Vol. A57 (1980) ACTA PHYSICA POLONICA No 3

# DIELECTRIC RELAXATION IN POTASSIUM FERROCYANIDE TRIHYDRATE

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*(Received June 7, 1979)*

Dielectric permittivity and dielectric losses of $K_4Fe(CN)_6 \cdot 3H_2O$ along the ferroelectric direction have been measured at 1 kHz, 10, 85, 150, 250, 600, 1000 and 1500 MHz as a function of temperature. Dielectric relaxation was observed in the paraelectric region. The former relaxation was of the Debye type with a single relaxation time even in the immediate vicinity of the Curie point. It was found that the distribution of the relaxation times is observed only in the case of twinned crystals and other crystals with a certain amount of dislocations and imperfections.

## 1. *Introduction*

Potassium ferrocyanide trihydrate $K_4Fe(CN)_6 \cdot 3H_2O$ in the paraelectric phase crystallizes in the monoclinic system, space group $C_{2h}$ [1], with four molecules per unit cell.

The basis vectors of the unit cell are

$$a = c = 9.32\ \text{Å} \quad \text{and} \quad b = 16.64\ \text{Å}, \quad \beta = 100°.$$

At 26.5°C the substance undergoes a second order phase transition and the space group becomes $C_s^4$ [2]. The crystal has an inversion symmetry centre and a twofold rotation axis along [010] above $T_c$; below $T_c$ the only elements of symmetry reflection plane perpendicular to [010] are observed. The water molecules are located in two-dimensional layers perpendicular to the [010] axis (Fig. 1).

Between the two layers of water molecules there are two layers of $[Fe(CN)_6]^{-4}$ groups and interspersed potassium ions with the iron nuclei located at the centre of a regular octahedra of cyanide ions (Fig. 2). It seems that in many respects, potassium ferrocyanide trihydrate provides a good system for a detailed study of the ferroelectric state by dielectric relaxation measurements. Although the crystal structure is fairly complicated, one expects that a major contribution to ferroelectricity arises from the water molecular-dipole mo-

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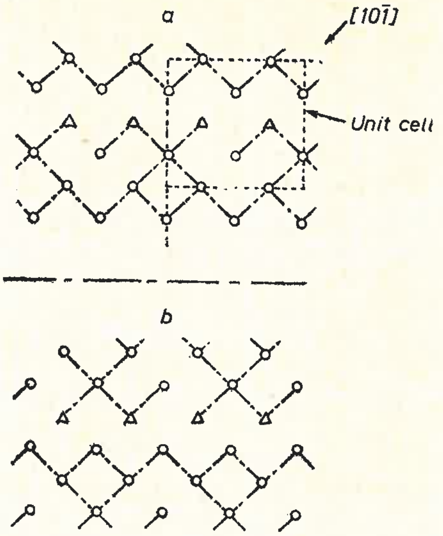

**Fig. 1.** a) Hydrogen bonding between a layer of water molecules in potassium ferrocyanide trihydrate, b) The polarization reversed state Oxygen: ○, Nitrogen: △

