Constrained Relaxation and the Glass Transition in KBr_{1-x}-KCN_x

D. Walton
Physics Department, McMaster University, Hamilton, Ontario, Canada L8S 4M1

(Received 6 November 1989; revised manuscript received 9 April 1990)

Using a model based on the theory for hierarchically constrained relaxation of Palmer *et al.*, it has been possible to account for the quadrupolar freezing of the CN ion in KBr-KCN alloys observed in both Brillouin scattering and low-frequency shear resonance. In particular, the small change in the glass transition temperature with probe frequency can be accounted for.

PACS numbers: 64.70.Pf, 61.42.+h

The relaxation of anisotropic defects in a crystalline matrix can be of two limiting distinct kinds depending on whether the energy barriers are independent of the defect configuration or whether these barriers are determined by the configuration. In the former case, if the sample is cooled from an elevated temperature, the relaxation rate simply goes smoothly to zero as the temperature goes to zero. In the latter, the relaxation rate slows rapidly when the thermal energy kT is on the order of the interaction energy, and may go to zero at some finite temperature. It can lead to an orientational glass phase of the defects.

The alloys of KCN with other alkali halides provide a particularly interesting system because the CN ion actually plays both roles: The CN ion has both an electric dipole moment (referred to here as the "dipole"), and an elastic moment, often referred to as an elastic "quadrupole" moment (which we will call the "quadrupole"). An electric quadrupole moment also exists, but is usually neglected. It is generally agreed that the elastic quadrupolar interactions are responsible for a glassy phase at concentrations x between about 0.2 and 0.6.

At temperatures below the glass transition temperature it is believed[1-3] that the dipoles are free to "flip," head to tail, leading to strong dielectric relaxation phenomena.[1] The dielectric relaxation peak is very broad in frequency. Its temperature and frequency dependence are fitted very well by a Gaussian distribution of energy barriers[1-3] which neglects any interaction between the dipoles. The barriers responsible for the dielectric relaxation are provided by the elastic interaction between the CN ions, i.e., the quadrupoles. Although the behavior of the dipoles can be explained, at present no model exists for the relaxation and freezing of the quadrupoles.

The relaxation of the quadrupoles is evident via their broadening of acoustic phonons,[4,5] and in torsion-pendulum results.[6] The torsion-pendulum results, reproduced in Fig. 1, show two peaks in the temperature dependence of the internal friction. The lower-temperature secondary peak has been associated with dipole relaxation,[6] while the higher-temperature primary peak is due to the quadrupoles. Ultrasonic results do not reveal the attenuation because the echoes are lost for the concentrations of interest here. However, Brillouin data clearly show a strong broadening which is large enough to be easily measured. The width of the phonon increases to a sharp maximum[4,5] at a temperature T_g which is slightly lower than that of the minimum in the velocity of sound; see Figs. 2 and 3.

What is particularly interesting is how little the temperature of the quadrupole peak T_g changes for a change in frequency of 6 orders of magnitude: For $x=0.5$, T_g is 78 K from Brillouin data,[4,5] whereas from the torsion-pendulum results T_g is 68 K. The dipole peak, on the other hand, moves from about 70 to 38 K.

This behavior is characteristic of a glass transition: As the temperature is lowered interactions become increasingly important, and, in order to relax, a quadrupole must overcome the barrier imposed by its neighbors. The temperature at which this occurs is determined more by the strength of the quadrupole interaction than the frequency of measurement.

The purpose of this Letter is to show that a model based on the theory of hierarchically constrained relaxation of Palmer *et al.*[7] cannot only account for the quadrupole relaxation, and can fit the data in Figs. 1-3, but

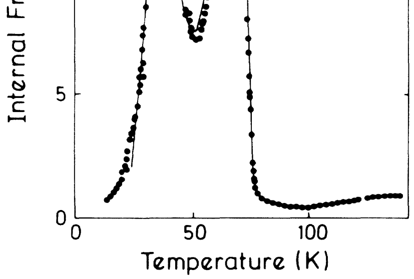

FIG. 1. The temperature dependence of the internal friction for a concentration of 0.53 determined by Knorr, Volkmann, and Loidl (Ref. 6). The solid line was calculated as described in the text.

