

## STUDY OF THE REACTION $K_4Fe(CN)_6 \cdot 3H_2O \rightarrow K_4Fe(CN)_6 + 3H_2O$ BY THE DERIVATOGRAPH AND DIELECTRIC CONSTANT MEASUREMENTS

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$K_4Fe(CN)_6 \cdot 3H_2O$  was studied by a derivatograph in the temperature range  $+20^\circ$  to  $+300^\circ$  and dielectric constant ( $\epsilon$ ) measured from  $-80^\circ$  to  $+150^\circ$ . The loss of the three water molecules occurs at  $105^\circ$  and the  $\epsilon$  vs  $T$  curve shows a Debye relaxation behavior. By using Mason's theory it was possible to classify  $K_4Fe(CN)_6 \cdot 3H_2O$  in the temperature range  $-25^\circ$  to  $+100^\circ$  C as a para-electric order-disorder crystal.

In a recent article [1] we discussed the applications of the combined techniques – the derivatograph and dielectric constant measurements. The main conclusions in that work, which shall also be applied in this article were: 1. Transitions involving loss of gas molecules,  $H_2O$  in  $CuSO_4 \cdot 5H_2O$ , and ferroelectric-para-electric transition,  $NaNO_2$ , show the same behavior for the DTA curve. 2. The dielectric constant vs temperature curves are very different; in  $CuSO_4 \cdot 5H_2O$  they are step-wise, and in  $NaNO_2$  a Debye relaxation behavior [2] is observed. These observations were explained by assuming that  $NaNO_2$  is an order-disorder ferroelectric crystal.

A crystal is of order-disorder type if it has one sublattice consisting of particles which have two or more equivalent positions. These particles have an extra degree of freedom compared to those particles which form the order lattice. In this sense, an order-disorder crystal is a crystal having at least two intermixed sub-lattices. The order lattice is a lattice formed by particles under a displacement motion, i.e. oscillate around their equilibrium positions. They are normal oscillators. The disorder sub-lattice is a lattice formed by particles having the possibility of assuming at least two positions along a direction overcoming a potential barrier. These particles are random or Brownian particles. These random particles have time-dependent statistical behavior. The dielectric constant for this kind of crystal can be expressed by

$$\epsilon = \epsilon' + \epsilon_d \quad (1)$$

where  $\epsilon'$  is associated with the normal oscillator sub-lattice and  $\epsilon_d$  is associated with the sublattice of Brownian particles [3]. The dielectric behavior of  $\epsilon$  vs  $T$  for ferroelectric materials can be explained by a theory first advanced by Mason [4]. Known examples of order-disorder ferroelectric crystals are [3]

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$NaNO_2$ ,  $NaClO_3$ ,  $NaNO_3$ ,  $KNO_3$ ,  $Cu(HCOO)_2 \cdot 4H_2O$  and  $K_4Fe(CN)_6 \cdot 3H_2O$ . The last compound becomes ferroelectric [5] below 294 K. Its dielectric properties below zero degree centigrade have been investigated by several workers [6, 7]. R. Kiriya [8] et al. have carried out X-ray and NMR experiments mainly with single crystals. Andrade and Porto [3], based on the above investigations and on Mason's theory, concluded that  $K_4Fe(CN)_6 \cdot 3H_2O$  is an order-disorder crystal in its ferroelectric phase. By analyzing Mason's theory it is possible to predict the existence of para-ferroelectric order-disorder crystals. Following this line of reasoning we investigated the compound  $K_4Fe(CN)_6 \cdot 3H_2O$  by a derivatograph and dielectric constant measurements in both ferroelectric and paraelectric phases.

### Experimental results and discussion

Thermal analysis was carried using a Paulik – Paulik – Erdey type derivatograph model 1969 manufactured by MOM. This equipment gives simultaneously TG, DTG, DTA and T curves.

