also close to a critical concentration. Presumably the rounding of the maximum of $s_{44}(T)$ and of $\delta(T)$ in the latter sample is due to strong random fields.

The bromides with $x=0.41$ and 0.53 show a second loss peak, as has already been established in the torsion pendulum experiment.[22] This secondary loss peak is thought to reflect the freezing of the CN electric-dipole moments since it coincides with the loss peak of dielectric measurements. Guided by the pure cyanides one thinks that the freezing of the dipoles couples to the elastic de-

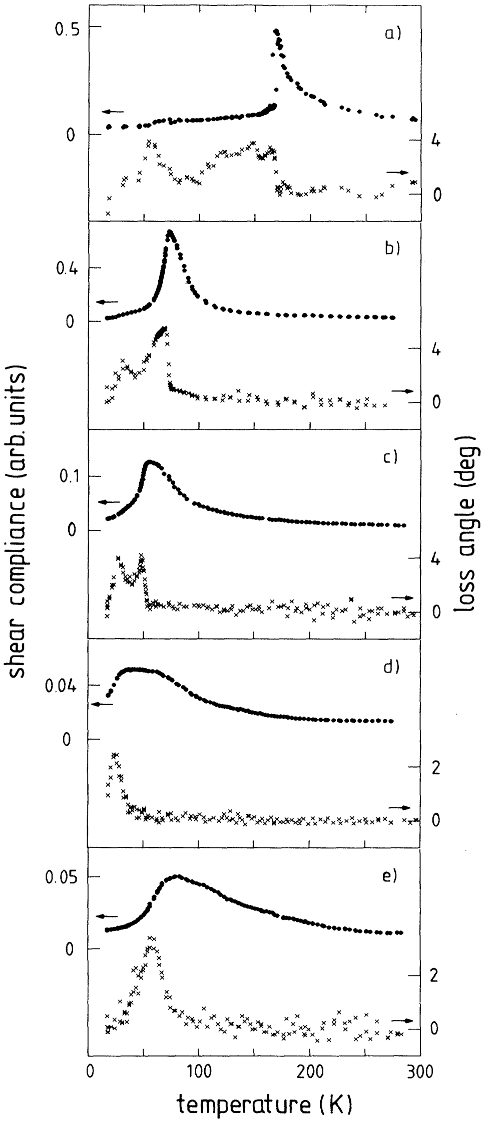

FIG. 2. The temperature dependence of the shear compliance s_{44} and of the loss angle. The samples are, from top to bottom, KCN, $(KBr)_{0.47}(KCN)_{0.53}$, $(KBr)_{0.59}(KCN)_{0.41}$, $(KBr)_{0.77}(KCN)_{0.23}$, $(NaCN)_{0.15}(KCN)_{0.85}$. The measuring frequency is 0.05 Hz for KCN and 2 Hz for the other samples.

grees of freedom as well. For the low-x bromide, $x=0.23$, the secondary loss peak is expected to occur around 14 K by extrapolation of the dielectric loss[36,37] data down to the present measuring frequency of 2 Hz. 14 K is, however, below the lowest temperature accessible with our equipment. For the NaCN:KCN sample, the extrapolation of the dielectric data yields a temperature of 37 K for the maximum of the secondary loss.[12] This temperature falls on the low-T wing of the primary loss peak. An inspection of the elastic loss peak shows that there is definitely not a second peak, but perhaps a weak shoulder. Thus, it appears safe to conclude that the dipolar degrees of freedom of NaCN:KCN couple to the quadrupolar ones to a much lesser degree than they do in KBr-KCN. This might be another indication for stronger random fields in the NaCN:KCN series.

HISTORY EFFECTS

Guided by analogous experiments in spin glasses,[6,29] the shear strain M of the mixed cyanides has been studied with the following sample history.

(1) The samples have been cooled down into the glassy state with no torque applied (ZFC).

(2) The field is switched on and the induced shear strain M_{ZFC} is measured while the samples are heated up into the paraelastic phase.

(3) The field-cooled strain M_{FC} is recorded on second cooling.

(4) The field is switched off at a temperature within the glassy state and the remanent strain M_{rem} is observed upon heating back into the paraelastic phase.

