Dielectric Susceptibility of $(KBr)_{0.50}(KCN)_{0.50}$: Is It a Dipole Glass?

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Dielectric susceptibility measurements for the mixed crystal $(KBr)_{0.50}(KCN)_{0.50}$ are reported in the frequency range 20 Hz $< f <$ 80 kHz. An anomaly is found at temperatures far below that where neutron and Brillouin studies find mode softening. The results are interpreted in terms of a possible dipole-glass phase that has been recently proposed for this system.

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There are several examples of systems that freeze into a disordered phase. The spin-glass phase in magnetic systems is one example where the spins have random orientations with no long-range directional order. Another example of this phenomenon is when a liquid freezes into a glass with no positional long-range order. In neither case, despite considerable experimental and theoretical activity, is there unanimous agreement that a true phase transition exists between the frozen glass and the disordered liquid or paramagnet. If a phase transition does indeed take place there is even more controversy concerning its nature. In the present paper we will report on a more unusual type of disordered system, a crystal containing rod-shaped molecules at random sites that interact via electric dipole and strain fields. Does this system form a glass as has been suggested?

Cyanogen-substituted alkali halides are prototypes of systems with coupled translational and orientational degrees of freedom.[1] Several authors suggested, on theoretical grounds,[2,3] that this system should be analogous to a spin-glass. Extensive studies of the soft modes in these systems have been reported.[4] CN^- carries an electric dipole moment ($0.07\ e\cdot$Å). Dielectric studies have demonstrated that the dielectric constant is a sensitive probe of the reorientation of CN^- dipoles.[5] In the magnetic spin-glass the onset of this phase is signified by a cusp in the magnetic susceptibility. If an analogous cooperative process occurs in the electric dipole system, a similar effect is expected to manifest itself in the dielectric constant $\epsilon = \epsilon_1 + i\epsilon_2$.

Recently an inelastic neutron scattering study[6] of the random mixed crystal $(KBr)_{0.5}(KCN)_{0.5}$ reported an increase in the strength of the central elastic peak around 90 K associated with a minimum in the transverse acoustic phonon frequency near 100 K. This result is interpreted in terms of the formation of an orientationally disordered, static, dipole arrangement of CN molecules—the dipole-glass phase. A model of this phase has been formulated.[7]

In this Letter we report the observation of a dielectric anomaly in the mixed crystal $(KBr)_{0.50}$-$(KCN)_{0.50}$ at low frequencies (20 Hz–80 kHz). The measurements were performed using a General Radio 1615 capacitance bridge and a PAR 124A lock-in amplifier as the phase-sensitive null detector. The capacitance could be measured to an accuracy of one part in 10^5. The accuracy in the conductance measurement depends on f. At 10 kHz, it was 1 part in 10^3. Our samples were from the same batch as those used in Ref. 6.

The inset of Fig. 1 shows the temperature dependence at 75 kHz of ϵ_1 plotted relative to its value at 4.2 K. Above 100 K ϵ_1 rises monotonically with T in the same way as it does for pure KBr. As T is lowered ϵ_1 flattens and then starts to rise again, reaching a peak at 49.5 K. On further cooling it drops precipitously. Associated with the drop is a strong peak in ϵ_2 reminiscent of a Debye relaxation peak.

The presence of an anomaly at a substantially lower temperature and the absence of any feature

