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# Dielectric Properties of $(\text{KBr})_{1-x}(\text{KCN})_x$

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The temperature dependence of the dielectric constant of  $(\text{KBr})_{1-x}(\text{KCN})_x$  was measured at frequencies of 87.5 Hz, 1, 10 and 100 kHz for concentrations of  $x=0, 0.01, 0.04, 0.14, 0.25,$  and  $0.50$ . Both the real and the imaginary part showed maxima at characteristic temperatures which depend on the measuring frequency and the concentration. The results are analogous to the behaviour of the magnetic susceptibility in spin glasses and support the existence of an orientational glass state.

## I. Introduction

KCN and the pseudobinary compounds  $(\text{KBr})_{1-x}(\text{KCN})_x$  are molecular crystals with a pseudocubic structure (NaCl) in the high temperature phase. The aspherical CN molecule resides in an octahedral Devonshire potential. At low concentrations  $x$  the CN molecules are known to be oriented along the  $\langle 111 \rangle$ -directions [1]. In pure KCN the orientation of the CN molecules is described by a temperature dependent probability distribution with maxima along  $\langle 111 \rangle$  [2]. In a concentration range  $0.56 < x < 1$  these crystals undergo structural phase transitions into an orthorhombic structure which occur as a consequence of a strong coupling between the rotational and the translational modes [3-7].

For  $x < 0.56$  there exists a low temperature glass state [8-10] which results from a frustration of the multipole interaction between CN pairs into which not only the orientations but also the bond vectors enter. The freezing temperatures  $T_F$  are concentration and frequency dependent [11] indicating that the freezing in  $(\text{KBr})_{1-x}(\text{KCN})_x$  is not a static process but rather a relaxational phenomenon.

It should be possible to study the freezing by dielectric measurements since the CN dump-bells carry a dipole moment of about  $0.30D$  (the values in the literature range from  $0.2$  [12] to  $0.74D$  [13]). In analogy to magnetization measurements in spin glasses one expects a cusp in the dielectric susceptibility at  $T_F$ . An early dielectric investigation of a

very dilute concentration ( $x < 0.003$ ) of CN ions in a KCl matrix have been reported by Sack and Moriarty [14]. Here the increase of the dielectric constant  $\epsilon'(T)$  below 20 K followed a  $1/T$ -law and yielded a dipole moment of  $0.3D$ . More recent dielectric measurements in  $(\text{KCl})_{1-x}(\text{KCN})_x$  have been reported by Julian and Lüty [15]. In the dilute limit ( $x \leq 0.09$ ) a Curie law for  $\epsilon'(T)$  is apparent from their results, while in an intermediate concentration range ( $0.19 \leq x \leq 0.81$ ) the dielectric constant exhibits a cusp which is shifted to higher temperatures with increasing  $x$ . Finally for  $x \geq 0.87$  the system undergoes a structural phase transition as can be seen from the discontinuities observed in  $\epsilon'(T)$ .

In the present work we report dielectric measurements in a concentration range  $0.01 < x < 0.50$  using measuring frequencies from 87.5 Hz to 100 kHz down to 3 K.

## II. Experiments and Results

The  $(\text{KBr})_{1-x}(\text{KCN})_x$  single crystals were obtained from the Crystal Growth Laboratory of the University of Utah. They were grown from the melt starting with zone refined KBr and KCN materials. Samples with concentrations  $x=0, 0.01, 0.04, 0.14, 0.25,$  and  $0.50$  were investigated; the values  $0.01, 0.25$  and  $0.50$  give the composition of melt, the figures  $0.04$  and  $0.14$  have been determined by chemical