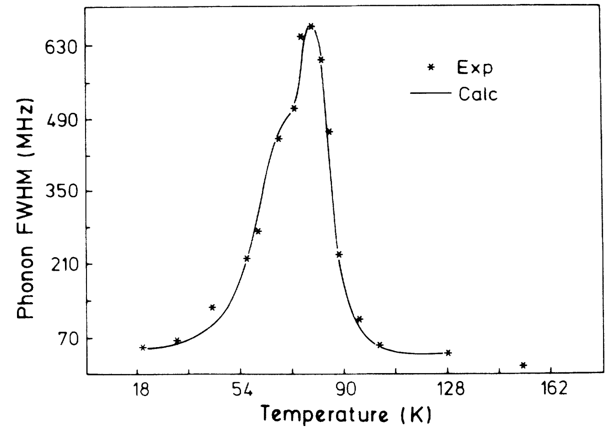

FIG. 2. The temperature dependence of the phonon width determined by Hu, Vanderwal, and Walton (Ref. 5) for a concentration of 0.5. The solid line was calculated as described in the text, with the same parameters as used for the solid line shown in Fig. 1.

also results in a distribution of barrier heights in agreement with that used to fit the dielectric data.

The quadrupolar results also show a peak due to the dipolar relaxation. While it is a little surprising that the dipole transition should couple so strongly to the elastic properties the secondary peak is not of interest here, and we will simply fit it by the dielectric function appropriate to the frequency of measurement.

Elastic properties are conveniently described in terms of a complex elastic compliance J such that the velocity v of a sound wave of frequency ω is given by the real part, and its attenuation α by the imaginary part:[8]

$$1/v - i\alpha/\omega = [\rho(\mathrm{Re}J + i\,\mathrm{Im}J)]^{1/2}. \qquad (1)$$

In general,[8] the compliance J measures the strain produced when a stress is applied. There is an instantaneous response followed by a slower change as the system relaxes. If the system has a single relaxation time τ,

$$J(t) = J_0 + \delta J[1 - e^{-t/\tau}]. \qquad (2)$$

In this expression J_0 accounts for the instantaneous strain, and the second term accounts for the subsequent relaxation.

Often, there is a spectrum of relaxation times. In that case Eq. (2) becomes

$$J(t) = J_0 + \sum_n \delta J_n e^{-t/\tau_n}. \qquad (3)$$

In the frequency domain, the Fourier transform yields

$$J(\omega) = J_0 + \sum_n \delta J_n/(1 - i\omega\tau_n). \qquad (4)$$

If there is only one relaxation time, the fact that the velocity of sound is proportional to the real part, and the attenuation to the imaginary part, can be used to estimate δJ and obtain the relaxation time.[8,9] If this is done with the data shown in Figs. 1 and 2, it is found that[5] the relaxation of the CN exhibits Arrhenius behavior at high temperatures, suggesting that a single-relaxation-time approximation is valid. But at lower temperatures, just above T_g, it is found that the temperature dependence of the relaxation time leads to a high value for the activation energy and an unphysical magnitude for the preexponential, suggesting that more than one CN is involved.[5] These results are shown in Fig. 4. In order to describe the relaxation at these temperatures it is necessary to employ a theory which will be able to take the interactions into account.

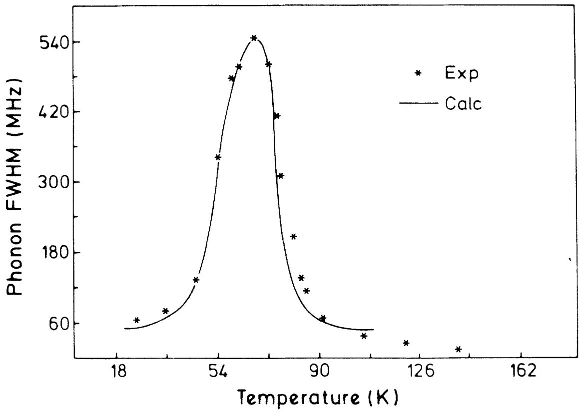

FIG. 3. The temperature dependence of the phonon width determined by Hu, Vanderwal, and Walton (Ref. 5) for a concentration of 0.35. The solid line was calculated as described in the text.

