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LETTER TO THE EDITOR

Dielectric echoes in an orientational glass: $\text{KBr}_{1-x}(\text{CN})_x$

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Abstract. Dielectric echoes have been observed in the mixed crystal $\text{KBr}_{1-x}(\text{CN})_x$ for $x = 0.034, 3, 20, 50,$ and 70% at 0.8 GHz and 10 mK. At 50% , the dephasing rates are comparable to structural glasses; however, the concentration dependence of these rates seems anomalous when compared to other properties. We explain this result in terms of the tunnelling model for glasses with concentration-dependent distributions that favour symmetric potentials as $x \rightarrow 0$.

The mixed crystal $\text{KBr}_{1-x}(\text{CN})_x$ forms an ‘orientational glass’ for concentrations $0.03 < x < 0.56$ in which, at low temperature, the CN molecules freeze into random orientations (region VI in figure 1) [1]. Below 1 K, localised low-energy excitations believed to arise from CN tunnelling are responsible for physical properties remarkably similar to structural glasses [2]. For $0.56 < x < 0.80$ and below 1 K, although the dipole axes are aligned in a ferroelastic phase (V in figure 1), these glassy excitations still exist due to the electric dipolar and substitutional disorder [2, 3].

Glasses, as is well known, possess nearly universal low-temperature properties that have been explained by broad distributions of tunnelling entities, although no first-principles calculation of the distributions yet exists. In contrast to structural glasses, the concentration of tunnelling species in a substitutional orientational glass such as $\text{KBr}_{1-x}(\text{CN})_x$ can be varied over a broad range. At very low x no collective behaviour occurs; the CNs act as weakly interacting impurities. As x increases from 0.03 to 0.8 , interactions between the randomly situated CNs increase dramatically, broadening the distributions towards those of a glass, and rapidly decreasing the number of states able to tunnel at low temperature.

Although some progress has been made in understanding the distribution of barrier heights required to describe activated processes [4], the description of the distribution functions governing the tunnelling process has been less successful. In the present work we describe electric dipolar echo experiments [5] below 0.1 K and measurements of the temperature-dependent microwave dielectric response in order to address this question. We find the surprising result that echo dephasing rates T_2^{-1} are not proportional to the density of tunnelling states, as one would expect. We explain this by proposing a qualitative model of the tunnelling distribution functions in which the CN potentials become more symmetric at low x , resulting in a weaker CN–CN coupling. We suggest, therefore, that the salient aspect of ‘glassiness’ is the existence of a broad distribution of *asymmetric* tunnelling potentials.

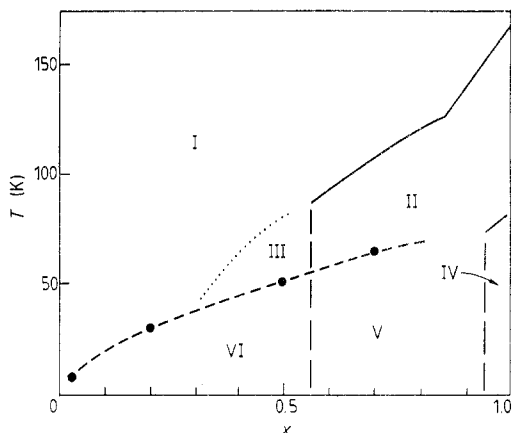


Figure 1. Approximate phase diagram for $\text{KBr}_{1-x}(\text{CN})_x$. At high T the CNs are free to reorient (I). As T decreases, the elastic dipoles freeze into a ferroelastic phase (axes aligned, II) or an orientationally disordered phase (III), in both of which the electric dipoles can still reorient by thermally activated 180° flips. At still lower T the dipoles freeze into an antiferroelectric phase (IV), an elastically ordered but electric dipolar disordered phase (V), or an orientational and electric dipolar glass (VI). Tunnelling occurs in phases VI and V. The data points and the broken curve through them are dipolar freezing temperatures at 0.79 GHz determined from our dielectric measurements.