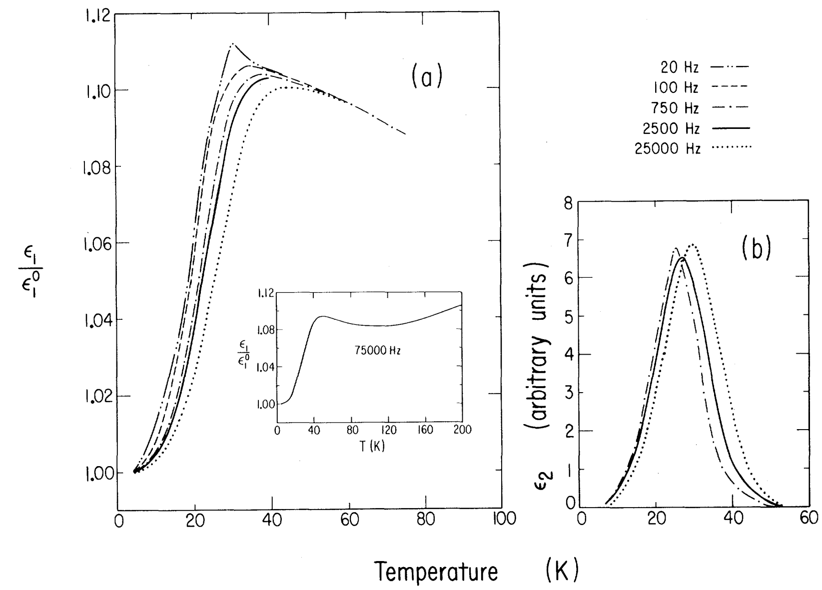

FIG. 1. (a) ϵ_1 vs temperature for several frequencies. Inset: 75-kHz data up to 200 K. (b) ϵ_2 vs temperature for several frequencies.

around 90 K, where the neutron measurements find a mode softening, is certainly very surprising. In order to understand the nature of this anomaly we repeated the measurements at various frequencies. The results are shown in Fig. 1. The dispersion is very pronounced at temperatures between 20 and 50 K and decreases to a small value at 4.2 K. Associated with the dispersion is the strong peak in ϵ_2. The peak in ϵ_1 becomes more pronounced as f is lowered. At 20 Hz it is indeed very cusplike. The analogy with spin-glasses is obvious. However, the position of the peak in ϵ_1, defined as the freezing temperature in analogy with spin-glasses, is strongly frequency dependent; it shifts to lower T with lower f. The peak in ϵ_2 also shifts in a similar fashion. In the magnetic spin-glass systems, however, two different classes are experimentally observed. In one the position of the cusp is insensitive[8] to f, while in the other it shifts[9,10] to lower T for lower f in an analogous way to what we have discovered. So if indeed a glass phase is forming, it is more akin to the second class of spin-glasses.

A second point is that the relaxation peaks are too broad to be attributable to a single relaxation time in a Debye model. In order to test the nature of the frequency dispersion we scanned through f at a fixed T. Figure 2 shows these results.

In the Debye model of dielectric relaxation $\epsilon(\omega)$ is given by

$$\epsilon(\omega) = \epsilon_\infty + (\epsilon_0 - \epsilon_\infty)/(1 - i\omega\tau),$$

where ϵ_0 and ϵ_∞ are the low- and high-frequency limits of $\epsilon_1(\omega)$ and where τ represents the single relaxation time. In Fig. 2 it is clear that no single-relaxation-time approximation can fit the data.

One particular point deserves attention. With

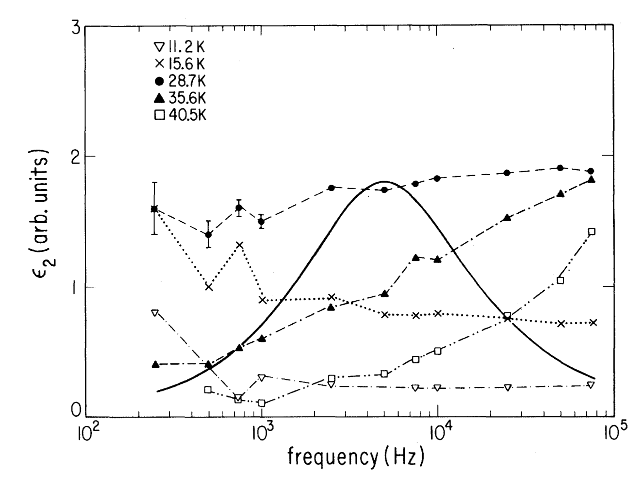

FIG. 2. ϵ_2 vs frequency at several temperatures. The solid curve represents the prediction of the Debye relaxation model with a single relaxation time, $\tau = 3.18 \times 10^{-3}$ sec. The data cannot be fitted by a single-relaxation-time model.

temperature the frequency dependence does change. At 11 K ϵ_2 has a significantly larger value at lower frequencies while at 40 K the higher-frequency values are substantially larger. The progression indicates that the entire distribution itself shifts to lower temperature. These results indicate that the anomaly is extremely sensitive to the time scale of the measurement. In order to test this dependence we plot in Fig. 3 the position of the peaks in ϵ_1 and ϵ_2 vs f in an Arrhenius form $[f=f_0\exp(-E/kT_{\text{peak}})]$. The straight-line fits are quite good. In contrast with the so-called nonideal spin-glass where Arrhenius fits sometimes yield unphysical results,[10] in this case the fit parameters are extremely reasonable. We believe that the difference between the fits for ϵ_1 and ϵ_2 is due primarily to the background contribution for ϵ_1 which does not exist for ϵ_2, thereby making the latter a more direct measure of the orientational contribution to $\tilde{\epsilon}$.