Such a theory was provided by Palmer *et al.*[7] It postulates an assembly of N Ising spins distributed over a number of levels such that each spin in level $n+1$ is only free to change its state if μ_n spins in level n attain one particular state of their 2^n possible ones. The relaxation times in the theory of Palmer *et al.* are related by

$$\tau_{n+1} = 2^{\mu_n}\tau_n, \qquad (5)$$

leading to

$$\tau_n = \tau_0 2^{\sum_{k=0}^{n-1}\mu_k}. \qquad (6)$$

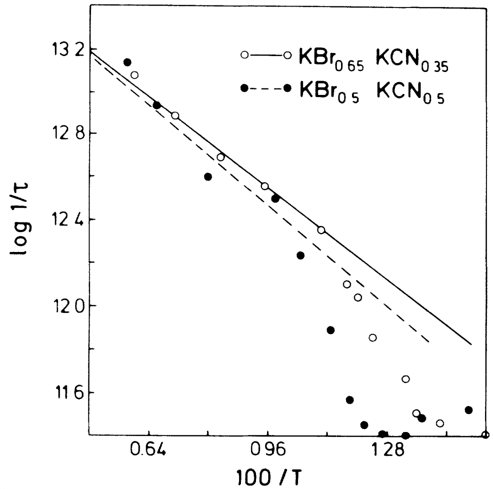

FIG. 4. The reciprocal relaxation time deduced from the data in Figs. 2 and 3 assuming a single relaxation process. The solid circles represent experimental results for a concentration of 0.50, and the open circles 0.35. The dashed line represents the relaxation time of ions with no neighbors as described in the text for 0.50, and the solid line for 0.35.

The Palmer-Stein-Abrahams-Anderson (PSAA) model is abstract, and does not specify any model for the levels of the system, except the requirement that spins in one level constrain spins in the level immediately above it. The CN ions constrain neighboring CNs via their elastic strain fields; so, it is logical to associate the levels with the number of near neighbors. Crudely, a CN with, say, six nearest neighbors cannot relax until μ_5 CNs with five nearest neighbors have relaxed. In turn this implies that those spins with fewest neighbors relax first, and those with the most relax last. This model neglects any "jumps" in the hierarchy, i.e., a situation in the above example where some of the spins constraining the level-6 CN have less than five nearest neighbors.

The PSAA theory implies that some short-range correlation exists between the spins, i.e., that the temperature is below some ordering temperature. At high temperatures, the constraints must disappear, and a single relaxation time recovered.

The CN can take up various possible orientations in the unit cell, and the Ising model is not appropriate. For instance, the molecule could be oriented along one of the six possible $\langle 110\rangle$ directions, and, because the molecule is not perfectly symmetrical, there may be an elastic interaction when the CN flips head to tail, leading to twelve possible configurations. Thus μ_n spins have p^{μ_n} possible states where p can be 12, corresponding to orientation along a $\langle 110\rangle$ axis, 8 if the CN lies along a $\langle 111\rangle$ axis, or 6 for a $\langle 100\rangle$ orientation. Of course, other possibilities exist, but for simplicity's sake these will be the only ones considered.

The first spins to relax are those in level 0, which have effectively no nearest neighbors, but will have next-nearest neighbors, next-next neighbors, etc. Their relaxation time is τ_0. Next, those in level 1 relax, and their relaxation time will be $\tau_1 = p^{\mu_0}\tau_0$, where μ_0 is the average number of spins in level 0 which must relax for one spin in level 1 to relax. It is, of course, inconsistent to postulate a spin in level 1 constrained by interacting with a spin in level 0 which has no nearest neighbors. However, the interaction is long range, and the further neighbors are also important. To account for this approximately the discrete distribution will be replaced by one that is continuous. The level-0 spins can then be interpreted as those that are only constrained by some minimal average field. Following the argument in PSAA outlined above, $\tau_n = p^{\mu_{n-1}}\tau_{n-1}$.