The heating and cooling rates are about 4 mK/s. The isothermal waiting times after field switching are of the order of half an hour. The results are shown in Fig. 3. The $M_{\mathrm{ZFC}}(T)$ curves are identical to the $s_{44}(T)$ curves of the last paragraph, with the exception that the cusp and the low-T wing are slightly shifted to lower temperatures. This can be understood in terms of the relaxational model. Finite cooling and heating rates block the evolution of slow relaxations in very much the same way as finite frequencies of oscillating fields. Our heating and cooling rate corresponds to an effective frequency of less than 10^{-3} Hz. M_{FC} and M_{ZFC} deviate from one another below a characteristic temperature $T_F^{\mathrm{ZFC-FC}}$. M_{rem} vanishes above another characteristic temperature T_F^{rem}. The various T_F's give the freezing and thawing temperatures of the shear strains coupled to the orientational quadrupolarizations on a time scale set by the measurement. $T_F^{\mathrm{ZFC-FC}}$ and T_F^{rem} should be about equal since these temperatures are obtained with the same heating and cooling rate, they are both lower than T_F (2 Hz). In comparing the ZFC-FC-rem cycles of the four samples, one notices that $T_F^{\mathrm{ZFC-FC}}$ and T_F^{rem} of the mixed bromides with $x=0.53$ and 0.41 are well defined whereas the splitting between the $M_{\mathrm{ZFC}}(T)$ and $M_{\mathrm{FC}}(T)$ curves and the decay of M_{rem} with the temperature of the other two mixed crystals are rather gradual. This different behavior might have been expected from the different shape of the cusp and of the loss peak of the 2 Hz measurement.

So far our reasoning is guided for a relaxational concept of the freezing process. Nevertheless, one should ask the question whether M_{FC} or M_{ZFC} is closer to thermal equilibrium, that is, which of the two quantities, if any, is independent of the sample history. For spin glasses the so-called folklore mapping between the experiment and the mean-field theory proposes that M_{ZFC} probes just one valley of the free-energy landscape in phase space, but that field cooling provides an average over all states.[38] For the moment we remark that we followed M_{FC} at a constant field with time over several hours at constant temperature without noticing any significant change. Further, below we will show that

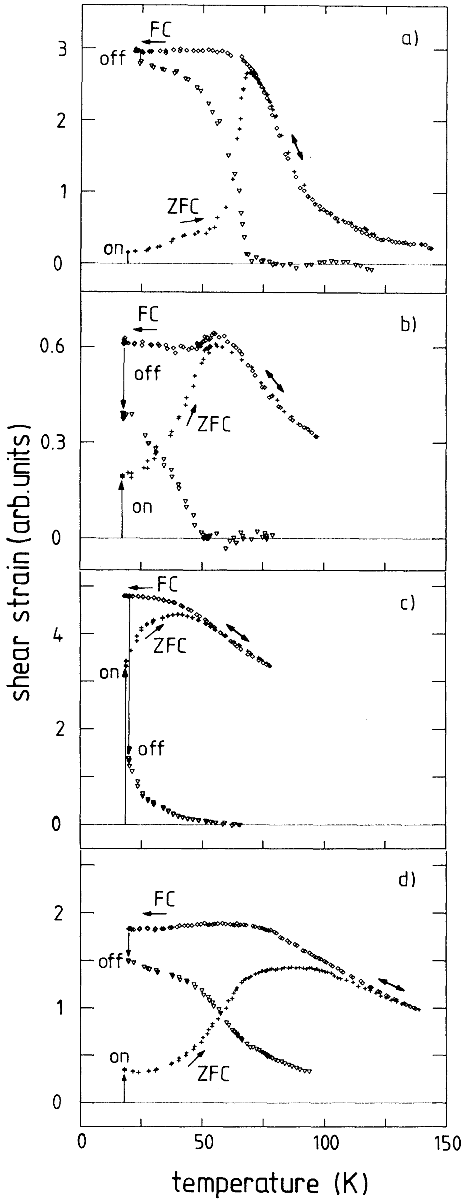

FIG. 3. The shear strain as a function of temperature in a ZFC-FC-rem cycle. The samples are, from top to bottom, $(\mathrm{KBr})_{0.47}(\mathrm{KCN})_{0.53}$, $(\mathrm{KBr})_{0.59}(\mathrm{KCN})_{0.41}$, $(\mathrm{KBr})_{0.77}(\mathrm{KCN})_{0.23}$, $(\mathrm{NaCN})_{0.15}(\mathrm{KCN})_{0.85}$.

