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DIELECTRIC RESPONSE OF KCN CRYSTALS AT ULTRA-LOW FREQUENCIES

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We describe an ultra low frequency equipment employing programable digital technique. The system is used to measure the dielectric parameters ε', ε'' and tg δ of pure KCN crystals as a function of temperature in the frequency range 10^{-2} Hz to 40 Hz. The relaxation time of the CN^- dipoles presents a classical temperature activated reorientation behavior characterized by an Arrhenius law $\tau = \tau_0 \exp(U/kT)$ with $\tau_0 = 7.26 \times 10^{-15}$ s and $U = 0.147$ eV.

INTRODUCTION

Pure alkali cyanides crystals have been extensively studied experimentally and theoretically for the interesting anisotropic properties of reorientation and collective ordering behavior of the CN^- molecular ion. The CN^- can be described as an elastic dipole tensor due to its non spherical shape and as an electric dipole vector due to its asymetric head and tail charge distribution. Pure KCN suffers a first order structural phase transition from a cubic NaCl structure to a body centered orthorhombic one at 168 K.[1,2] The CN^- axis aligns along the $\langle 110 \rangle$ directions of the original cubic structure with ordered elastic quadrupole moments while the electric dipoles are still disordered relative to their head and tail. The order is therefore purely elastic.

A second order phase transition occurs at about 83 K in which the CN^- ions order antiferroelectrically.[3] The head and tail reorientation of the CN^- occurs at a much lower rate and gradually diminishes with the temperature becoming fully ordered at 0 K. The crystallographic structure is primitive orthorhombic.

Several techniques have been already used to measure the average time between CN^- reorientations. We describe an ultra-low frequency equipment employing digital technique[4] which has been adapted to obtain new data of the dielectric parameters of pure KCN (ε', ε'' and tg δ) in the frequency range 10^{-2} to 40 Hz filling the frequency range between ITC[5] and the high frequency data.[5–7]

DESCRIPTION OF THE LOW FREQUENCY EQUIPMENT

At low frequency a dielectric material can be represented by a resistance R and a capacitor C mounted in parallel or in serie. In the first case the current $i(t)$ (amplitude I) flowing through the dielectric leads the voltage $v(t)$ (amplitude V) by the phase angle $((\pi/2) - \delta)$.

$$i(t) = (R^{-1} + j\omega C)v(t) = C_0(\varepsilon'' + j\varepsilon')v(t)$$

where C_0 is the geometrical capacitance of the sample. In a complex plane

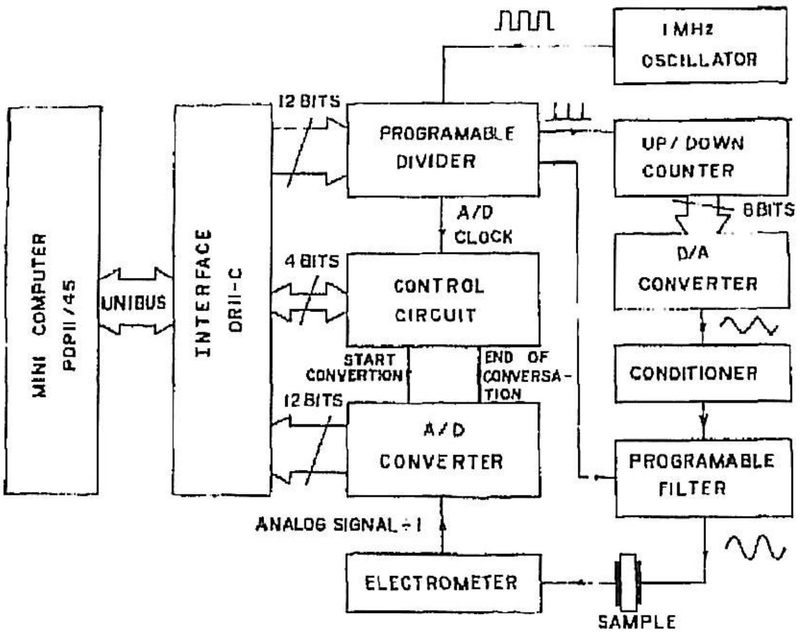

FIGURE 1 Block diagram of the ultra-low frequency equipment.

