



DIELECTRIC RESPONSE OF KCN CRYSTAL AT ULTRA LOW FREQUENCIES

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The dielectric response of pure KCN crystals (ϵ' , ϵ'' and $\text{tg } \delta$) has been measured as a function of temperature in the frequency range 10^{-2} Hz to 10^4 Hz. In the antiferroelectric phase the width of the loss peak are found practically independent of temperature (1.4 decades) and close to a Debye behavior; the relaxation time of the CN^- dipoles is characterized by an Arrhenius behavior $\tau = \tau_0 \exp(U/KT)$ with $\tau_0 = 7.26 \times 10^{-15}$ s and $U = 0,147$ eV confirming a classical temperature activated reorientation of the dipoles.

The study of the reorientation and collective ordering behavior of linear diatomic ions in ionic solids is a field of great interest. Pure alkali cyanides (NaCN, KCN, RbCN and CsCN) are among the many components which have been extensively investigated both experimentally and theoretically. The anisotropic properties of the CN^- molecular ion are of two types:

- a) an elastic dipole tensor due to the non spherical shape of the molecular ion.
- b) an electric dipole vector due to the asymmetric head and tail charge distribution of the molecule.

KCN crystallizes from the melt in the NaCl structure^{1,2}. At high temperature anion sites have an octahedral pseudocubic symmetry due to the fast reorientation of the CN^- ions^{3,4}. As the temperature is lowered this compound exhibits at 168 K a structural phase transition of first order to a body centered orthorhombic structure^{5,6}. The CN^- axis align along the $\langle 110 \rangle$ directions of the original cubic structure but the sense of the ions do not. This means that the electric quadrupolar moment orders but the electric dipole moment does not; the CN^- ions are still rapidly orienting head and tail. The order is purely elastic⁷. A second transition occurs at 83 K where the CN^- ions become ordered in an antiferroelectric manner⁸⁻¹⁰. In this phase the head to tail reorientations of the CN^- ions are still present but occur at a much lower rate which gradually diminishes with the temperature until obtaining a full ordering at 0 K. The structure is primitive orthorhombic. Reorientation and ordering involve the rotation of the molecule within a rigid fixed lattice as well as sizeable deformations of the lattice due to strong anisotropic coupling of the CN^-

with its surrounding.

The average time between the reorientation of CN^- ions in alkali cyanides has been experimentally measured over eleven decades of value using NMR technique¹¹⁻¹³, dielectric techniques¹⁴⁻¹⁷ in the frequency range 50 Hz to 100 KHz and ionic thermal conductivity (ITC)¹⁷, a practically dc technique.

In this communication we present new data of the dielectric response of pure KCN single crystals measured in the frequency range 10^{-2} to 40 Hz as well as data for higher frequencies¹⁸ confirming the previous results. The new data fill partly the frequency range between ITC and earlier high frequency measurements.

The dielectric response (ϵ' , ϵ'' and $\text{tg } \delta$) has been measured at high frequency with a commercial capacitance bridge (General Radio model 1615-A). The response at low frequency was obtained with an equipment developed in our laboratory¹⁹⁻²⁰. This equipment measures the current amplitude flowing through the sample $I = I_0 e^{j(\omega t + \phi)}$ and its phase difference with the applied voltage $V = V_0 e^{j\omega t}$ using modern digital techniques; the frequency range is automatically scanned. The dielectric parameters are given by

$$\epsilon' = \frac{I_0}{\omega C_0 V_0} \cos \delta \quad \epsilon'' = \frac{I_0}{\omega C_0 V_0} \sin \delta$$

$$\text{tg } \delta = \frac{\epsilon''}{\epsilon'}$$

where C_0 is the geometrical capacitance of the sample $C_0 = \epsilon_0 \frac{S}{d}$.