M_{ZFC} relaxes towards M_{FC} and that therefore $M_{FC}(H,T)$ is the equilibrium response $M(H,T)$, which is consistent with the view cited above.

On the basis of the mean-field theory, it has been proposed for the spin glasses[38] and dipolar proton glasses[39] that the deviation of $M(H,T)$ from the extrapolated paramagnetic Curie or Curie-Weiss-type behavior $M_{para}(H,T)$ gives the glass order parameter q, thus for the Curie case $q=1-M/M_{para}$. Unfortunately, such an extrapolation of the paramagnetic behavior is not free from the arbitrariness in the mixed cyanides. We discuss the situation for the $x=0.53$ bromide: The mean-field expression [Eq. (1)] and modifications thereof, with and without random-field contributions,[28,17] have been fitted to the data. The fits suggest that the extrapolated paraelastic response diverges at an ordering temperature T_0, $65<T_0<78$ K (within these limits the value of T_0 depends on the expression chosen and on the T range of the fit). Thus, T_0 is larger than T_F, which makes the quantitative extraction of $q(T)$ from M_{para} and M_{FC} impossible. Nevertheless, on a qualitative basis the present data suggest that $q(T)$ increases most strongly in the narrow T range in which $M_{FC}(T)$ bends over into the low-T plateau. This happens around 65 K. The strong increase of the central peak intensity of the neutron experiment occurs, however, already at 95 K. Similar discrepancies exist for the other two samples for which neutron data are available, namely, the bromide with $x=0.23$ (Ref. 40) and the mixed Na cyanide.[12] According to the random-field theory of Bostoen and Michel, the strong onset of the central peak intensity and the kink of $s_{44}(T)$ should coincide in temperature.[41] One may speculate that the elastic behavior and the central peak at higher temperatures are indeed strongly influenced by random-field effects, but that the onset of the glassy state, as indicated by the splitting of the FC and ZFC curves and by the anomaly of the nonlinear response (see below), is a consequence of random bonds.

CREEP AND AFTEREFFECT MEASUREMENTS

The isothermal time evolution of M of the $x=0.53$ bromide has been followed after field switching for two types of transients: The field has been switched on after ZFC (creep), the field has been switched off after FC (aftereffect). In both cases the sample responds by a spontaneous change of the shear strain followed by a relaxing change. See Fig. 4 for an overview and definitions. In the following the time law of the relaxing part is discussed. Among the simple decay laws [$\sim\ln(t), \sim\exp(-t/\tau), \sim t^{\alpha}$] the logarithmic decay is closest to the experiment. This is evident from the roughly linear curves in strain versus $\log_{10}(t)$ plots, see Fig. 5 for the creep and Ref. 32 for the aftereffect. Since the $\ln(t)$ law is by no means satisfactory over the T range investigated, two more sophisticated relaxation laws have been applied, the KWW or stretched exponential $\sim\exp[-(t/\tau_{KWW})^{\beta}]$ and an exponential law with a log-normal distribution of the relaxation time, i.e., a Gaussian distribution on a $\log_{10}(\tau)$ scale centered at τ_0 with a standard deviation σ. Both models have two free param-

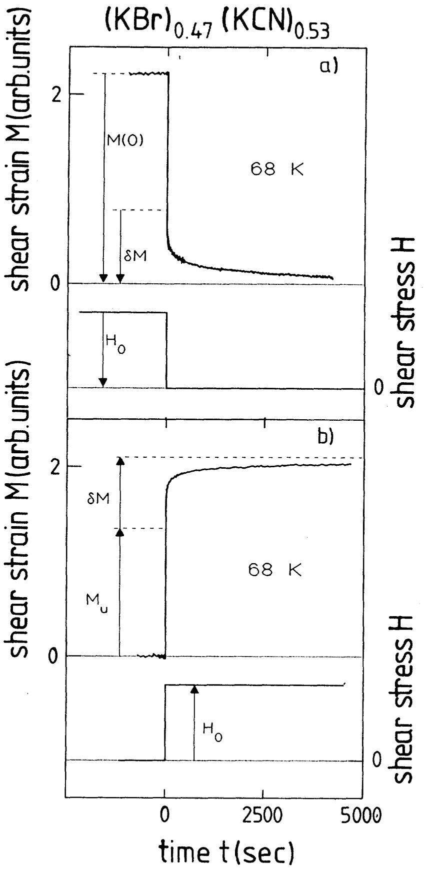

FIG. 4. Time profiles for the torque H and the shear strain M in (a) aftereffect measurements after field cooling and (b) creep measurements after zero-field cooling. The instantaneous and relaxing parts of the strain are defined as shown.