$\text{KBr}_{1-x}(\text{CN})_x$ samples [6] with nominal CN concentrations of 0.034, 3, 20, 50, and 70% were cut into roughly circular discs 2 mm thick and 1 cm in diameter. We placed these discs in the uniform electric field region of re-entrant cavities resonant at 0.79 GHz with the electric field along a $\langle 100 \rangle$ direction. The cavities were in thermal contact with the mixing chamber of a ^3He - ^4He dilution refrigerator. Dielectric constant measurements involved monitoring the cavity resonance frequency as a function of temperature. When applying microwave pulses during the echo experiments, care was taken to keep the duty cycle low enough that bulk heating of the samples did not occur. Input pulses were about $0.4 \mu\text{s}$ long, and were of an intensity about 1–4 dB below that required for maximum echo generation.

Results of the dielectric measurements are shown in figure 2. The increase of dielectric constant with decreasing temperature for $T \leq 1$ K is typical of glasses and is given by [7]:

$$\Delta\epsilon/\epsilon \propto p^2 P \log T$$

where p is the induced dipole moment and P is the density of states of the quickly relaxing systems. This logarithmic dependence results from the broad energy distribution of the states. In the 0.034% sample the increase in ϵ extends to lower temperature than would be expected for isolated CNs in KBr, so apparently there is already enough disorder at $x = 0.034\%$ to broaden the energy spectrum in this energy range. The increase in dielectric constant with temperature for $T \geq 1$ K seen in all but the 0.034% sample is due to relaxation processes [8].

Two-level, low-energy excitations in solids are equivalent to spin- $\frac{1}{2}$ systems, and can be probed with coherent resonant fields [5]. During a two-pulse echo excitation sequence, any process which changes the frequency (energy splitting) of a state slightly will contribute to dephasing of that state. Only the static dephasing due to inhomogeneous broadening is reversible, so the size of the echo depends on the dynamical dephasing which changes the frequency during the echo process. In glasses it is assumed that these dephasing processes are the result of spectral diffusion [9], in which thermally active states, ('B states'), make transitions, and their coupling to those states observed directly in the echo experiment, ('A states'), results in the dephasing of these states. In glasses, the echo decay for a two-pulse sequence is given by [10]:

$$E(2\tau) = E_0 \exp(-C\tau^{3/n}).$$

Here interactions between states i and j are assumed to vary as r_{ij}^{-n} . The echo amplitude

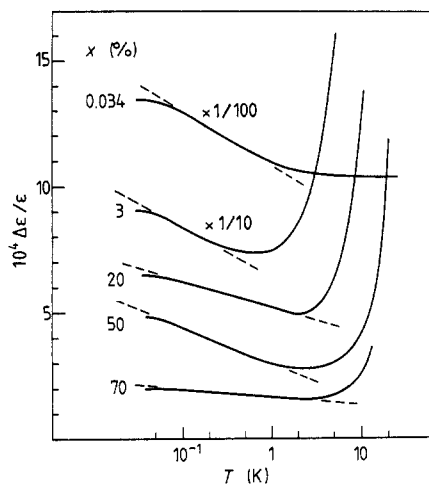


Figure 2. The variation of the real part of the 0.79 GHz dielectric constant versus temperature for the five CN concentrations x . The data are offset from each other vertically for clarity. Note that the $x = 3\%$ data are reduced by a factor of 10 and the $x = 0.034\%$ data by a factor of 100. Broken lines represent the logarithmic dependence for $0.1 \text{ K} \leq T \leq 1 \text{ K}$.

E_0 is proportional to the density of A states, P . The quantity C is proportional to the density of B states, and additionally reflects the average coupling between A and B states. The two-pulse echo decays in our experiment were approximately of this form, but varied slightly among samples. We define a dephasing time T_2 as the time for an echo to decay to $1/e$ of its initial value. For $n = 3$ one expects exponential echo decay with $C = T_2^{-1}$.

Spin-lattice relaxation time (T_1) measurements used a three-pulse technique described in [5] in which an initial pulse partially inverts the population of states, and recovery from inversion is monitored by generating echoes with two pulses at a later time. We assume that one-phonon processes can account for T_1 below 1 K.