The crystals have been grown in our labo-

boratory by the Czochralsky technique using Merck pro analysis material. The samples (area $15 \times 10 \text{ mm}^2$) have been cleaved or cut in thin slices and then finely polished until obtaining thicknesses of the order of $d = 0,4$ to $0,5 \text{ mm}$. Gold electrodes with guard rings have been evaporated on both faces. The sample holder was designed such that the crystal is standing almost free in the cell in order to avoid mechanical stresses¹⁸. Miniature coaxial cable are soldered on the electrodes with silver paint. The measurements have been performed in a Supravartemp Janis cryostat (helium gas cooling) where the crystal temperature is measured with a calibrated diode sensor and regulated to $\pm 0,1 \text{ K}$.

Figure 1 shows the temperature behavior of the dielectric constant ϵ' measured at 1 KHz (dotted line) and at lower frequencies: ~ 40 , 10 , 1 , 10^{-1} and 10^{-2} Hz . All the data have been taken with decreasing temperatures. For $T < 250\text{K}$

the curves appeared slightly shifted toward higher values of ϵ' as the frequencies decrease. The same behavior has been observed for pure KBr crystals; this peculiar behavior are thought to arise from electronic difficulties in the precise calibration of the electrometer response as a function of the frequency¹⁸⁻²⁰. The increase observed at low frequency for $T > 250 \text{ K}$ is however a real effect of polarization which becomes important at extremely low frequencies already near room temperature²¹. The jump in ϵ' at the ferroelastic phase transition and which is not accompanied by a dielectric loss occurs always at the same temperature $T = 168 \text{ K}$ independently of the frequency of the applied field. It shows however a thermal hysteresis (not shown).

Figure 2 shows in more details the behavior of ϵ' and $\text{tg } \delta$ in the antiferroelectric phase as a function of temperature measured for different frequencies (10^{-2} to 10^4 Hz). The curves

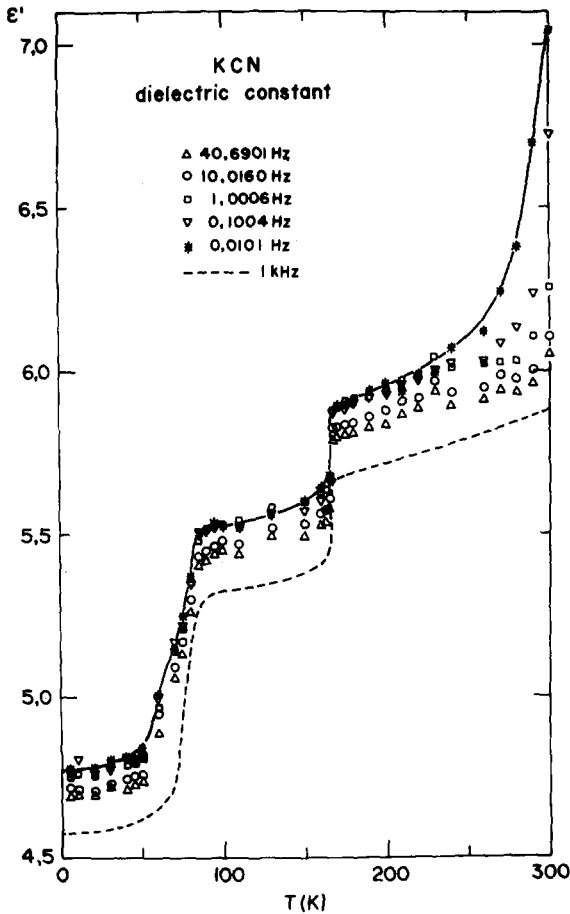


FIG. 1 Temperature dependence of the dielectric constant ϵ' of pure KCN measured at 40 Hz (Δ), 10 Hz (\circ), 1 Hz (\square), 10^{-1} Hz (∇) and 10^{-2} Hz ($*$) with our low frequency equipment. The dotted curve, shows as reference, has been obtained at 1 KHz with a commercial bridge Genrad 6015-A.