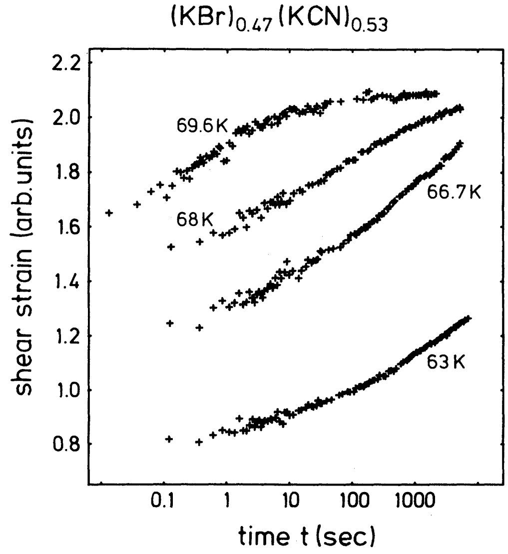

FIG. 5. The isothermal time evolution of the shear strain in creep measurements at various temperatures.

eters and give fits to the measurement of comparable quality. The fit parameter are most accurately determined in the (narrow) temperature range around 68 K where τ_{KWW} and τ_0, respectively, fall into the experimental time window (Fig. 6). A complete analysis of the data has been carried out with the KWW law. The T dependence of τ_{KWW} and β is shown in Fig. 7. The values obtained from the creep and the aftereffect measurements are identical. The β values are between 0.15 and 0.3, indicating that the distribution of τ is very broad.[42] Comparable values of β have been obtained in spin glasses. Since the translation of the KWW parameters into a τ distribution is not straightforward, we alternatively quote the result of the log-normal fit. For $T = 68.1$ K, $\tau_0 = 251$ s, σ is 3.6 decades, whereas $\tau_{\mathrm{KWW}} = 146$ s. For $T > 67.5$ K, $\tau_{\mathrm{KWW}}(T)$ roughly follows an Arrhenius law with an attempt frequency of 10^{125} Hz and an activation enthalpy of 20 000 K. Corresponding figures from previous work based on high-frequency results are 10^{60} kHz and 8000 K (Ref. 36). Note, however, that these values have been determined from the cusp of the real part of the elastic response function at T_F' rather than from the maximum of the dissipative part at T_F''. The only other data point on T_F'', namely, that of the torsion pendulum experiment, is, in fact, consistent with the present Arrhenius law. At lower T, $\tau_{\mathrm{KWW}}(T)$ deviates from the high-T Arrhenius law in a way which is contrary to what is expected from the Vogel-Fulcher law. In fact, Fig. 7 suggests that the relaxation time settles at low T at a finite maximum value of the order of 10^6 s. The same type of behavior in the dipolar glassy system $K_{1-x}Li_xTaO_3$ has been interpreted in terms of a special relaxation model.[43] We are rather convinced that this low-T limit of τ is imposed by the slow but nevertheless finite cooling and heating rates and by too short a waiting time before field changes. One cannot expect to observe long τ's if the system has not had time enough to condense these slow modes.

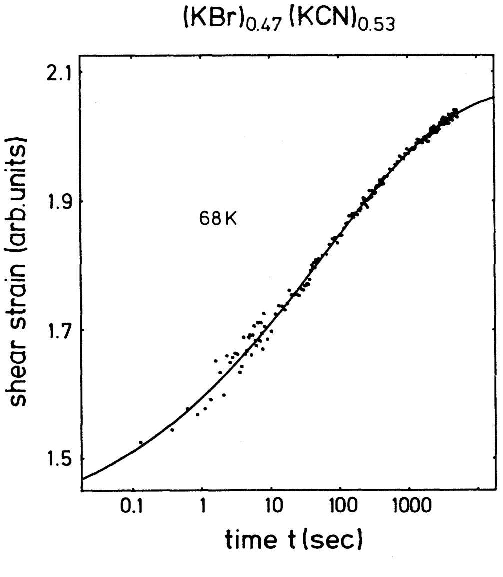

FIG. 6. Fit of the KWW time law to a creep shear-strain transient ($\tau_{\mathrm{KWW}} = 61$ s, $\beta = 0.23$).

