Unusual dielectric relaxation of the mixed crystal $(KBr)_{1-x}(KCN)_x$ at low temperatures and at low defect concentrations

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(Received 23 May 1989)

For a study of the transition from a crystalline system with isolated defects to an orientational glass with the typical low-temperature anomalies of glasses we have investigated the complex dielectric constant of $(KBr)_{1-x}(KCN)_x$ below 1 K for $0.05 \leq x \leq 0.12$. For $x < 0.1$ we have observed an unusual relaxation behavior with rates increasing on cooling. This effect can be explained with a relaxation within the system of CN^- dipoles. At higher concentration this relaxation mechanism loses importance and the dielectric properties approach those of a structural glass.

I. INTRODUCTION

It has long been known that at low temperatures there are fundamental differences between the behavior of amorphous materials and that of crystalline solids.[1] These anomalies are brought about by low-energy tunneling states with a broad distribution of their characteristic parameters.[2] However, a microscopic description of these anomalies is still lacking. A possible access to a deeper understanding is the investigation of crystals containing tunneling defects. At defect concentrations exceeding a few percent, these systems have low-temperature properties almost indistinguishable from those of glasses. Microscopically, however, the nature of the tunneling species, i.e., the defect, is well known and has been investigated in detail in many cases. Therefore, by varying type and concentration of the defects, it is possible to control disorder both qualitatively and quantitatively.

For such experiments the mixed crystal $(KBr)_{1-x}(KCN)_x$ is especially well suited because samples with arbitrary concentration ratios can be produced. The phase diagram[3] shows that at low temperatures in the concentration range between about $x = 0.03$ and 0.56, the orientation of the CN^- ions is random. Therefore it was tempting to look for a glasslike low-temperature behavior at these concentrations. Measurements by other groups have shown that the thermal,[4] acoustic,[5] and dielectric[6] properties are—at least for higher concentrations—similar to those of amorphous materials. Furthermore, an analysis of rotary echo experiments[7] showed that at a concentration of $x = 0.2$, the distribution of the tunneling parameters corresponds largely to that of a glass.

Theoretical work[8,9] has shown that the "glassy" low-temperature properties can be explained with the tunneling of the CN^- ions between opposite orientations. The broad distribution of energy splittings of these two-level tunneling systems was ascribed to a distribution of barrier heights[8] or to dipole-dipole interaction.[9]

In this work we shall report on measurements of the complex dielectric constant of the mixed crystal $(KBr)_{1-x}(KCN)_x$ at temperatures below 1 K and for concentrations between $x = 0.05$ and 0.12. Our measurements were centered around lower concentrations in order to better understand the transition from the behavior of a well-defined isolated defect into the regime of orientational disorder. In this range we have observed a very unusual relaxational behavior which can be explained with a relaxation within the system of the CN^- dipoles themselves.

II. EXPERIMENTAL TECHNIQUE

In dielectric measurements at very low temperatures, because of its low magnitude and the low permissible excitation levels, it is extremely difficult to determine the absolute value of the absorption. Therefore we could not use a commercial capacitance bridge in our experiment. Instead we have used a modified bridge circuit which allowed us to perform such measurements with sufficient resolution. Our capacitance bridge consisted of an inductive voltage divider, a resistance decade, and a reference capacitor [Fig. 1(a)]. The essential difference from conventional techniques is that our reference capacitor was integrated into the sample holder [Fig. 1(b)]. This capacitor consisted of a sapphire disk 2 mm thick and 20 mm in diameter with a gold layer evaporated onto both sides. At temperatures below 1 K the dielectric absorption of this material is negligible. One side of the reference capacitor also served as a sample electrode and was surrounded by a grounded guard ring. Connection between the room-temperature components of the bridge and the sample holder was made with three coaxial cables.

The $(KBr)_{1-x}(KCN)_x$ samples (thickness 2 mm, diameter 12 mm) (Ref. 10) were pressed onto the reference capacitor with a spring-loaded gold-plated copper disk [Fig. 1(b)]. Good thermal contact to the sample was ensured by the high thermal conductivity of the sapphire crystal clamped between the two halves of the copper sample holder. The sample holder was attached to the mixing chamber of a ^3He-^4He dilution refrigerator. The

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high symmetry and stability of this design resulted in a very low level of interference pickup from outside sources and allowed the measurement of losses as low as $\tan\delta = 10^{-6}$ at cryogenic temperatures.