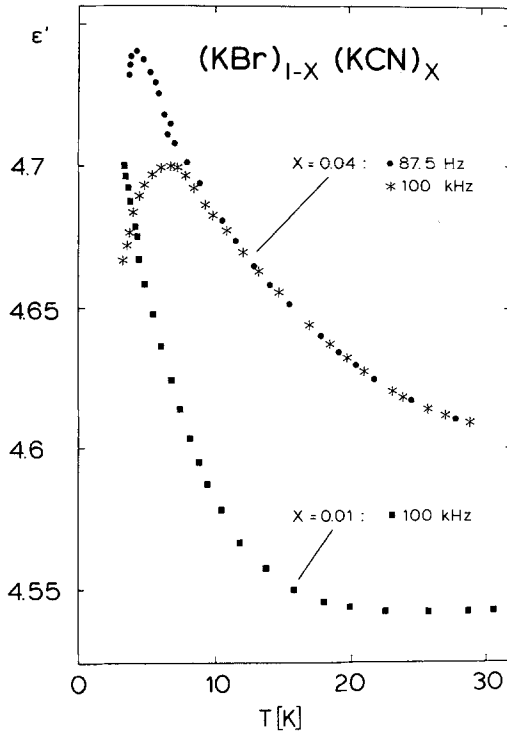


Fig. 1. The real part of the dielectric constant as a function of temperature

analysis: the composition of melt in these two cases was 0.05 and 0.20. Thin slabs with  $\langle 100 \rangle$  faces were cleaved to dimensions of roughly  $10 \times 10 \times 1$  mm. Nine slabs were fixed with vacuum grease in a stress free configuration to one of the two flat copper electrodes of the condenser which were covered with a Mylar foil to avoid chemical reactions.

Both the capacitance  $C$  and the conductance  $G$  were measured at 87.5 Hz using a three terminal capacitance bridge in conjunction with a lock-in amplifier. At higher frequencies (1, 10, and 100 kHz)  $C$  and  $G$  were recorded fully automatically with a multi-frequency LRC meter. The measurements were performed in a range of excitation voltages from 0.1 to 5 V with no change in  $C$  and  $G$  showing that the regime of linear response was never passed. Characteristic values of the capacitance and the conductance were 20 pF and  $100 \mu\text{mho}$ , respectively. The resolution was never worse than  $10^{-4}$  for  $C$  and 0.01 for  $G$ . The real and imaginary part  $\epsilon'$  and  $\epsilon''$  of the dielectric constant  $\epsilon = \epsilon' - i\epsilon''$  is related to  $C$  and  $G$  via  $\epsilon' = C/C_0$  and  $\epsilon'' = G/\omega C_0$  where  $C_0$  is the capacitance of the flat plate condenser with the sample removed. The absolute values of  $\epsilon'$  and  $\epsilon''$  may be inaccurate up to 10% due to the incomplete filling of the condenser with the dielectric medium.

The results on the temperature, frequency and concentration dependence of the dielectric constant  $\epsilon'$

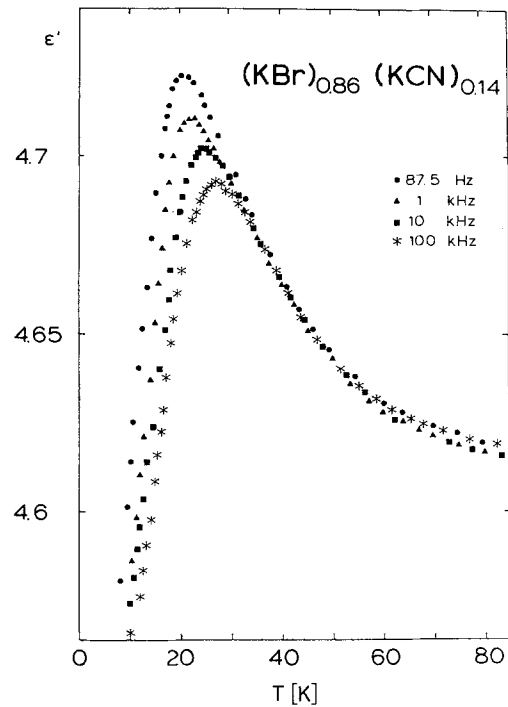


Fig. 2. The real part of the dielectric constant as a function of temperature

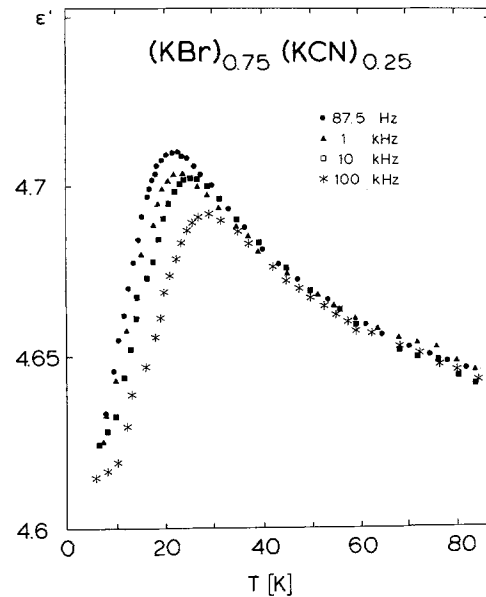


Fig. 3. The real part of the dielectric constant as a function of temperature

are shown in Figs. 1-4.  $\epsilon'$  of the 1%-sample is frequency independent and follows a  $1/T$ -law down to 3 K, the lowest temperature which could be reached in the variable temperature cryostat used in the present study (Fig. 1). In samples with higher CN concentrations  $\epsilon'$  exhibits a maximum at a charac-