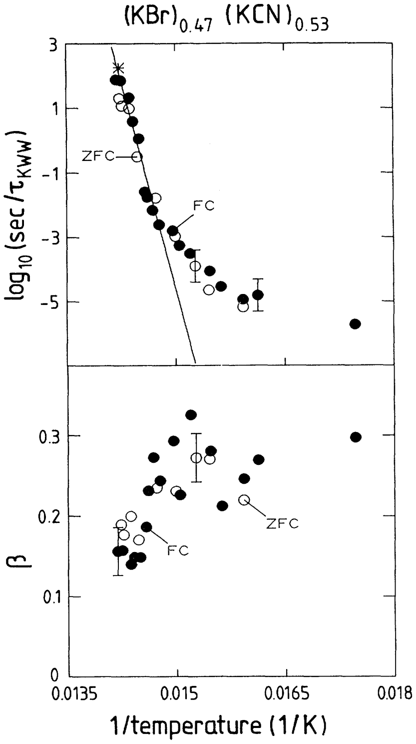

FIG. 7. The temperature dependence of the KWW parameters τ_{KWW} and β for aftereffect (FC) and creep (ZFC) transients. The solid line is the Arrhenius law described in the text. One data point ($*$) is from the elastic loss of the torsion pendulum experiment (Ref. 22).

The parametrization of the strain decay in terms of the KWW law gives values for the instantaneous and relaxing part of $M(t)$, and allows the extrapolating to $M(t=\infty)$. For the creep measurements the instantaneous shear after field application, M_U, and $\delta M(t=\infty)$ are free fit parameters. The resulting total strain at $t=\infty$, i.e., $M_U + \delta M(t=\infty)$ is within the scatter of the data points identical to M_{FC} (Fig. 8). This is a central result of the present study: field cooling gives to a good approximation the static limit for the elastic response, M_{FC} is close to, if not identical with, the equilibrium strain. As a consequence of this result, the cusp of s_{44} and c_{44} in finite-frequency measurements, the cusp of M_{ZFC}, the decrease of $s_{44}(T)$, and the stiffening of $c_{44}(T)$ at low temperatures is a purely relaxational effect and has little to do with a static order parameter q. Of course, we can make this strict statement at higher temperatures only, namely, $T > 63$ K, in which the relation time is not too far outside of our time window. The relaxing part and the instantaneous part are comparable in size, the δM fraction increasing somewhat towards lower T (Fig. 8).

In first fits of the aftereffect after field-cooling measurements, the value of $M(t=\infty)$ (Fig. 4) was considered a free parameter. In the T range where the fit is most reliable, that is for temperatures where $\tau_{\mathrm{KWW}}(T)$ falls into the experimental time window, values around zero have been obtained for $M(t=\infty)$. Thus, the field-cooled

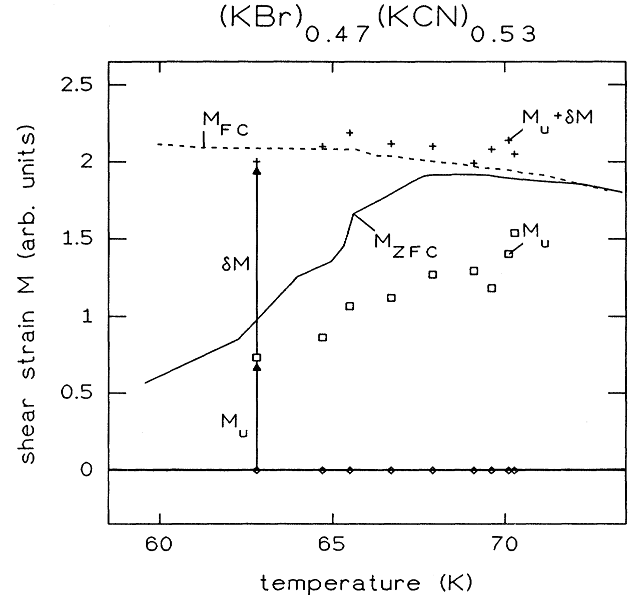

FIG. 8. The temperature dependence for various forms of shear strains in creep measurements. M_U is the instantaneous part of the transient, $M_U+\delta M$ the $t=\infty$ limit, as obtained from KWW fits. The field-cooled strain (dashed line) and the zero-field-cooled strain, reproduced from Fig. 3, are shown for comparison.

strain M_{FC} decays eventually to zero after field removal. Any remanent strain exists only because of insufficient waiting time after field removal. In subsequent fits outside the favorable T range, $M(t=\infty)$ was held at zero value and only the partition into the spontaneous and the relaxing part was allowed to vary. As for the creep the relaxing part amounts to roughly one-half of M_{FC} with some increase towards lower T.