representation

$$\varepsilon' = \frac{I}{\omega C_0 V}\cos\delta \qquad \varepsilon'' = \frac{I}{\omega C_0 V}\sin\delta$$

The block diagram of the system is shown in Figure 1; it measures accurately the variables I and δ for a given applied voltage (V, ω). It consists mainly of a programable ultra-low frequency generator (ULF) whose output (up to 10 V) is applied to the sample. An electrometer based on an Analogic Devices AD42L integrated circuit measures the current flowing through the dielectric with a minimum current sensitivity of 10^{-13}A and converts it into a voltage having a phase difference ϕ with respect to the applied voltage on the sample. The output voltage is digitalized. Its amplitude and the phase difference ϕ are determined using Fourier series analysis technique. ε', ε'', tg δ and other control parameters such as the reproducibility and the harmonic distortion are then calculated. The whole system is controlled by a computer which allows a totally automated data acquisition scan between 10^{-4} and 40 Hz. The phase angle φ introduced by the sample only is slightly different from the measured phase angle ϕ, and corrections determined experimentally must be taken into account.

Comparing tests using different calibrated capacitors at 50 Hz, made with a General Radio bridge 1615-A, show that determination of the capacitance agrees within 3% for a capacitor of the order of 1 to 10 pF and 0.5% for capacitor larger than 10 nF.

EXPERIMENTAL RESULTS[8,9]

Pure KCN crystals grown in our department were cleaved or cut and polished to a size of about $15 \times 10 \times 0.5$ mm^3. Gold electrodes with guard rings were evaporated on both faces. The samples were mounted in a Supervaritemp Janis cryostat on a sample holder especially designed in order to avoid crystal stress.