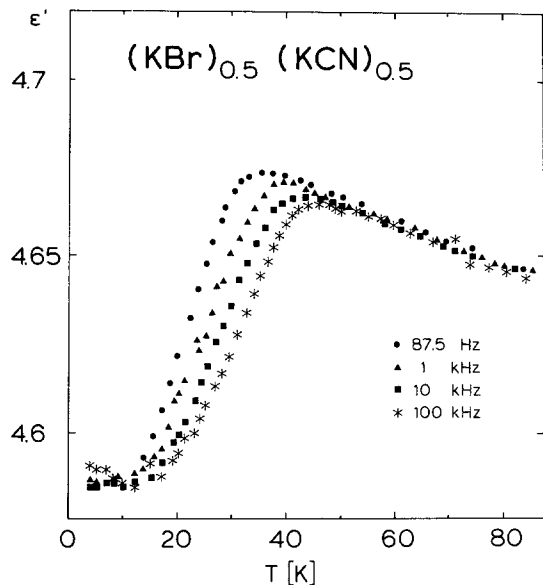


Fig. 4. The real part of the dielectric constant as a function of temperature

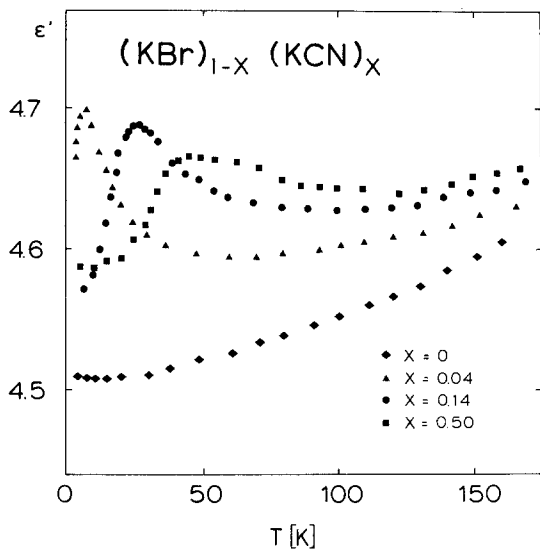


Fig. 5. The real part of the dielectric constant at 100 kHz as a function of temperature

Table 1. The temperatures of maximum  $\epsilon'(T)$  in  $(\text{KBr})_{1-x}(\text{KCN})_x$

$x$	0.04	0.14	0.25	0.50
87.5 Hz	$4.3 \pm 0.3$	$20.5 \pm 0.5$	$22.5 \pm 0.5$	$35.5 \pm 1.0$
1 kHz	5.0	22.8	23.5	39.5
10 kHz	6.0	25.0	26.0	42.5
100 kHz	6.5	27.0	29.5	46.0

teristic temperature  $T_F$ . For higher frequencies and higher concentrations  $T_F$  is increased, the maximum broadens and deviations from a Curie law become more and more apparent (Figs. 1-4). Figure 5 gives a comparison of  $\epsilon'$  measured at 100 kHz for three concentrations, complemented with the results on the

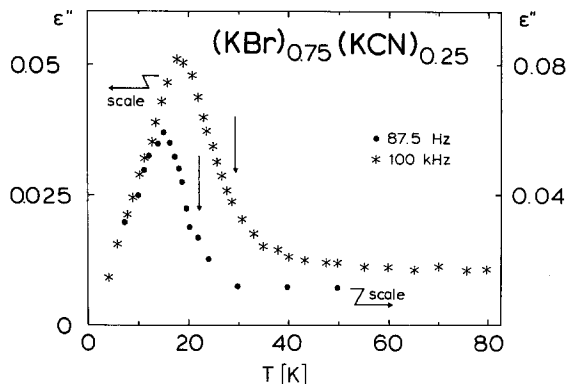


Fig. 6. The imaginary part of the dielectric constant as a function of temperature. The arrows indicate where the maxima of the corresponding real parts occur