NONLINEAR RESPONSE

The experiments have been carried out with a sinusoidal field H, $\nu=85$ Hz, with the lock-in amplifier. The ν signal is proportional to the linear part of s_{44}, the 3ν signal proportional to the leading component of the nonlinear part of s_{44} weighted with either the third[44] or the fourth power[45] of the linear response. The 3ν signal is unmeasurably small except in a small-T-range. At its maximum intensity it is still 10^4 times smaller than the ν signal. The weakness of the 3ν signal prevented us from working at lower frequencies which would give a better approximation to the static limit but where the performance of the amplifier is worse.

Figure 9 shows the results on the 3ν signal, and on the ν signal for comparison, for the two samples studied, namely, the bromides with $x=0.41$ and 0.53. For both samples the T dependence shows a cusp of the 3ν signal, defining a temperature T_{n1}, 52 K for $x=0.41$, 66.2 K for $x=0.53$. T_{n1} is comparable to the freezing temperatures of the previous chapters. The cusps are relatively sharp, they cannot be explained by merely considering the T variation of the linear response (taken to the third or fourth power), since around T_{n1} the change of the linear response with temperature is quite moderate. The high T wing is reminiscent of a Curie-Weiss law $[\sim(T-T_g)^{-\gamma}]$. The best fit is obtained with $T_g=(44.5+1)$ K and $\gamma=0.95\pm0.05$ for $x=0.41$, $T_g=(63.5\pm1)$ K, and $\gamma=1.7\pm0.1$ for $x=0.53$. The decrease of the 3ν signal for $T<T_{n1}$ might be again due to relaxations although the out-of-phase component of the 3ν signal was never above the noise level. For the two samples the values of T_{n1} compare differently with the cusp temperatures of the linear response. For $x=0.41$ the cusps of the linear and the nonlinear response roughly coincide, whereas for $x=0.53$ the cusps of the nonlinear response is at a significantly lower temperature.

For spin glasses the Curie-Weiss-type T dependence of the nonlinear susceptibility is considered the strongest evidence for the transition into the glassy state being phase-transition-like, with a divergence of a characteristic length. We recall that the inevitable appearance of random fields in quadrupolar glasses is expected to modify this picture, in particular, random fields are expected to suppress the divergence of χ_{n1}. Furthermore, χ_{n1} when measured at a finite frequency is affected by relations of the glass order parameter. The fact that the

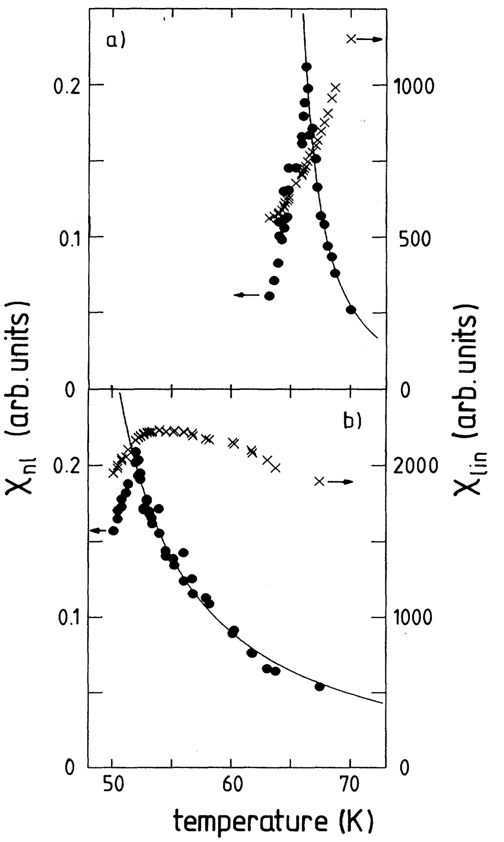

FIG. 9. The ν and 3ν responses as a function of temperature, $\nu=85$ Hz, for (a) $(\mathrm{KBr})_{0.47}(\mathrm{KCN})_{0.53}$ and (b) $(\mathrm{KBr})_{0.59}(\mathrm{KCN})_{0.41}$. The solid lines are fits to power laws $\sim(T-T_g)^{-\gamma}$.

anomaly of χ_{n1} is weak but nevertheless sharp proposes that random fields are significant but that order parameter relaxations are of secondary importance.