After equilibration of the bridge, the dielectric constant was determined from the setting of the ratio transformer and the value of the reference capacitance. Absorption was compensated by the resistance decade in the reference branch. The absolute error in the absorption measurement is mainly due to difficulties in precisely determining the residual absorption of the experimental setup. This absorption is caused by losses in the cables and the ratio transformer and by the resistance decade itself. The error depends on the measuring frequency; for low frequencies it was about 10%. At frequencies above 20 kHz the difference between the residual resistance and that required for equilibration of the bridge was so small that errors exceeding 50% cannot be excluded. The measuring frequency could be varied between 100 Hz and 100 kHz, the limits were mainly given by the components of the bridge.

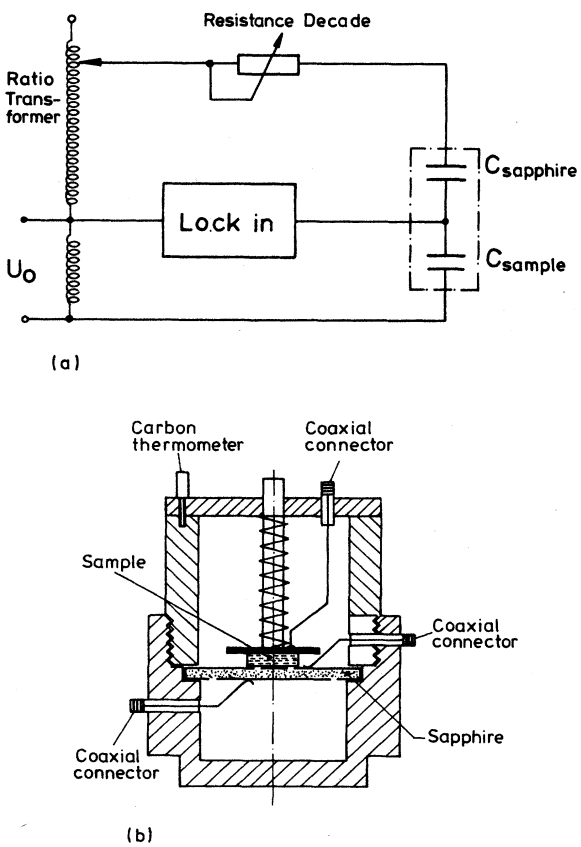

FIG. 1. The capacitance bridge. (a) Electrical circuit. In equilibrium the excitation voltage U_0 is divided by a ratio transformer between the reference capacitor and the sample according to their capacitance ratio. The dielectric loss of the sample is compensated by the decade resistor. Bridge null is detected by a lock-in amplifier. The dash-dotted line encloses components located in the cryostat. (b) Sample holder. The sample is mounted on a sapphire disk which simultaneously served as a reference capacitor. The surrounding sample holder is made of copper. All electrical leads outside the sample holder are coaxial.

III. EXPERIMENTS ON GLASSES REVIEWED

For a discussion of the transition from a crystalline solid to an amorphous one it will be useful to review the dielectric properties expected for a typical glass.[11]

As mentioned above, the low-temperature properties of glasses are governed by low-energy tunneling systems. These are characterized by a tunnel splitting Δ_0, an energy asymmetry Δ of the two wells, a phonon coupling constant γ, and a dipole moment **p**. The fundamental assumption of the tunneling model for glasses is that Δ and Δ_0 are distributed like $P(\Delta,\Delta_0)d\Delta\, d\Delta_0 = (\bar{P}/\Delta_0)d\Delta\, d\Delta_0$. This leads to an almost constant density of states $n(E)$ with $E = (\Delta + \Delta_0)^{1/2}$.

Tunneling systems of a given energy E can be composed of any combination of Δ and Δ_0. Since the matrix element for resonant interaction with phonons is $\gamma(\Delta_0/E)$, a broad distribution of the rate for one-phonon relaxation is expected and observed. This relaxation process and resonant interaction with the tunneling systems leads to a dielectric behavior of glasses summarized in the following.

Absorption: $\tan\delta$ first increases as T^3 and becomes temperature and frequency independent above a temperature T^*, where relaxation rates are high enough so that $\omega\tau_{\min} \leq 1$ for tunneling systems with $E \approx k_B T$ ($\tau_{\min}$ is the relaxation time for $E = \Delta_0$). At audio frequencies this transition usually occurs at temperatures between 50 and 500 mK. Absorption due to resonant interaction with the tunneling systems has only been observed at microwave frequencies.

Dielectric constant: ϵ starts with a negative logarithmic temperature dependence $\Delta\epsilon/\epsilon = -c\ln T + \text{const}$ due to resonant interaction with the tunneling systems. The relaxation contribution is negligible at the lowest temperatures and results in a positive logarithmic temperature dependence above T^*. If the resonant part has a slope $-c$ then that of the relaxation contribution is $3c/2$, so that for $T > T^*$ we expect an increase of ϵ with $c/2$.