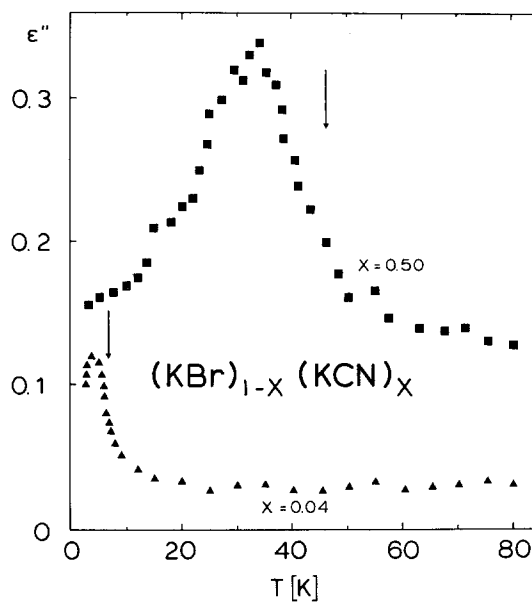


Fig. 7. The imaginary part of the dielectric constant as a function of temperature. The arrows indicate where the maxima of the corresponding real parts occur. The measuring frequency is 100 kHz

reference system KBr. The values for  $T_F$  are collected in Table 1.

Related anomalies were observed in the temperature dependence of the imaginary part  $\epsilon''$ . The temperatures of the maximum of  $\epsilon''$  were always somewhat lower than the temperatures of maximum  $\epsilon'$ , but showed the same increase with frequency and CN-concentration (Figs. 6 and 7).

### III. Analysis of the Results

The complex dielectric constant of a cubic crystal is defined via the susceptibility  $\chi$  by the scalar equation

$$\varepsilon = 1 + 4\pi\chi. \quad (1)$$

The dipolar susceptibility  $\chi_0$  for a system of non-interacting classical dipoles with the dipole moments  $p_0$  is given by

$$\chi_0 = \frac{N}{V} \frac{p_0^2}{k_B T}. \quad (2)$$

$N$  is the number of dipoles per volume  $V$ . Assuming a paraelectric relaxation process one can use Debye's formula for the frequency dependent susceptibility

$$\chi(\omega) = \chi_0 \cdot (1 - i\omega\tau)^{-1} \quad (3)$$

where  $\omega$  is the measuring frequency and  $\tau$  is the relaxation time. This form implies that reorientation processes which are much slower than the measuring time  $1/\omega$  no longer contribute to the response. The simplest form for the temperature dependence of  $\tau$  is the Arrhenius law:

$$\tau = \tau_0 \exp(E_0/k_B T). \quad (4)$$

$1/\tau_0$  is the attempt frequency and  $E_0$  the energy barrier of the hindering potential.

On the basis of the Clausius-Mosotti-equation the dielectric constant of the mixed system  $(\text{KBr})_{1-x}(\text{KCN})_x$  is given by

$$\frac{\varepsilon'(\omega) - 1}{\varepsilon'(\omega) + 2} = \frac{\chi'(\omega)}{\chi'(\omega) + 3/4\pi} - \frac{\varepsilon_0 - 1}{\varepsilon_0 + 2} \quad (5)$$

with

$$\chi'(\omega) = \chi_0 (1 + \omega^2 \tau^2)^{-1}. \quad (6)$$

$\varepsilon_0$  is the dielectric constant of the background system which describes the ionic polarizabilities of the  $\text{K}^+$ ,  $\text{Br}^-$  and  $\text{CN}^-$  ions. The imaginary part of the dielectric constant follows from equation (1) as

$$\varepsilon''(\omega) = 4\pi\chi''(\omega) \quad (7)$$

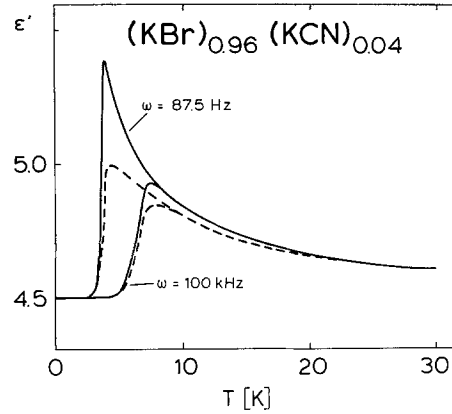
where  $\chi''(\omega)$  is the imaginary part of the susceptibility of equation (3)

$$\chi''(\omega) = \omega\tau\chi_0 \cdot (1 + \omega^2\tau^2)^{-1}. \quad (8)$$

For a calculation of  $\varepsilon(\omega)$  we used a CN dipole moment of  $0.2D$  and the experimental values of KBr as background. The parameters  $\tau_0$  and  $E_0$  were determined from a fit to the freezing temperatures over ten decades of frequency as described in our recent publication [11]. The resulting values are listed in Table 2. Figure 8 shows the temperature dependence of the dielectric constant calculated for the concentration  $x=0.04$  and frequencies of 87.5 Hz and