In the following we compare the various characteristic temperatures which have been defined in the present study. For $x=0.53$, $T_g=63.5$ K, $T_{n1}=66$ K, the maximum of s_{44} is at $T_F'=74.8$ K for 85 Hz, at 72.5 K for 2 Hz, $T_F^{\mathrm{ZFC-FC}}=T_F^{\mathrm{rem}}=68.5$ K. This compilation suggests that T_g might be the static limit of the freezing temperatures. In this sense the transition into the glassy state is the consequence of slowing-down relaxations similar to the standard view for real glasses. In spin glasses, however, T_g is usually larger than the freezing temperature[45] (defined from the maximum of the susceptibility), which means that the relaxations evolve only after the system has entered into the glass phase.

COMPLEMENTARY MEASUREMENTS ON KCN

The $s_{44}(T)$ data on KCN have already been shown and discussed before. In the paraelastic phase, the $s_{44}(T)$ phase is proportional to $(T-T_0)^{-\gamma}$, $T_0=(151\pm4)$ K, $\gamma=0.97\pm0.04$. The background term, which according to Eq. (1) represents the unrenormalized shear compliance s_{44}^0, is negligible in the T range investigated. These parameters are in agreement with previous ones[46,47] derived from measurements of $c_{44}(T)$ at ultrasonic frequencies. In addition, we have measured creep curves after ZFC and aftereffect curves after FC into the ferroelastic phase. The end point of cooling was 162 K for ZFC and 160 K for FC, these temperatures are slightly below the ferroelastic transition temperature ($T_c=163$ K on cooling).

Again the $M(t)$ transients show a spontaneous part and a slowly relaxing part. The latter part could be parametrized in terms of the KWW law with $\tau_{\mathrm{KWW}}=10^{4.8}$ s, $\beta=0.22$ for the creep, $\tau_{\mathrm{KWW}}=10^{5.0}$ s, $\beta=0.27$ for the aftereffect. Already these τ values are outside of our t window. For lower T the fits become less and less trustworthy, but they give nevertheless the impression that the increase of τ_{KWW} with decreasing T is much weaker than for the glass-forming cyanides. The ferroelastic phase exists in a multidomain state, thus it is natural to think of the creep and aftereffect as being due to domain-wall motion. A second suggestion is that the low value of c_{44} just above T_c (and at T_F for $x=0.53$) makes the creation of screw dislocations possible, which, in turn, might contribute to the elastic relaxations.[48] In any case the similarity of the $M(t)$ transients in pure KCN on one side and in the glass-forming cyanides might indicate that an understanding of the ferroelastic transition, including the mesoscopic domain structure, might be very helpful for the understanding of the glass state. In this sense the shape memory effect which occurs when cooling a sample through a ferroelastic or martensitic transformation may be of importance for the ZFC-FC-rem cycles of the mixed cyanides. We carried out a simple cooling-heating cycle in zero field. For the mixed cyanides such an experiment gives no indication for a spontaneous bending or twisting of the sample. For KCN, however, the sample bends and twists as shown in Fig. 10(a). The ferroelastic multidomain crystal shows a spontaneous change of its macroscopic shape which is due to an incomplete compensation of the 24 domain states, presumably induced by preexisting stresses. The shape change is by no means completed just below T_c but varies with T, even reverses, down to the lowest temperature investigated. Thus, the domains rearrange at least down to this temperature an effect which necessarily leads to elastic loss in s_{44} measurements. Upon heating back into the paraelastic phase the sample eventually finds back to the original shape. This is analogous to the two-way-shape-memory effect of the martensites.[49] The reverse transition starts at about 170 K and is completed around 177 K. Similar hysteresis cycles have been observed by optical transition.[50] Figure 10(b) shows the one-way-shape-memory effect: the sample is zero-field