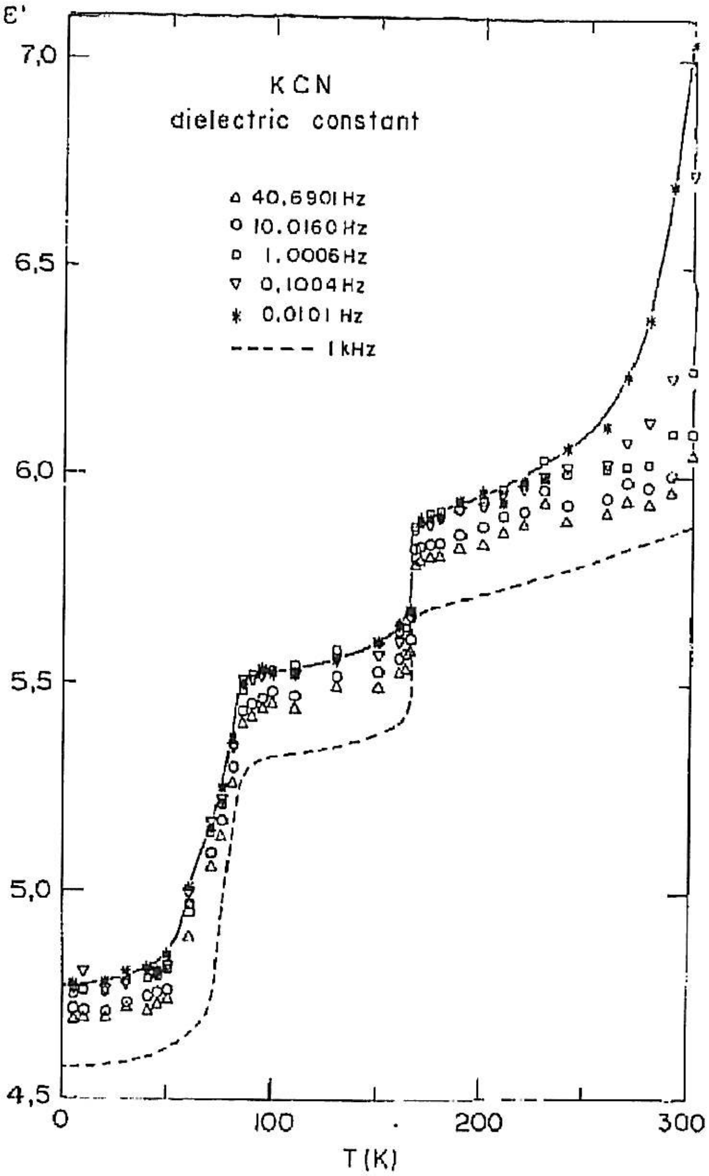

FIGURE 2 Temperature dependence of the dielectric constant ε' of pure KCN measured at 40 Hz (△), 10 Hz (○), 1 Hz (□), 10^{-1} Hz (▽) and 10^{-2} Hz (*). The dotted curve, shown as reference, has been obtained at 1 kHz with a commercial bridge Genrad 1615-A.

Figure 2 shows the temperature behavior of the dielectric constant ε' measured at 1 kHz (Genrad bridge 1615-A) and at lower frequencies with the ULF equipment. The curves appeared slightly shifted toward higher value of ε' as the frequency decreases. Such a behavior has also been observed for pure KBr crystals, and arises from electronic difficulties in the calibration on the frequency response of the electrometer. For $T > 250$ K the increase of ε' for the lower frequencies is a real polarization effect which becomes important at room temperature for these low frequencies.[10] The jump at 168 K always occurs at the same temperature, independently of the frequency and is not accompanied by a dielectric loss.

Figure 3 shows in more detail the behavior of ε' and tg δ in the antiferroelectric phase as a function of the temperature for frequencies varying from 10^{-2} to 10^{4}Hz. The curves have been shifted downwards in order to coincide at $T < 40$ K. A clear shift toward lower temperature and a decrease of ε' and tg δ is seen when the frequency diminishes. This shows that the dipoles still reorient even at the lowest temperatures.