IV. EXPERIMENTAL RESULTS

Let us start with the highest concentration, $x = 0.12$, investigated. According to thermal and acoustic experiments, the glasslike behavior discussed above is expected for this sample. The dielectric constant (Fig. 2) and the absorption (Fig. 3) steadily increase with temperature, although the slope for the absorption is rather small up to 500 mK. Absorption is frequency independent within the accuracy of our experiment. Unfortunately, due to technical problems, this sample could only be measured above 70 mK, whereas a calculation of T^* from acoustic data[5] yields values around 40 mK. Therefore, T^* and the corresponding minimum of the dielectric constant could certainly not be reached.

Although this result does not strongly support the applicability of the tunneling model to $(KBr)_{1-x}(KCN)_x$, it

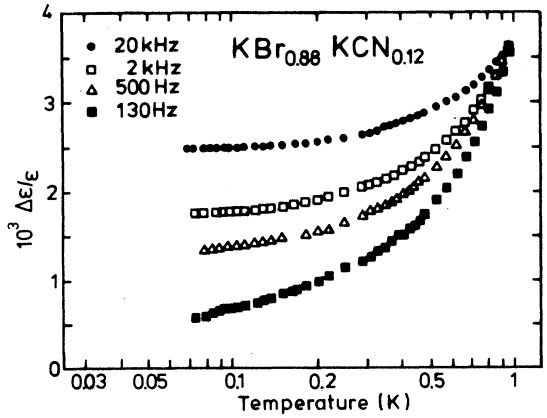

FIG. 2. Dielectric constant of $(KBr)_{0.88}(KCN)_{0.12}$ between 0.07 and 1 K.

also does not contradict it. This situation changes for the lower concentrations investigated by us.

The results for $x=0.08$ are shown in Figs. 3 and 4. The dielectric constant decreases until a frequency-dependent minimum between 70 and 200 mK is reached. Above this temperature ϵ increases rapidly. Roughly at the same temperature, tanδ changes from a temperature- and frequency-independent behavior to a frequency-dependent increase. The magnitude of tanδ and the variation of ϵ in our temperature range are larger by a factor of 5 compared to $x=0.12$. The rapid increase of ϵ above 0.2 K can mainly be associated with the transition from dipolar glass where the orientation of the CN^- is frozen to a system with freely rotating dipoles.[12,13] A phase diagram derived from neutron scattering studies[3] shows that at low x this glass-transition temperature goes to zero with concentration.

The decrease of ϵ at the lowest temperatures, however, cannot be associated with a "glassy" behavior. If the minimum in ϵ were identical with the minimum at T^* in glasses, absorption should incresae rapidly in this temperature range.

This situation becomes even more pronounced for $x=0.05$ (Figs. 5, 6, and 7), except that for frequencies

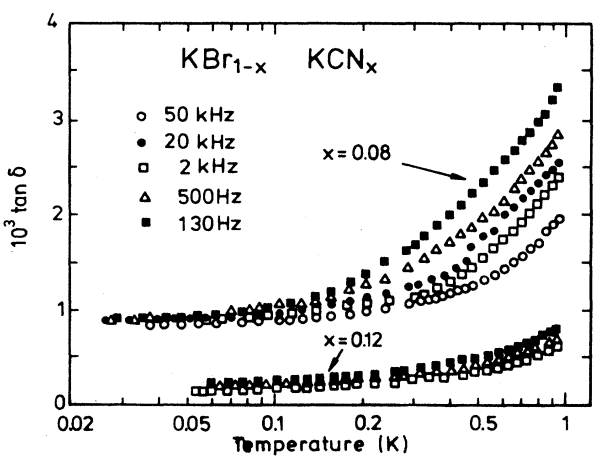

FIG. 3. Dielectric loss tanδ of $(KBr)_{0.92}(KCN)_{0.08}$ and of $(KBr)_{0.88}(KCN)_{0.12}$ between 0.03 and 1 K.

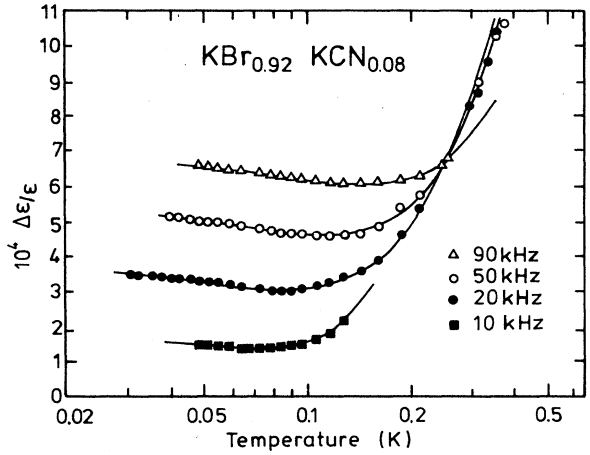

FIG. 4. Real part of the dielectric constant of $(KBr)_{0.092}(KCN)_{0.08}$ between 0.03 and 0.4 K. Solid lines are fits with parameters shown in Table I. Data at different frequencies have been offset arbitrarily.