To proceed further, the dependence of μ_n on n is required. Assume that elastic strain fields from the neighbors deepen the potential well in which the spin finds itself. Therefore, at $T=0$, if roughly one-half the neighbors flip, their effect will disappear, and the barrier height will be approximately equal to that for a spin with no nearest neighbors. At $T=0$,

$$\mu_n = (n+1)/2 . \tag{7}$$

At finite T some of the neighbors will have flipped via thermal activation and this will reduce μ_n. Thus

$$\mu_n = [(n+1)/2]F(T) \tag{8}$$

and

$$\tau_n = \tau_0 p^{\sum_{k=0}^{n-1}\mu_k} = \tau_0 p^{n(n+1)F(T)/2} . \tag{9}$$

Substitution of the above equation into Eq. (4) yields

$$J(\omega) = J_0 + \sum_n \delta J_n / (1 - i\omega\tau_0 p^{n(n+1)F(T)/2}) . \tag{10}$$

The simplest way to specify $F(T)$ is with mean-field theory. Below some temperature T_c

$$F(T) = (1 - T/T_c)^{1/2} . \tag{11}$$

If $T > T_c$, $F(T)=0$, which has the effect of removing the constraints at high temperatures. T_c should be a function of the number of neighbors, but in view of the approximation already present in using mean-field theory, this dependence will not be introduced here.

It is necessary to specify δJ_n: Assume that each CN contributes an equal amount δJ, so that

$$\delta J_n = (N_n/N)\delta J , \tag{12}$$

where N_n is the number of CN ions in level n (i.e., with n nearest neighbors). N_n is approximated by a Gaussian distribution about the most probable number of neighbors. This distribution must be the same as that used to fit the dielectric relaxation results, and we require that the ratio of the mean value to the standard deviation be the same in both cases. Values between about 2.5 and 3 are quoted in the literature.[1,2] The fit is not overly sensitive to the value chosen, but 3 appears to work well.

Palmer *et al.*, arguing that n is large, replace the sums over n by integrals. Zwanzig[10] evaluated the sums and has questioned the accuracy of the results; however, Palmer *et al.*, in their Reply,[11] argue that the integral has greater physical significance, and that the sum is only a device to introduce the model.

In our case the maximum number of nearest neighbors is not large; it is in fact twelve. However, we assume that the effect of the longer-range interactions with the more distant neighbors has the effect of making the levels closely spaced and numerous; so we also replace the sum by an integral,

$$J(\omega) = A\int_0^{12} dn\, e^{-[(n-12x)/4x]^2} \Big/ (1 - i\omega\tau_0 p^{F(T)n(n+1)/4}) , \tag{13}$$

where A is an arbitrary constant.

First, the torsion-pendulum results shown in Fig. 1 will be fitted. The points are the data; the solid line was calculated as follows:

We assume that the secondary peak is due to dipole relaxation; its amplitude is given by $D\epsilon''$, where D is a constant and ϵ'' is the imaginary part of the dielectric constant. Ernst *et al.*[12] find that a log-normal distribution accounts well for the dielectric relaxation,

$$\epsilon'' = (\epsilon_0 - \epsilon_\infty)W^{-1}\exp\{-[(\log_{10}\omega - \log_{10}\omega_p)/W]^2\} , \tag{14}$$

and we use $\omega_p = 2\times 10^{14} e^{-350/T}$ and $W = 110/T - 0.6$. These parameters are within the range of those deduced by Ernst *et al.*,[12] and those employed by Eisele[13] for a frequency of 700 Hz. D is left as an adjustable constant.

We now consider the primary peak, due to elastic relaxation. Using Eq. (13) above, with

$$\tau_0 = 2\times 10^{-13} e^{350/T} \qquad (15)$$

(this equation is plotted as the dashed line in Fig. 4), 81.5 K for T_c, and 12 for p, the solid line in Fig. 1 was obtained. It was not possible to fit the torsion-pendulum data with p equal to 8 or 6.

Next consider the Brillouin data for $x=0.5$, shown in Fig. 2. The solid line was calculated with the same parameters. A and D were again adjustable constants.

The Brillouin data for the $x=0.35$ sample were fitted with the results shown by the solid line in Fig. 3. The parameters for the dielectric contribution were $\omega_p = 2\times 10^{14} e^{-300/T}$ and $W=100/T$. Changes in the parameters for the quadrupolar relaxation from preceding fits were $T_c=70$ and 300 K for the activation energy for τ_0. With this value of the activation energy, Eq. (15) yields the solid line in Fig. 4. The calculated values drop somewhat more sharply with temperature on the high-temperature side of the peak than the experimental data, but the fit is still within experimental error. If T_c is allowed to vary with n, the fit is much improved.