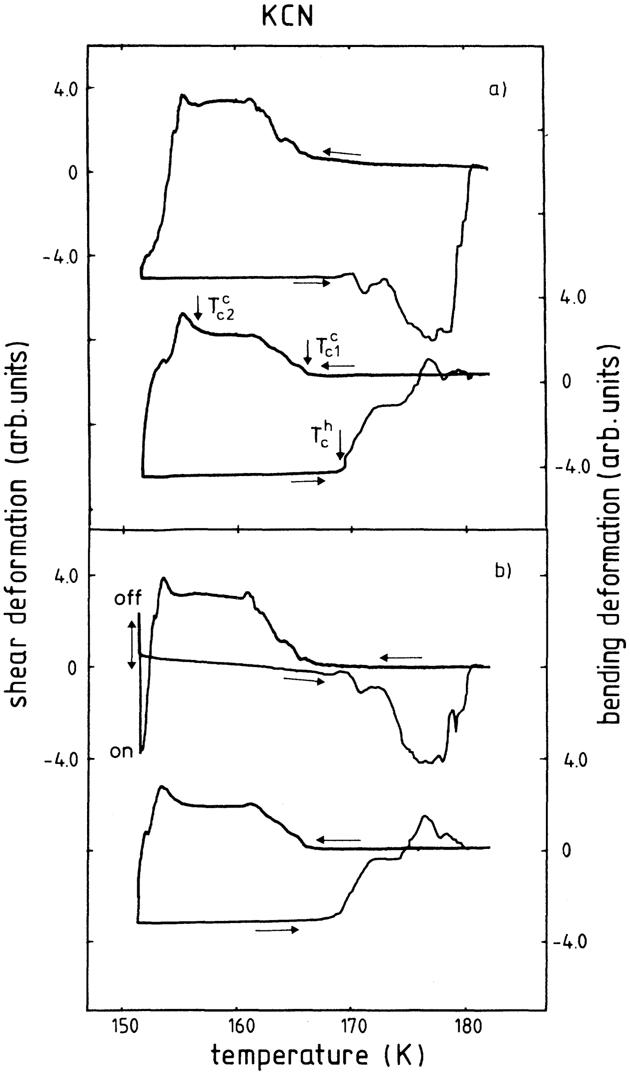

FIG. 10. The macroscopic deformation, separated for twisting (=shear) and bending, of a KCN single crystal on thermal cycling through the ferroelastic phase transition. (a) No fields applied. (b) Application and subsequent removal of a troque in the ferroelastic phase.

cooled into the ferroelastic phase. The field is switched on, a net shape change is induced, this change is only along the field direction, i.e., is only twist without bending. Field removal leaves a remanent shear deformation with respect to the shape before field application. This means that the majority domains have been enlarged. On heating back into the paraelastic phase, the original shape is again restored.

From these measurements one has good reason to think that it would be difficult to distinguish a ZFC-FC-rem cycle of KCN from that of a glassy mixed cyanide. Perhaps the only difference between the conventional ferroelastic multidomain state of KCN and the cyanide glass is a different domain size. This view may be particularly helpful for the glassy samples with concentrations close to the threshold concentration for ferroelastic ordering. In fact, to some extent different behavior of the bromide with $x = 0.23$ as compared to that with $x = 0.53$ supports the idea that the glass state is divided into subregimes.[51]

CONCLUSIONS

From the present results we can make a definite statement (for an admittedly limited T range): It is the $M_{\mathrm{FC}}(T)$ curve which represents the static limit. The cusps of $s_{44}(T)$ and $c_{44}(T)$ curves obtained in finite-frequency measurements are relaxational effects and have nothing to do with the glass order parameter q. The static compliance, as measured by $M_{\mathrm{FC}}(T)$ and as obtained by the $t = \infty$ limit of creep curves, follows what is called in spin-glass physics a Parisi-type T dependence. This T dependence is also obtained in the most advanced version of the random-field model.[41]

The present results raise doubts whether the central peak is an appropriate measure of the glass order parameter since it increases strongly at temperatures much higher than those which are considered characteristic for the onset of the glassy state in the static elasticity data.

The present results emphasize the analogy of the cyanide glasses and the spin glasses on a level much higher than this was possible before. The behavior of $s_{44}(T)$, the t law of the relaxations, and the ZFC-FC-rem curves are qualitatively identical to the corresponding quantities in spin glasses. Clearly relaxational effects are much stronger in the cyanides, since the CN reorientation couples much stronger to the crystalline environment than the reorientation of a spin. Guided by the spin glasses we think that the behavior of the nonlinear response strongly suggests that the orientational glass state is a phase in the thermodynamic sense.

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