**Table 2.** The energy barriers  $E_0$  and the attempt frequencies  $\tau_0$  in  $(\text{KBr})_{1-x}(\text{KCN})_x$  (from [11])

$x$	$E$ (K)	$\tau_0$ (s)
0.04	57	1.2E-9
0.14	550	1.0E-16
0.25	600	1.0E-15
0.50	1,160	1.2E-17

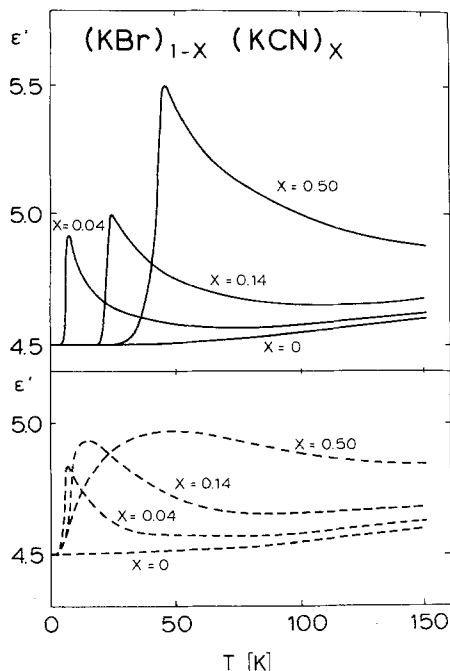


**Fig. 8.** The calculated temperature dependence of the real part of the dielectric constant. The solid line is the result of the Debye model with an Arrhenius law for the relaxation time; the broken line is obtained by considering additionally mean random fields

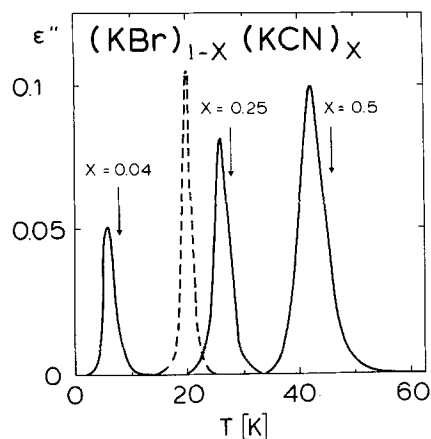
100 kHz as solid lines. Here the concentration  $x$  enters via the number of dipoles per unit volume  $N/V$  in (2). Comparing to the corresponding experimental results of Fig. 1 one notes a general qualitative agreement, but the cusp of the calculation is by far too sharp and too high. Figure 9 shows  $\varepsilon'(T)$  as predicted for  $x=0.04$ , 0.14 and 0.50. Even at these higher concentrations the model yields relatively sharp cusps, the height of which increases strongly with  $x$ , and a Curie behaviour on the high temperature side. This is in contradiction to the experimental data (Fig. 5) where broad maxima of about concentration independent height were observed.

Related discrepancies exist between the experimental and the calculated temperature dependence of  $\varepsilon''$ . Again the maxima calculated for  $\varepsilon''(T)$  are too sharp (Fig. 10). The calculation reproduces however correctly that the maxima of  $\varepsilon''(T)$  occur at slightly lower temperatures than the maxima of  $\varepsilon'(T)$ .

The Debye model complemented by an Arrhenius law for the relaxation time  $\tau$  gives a qualitative understanding for the occurrence of a cusp in  $\varepsilon(T)$ . The shortcoming of the model is that it fails to explain the concentration dependence of  $\varepsilon$  in a satisfactory way even if the free parameters  $\tau_0$  and  $E_0$  are adjusted for each CN concentration separately.