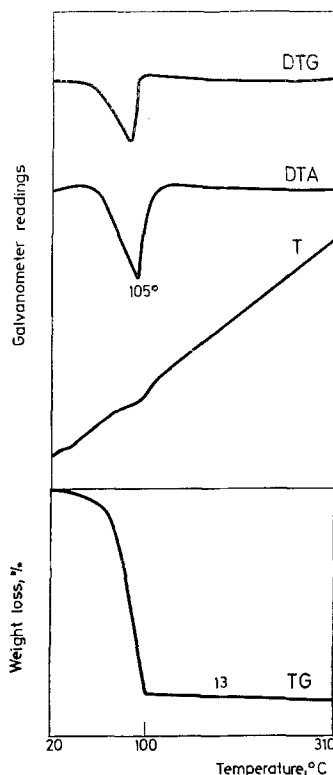


Fig. 1. Thermal curves for the decomposition of  $K_4Fe(CN)_6 \cdot 3H_2O$  at a heating rate of  $2^\circ/min$

Measurements of the dielectric constant as a function of the temperature were carried out using a wide range linear capacitance meter described elsewhere [9]. This equipment has proven useful for locating phase transitions in ferroelectric materials, and is sufficiently sensitive to detect other types of transitions. Figure 1 shows the thermal curves for  $K_4Fe(CN)_6 \cdot 3H_2O$  in the temperature range  $25^\circ$  to  $300^\circ$ . The minimum on the DTA curve at  $105^\circ$  and the mass loss indicated by the TG curve show the loss of three water molecules as endothermal reaction with no oxidation in this temperature range. Several heating rates were tried but the temperature of the transition changed very little.

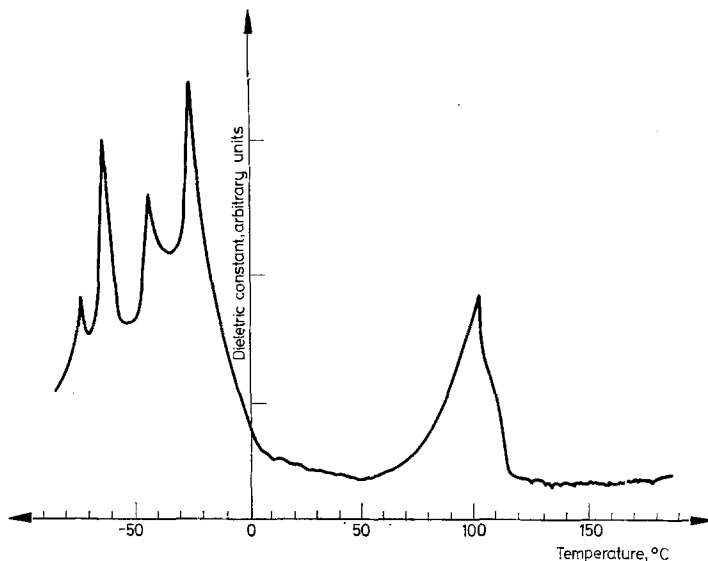


Fig. 2. Dielectric constant *vs.* temperature for  $K_4Fe(CN)_6 \cdot 3H_2O$  for a frequency of 1 kHz and temperature range  $-80^\circ$  to  $+150^\circ$

Figure 2 shows the  $\epsilon$  *vs.*  $T$  curve for the temperature range  $-80^\circ$  to  $+150^\circ$ . The low temperature range was included because we used powder samples in our measurements. Most literature data refer to the dielectric properties of single crystals of  $K_4Fe(CN)_6 \cdot 3H_2O$ .

The four peaks observed on the  $\epsilon$  *vs.*  $T$  curve in the temperature range  $-80^\circ$  to  $-25^\circ$  are comparable to the findings of S. Waku et al. [7]. Using single crystals they found five peaks from  $-80^\circ$  to  $-22^\circ$  for each of the directions  $[101]$  and  $[\bar{1}0\bar{1}]$  and observed a ferroelectric hysteresis loop from  $-22^\circ$  to  $-140^\circ$ .

It is important to note that all the four peaks that appear in Fig. 2 are similar to that observed in  $NaNO_2$  [1] at  $165^\circ$ .