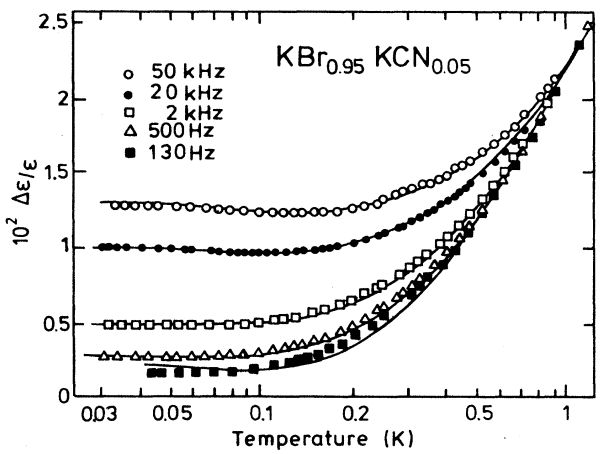

FIG. 5. Real part of the dielectric constant of $(KBr)_{0.95}(KCN)_{0.05}$ between 0.03 and 1 K. Solid lines are fits with parameters shown in Table I.

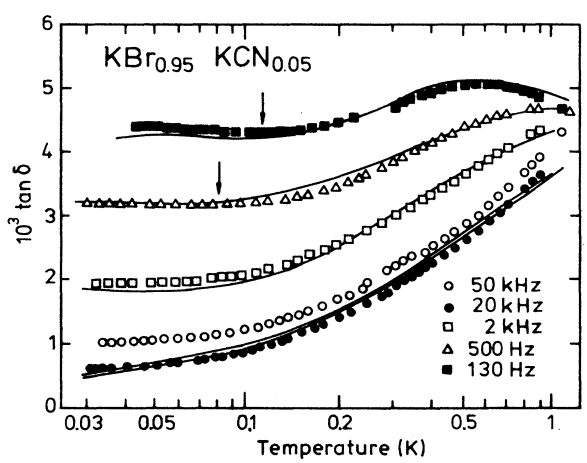

FIG. 6. Dielectric loss tanδ of $(KBr)_{0.95}(KCN)_{0.05}$ between 0.03 and 1 K. Solid lines are fits with parameters shown in Table I.

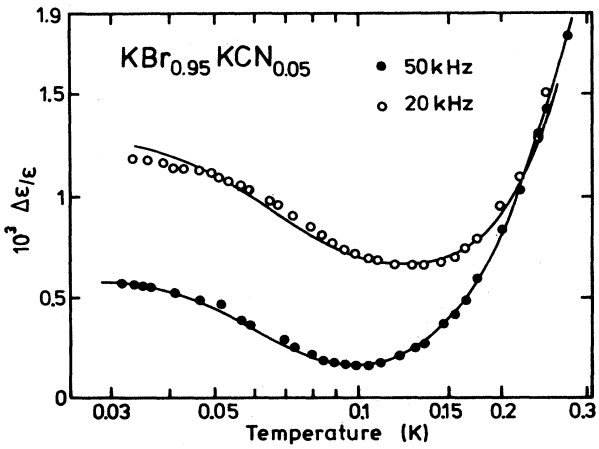

FIG. 7. Enlarged section of Fig. 4 for two frequencies. The negative temperature dependence of ϵ below 100 mK is clearly visible.

below 2 kHz no minimum in ϵ was observed. Compared to $x=0.08$ the change of ϵ in our temperature range has increased by a factor of 5. Absorption is now frequency dependent in the plateau region. At the lowest frequency of 130 Hz an absorption peak appears around 0.7 K which we associate again with the orientational glass transition.

These low-temperature properties strongly deviate from those of a structural glass. They are an indication that at low concentration an additional process comes into play. It can only be a relaxation process for two reasons: At our measuring frequencies, resonant systems are too low in energy to contribute to absorption. The negative temperature dependence of ϵ at the lowest temperatures cannot be caused by the resonant process either: if this were the case, absorption should rapidly increase at these temperatures. The initial decrease of ϵ with temperature can only be explained if the new relaxation process leads to rates that decrease when temperature is raised. Indications for a relaxation process with this surprising temperature dependence have already been found in other defect crystals. A first observation was reported by Knop and Känzig in dielectric measurements on alkali halides with OH^- defects. These investigations on $KCl:OH^-$ under biaxial pressure and on $RbCl:OH^1$ are reviewed in Ref. 14. An analogous relaxation behavior was found in γ-irradiated quartz.[15] Besides, measurements of the complex dielectric constant of $KBr:OH^-$ (Ref. 16) and of $NaBr:F^-$ (Ref. 17) revealed properties similar to those found in this experiment.