At temperatures below the glass transition temperature, the frozen distribution of quadrupoles should yield a distribution of barrier heights which is consistent with that deduced from the dielectric relaxation: In mean-field theory the average contribution of the nearest neighbors to the barrier is $3T_c$; thus the most probable barrier height would be 636 K for the 0.5 sample, which agrees rather well with previous reports.[1] It is 510 K for the 0.35 sample. The width of the distribution was assumed from the outset to be in agreement. In fitting the dielectric data it is necessary to use a temperature-dependent width, and sometimes a temperature-dependent barrier height.[1] Equation (13) yields an effective temperature dependence for these quantities because the lower barriers will not be frozen in position at the higher temperatures. However, the structure of the equation is such that it has not been possible to demonstrate a correspondence with the dielectric relaxation models.

Using the theory for hierarchically constrained relaxation of PSAA it has been possible to account for the temperature, and concentration dependence of the quadrupolar relaxation time of CN in KBr at temperatures above and below the glass transition temperature, and for concentrations in the glass-forming range. Only the imaginary part of the elastic constant has been considered here. The real part, of course, is also affected by the relaxation. Michel[14] has shown that the rotational modes of the CN ion couple to the translational modes of the lattice, leading to a strong softening of the C_{44} elastic constant, and his theory agrees very well with experiment. This can take place whether or not a direct interaction exists between the defects such as has been considered here. Michel's mechanism, therefore, yields a change in the bulk elastic constants, to which should be added the changes in the real part provided by the model introduced here. The results of such a calculation will be presented in a future publication.[15]

Finally, it should be mentioned that it is possible to obtain an average CN relaxation time from Eq. (13). This was done in an earlier version of this work, and the results reproduced the data in Fig. 4. Measurement of the CN relaxation rate in NaCl-CN alloys using NMR (Ref. 16) reveals similar behavior to that shown in Fig. 4, and the analysis presented above also accounts for these data. Space does not permit any further discussion which will be left for another publication.[15]

This research was supported by a grant from the Natural Sciences and Engineering Council of Canada. It is a pleasure to acknowledge fruitful discussions with G. P. Johari and A. J. Berlinsky. A major portion of this Letter was written during a visit to the Institut fur Physik at the Johannes Guttenburg Universitat in Mainz, West Germany, whose hospitality is gratefully acknowledged. It is also a pleasure to acknowledge fruitful conversations with K. Knorr, A. Loidl, and R. Bohmer.

---

[1] N. O. Birge, Y. H. Jeong, S. R. Nagel, S. Battacharya, and S. Sussman, Phys. Rev. B **30**, 2306 (1984).

[2] J. P. Sethna and K. S. Chow, Phase Transitions **5**, 317–340 (1985).

[3] M. Meissner, W. Knaak, J. P. Sethna, K. S. Chow, J. J. DeYoreo, and R. O. Pohl, Phys. Rev. B **32**, 6091–6093 (1985).

[4] J. J. Vanderwall, Z. Hu, and D. Walton, Phys. Rev. B **33**, 5782 (1986).

[5] Z. Hu, J. Vanderwal, and D. Walton, Phys. Rev. B **38**, 10830 (1988).

[6] K. Knorr, U. G. Volkmann, and A. Loidl, Phys. Rev. Lett. **57**, 2544 (1986).

[7] R. G. Palmer, D. L. Stein, E. Abrahams, and P. W. Anderson, Phys. Rev. Lett. **53**, 958 (1984).

[8] A. S. Nowick, in *Physical Acoustics,* edited by W. P. Mason and R. N. Thurston (Academic, New York, 1977), Vol. 13, p. 3.

[9] P. W. Young and J. F. Scott, Phase Transitions **6**, 175–234 (1986).

[10] R. Zwanzig, Phys. Rev. Lett. **54**, 364 (1985).

[11] R. G. Palmer, D. L. Stein, E. Abrahams, and P. W. Anderson, Phys. Rev. Lett. **54**, 365 (1985).

[12] R. M. Ernst, L. Wu, S. R. Nagel, and S. Sussman, Phys. Rev. B **38**, 6246 (1988).

[13] B. Eisele, Diplomarbeit, Johannes Guttenberg Universitat, Mainz (unpublished).

[14] K. H. Michel, Phys. Rev. Lett. **57**, 2188 (1986); Phys. Rev. B **35**, 1405 (1987); **35**, 1414 (1987).

[15] D. Walton (to be published).

[16] S. Elschner and J. Petersson, Z. Naturforsch. **41a**, 343 (1986).