PHYSICAL REVIEW B VOLUME 51, NUMBER 6 1 FEBRUARY 1995-II

Brief Reports

Brief Reports are accounts of completed research which, while meeting the usual **Physical Review** *standards of scientific quality, do not warrant regular articles. A Brief Report may be no longer than four printed pages and must be accompanied by an abstract. The same publication schedule as for regular articles is followed, and page proofs are sent to authors.*

Shear relaxation of $(NaCN)_{1-x}(KCN)_x$ quadrupolar glasses

Chr. Kaiser, J. Albers, A. Klöpperpieper, and Klaus Knorr
Technische Physik, Universität des Saarlandes, 66123 Saarbrücken, Germany

(Received 27 June 1994)

Shear-torque experiments have been performed on $(NaCN)_{1-x}(KCN)_x$ mixed crystals, $x=0.85$, 0.45. The shear strain relaxation time follows an Arrhenius law. The results support recent molecular-dynamics simulations.

$(KBr)_{1-x}(KCN)_x$ and other alkali halide–alkali cyanide mixed crystals form an orientational glass state[1] at low temperatures for CN concentrations x below a certain threshold value x_C. This behavior is in many respects similar to diluted magnetic systems with a spin-glass state, the quadrupole moment of the CN ion playing the role of the spin. In contrast to the chemically simpler quadrupolar glasses Ar:N_2 and ortho-para-H_2, the relevant bulk orientational susceptibility of the cyanides is accessible experimentally through the elastic shear constant c_{44} (or the shear compliance $s=1/c_{44}$). The quadrupolar glass state appears alike in $(NaCN)_{1-x}(KCN)_x$ at intermediate concentrations $x_1<x<x_2$, in spite of the fact that the CN sublattice is undiluted and the terminal compounds NaCN and KCN are isomorphic in the NaCl-type room-temperature phase and in the orthorhombic low-temperature phases.[2,1]

Recent molecular-dynamics (MD) simulations[3] on $(NaCN)_{1-x}(KCN)_x$ show that CN molecules with direct Na neighbors lock into $\langle 100\rangle$ orientations already at relatively high temperatures whereas the others which do not have such neighbors play an active role in the translation-rotation coupling, thereby supporting the softening of c_{44}. This species eventually freezes into $\langle 111\rangle$ directions. For $x=0.5$ virtually all CN molecules have Na neighbors, hence the latter species is absent and the softening of c_{44} is only little developed. NMR measurements strongly support this picture.[4]

The shear elasticity of $(NaCN)_{1-x}(KCN)_x$ has been investigated so far by neutron[5] and Brillouin scattering,[6,7] by shear-torque experiments,[8] and most systematically by the ultrasonic studies of Hu, Wells, and Garland.[9,10] Hu, Wells, and Garland have extracted the temperature dependence of the cooperative quadrupolar relaxation time τ from the measured ultrasonic attenuation and suggest a peculiar temperature dependence, namely $\ln\tau(T)=A-B\ln T$, which is distinctly different from the Arrhenius or the Vogel-Fulcher law usually observed in glassy systems, including $(KBr)_{1-x}(KCN)_x$, Ref. 8. Our study is motivated by this finding of Hu, Wells, and Garland and by the unsuspected MD result.

We have investigated two single crystals with concentrations of $x=0.85$ and 0.45. The x values are based on the cubic lattice constant as obtained from x-ray diffraction. The sample with $x=0.85$ is representative for those slightly below the upper threshold concentration x_2 which show a deep softening of c_{44}, whereas the second one falls into the middle of the concentration region in which the variation of s with T is much weaker[9] and where practically all CN molecules have Na first neighbors. We employed the shear-torque method which allows different modes of operation.[8] For the "soft" sample with $x=0.85$ we performed measurements in a constant external shear stress with a zero-field-cooling (ZFC)/field-cooling (FC)/thermal remanence history (Fig. 1), measurements with ac excitation with frequencies f in the Hz to 100 Hz range and measurements of the fundamental torsional resonance of the sample in the kHz region (Fig. 2). For the "hard" sample, $x=0.45$, the shear strain signal is weak and only the two latter and

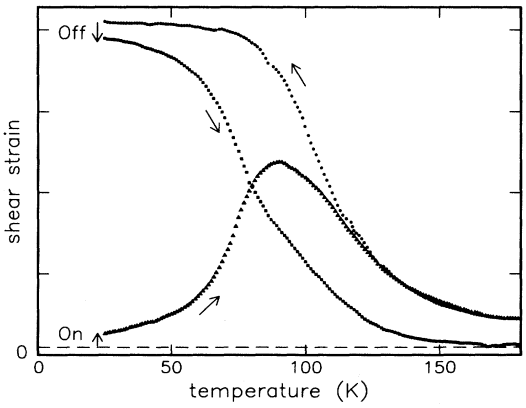

FIG. 1. The shear strain of $(NaCN)_{1-x}(KCN)_x$, $x=0.85$, on heating after zero-field cooling, on field cooling, on zero-field heating after field cooling (thermal remanence).