Already in 1972, immediately after the measurements of Knop and Känzig on $KCl:OH^-$, Janssen[18] suggested a relaxation process which leads to an increasing rate with decreasing temperature. We have used this mechanism for the interpretation of our experimental results. The theoretical background of this analysis shall be discussed in the following paragraph.

V. RELAXATION INTO THE DIPOLE BATH

For a relaxation of the tunneling systems into thermal equilibrium it is usually assumed that only interaction with thermal phonons can perform the exchange of energy. With this process, however, a decrease of the rate with increasing temperature cannot be explained.

Janssen[18] suggested to take into account a relaxation into thermal equilibrium by an exchange of energy within the bath of dipoles themselves. Two or more dipoles should flip collectively and thus change states with the sum of their energies being conserved. The most probable origin of this mechanism is the electrical dipole-dipole interaction. For a calculation of this process a system of dipoles with (other than in glasses) a fixed tunnel splitting Δ_0 is considered. Because of internal electric fields $\mathbf{F}$, the two energy minima have an asymmetry $\Delta=\mathbf{p}\cdot\mathbf{F}$ (a possible additional asymmetry by internal strain fields has not been considered here). $\mathbf{p}$ is the dipole moment of the tunneling systems. The Hamiltonian of such a system is

$$H_0=\tfrac{1}{2}(\mathbf{p}\cdot\mathbf{F}\sigma_z-\Delta_0\sigma_x)\ , \tag{1}$$

where σ_x and σ_z are the Pauli spin matrices. The total energy of the system is given by

$$E=(p^2F^2+\Delta_0^2)^{1/2}\ . \tag{2}$$

Henceforth we shall drop the discussion in terms of internal fields[18] and replace $\mathbf{p}\cdot\mathbf{F}$ with the equivalent asymmetry energy Δ.

If dipole-dipole interaction is considered, one obtains for a system of N dipoles

$$H=\frac{1}{2}\sum_{i=1}^{N}(\Delta^i\sigma_z^i-\Delta_0\sigma_x^i)+\frac{1}{2}\sum_{i,j}f_{ij}\sigma_z^i\sigma_z^j\ , \tag{3}$$

where f_{ij} is the interaction energy between tunneling systems i and j. Under the assumption that perturbation theory is valid, the rate for a transition between two eigenstates α and β is given by Fermi's golden rule:

$$W(\alpha\rightarrow\beta)=\frac{2\pi}{\hbar}|\langle\beta|M|\alpha\rangle|^2\delta(E)\ . \tag{4}$$

$\langle\beta|M|\alpha\rangle$ has the following form in first and second order:

$$\langle\beta|M|\alpha\rangle=\langle\beta|(H-H_0)|\alpha\rangle+\sum_m\frac{\langle\beta|(H-H_0)|m\rangle\langle m|(H-H_0)|\alpha\rangle}{E_i-E_m}\ , \tag{5}$$

where m is an intermediate state, E_i and E_m are the energies of the initial and the intermediate states, respectively. The first-order term vanishes if more than two dipoles change their states in the relaxation process, the second-order term if more than four dipoles contribute. The transition between two eigenstates will only contribute to relaxation absorption and dispersion if the total polarization $\sum_i(\Delta_i/E_i)\mathbf{p}$ of the dipoles changes. Because this relaxation process is associated with an energy exchange within the dipole bath, the total energy in the dipole bath must be conserved. Therefore, for a two-dipole process, a distribution of the tunneling splitting Δ_0 or of the orientation of $\mathbf{p}$ is required. As will be seen later, these distributions are very narrow and cannot be separated. There-

fore we only consider a distribution of Δ_0. Multidipole processes are only possible if the energy E of the dipoles is distributed. This can happen by a distribution of the tunnel splitting Δ_0 or—more important in our case—by a distribution of the asymmetry energy Δ and thus of the internal electric fields.