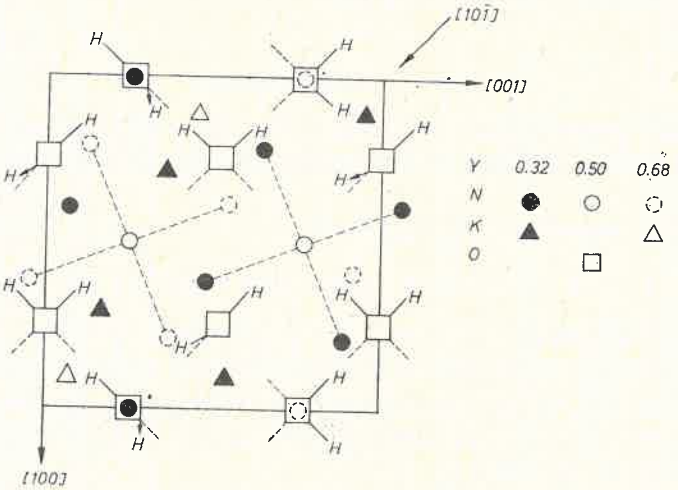

Fig. 2. Orientation of the water molecular $y = 0.50$ layer only in potassium ferrocyanide trihydrate. The O—H bonds that are approximately in the *ac* plane or approximately parallel to the *b* axis are shown as ——— or ———→ respectively. The orientation on polarization reversal is shown by dotted lines

ments. The water molecules in $K_4Fe(CN)_6 \cdot 3H_2O$ are bound chiefly by the relatively weak hydrogen bonds. Thus to obtain a satisfactory approximation, it is necessary to consider only electric dipole-dipole and hydrogen-bonding forces in the construction of a model for ferroelectricity in this crystal.

## 2. *Experimental*

Crystals of $K_4Fe(CN)_6 \cdot 3H_2O$ were obtained by slow evaporation of saturated aqueous solutions containing, a small amount of KCN. The quality of the crystal was found to be improved by the presence of KCN which prevent the formation of twinning. The crystals should be grown from fresh solutions, because solutions more than two weeks old become dark, even if stored in darkness and tend to produce the twinning crystals in the $a-c$ plane.

Only the well formed optically transparent and untwinned crystals were used in our experiments. To check whether the crystals were untwinned, observations were performed under a microscopic in polarized light.

The crystals were cut perpendicularly to the cleavage plane (010) and polished to the required dimensions. After polishing the sample, electrodes of conducting silver paint were applied to the polished parallel surfaces, which were exactly perpendicular to the [101] direction (ferroelectric direction).

The static dielectric permittivity was measured at 1 kHz using a MERATRONIK Automatic C Bridge type E-315 A. The crystal was placed in a special sample holder [3] which was cooled down along with the liquid nitrogen, which passed through the heat exchanger provided in the heater and temperature sensor connected to the I — D — P temperature controller. The temperature of the crystal was measured with a copper--constantan thermocouple to accuracy of ±0.1 K.

The dielectric permittivity and dielectric losses were measured in the range 10 kHz--30 MHz on an Inco Q-meter MQL-5 type; in the range 30 MHz–4 GHz by means of coaxial measuring lines. Rohde-Schwarz LHMBN — 3916/50 for 80–300 MHz and Orion type EZN-1 for 500 MHz–4 GHz supplied by generators Orion type 1271, Rohde-Schwarz type SLSV-BN 41002, Soviet G4 374 and G48. The standing wave ratio was measured by means of a VSWR meter Orion type T2A 201 or Unipan 327. In all cases a frequency modulation of 1 kHz was used. The principles of measurements were described previously [4, 5].

## 3. *Results and discussion*

Static dielectric permittivity has been measured over a wide temperature range 298--173 K in the $[10\bar{1}]$ direction. The results shown in Fig. 3 are in good agreement with previously published data [6]. In some cases the secondary anomalies below the transition temperature are observed, but they seem to be only due to the inhomogenities of the crystal. In the present experiment only crystals exhibiting the single well-defined peak were used. Another proof of the high quality of our crystals was the spontaneous polarization value. The highest quality of a crystal is indicated by the highest spontaneous polarization value (Fig. 4).

Fig. 5 and 6 show $\varepsilon'$ vs $T$ and $\varepsilon''$ vs $T$, respectively. In the case of higher frequency in the vicinity of the Curie point a sharp minimum is observed.