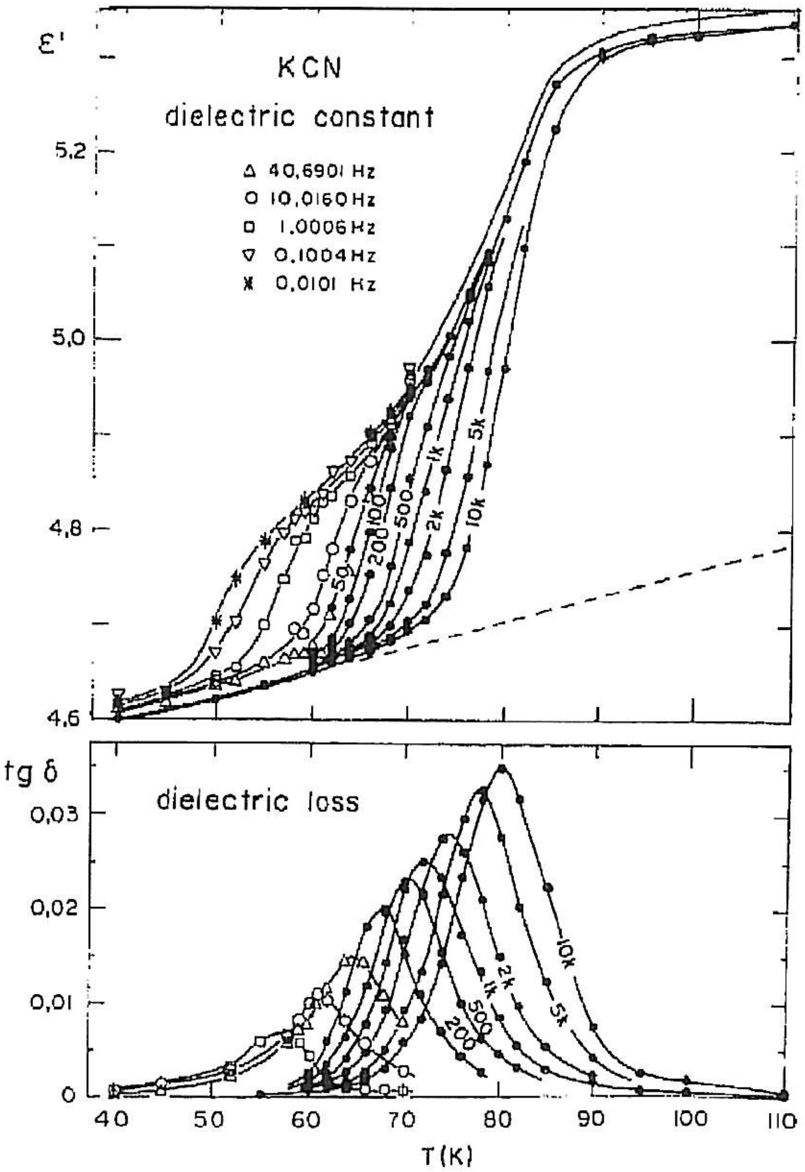

FIGURE 3 Temperature dependence of the dielectric constant ε' and tg δ of pure KCN in the antiferroelectric region. The dotted line is an extrapolation and represents the expected temperature variation of the dielectric constant at high frequencies (see also Figure 5).

The temperature dependence of the dielectric loss peak shift in frequency is shown in Figure 4; the experimental points are taken from the maximum of the loss peak measured as a function of the frequency. The result of an ITC measurement[5] is also shown. The temperature dependence is fitted with an Arrhenius law $\tau = \tau_0 \exp(U/kT)$ with $\tau_0 = 7.26 \times 10^{-15}$ s and $U = 0.147$ eV, showing good agreement with the values obtained by Lüty *et al.*[5] The shape of the peaks is close to that predicted by the Debye equation and their width at half maximum($\sim$1.4 decades) is practically constant in the temperature range studied. The area A(ε'') under the ε'' curves plotted in a $\log_{10}\omega$ scale is related to the static susceptibility of the crystal $\chi_s/\varepsilon_s - \varepsilon_\infty = 4\pi\chi_s = 1.466$ A (ε'').

The difference between the curves $\varepsilon'(10^{-2}$ Hz) and $\varepsilon'(\infty)$ is compared in Figure 5 with the results of A(ε'') of Ortiz-Lopez;[7] the agreement is 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 $E_B = 0$ proposed by this author. The curve $\varepsilon'(10^{-2}$ Hz) is therefore a good approximation of the static value of the dielectric constant $\varepsilon'(0)$. The drop