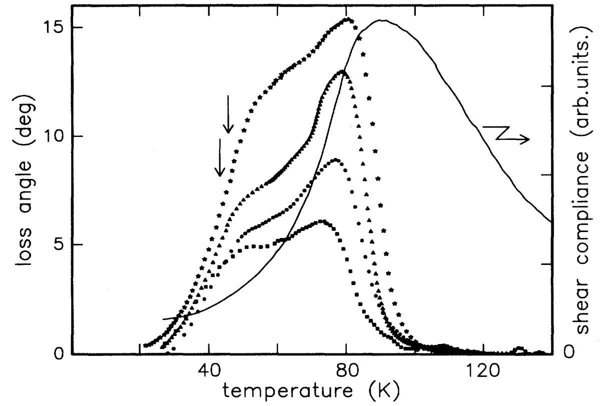

FIG. 2. The shear compliance of $(\mathrm{NaCN})_{1-x}(\mathrm{KCN})_x$, $x=0.85$, measured at $f=2$ Hz (solid line), and the elastic loss angle (■: 2 Hz, ●: 80 Hz, ▼: 130 Hz, ☆: from the torsional resonance with $fo=2$ kHz at 80 K). The arrows indicate the maximum dielectric loss as obtained in Ref. 5 on a sample with $x=0.73$ at 2 Hz and 2 kHz.

more sensitive modes were feasible. The data on this sample are of relatively poor quality, but are nevertheless sufficient to localize the maximum of the loss (Fig. 3). Figure 4 shows the temperature of the maximum loss $T_{\max}$ in an Arrhenius plot, that is $\ln f$ vs $1/T_{\max}$.

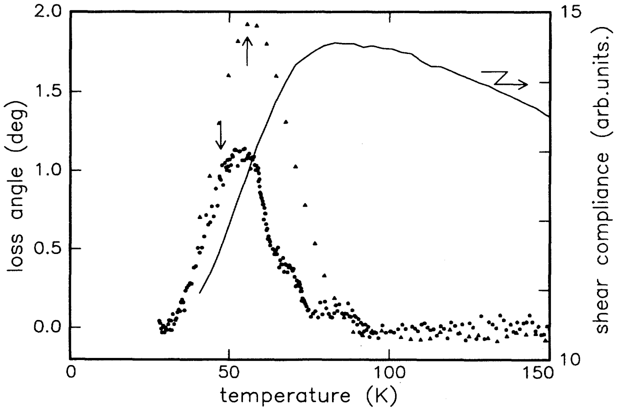

FIG. 3. The shear compliance s of $(\mathrm{NaCN})_{1-x}(\mathrm{KCN})_x$, $x=0.45$ (solid line) as obtained from the torsional resonance frequency fo (which is 8.6 kHz at 80 K), and the elastic loss angle (●: 65 Hz, ▼: from the torsional resonance). Note that the origin of the s scale is suppressed. The arrows indicate the maximum of the dielectric loss as obtained in Ref. 5 on a sample with $x=0.59$.

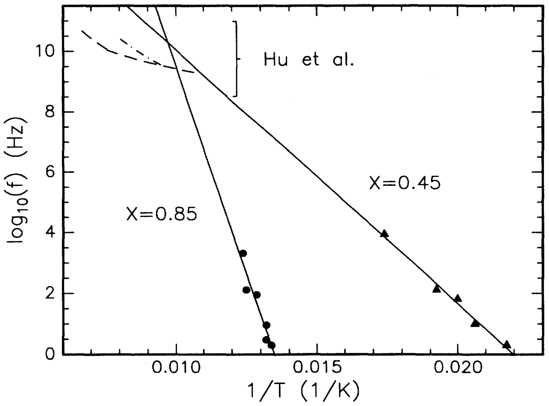

FIG. 4. Arrhenius plot of the temperature dependence of the primary elastic loss maxima, ●: $x=0.85$, ▼: $x=0.45$. Also shown is the $\tau^{-1}(T)$ law of Hu, Wells, and Garland (Ref. 10) (dashed line: $x=0.44$, dash-dotted line: $x=0.73$).