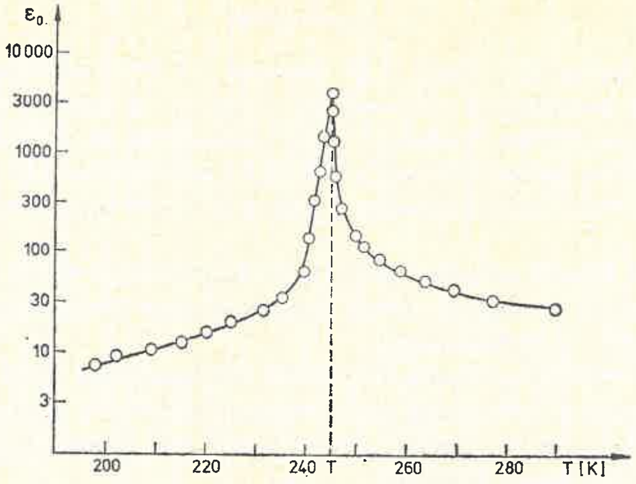

Fig. 3. Temperature dependence of the dielectric permittivity in $K_4Fe(CN)_6 \cdot 3H_2O$

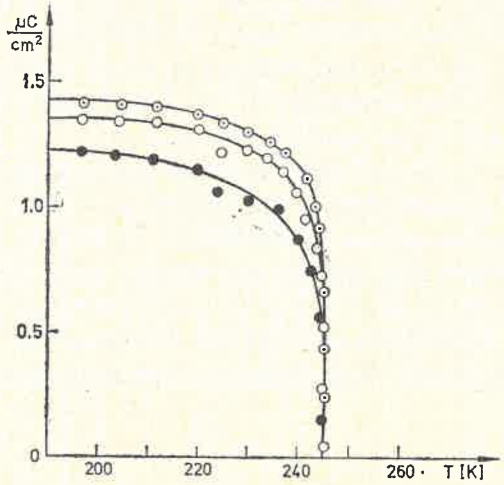

Fig. 4. The spontaneous polarization of $K_4Fe(CN)_6 \cdot 3H_2O$ versus temperature. ● — $P_s$ for a twinned sample, ○ — $P_s$ for the sample of optically transparent but with "nonsymmetrical" conoscopic figures, ⊙ — $P_s$ for the sample of optically transparent and "symmetrical" conoscopic figure

From the representation of the relaxation in terms of the Cole–Cole relation

$$\varepsilon(i\omega)-\varepsilon(\infty) = \frac{\varepsilon(0)-\varepsilon(\infty)}{1+(i\omega\tau)^{\beta}}, \tag{1}$$

the values of $\beta$ and $\tau$ were calculated using the following equation

$$\tau = \left\{\frac{\varepsilon''(\omega)}{[\varepsilon'(\omega)-\varepsilon(\infty)]\left[\sin\left(\beta\frac{\pi}{2}\right)-\varepsilon''(\omega)\cos\left(\beta\frac{\pi}{2}\right)\right]}\right\}^{\frac{1}{\beta}}\cdot\frac{1}{\omega}. \tag{2}$$

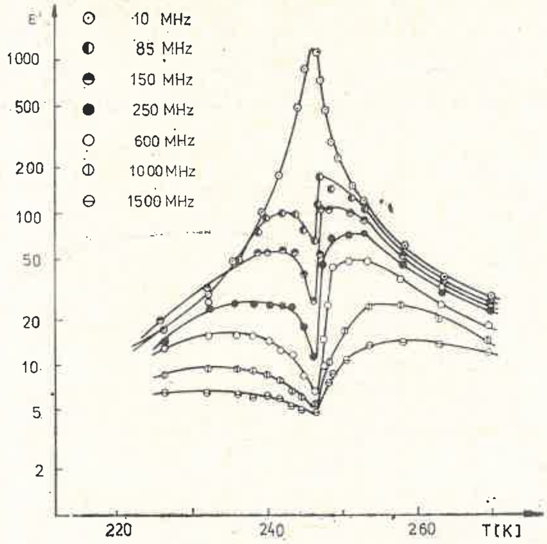

Fig. 5. The real part of the dielectric permittivity of $K_4Fe(CN)_6 \cdot 3H_2O$ versus temperature at various frequencies