A summary of several results is given in figure 3. The three sets of data points which follow the top curve represent the normalised density of states, P , at energy $E \sim 0.1 \text{ K}$ as derived from three independent experiments: time-dependent specific heat [2] (triangles), dielectric echo amplitudes (squares), and the $\log T$ part of the dielectric constant (full circles). At low x the density of states should increase linearly with cyanide concentration. In the range $x = 0.001$ to 0.70 , however, increased interactions between cyanides freeze many of the CN molecules, *decreasing* the density of states with increasing x .

The lower curve in figure 3 shows the dephasing rates T_2^{-1} from two-pulse echoes normalised to the $x = 70\%$ value of $16 \mu\text{s}^{-1}$ at 10 mK . If the coupling between states is independent of concentration, this quantity should follow the density of states, since T_2^{-1} is proportional to the number of B states. The dramatic deviation from this behaviour indicates large changes in the coupling between states as x changes. Since this coupling is via elastic or electric fields, a possible explanation is that the bare coupling of states to these fields changes with cyanide concentration. This is not the case. Our spin-lattice relaxation time (T_1) measurements give couplings to phonons that are essentially independent of x (values range from $\gamma = 0.1 \text{ eV}$ to 0.2 eV), based on materials parameters from [2] and a one-phonon decay [4]. In addition, the two-pulse echo amplitude as a function of excitation amplitude which measures the dipole moment [4] indicates no significant changes in the coupling to electric field, within a factor of 1.5, our measurement uncertainty. We suggest, therefore, that the large changes in the CN-CN coupling are due to changes in the distributions of these low-energy states.

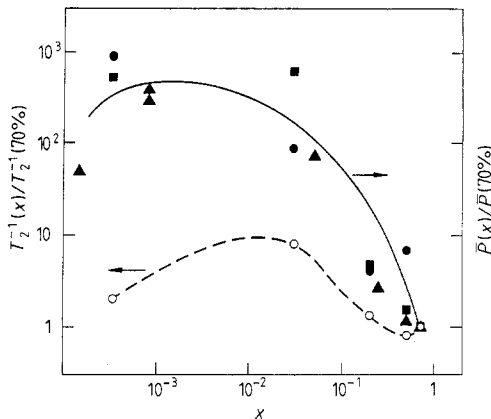


Figure 3. The top three sets of data are density of states at $E \approx 0.1$ K versus CN concentration x . Triangles: short-time specific heat at 0.1 K and 1 ms [9]; full circles: logarithmic slope of 0.79 GHz dielectric constant at $0.1 \text{ K} \leq T \leq 1 \text{ K}$; squares: 0.79 GHz two-pulse echo amplitudes at 10 mK. Lower data points (open circles) are T_2^{-1} from two-pulse echoes at 10 mK. All sets of data are normalised to their value at $x = 70\%$. The full and broken curves are guides to the eye.

We describe these distributions in terms of the tunnelling model for glasses [8]. In this model, an atom or group of atoms (possibly a single CN in $\text{KBr}_{1-x}(\text{CN})_x$) resides in a double-well potential. The asymmetry energy between the two wells is represented by Δ and the tunnelling (overlap) energy by Δ_0 , giving an energy separation between eigenstates $E = (\Delta_0^2 + \Delta^2)^{1/2}$. In glasses the Δ distribution is constant and the Δ_0 distribution varies as $1/\Delta_0$. States of a given energy E have values of these parameters ranging from 0 to E . Those symmetric states with $E \approx \Delta_0$ have strong resonant coupling to phonons and electric fields, so they can be seen in dielectric, acoustic, echo, and short-time specific-heat experiments below 1 K. The density of this group of states at $E \sim 0.1$ K is therefore represented by the upper curve in figure 3.