An analysis of dielectric rotary echoes in $(KBr)_{0.97}(KCN)_{0.03}$ has shown[7] that the tunnel splitting is not distributed, or is at most distributed in a very narrow range. Therefore in our calculations we have assumed a constant tunnel splitting and a Gaussian distribution of the asymmetry Δ. This leads to a distribution function $P(E)$ of the form

$$P(E)=\frac{P_0 E}{(E^2-\Delta_0^2)^{1/2}}\exp\left[-\frac{[(E^2-\Delta_0^2)^{1/2}-\bar{\Delta}]^2}{\Gamma^2}\right] . \quad (6)$$

P_0 is a scaling factor chosen such that integration over Eq. (6) gives the number of tunneling systems. $\bar{\Delta}$ and Γ are the center and the width of the Gaussian distribution of Δ, respectively. In fitting the data it turned out that two-dipole relaxation cannot be neglected in spite of the narrow distribution of the tunnel splitting. An exact calculation of this contribution would require assumptions on a corresponding distribution function and thus a more complicated model. We therefore have kept the distribution of Eq. (6) and taken into account the two-dipole process by a modified scaling factor ηP_0 ($\eta \ll 1$). This simplification turned out to be sufficient for a description of our measurements on $(KBr)_{0.95}(KCN)_{0.05}$. At higher CN^- concentrations, however, this is not the case, since already for $x=0.08$ a distribution of tunnel splittings with $\Delta_{0,\max}/\Delta_{0,\min} \geq 50$ must be assumed in order to explain the frequency-independent plateau of the absorption. From Eqs. (4), (5), and (6) the relaxation rates for the two- and three-dipole processes can be calculated. According to Ref. 18 the result is

$$\tau_2^{-1}(E)=A_2(E)\eta P(E) , \quad (7)$$

with

$$A_2(E)=\frac{2\pi}{\hbar}\bar{f}^2\left[\frac{\Delta_0}{E}\right]^4$$

for the two-dipole process and

$$\tau_3^{-1}(E)=\int_{\Delta_0}^{E-\Delta_0}dE_1\int_{\Delta_0}^{E-\Delta_0}dE_2\left[\delta(E-E_1-E_2)V^2P(E_1)P(E_2)A_3(E,E_1,E_2)\frac{\cosh(E/k_BT)}{\cosh(E_1/k_BT)\cosh(E_2/k_BT)}\right] , \quad (8)$$

with

$$A_3(E,E_1,E_2)=\frac{2\pi}{\hbar}\bar{f}^4\left[\frac{(\Delta_0^3)^{1/2}}{EE_1E_2}\right]^4[E_1(\Delta+\Delta_2)+E_2(\Delta+\Delta_1)-E(\Delta_1+\Delta_2)]^2$$

for the three-dipole process. V is a measure for the volume around a dipole within which electrical dipole-dipole interaction is important for the process here. A_2 and A_3 designate the off-diagonal coupling between the dipoles under consideration[18] with an average coupling strength $\bar{f}$.

The relaxation rate for one dipole is the sum of the rates for all relaxation channels. Of course the one-phonon relaxation rate has to be considered here, too. It is given by[19]

$$\tau_{\rm Ph}^{-1}(E)=A_{\rm Ph}\Delta_0^2 E\coth\left[\frac{E}{2k_BT}\right] . \quad (9)$$

$A_{\rm Ph}$ contains material constants like the velocity of sound and the coupling between tunneling systems and strain fields.

The temperature and energy dependence of the total rate $\tau^{-1}=\tau_2^{-1}+\tau_3^{-1}+\tau_{\rm ph}^{-1}$ for dipoles of energy E is shown in Figs. 8 and 9. For high energies dipole-dipole relaxation is inefficient due to the high exponent of (Δ_0/E) in A_2 and A_3 [Eqs. (7) and (8)]. Therefore the almost-energy-independent phonon relaxation dominates. For E approaching $2\Delta_0$ the three-dipole rate increases by several orders of magnitude and diverges for $E\rightarrow 2\Delta_0$ because of the diverging densities of state $P(E_1)$ and $P(E_2)$. Below this energy, phonon relaxation first takes over again, until, at lower energy, the two-dipole process dominates and diverges for $E\rightarrow\Delta_0$.

Temperature dependence of τ^{-1} at the lowest temperatures is dominated by the three-dipole process. It leads to decreasing rates with increasing temperature ($T\leq 100$ mK in Fig. 8). This unusual behavior can be made plau-

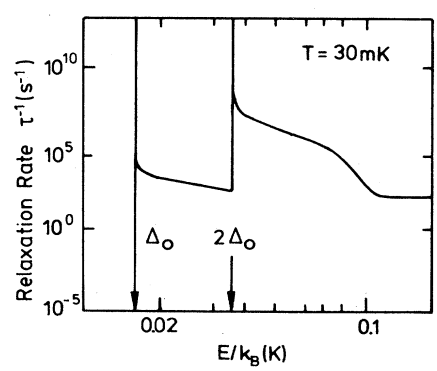

FIG. 8. Energy dependence of the relaxation rate including dipole-dipole relaxation. Above 0.1 K, phonon relaxation dominates. Below this temperature the rate increases due to the three-dipole process and divergences at $E=2\Delta_0$. Below this energy, phonon relaxation takes over again until the two-dipole process contributes. This process causes a second divergence at $E=\Delta_0$.