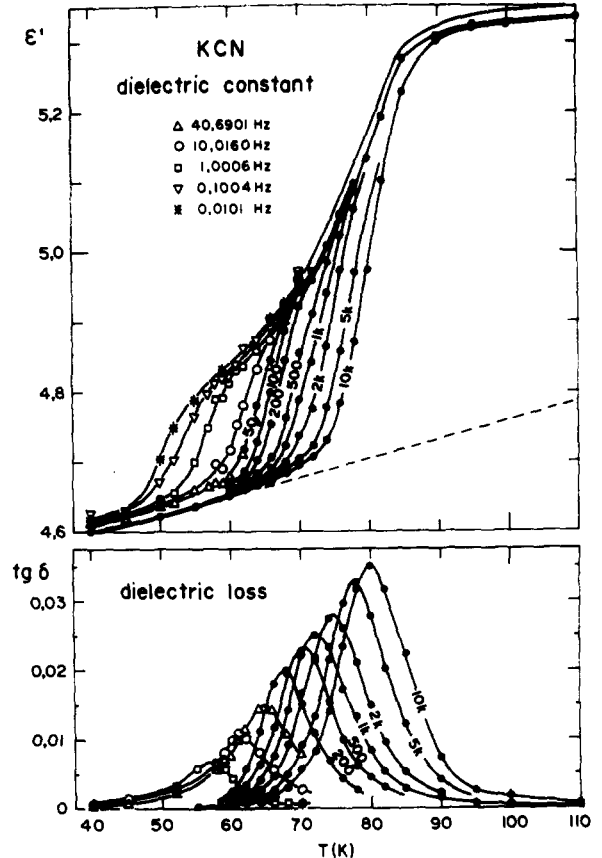


FIG. 2 Temperature dependence of the dielectric constant ϵ' and $\text{tg } \delta$ of pure KCN in the antiferroelectric region measured at various frequencies $f = 10^{-2}$ to $f = 10^4 \text{ Hz}$. The curves have been slightly shifted downwards (see text). The dotted line is an extrapolation and represents the expected temperature variation of the dielectric constant at high frequencies ϵ_∞ (see also fig.4).

of ϵ' have been slightly shifted downwards in order to practically coincide at $T < 40$ K. As the frequency diminishes we clearly observe a shift and a decrease of ϵ' and of the dielectric loss ϵ'' towards lower temperatures showing that the dipole still reorient even at lower temperatures.

The temperature dependence of the dielectric loss peak shift in frequency is shown in figure 3. The data have been obtained from the

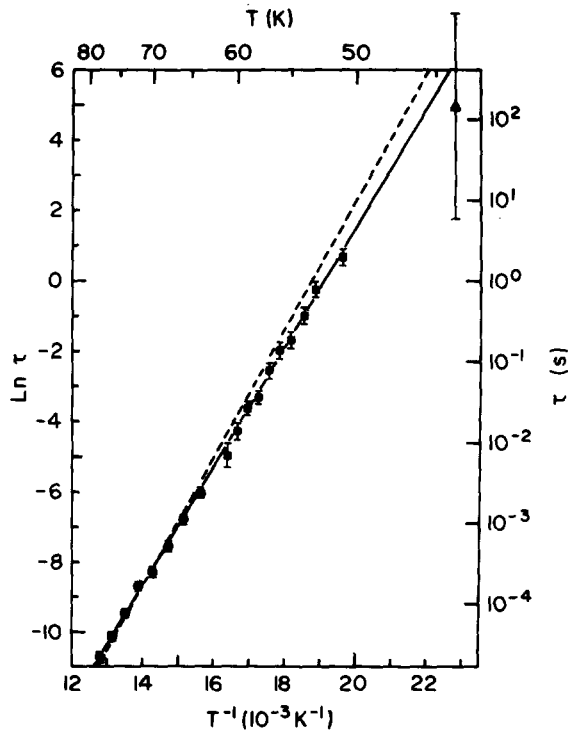


FIG. 3 Arrhenius plot of the relaxation time of CN^- dipoles versus inverse temperature $\tau = \tau_0 \exp(U/KT)$ with $\tau_0 = 7.26 \times 10^{-15}$ s, $U = 0,147$ eV obtained at high frequencies (\bullet) (Genrad bridge) and low frequencies (\blacksquare). The ITC result (\blacktriangle) is taken from reference 17. The bars represent the uncertainties of the measurements. The dotted line is the fit obtained by Luty et al¹⁷