The key point to understanding the seemingly anomalous behaviour of the dephasing rate T_2^{-1} as a function of concentration is that dephasing is determined by those relatively asymmetric states with large Δ . The dephasing rate is determined by those thermally active states (B states) which couple reasonably strongly to the A states. This coupling between states, in the tunnelling model [9], is given by

$$J_{ij} \propto (1/r_{ij}^n)(\gamma_i \Delta_i / E_i)(\gamma_j \Delta_j / E_j)$$

where γ is a phonon coupling parameter. It can be seen that those states with large Δ will couple strongly to other states so they will be the most effective at dephasing the A states. These B states must also have a non-zero Δ_0 so that they couple to phonons and can be thermally active on the timescale of the experiment. The states most effective at dephasing, then, come from the same general distributions as those observed directly in the echo experiment, but are fairly asymmetric; that is, they have larger values of Δ and smaller values of Δ_0 .

We can now explain the dephasing rate variation by postulating that as the concentration is decreased, the distribution of states at a given energy E is shifted towards larger values of Δ_0 . This has two effects on the dephasing rates. First, the typical A state will have a smaller value of Δ , and so will be affected less by the B states. In addition, the density of B states (states with reasonably large Δ) will decrease in relation to the density of A states. Both of these effects will result in less dephasing at low concentrations. The conclusion, then, is that at low cyanide concentrations the tunnelling states become more symmetric. This conclusion is physically reasonable. At low concentrations, the potential well seen by the cyanide is determined mostly by the KBr crystal field, so the asymmetries (Δ) will tend to be small and the distribution in Δ_0 will

be narrow and peaked around 1.5 K. This effect will tend to make states at a given energy E more symmetric than in the glassy region of $x \approx 50\%$.

Additional support for these ideas is found in the dielectric constant data at 0.034% (figure 2). Note the absence of the high-temperature relaxational contribution with positive slope seen at all other concentrations. The lack of this relaxational feature normally seen in glasses indicates a proportionally small number of large- Δ , asymmetric states.

A previous study of $\text{KBr}_{1-x}(\text{CN})_x$ considered modification of the distribution functions [11]. Variation of the velocity of sound and ultrasonic absorption with temperature were measured for $x = 25\%$ and 50% . Fitting ultrasonic data to a modified tunnelling model, it was concluded that for lower x , the distribution is weighted towards larger values of Δ , in direct contrast to our conclusions. We suggest that their fits, which included data up to about 8 K, may have been influenced by the thermally activated processes expected at the higher end of their range, rather than by tunnelling.

The density of quickly relaxing states, \bar{P} , derived from our dielectric measurements agrees reasonably well (within a factor of four) with time-dependent specific heat measurements [9] on samples of $x = 25, 50$ and 70% , taking [12] $p = 0.5$ D. The specific heat experiments also see an anomalously large number of very slowly relaxing states. An explanation within the framework of the tunnelling model for the presence of these slow states would require a large number of large- Δ states. Although this is not predicted by our model, it is not inconsistent with our measurements, since the slowly relaxing states seen in specific heats have lifetimes much too long to contribute to dephasing within the timescale of our experiments ($100 \mu\text{s}$). A possible alternative explanation is that these slow states are small clusters of cyanide molecules that must undergo some collective reorientation in order to relax.

An additional conclusion that our study provides concerns the thermal conductivity mechanism at moderate (1–10%) cyanide concentration. Usually it is assumed that heat is transported solely by phonons, and that the localised excitations play the role of scattering centres. It has been suggested [13], however, that at moderate cyanide concentrations some of the thermal transport may be from energy transfer between these excitations via mutual flips between pairs of states having nearly the same energy. These mutual flips would increase the dephasing rates at $x \approx 1$ –10% by several orders of magnitude over those of glasses (or $\text{KBr}_{0.5}(\text{CN})_{0.5}$). Figure 3 clearly shows that this is not the case. We therefore conclude that our echo experiments are inconsistent with this additional thermal conductivity mechanism.

In conclusion, echo measurements over a wide range of concentration in an orientational glass have provided unique information on the tunnelling centre interactions. Constraints placed on the tunnelling distribution functions by the data have led to a qualitative model that explains the evolution of low-temperature glassy properties. The distribution of double-well asymmetry energies is shown to be relevant to the realisation of typical 'glassy' behaviour.

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