The best fit of an Arrhenius law to the data is included in the figure. The Arrhenius law extrapolates approximately to the $\tau(T)$ data given by Hu, Wells and Garland for samples with neighboring compositions x. (We refer to constant stress relaxation time for $x=0.44$ and $x=0.73$ as parametrized in Table I of Ref. 10.) On the other hand the extrapolation of the ($\ln\tau = A - BT$) law of Hu, Wells, and Garland to our range of measuring frequencies is not consistent with our results. Obviously the Arrhenius law describes the overall variation of τ with T better than the $\ln\tau = A - BT$ law. We suspect that the analysis of Hu, Wells, and Garland heavily depends on the assumptions made on the distribution $g(\tau)$. Since we refer to the temperatures of maximum loss, it is clear that our Arrhenius law considers the most probable relaxation time, i.e., the τ at which $g(\tau)$ is maximum. The large width of the loss peak and the relatively low value of the maximum loss angle indicate that $g(\tau)$ must be very broad. Furthermore the T dependence of the loss suggests that the distribution $g(\tau)$ is bimodal, as has been noticed before (Refs. 11, 8, and 1). This is reminiscent of the α and β peak observed in many real glasses.[12] In the cyanides the primary loss can be observed in shear elasticity measurements, only. The primary peak is connected with the freezing in of the CN quadrupole moments. Pertinent models have been developed.[13,14] The secondary relaxations can be probed by elasticity and dielectric measurements. The temperatures of maximum dielectric loss, measured at comparable frequencies, are indicated in Figs. 2 and 3 by arrows. (These temperatures are taken from the data of Ref. 5 on samples with $x=0.85$ and 0.59.) For $x=0.85$ the dielectric loss maxima coincide approximately with the low-T shoulder of the loss profile. It is therefore adequate to say that this secondary loss is due to relaxational modes which involve changes of both, electric polarization and shear strain. One thinks of 180° reorientations of the CN molecules as the major source for the secondary loss.[1] 180° flips contribute in first respect to dipolar response, but since the shape of the CN molecule has a slight head-tail asymmetry, some quadrupolar response is expected, too.

For $x=0.45$ there is little T dependence of the shear compliance s and only one structure in the T dependence of the elastic loss. The temperature of maximum elastic and of maximum dielectric loss occur at approximately the same temperature (Fig. 3). Thus the loss is of mixed quadrupolar and dipolar character. These observations suggest that the T_{2g} translation-rotation coupling is not very effective for this CN concentration. According to MD calculations this situation is intimately related to the dominance of the ⟨100⟩ species at this concentration.

Is there any support for two different CN species in the "soft" sample, $x = 0.85$? Clearly, the active $\langle 111 \rangle$ species gives rise to the dramatic growth of s and the well developed quadrupolar freezing process which is apparent from the primary loss peak and the concomitant decrease of s. It is however remarkable that the splitting of the FC and the ZFC branch as well as "thawing" of the remnant shear strain of Fig. 1 proceed in a way much more gradual than in $(\mathrm{KBr})_{1-x}(\mathrm{KCN})_x$ with x slightly below x_C, Ref. 8. We suggest that this is due to CN molecules which are orientationally locked already at relatively high temperatures and identify these molecules as the $\langle 100 \rangle$ species of the MD simulation.

In summary we have given evidence that the freezing process of $(\mathrm{NaCN})_{1-x}(\mathrm{KCN})_x$ is governed by Arrhenius-type thermally activated reorientation processes. This is in marked contrast to the T dependence of the relaxation time reported by Hu, Wells, and Garland. Furthermore the present results strongly support a view which has emerged from recent MD simulations, namely that two sorts of CN molecules have to be distinguished, those locked into $\langle 100 \rangle$ pockets by direct Na neighbors and others which take an active role in the T_{2g} rotation-translation coupling.

This work has been supported by the Deutsche Forschungsgemeinschaft through the Sonderforschungsbereich 262 and through Project No. Kn 234/8-1.

---

[1] U. T. Höchli, K. Knorr, and A. Loidl, Adv. Phys. **39**, 405 (1990).

[2] F. Lüty and J. Ortiz-Lopez, Phys. Rev. Lett. **50**, 1289 (1983); J. Ortiz-Lopez, Ph.D. thesis, University of Utah, 1983.

[3] A. Cheng, M. L. Klein, and L. J. Lewis, Phys. Rev. Lett. **66**, 624 (1991); Phys. Rev. B **44**, 13 (1991).

[4] N. L. Adolphi and M. S. Conradi, Phys. Rev. B **45**, 13 057 (1992).

[5] A. Loidl, T. Schräder, R. Böhmer, K. Knorr, J. K. Kjems, and R. Born, Phys. Rev. B **43**, 1238 (1986).

[6] J. F. Berret and R. Feile, Z. Phys. B **80**, 203 (1990).

[7] R. Jimenez, B. Jimenez, J. K. Krüger, F. Savetat, and F. Mauvy, in Proceedings of the 8th International Meeting on Ferroelectricity, Gaithersburg, MD, 1993 [Ferroelectrics (to be published)].

[8] J. Hessinger and K. Knorr, Phys. Rev. Lett. **65**, 2674 (1990); Phys. Rev. B **47**, 14 813 (1993).

[9] Z. Hu, C. W. Garland, and A. Wells, Phys. Rev. B **40**, 5 757 (1989).

[10] Z. Hu, A. Wells, and C. W. Garland, Phys. Rev. B **44**, 6731 (1991).

[11] U. Volkmann, R. Böhmer, A. Loidl, U. T. Höchli, and S. Haussühl, Phys. Rev. Lett. **56**, 1716 (1986).

[12] G. P. Johari, Philos. Mag. B **46**, 549 (1982).

[13] C. Bostoen and K. H. Michel, Phys. Rev. B **43**, 4415 (1991).

[14] D. Walton, Phys. Rev. Lett. **65**, 1599 (1990).