The difference between this case and one where a single-relaxation-time approximation holds should be pointed out. As shown in Fig. 2, a Debye-fit where the peak in $\epsilon_2(\omega)$ occurs at $\omega\tau=1$ is inapplicable. However, in this system $\epsilon_2(\omega)$ still has a well-defined, albeit broad, peak at every temperature. We have plotted the temperature dependence of this frequency where $\epsilon_2(\omega)$ is a maximum. This process has been used widely for structural glasses where such slowing down of the entire distribution is seen.[11]

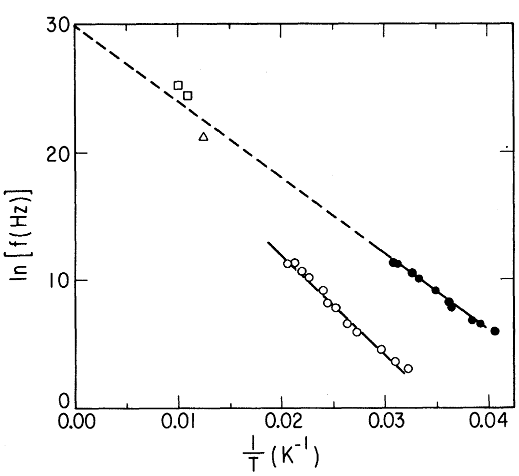

FIG. 3. The value of $\ln f$ in hertz vs the inverse temperature for the peaks in ϵ_1 (open circles) and ϵ_2 (closed circles). A good fit is obtained with the Arrhenius form: $f=9.30\times10^{11}\exp(-781/T_{\text{Hz}})$ for ϵ_1 and $f=8.52\times10^{12}\exp(-593/T_{\text{Hz}})$ for ϵ_2. The triangle represents the Brillouin data of Ref. 9 for the soft mode and the squares represent the neutron data of Ref. 1 for the soft mode and the onset of the elastic peak. The dashed line is the extrapolation of the best fit for the ϵ_2 data to higher temperature and frequency.

Experiments performed with a static electric field up to 2.2 kV/cm produced no appreciable change in the results. This confirms the speculation that the interaction between the CN^- through lattice strains is stronger than the dipole-dipole interaction. In this respect the straightforward spin-glass analogy does not hold. External stress is expected to have a significantly stronger effect on the dielectric anomaly than does an external electric field.[12]

Taken together these data suggest a new kind of electric-dipole–glass phase in the mixed crystal $(KBr)_{0.5}(KCN)_{0.5}$. The orientation of the CN^- dipoles slows down with decreasing temperature. Depending upon the time scale of the measurements, the dipoles may or may not appear frozen. This qualitatively explains the frequency dependence of the position of the anomaly. The precipitous drop in ϵ_1 then reflects the inability of the dipoles, or clusters of dipoles, to respond to the probing frequency because of their slow characteristic times. This reduces the number of alignable dipoles and results in a decrease in ϵ_1. The distribution of relaxation times, on the other hand, is characteristic of structural glasses and spin-glasses, i.e., frozen disordered states.[13] A distribution of cluster sizes and barrier heights could quite conceivably be responsible for it.

This system then makes two connections with other disordered systems. The presence of a peak (cusp) in ϵ_1 reminds one of the spin-glass where a wide distribution of relaxation times is also seen.[14] On the other hand, the so-called freezing into a glassy state appears not to be a static phenomenon but a relaxational one as in structural glasses. The mean-field theories[2] are not suited to explain this phenomenon. Appropriate theoretical treatments are needed to explain the results.