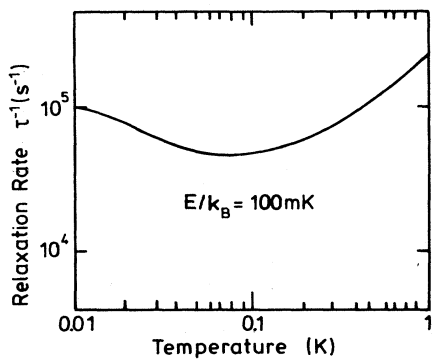

FIG. 9. Temperature dependence of the relaxation rate including dipole-dipole relaxation for tunneling systems with $E/k_B = 100$ mK. Increase of the relaxation rate below 0.1 K is due to dipole-dipole relaxation.

sible in a simple picture: For $T \to 0$, almost all tunneling systems are in the ground state. Then an excited system with energy E will have a high probability of finding two systems with energy $E/2$ in the ground state for relaxation. For $T \to \infty$ the probability of finding two systems with energy $E/2$ in the same state and thus the relaxation rate is reduced by a factor of 2. At higher temperature, dipole-dipole relaxation loses importance and a linear increase due to one-phonon relaxation follows.

From Fig. 8 one sees that close to $E = \Delta_0$ and $E = 2\Delta_0$ we have a distribution of relaxation rates over many orders of magnitude. The temperature independence of the absorption at low temperature is an experimental consequence of this phenomenon. Because one-phonon relaxation is almost energy independent, the width of this distribution decreases at higher temperature. Due to the limited frequency range a direct determination of the distribution of rates was not possible in this experiment. However, other measurements on KCL:OH$^-$,[14] RbCl:OH,[14] and γ-irradiated quartz[15] agree very well with this theory.

When the contributions of all relaxation channels are added, the fact must be taken into account that for a certain dipole, not all relaxation processes are necessarily possible. For instance, a relaxation via dipole-dipole interaction can occur only if the corresponding pairs or triples are available. Furthermore, because of energy conservation, the three-dipole process can only take place if the highest of the three energies is at least $2\Delta_0$. This is taken into account in Eq. (8) by the δ distribution in the integral.

For a calculation of the complex dielectric constant we have divided the tunneling systems into two classes. The relaxation rate for systems (I), which can only relax via two-dipole and one-phonon processes, is given by the sum of (7) and (9) as $\tau_{\rm I}^{-1} = \tau_{\rm Ph}^{-1} + \tau_2^{-1}$. For systems (II) which can also relax by three-dipole processes, the rate is $\tau_{\rm II}^{-1} = \tau_{\rm Ph}^{-1} + \tau_2^{-1} + \tau_3^{-1}$.

Finally, the contributions of the two classes have to be weighted. This is done by a parameter $c = c_{\rm I}/c_{\rm II}$ indicating the relative number of tunneling systems in the two classes. Then the complex dielectric constant $\epsilon(\omega, T)$ results as[20]

$$\epsilon(\omega,T) = \frac{p^2}{\epsilon\epsilon_0 k_B T}\left[\int_{\Delta_0}^{E_{\max}} dE \left[\frac{\Delta}{E}\right]^2 \operatorname{sech}^2\left[\frac{E}{2k_B T}\right]\frac{c}{c+1}P(E)\frac{1}{1+i\omega\tau_{\rm I}} + \int_{\Delta_0}^{E_{\max}} dE \left[\frac{\Delta}{E}\right]^2 \operatorname{sech}^2\left[\frac{E}{2k_B T}\right]\frac{1}{c+1}P(E)\frac{1}{1+i\omega\tau_{\rm II}}\right]. \tag{10}$$

At a first look it is very unsatisfactory that the theoretical description of the dipole-dipole relaxation requires a total of nine fitting parameters. These are the prefactor P_0 of the density of tunneling systems, the density ηP_0 of those systems which can perform two-dipole processes, the ratio c of the number of systems in the two classes, the tunnel splitting Δ_0, the center $\bar{\Delta}$ and the width Γ of the asymmetry distribution, the prefactor $A_{\rm Ph}$ of the one-phonon process, the mean dipolar interaction energy $\bar{f}$ and the mean interaction volume V.

In order to reduce the number of parameters, we have extracted the coupling of the tunneling systems to elastic fields and thus the parameter $A_{\rm Ph}$ from Ref. 5. The mean interaction energy $\bar{f}$ can be estimated from the measurements on KCl:OH$^-$, with a value of $\bar{f} = \frac{1}{2}\Delta_0$.[14] Since we have $\bar{f} = p^2/\bar{r}^3$, $\bar{r}$ and thus the interaction volume V can be calculated from Δ_0. The remaining six parameters were determined by fitting the experimental data [see Figs. (4)–(7)]. In these fits, the peak due to the orientational glass transition (see above) which appears at higher temperatures ($T \geq 1$ K) had to be taken into account. This process has already been investigated in detail; our empirical fit is based on Refs. 12 and 13, therefore the result will not be discussed here.