**Fig. 9.** The calculated temperature dependence of the real part of the dielectric constant at 100 kHz. The upper part shows the results of the Debye model with an Arrhenius law for the relaxation time; the lower part is obtained by considering additionally mean random fields



**Fig. 10.** The calculated temperature dependence of the imaginary part of the dielectric constant at 100 kHz – the arrows indicate the calculated maxima of the corresponding real parts – as predicted by the Debye model. The dashed line gives the result for  $x = 0.25$  at 87.5 Hz

It is obvious that for the high concentrations studied the CN–CN interactions are no longer negligible. The model from above is strictly speaking a single ion model, it incorporates artificially the effects of the interactions into the free parameters  $\tau_0$  and  $E_0$ , for  $x = 0.50$  for example it yields an unrealistic value of 1000 K for the potential barrier  $E_0$  between two easy orientations of the CN molecule.

The importance of the interion coupling can be gathered from the distinct deviations from the Curie law for  $T > T_F$  and from the fact that there is no simple scaling of  $\epsilon$  with the concentration  $x$ . The CN interactions are presumably rather complex. Not only direct dipolar and quadrupolar coupling may contribute but also an indirect coupling mediated by lattice strains. In order to consider the interactions we follow the mean random field approximation which was originally developed by Klein et al. [16] and applied to  $\text{OH}^-$  ions in KCl at very low concentrations. The electric mean fields  $E$  were described by a probability distribution  $P(E)$  of Gaussian or Lorentzian shape. The following results on the dipolar susceptibility were obtained: *i*) for  $T \rightarrow 0$   $\chi'$  approaches a concentration independent value, *ii*)  $\chi'(T)$  has a maximum at a temperature  $T_F$ , *iii*)  $\chi'(T_F)$  is independent of  $x$  and *iv*) the deviations from the Curie law at high temperatures are proportional to  $(x/T)^2$ . Later on this model has been extended on the problem of CN defects interacting via strain fields in alkali halide crystals [17].

This mean random field approach combined with an Arrhenius type susceptibility was used by Eiselt et al. [18] in a calculation of the magnetic susceptibility of clusters of spins in the magnetic insulator  $(\text{SrS})_{1-x}(\text{EuS})_x$ . Guided by Monte Carlo studies these authors modify the distribution  $P(E)$  to accommodate  $P(E \rightarrow 0) \propto E$ . The high temperature limit yields again the Debye behaviour of equation (6) whereas at low temperatures where only  $P(E \rightarrow 0)$  is important a correction factor has to be included which forces  $\chi' \rightarrow 0$  for  $T \rightarrow 0$ . An interpolation between the two limiting cases gives a temperature dependence of the form [18]

$$\tilde{\chi}'(\omega) = \chi'(\omega) [1 + (x \cdot g/T)^2]^{-1} \quad (9)$$

where  $g$  is a coupling constant.

Adapting these results to the present situation  $\epsilon'$  was calculated from equation (5) after replacing  $\chi'(\omega)$  by  $\tilde{\chi}'(\omega)$ . The results obtained with unique values for  $E_0$  and  $\tau_0$  independent of the concentration, namely 57 K and  $1.2 \cdot 10^{-9}$  s, and a coupling  $g$  of 90 K are shown in Figs. 8 and 9b as dashed lines. The improved model accounts in a semiquantitative way for the experimental observations on the dielectric constant over a wide range of concentrations by introducing only three parameters  $\tau_0$ ,  $E$  and  $g$ . This success may justify the application of the mean random field treatment in general and the assumptions on the distribution  $P(E)$  and the rigorous interpolation in particular. The results show that any description of the orientational glass state in  $(\text{KBr})_{1-x}(\text{KCN})_x$  will be confronted with the fact

that the single ion anisotropy, characterized by the parameter  $E_0$ , and the effective interion coupling, represented by the parameter  $g$ , are of comparable strength. A more sophisticated model should include the phonon modulation of the Devonshire potential and of the CN–CN coupling [9].

#### IV. Summary

In the present work we have shown that the dielectric response of  $(\text{KBr})_{1-x}(\text{KCN})_x$  is very similar to the magnetic susceptibilities of spin glass systems. The real and the imaginary part of the dielectric constant show maxima at characteristic temperatures which increase with the CN concentration and the measuring frequency. Thus the results strongly support the existence of an orientational glass state. A semiquantitative description was achieved with a Debye model for the single ion susceptibility where the relaxation time follows an Arrhenius law and a CN–CN coupling which is approximated by a mean field distribution of the shape proposed by Eiselt et al. [18].

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