The question then remains: How is the observed dielectric anomaly related to the neutron scattering results? Recently Michel and Rowe[7] showed that the generalized susceptibility for the orientational freezing is related to the shear elastic constant that is in turn related to the quadrupolar susceptibility. Hence the minimum in the phonon frequency implies a peak in the generalized susceptibility. While for neutron scattering ($f\sim1$ THz) the peak occurs at 100 K, for Brillouin scattering[15] ($f\sim1$ GHz) it occurs at 80 K. In Fig. 3 we included the temperature of the soft modes at the relevant frequency. Moreover, the central peak in the neutron data cannot distinguish elastic processes from inelastic ones of frequencies smaller than the resolution. Processes slower than the resolution (in Ref. 6 it is 0.16 meV) will appear to be elastic. We assume then that the characteristic frequencies are of the order of the resolution at 90 K where the peak starts to grow rapidly. We include that point too in Fig. 3. We note that an extrapolation of an Arrhenius fit to the peak in ϵ_2 agrees very well with the neutron and Brillouin data. Since it is the peak in the susceptibility that is related to the existence of the soft mode, it is appropriate to extrapolate our data for ϵ to compare with the frequencies and temperature where the neutron data indicate a soft mode. The agreement, if not fortuitous, is very suggestive. It is likely then that this experiment probes the same process as the neutron study but at widely different time scales; hence the apparent freezing occurs at widely different temperatures.

This study then raises several questions. First, is there a sharp glass transition? The answer for this system is in the negative. The freezing is not a static phenomenon, but a relaxational one. Finally, the question arises, how general is the result? Obviously a great deal of work needs to be done before an unambiguous answer can be given. But it is at least possible that a qualitatively similar behavior is present in other disordered systems except that the characteristic time scales are not easily accessible to experimental studies.

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[1]K. H. Michel, J. Naudts, and B. de Raedt, Phys. Rev. B 18, 648 (1978); J. M. Rowe, J. J. Rush, N. J. Chesser, K. H. Michel, and J. Naudts, Phys. Rev. Lett. 40, 455 (1978), and references therein.

[2]B. Fischer and M. W. Klein, Phys. Rev. Lett. 37, 756 (1976), and 43, 289 (1979).

[3]M. A. Klenin, Phys. Rev. Lett. 42, 1549 (1979).

[4]J. W. Kwiecien, R. C. Leung, and C. W. Garland, Phys. Rev. B 23, 4419 (1981), and references therein.

[5]M. Julian and F. Luty, Ferroelectrics 16, 201 (1977).

[6]J. M. Rowe, J. J. Rush, D. G. Hinks, and S. Susman, Phys. Rev. Lett. 43, 1158 (1979).

[7]K. H. Michel and J. M. Rowe, Phys. Rev. B 22, 1414 (1980).

[8]E. D. Dahlberg, M. Hardiman, R. Orbach, and J. Soutetie, Phys. Rev. Lett. 42, 401 (1978).

[9]F. S. Huang, L. H. Bieman, A. M. de Graff, and H. R. Rechenberg, J. Phys. C 11, L271 (1978).

[10]C. A. M. Mulder, A. J. van Duyneveldt, H. W. M. van der Linden, B. H. Verbeek, J. C. M. van Dongen, G. J. Nieuwenhuys, and J. A. Mydosh, Phys. Lett. 83A, 74 (1981).

[11]We have used a further check to ascertain the reasonableness of the fit. Using the fitting parameters to ϵ_2 from Fig. 3 we plotted ϵ_2 at all temperatures and frequencies. The resultant plot ascertained the approximate constancy of the spectral shape of ϵ_2 at all temperatures. The distribution is extremely wide, with the full width at half maximum extending over five and a half decades in frequency. See, for example, F. S. Howell, R. Bose, P. B. Macedo, and C. T. Moynihan, J. Phys. Chem. 78, 639 (1974), and references therein.

[12]D. Durand, L. C. S. doCarmo, A. Anderson, and F. Luty, Phys. Rev. B 22, 4005 (1980).

[13]See, for example, J. Wong and C. A. Angell, *Glass-Structure by Spectroscopy* (Marcel Dekker, New York, 1976), Chap. 11.

[14]A. P. Murani, J. Phys. (Paris), Colloq. 39, C6-1517 (1978), and references therein.

[15]S. K. Satija and C. H. Wang, Solid State Commun. 28, 1517 (1978).