Because the complex dielectric constant had to be fitted over a rather wide range in frequency and temperature, the parameters could be determined fairly well in spite of their large number. The quantities thus obtained are listed in Table I.

It turns out that all parameters have physically meaningful values or agree with other experiments. The density of states P_0 is about 3 orders of magnitude above that of glasses. This is understandable, since the distribution function employed here is considerably narrower than that of the tunneling model. With the assumption of a roughly equal total number of tunneling systems for both, the prefactor has to be correspondingly larger in our case. The value for η indicates that the density of states

TABLE I. CN^- tunneling parameters derived from dielectric data. The asterisk indicates that the fit was insensitive to these parameters.

x		0.05		0.08	
P_0	(10^{47}/J m^3)	25	(22–28)	1	(0.5–2)
η	(10^{-6})	4	(2–8)	*	
Δ_0	(mK)	17	(14–19)	10	(5–15)
$\bar{\Delta}$	(mK)	34	(25–45)	34	(25–45)
Γ	(mK)	34	(30–40)	50	(40–60)
c		3	(2.5–3.5)	*	

for which a two-dipole process is possible is smaller by 5 orders of magnitude against P_0. The very narrow distribution of Δ_0 derived from the echo experiments makes this plausible, where a tunnel splitting Δ_0 of 17 mK was found to result from the simultaneous tunneling of neighboring dipoles.[7]

For the interaction radius $\bar{r}$ we find a value of 200 Å. Considering the relatively long-range dipole-dipole interaction, this is a reasonable number. Because the electrical field at a dipole site $F=\bar{\Delta}/p$ is distributed with $\delta F=\Gamma/p$, the center $\bar{\Delta}$ and the width Γ of the asymmetry energy are a measure of magnitude and distribution of the internal electric fields. For F and δF we find 2.8 kV/cm. This value is similar to that measured in OH^--doped alkali halides.[14]

For the ratio c of systems in the two classes (with and without three-dipole process) we find a 3:1 ratio. This number is very well confirmed by Raman scattering experiments.[21] These experiments showed that up to a concentration of $x=0.06$, coupled modes of pairs and triples are observable, with the ratio of the scattering intensity just being 3:1 for pairs and triples.

The model discussed here is not adequate anymore for the higher-doped samples (≥ 0.08). The distribution of Δ_0 becomes too broad for the approximations made. This is clearly seen from the different reductions of the real and the imaginary parts of the dielectric constant when the CN^- concentration is increased from $x=0.05$ to $x=0.08$. The real part still is essentially determined by dipole-dipole relaxation. Therefore it is reduced much more strongly than the imaginary part, which is dominated by the total number of tunneling systems and their relaxation behavior. Obviously the increase of the CN^- concentration from $x=0.05$ to 0.08 causes the transition from the interaction of few dipoles to the collective behavior of a multitude of dipoles.

VI. CONCLUSION

In this work we have measured the complex dielectric constant of the mixed crystal system $(KBr)_{1-x}(KCN)_x$ in the concentration range from $x=0.05$ to 0.12. The results indicate an unusual relaxation behavior, in which the rate decreases with increasing temperature. This process is characterized by a relaxation within the dipole bath, where two or three dipoles change their states simultaneously. Theory based on this process gives a very good description of the complex dielectric constant at low concentration. This type of dipole-dipole relaxation is only significant if defect concentration is low enough to leave the tunnel splitting fixed or only narrowly distributed.

With increasing CN^- concentration ($x > \approx 0,1$) the interaction between the tunneling systems becomes stronger and leads to a broader distribution of the tunnel splitting. Thus, because of the selection rules for dipole-dipole relaxation, the probability of this process decreases rapidly.

Our results show that a high concentration of defects is necessary to obtain the distribution of tunnel splittings typical for structual glasses. A distribution of the asymmetry energy alone may cause glasslike properties in experiments sensitive to the energy density of states. A detailed investigation of the dynamical properties, however, shows that at low concentration, characteristics like the relaxation behavior may be totally different from those of a glass.

By comparing with older measurements we could show that dipole-dipole relaxation in defect systems with relatively low defect concentration is rather universal. One therefore can conclude that it is a characteristic of a "preglass" state in defect-rich crystals.

ACKNOWLEDGMENTS

We are indebted to S. Haussühl for preparation of the samples and to S. Hunklinger and G. Weiss for many helpful comments. This work was supported by the Deutsche Forschungsgemeinschaft (Contract No. Schi-238/1-2).

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