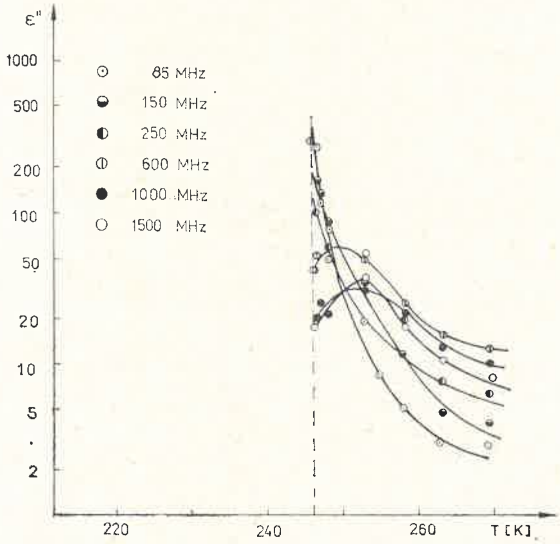

Fig. 6. The imaginary part of the dielectric permittivity of $K_4Fe(CN)_6 \cdot 3H_2O$ versus temperature at various frequencies

The Cole–Cole diagrams with the temperature as a parameter are presented in Fig. 7. The results reported in our article once more confirmed the monodispersive nature of the dielectric relaxation in ferroelectric crystals. However, a precise analysis of our results performed by means of the Yoshimitsu and Matsubara [7, 8] dispersion law in the immediate vicinity of the Curie point reveals a distribution for the relaxation times. The Yoshimitsu–Matsubara diagrams with $\beta$ as a parameter are shown in Fig. 8. In the vicinity of the Curie point the experimental results satisfy the curve with $\beta = 0.90$ and at $\frac{T-T_c}{T_c} > 0.01$ satisfied the curve with $\beta = 1$.

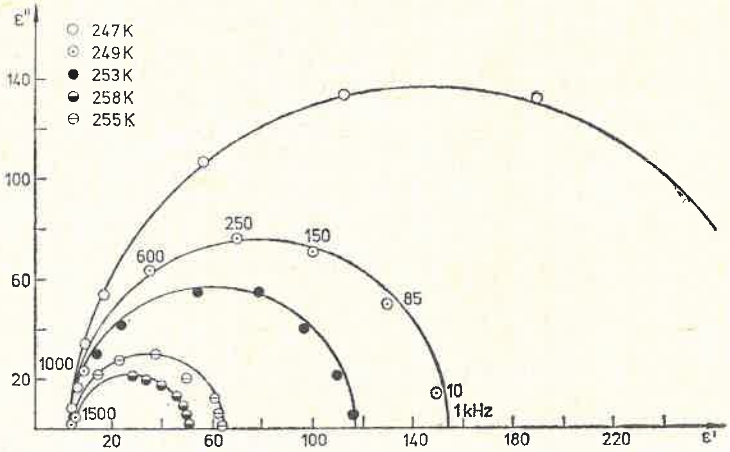

Fig. 7. Cole-Cole diagrams of $K_4Fe(CN)_6 \cdot 3H_2O$ with temperature as a parameter

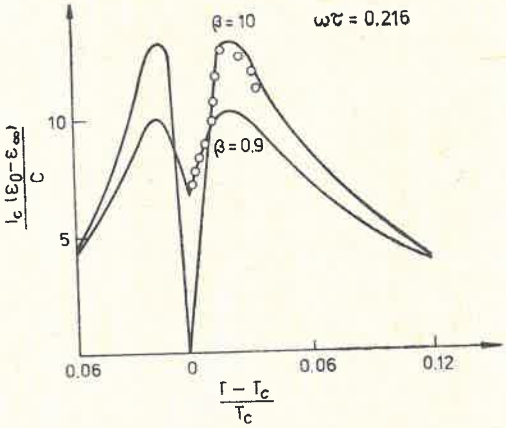

Fig. 8. Yoshimitsu-Matsubara diagrams of $K_4Fe(CN)_6 \cdot 3H_2O$ with $\beta$ as a parameter

It seems that inhomogenities of crystals are merely responsible for the distribution of the relaxation time, particularly in the immediate vicinity of the Curie point, where some kind of fluctuations become very active.