maximum of the loss peaks. Also plotted in the figure is the result of the ionic thermal conductivity (ITC) technique obtained by Ortiz-Lopez¹⁶. The temperature dependence is perfectly fitted to an Arrhenius law behavior $\tau = \tau_0 \exp(U/KT)$ with $\tau_0 = 7.26 \times 10^{-15}$ s and $U = 0,147$ eV in good agreement with the values obtained by Luty et al¹⁷ (dotted line). The shape of the peaks are close to that predicted by the Debye equations. Their width at half maximum is practically constant in the temperature range studied; it varies only from 1.36 decades at 68 K to 1.44 decades at 53 K (to be

compared with 1.144 decades for the Debye equation). This effect can be interpreted as being produced by a distribution of relaxation times such as the Cole-Cole distribution proposed by Ortiz-Lopez¹⁶. The area under the ϵ'' curves in $\log_{10} \omega$ scale $A(\epsilon'')$ is directly related to the static susceptibility of the material

$$\epsilon_s - \epsilon_\infty = 4\pi\chi_s = 1.466 A(\epsilon'')$$

where ϵ_s and ϵ_∞ are respectively the dielectric constant of the material measured at zero frequency $\epsilon_s = \epsilon'(0)$ and at infinite frequency.

This area decreases with decreasing temperatures and corresponds to a diminution in the number of the mobile CN^- dipoles as a consequence of the gradual formation of the antiferroelectric ordered state with frozen-in electric dipoles. The difference between the curves $\epsilon'(10^{-2}$ Hz) and $\epsilon'(\infty)$ (dotted line extrapolated in figure 2) is plotted in figure 4 with

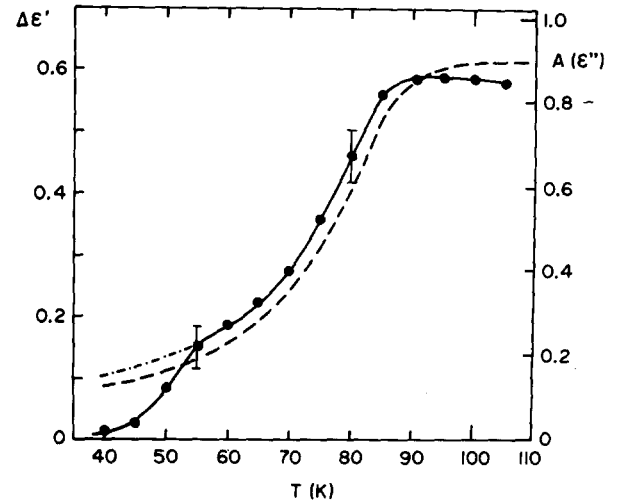


FIG. 4 Temperature dependence of the difference between the dielectric constant ϵ' measured at 10^{-2} Hz and at infinite frequency (dotted curve extrapolated of figure 2). For $T > 55$ K it represents the difference $\Delta\epsilon = \epsilon_s - \epsilon_\infty = 1.466A(\epsilon'')$ where $A(\epsilon'')$ is the integrated loss area (dotted line as measured by Ortiz-Lopez¹⁶). The drop of ϵ' observed for $T < 55$ K shows that the dipoles still not frozen-in cannot respond to the low frequency applied field (10^{-2} Hz).

the results of Ortiz-Lopez¹⁶ for $A(\epsilon'')$. The agreement is found reasonable for $T > 55$ K and confirms the model of random internal field with a simple block function distribution of local electric fields $P(E_B)$, symmetric with respect to $E_B = 0$. Down to 55 K the curve $\epsilon'(10^{-2}$ Hz) is therefore a good approximation of the static value of the dielectric constant $\epsilon'(0)$. At

T = 55 K most of the dipoles are frozen-in and the drop observed below this temperature reflects the fact that these dipoles still mobile cannot respond to the low frequency applied field (10^{-2} Hz).

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