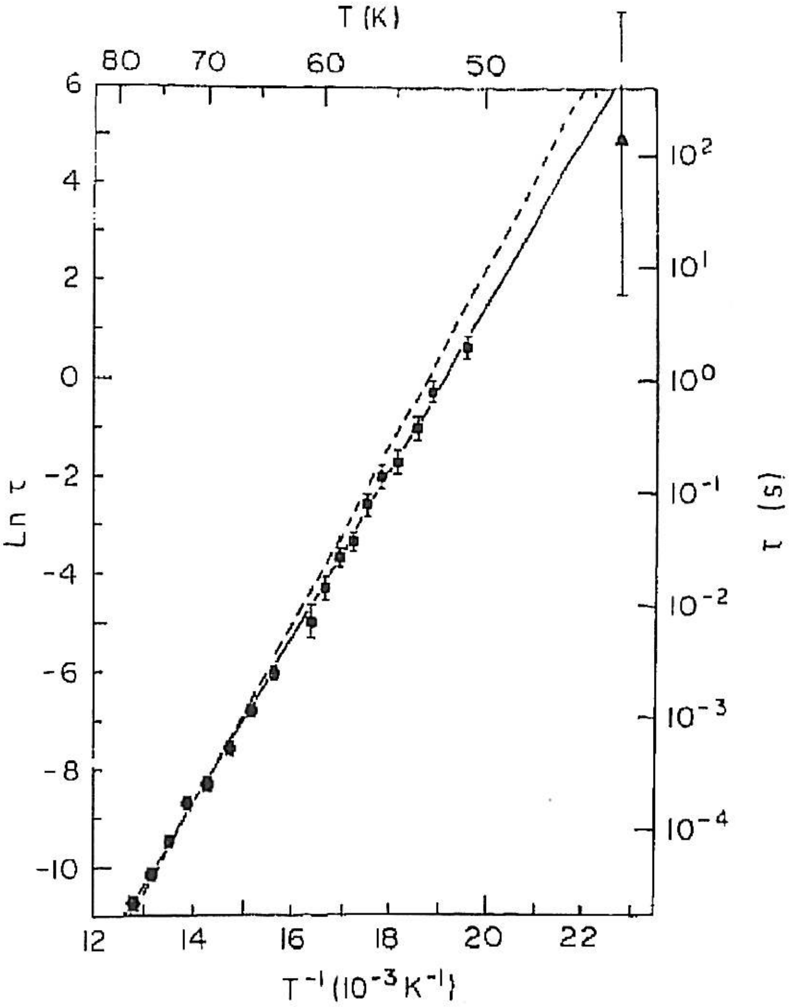

FIGURE 4 Arrhenius plot of the relaxation time of CN⁻ dipoles versus inverse temperature $\tau = \tau_0 \exp(U/kT)$ with $\tau_0 = 7.26 \times 10^{-3}$ s, $U = 0.147$ eV; (●) high frequencies data, (■) low frequencies ULF system. The ITC result (▲) and the dotted line are from Lüty *et al.*[5]

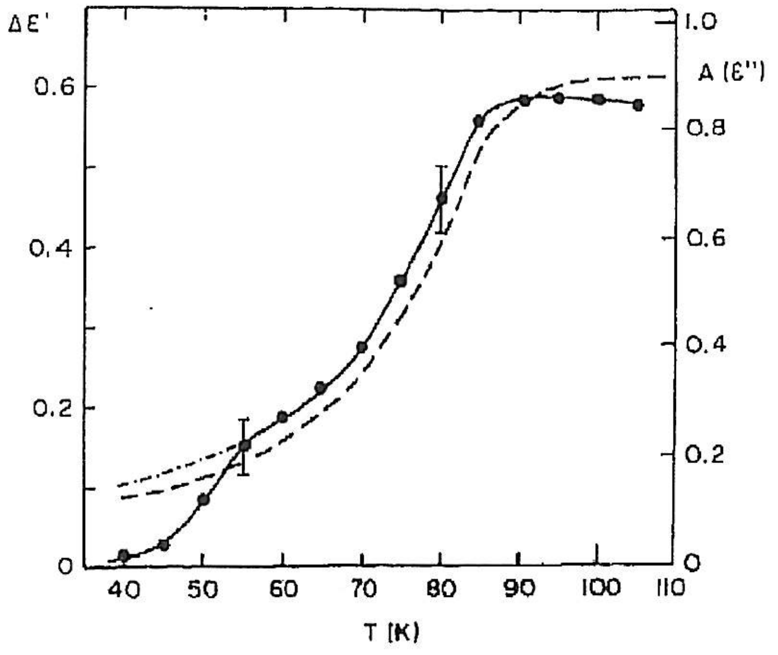

FIGURE 5 Temperature dependence of the difference between $\varepsilon'(10^{-2}$ Hz) and ε_∞ (dotted curve of Fig. 3) proprotional to the static susceptibility χ_s. The dotted line is the integrated loss area $A(\varepsilon'')$ measured by Ortiz-Lopez.[7]

observed below 55 K shows that the small number of dipoles still mobile at these temperatures cannot respond to the low frequency (10^{-2} Hz) applied field.

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