Assuming that a measured relaxation time (so-called macroscopic relaxation time) satisfies the equation:

$$\tau = \tau_0 \frac{\varepsilon(0)-\varepsilon(\infty)}{\varepsilon(\infty)}, \tag{3}$$

which is a slight modification of that given by Luther [9], the value for $\tau_0$ can be obtained. The results for several temperatures are shown in Fig. 9. By application of the above results the value of the Eyring free energy of dipole reorientation in the lattice can be calculated from

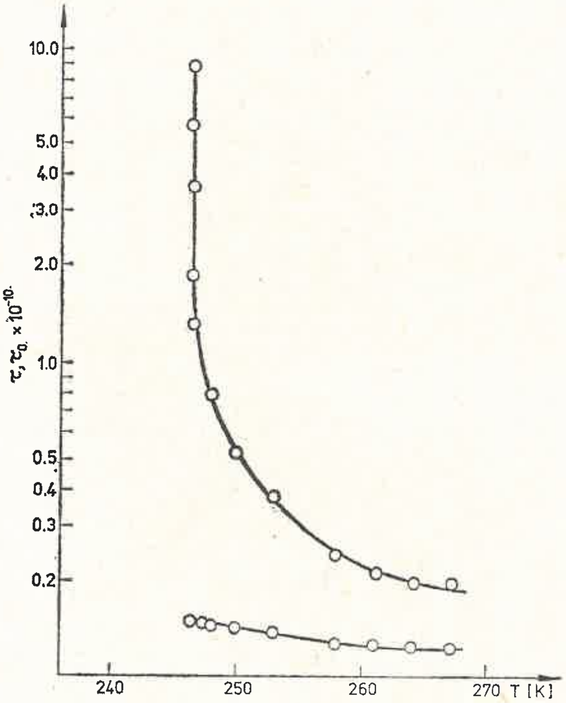

Fig. 9. The macroscopic and microscopic molecular relaxation times of $K_4Fe(CN)_6 \cdot 3H_2O$ versus temperature

$$\tau_0 = \frac{h}{kT} \exp \frac{\Delta F^*}{kT}. \tag{4}$$

In this case $\Delta F^* = 2.5 \pm 0.5$ kcal/mole.

Such a low energy barrier may perhaps indicate that the dielectric relaxation process is associated with the reorientation of rather weakly bonded water molecules. According to the layered structure of water molecules in the crystal shown in Fig. 1 [11] it can be suggested that the motion is highly correlated, that is, an $A \to C$ transition is always accompanied by a $B \to D$ transition and vice versa (see Fig. 2). Such a correlated motion seems to be quite reasonable, because some other uncorrelated motion reorientations will form the energetically unfavourable structures. However, O'Reilly and Tsang [10] have suggested from the NMR measurements that in the paraelectric phase may occur, some degree of independent reorientation of water molecules. If so, the degree of independent reorientation should be very low, otherwise a pronounced distribution of the dielectric relaxation times will have to be observed. In our experiments for selected high quality crystals only the single relaxation time was observed. Moreover, we have measured a pronounced distribution on other samples. Similarly, the distribution of the dielectric relaxation times was observed in the vicinity of the decomposition temperature (about 85°C) which is probably due to free water liberated in the dehydratation process, but these two effects are obviously not a property of the ideal crystal.

I would like to express my gratitude to Professor L. Sobczyk for his interest in the work and helpful discussions, and to Mr. L. Lasocki for his technical assistance.

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