The water molecules in  $K_4Fe(CN)_6 \cdot 3H_2O$  appear to be responsible for its ferroelectric behavior. The anhydrous compound was prepared by quenching a sample

from the derivatograph at 300° to room temperature. The dielectric constant of this compound was measured between -80° and +300° and no anomaly was observed.

The  $\epsilon$  vs  $T$  (Fig. 2) shows that the transition occurring at 105°, where the reaction  $K_4Fe(CN)_6 \cdot 3H_2O \rightarrow K_4Fe(CN)_6 + 3H_2O$  takes place, is quite different from those occurring at low temperatures and also from that in  $NaNO_2$  [1].

A typical relaxation process starts near 50° and continues until the temperature reaches 105° where a sudden drop occurs on the  $\epsilon$  vs  $T$  curve due to the loss of the water molecules. It seems clear that in this case we have a *para-electric order-disorder crystal*. To elaborate this point, we shall rely on Mason's paper [4]. His model was formulated to explain the behavior of the particles responsible for the ferroelectric properties of Rochelle Salt.

#### *Brief review of Mason's dielectric relaxation theory*

Let us begin considering Mason's rate equation for the dipole polarization along a direction,  $X$ , due to a self-diffusion process [10, 11]. The rate equation has the following form:

$$\frac{dP_d}{dt} = \left[ \frac{N_-}{\tau_c^-} - \frac{N_+}{\tau_c^+} \right] \mu \quad (2)$$

where  $\mu$  is the dipole moment per particle,  $\tau_c^+$  is a correlation time which defines the inverse of the probability per unit time of a particle jumping in the positive direction, and  $\tau_c^-$  is analogously the inverse of the probability of its jumping in the negative direction.  $N_+$  and  $N_-$  are populations in the wells along positive and negative directions (a double potential well disorder). The equation is based on the assumption that the particle transition rate for the two equivalent positions along  $X$  is described by a self-diffusion process with a correlation time given by  $\tau_c = \tau_0 \exp\left(\frac{\Delta U}{kT}\right)$  where  $\Delta U$  is the activation energy and  $\tau_0$  obeys the Eyring's relation  $\tau_0 = h/kT$ .

If an electric field  $E$  is applied, the activation energy becomes:

$$\left( \Delta U - \frac{1}{2} Fe\delta \right) \text{ and } \left( \Delta U + \frac{1}{2} Fe\delta \right) \quad (3)$$

where  $e$  is the electronic charge and  $\delta$  is the separation of the two potential wells. Assuming that the internal field is of the Lorentz type and the electronic and ionic polarization excited are proportional to the local field  $F$ , one has

$$\tilde{F} = (\tilde{E} + \beta \tilde{P}_d)(1 - \beta\gamma) \quad (4)$$

where  $\beta = \frac{4\pi}{3}$  for an isotropic medium and  $\gamma =$  polarizability per unit volume

due to all polarizations except that from the self-diffusion process defined by Eq. (1).

Using Eq. (4), we obtain from Eq. (2), for the static condition  $\left(\frac{dP_d}{dt}\right) = 0$ :

$$\tanh A \left[ \frac{E}{\beta N\mu} + \frac{P_d}{N\mu} \right] = \frac{P_d}{N\mu} \quad (5)$$

where the factor  $A$  is defined by:

$$A = \frac{e\delta\beta N\mu}{2(1-\beta\gamma)kT} \quad (6)$$

Putting  $E = 0$ , Eq. (5) yields an expression for the spontaneous polarization  $P_s$

$$\frac{P_s}{N\mu} = \tanh \left( \frac{AP_s}{N\mu} \right) \quad (7)$$

If the factor  $A$  is greater than unity, this equation will have positive and negative solutions other than zero, representing spontaneous polarization along the  $+X$  or  $-X$  direction. For values of  $A$  slightly greater than unity, we can replace  $\tanh \left( \frac{AP_d}{N\mu} \right)$  by the first two terms of the expansion and solving for  $P_s/N\mu$  one has

$$\frac{P_s}{N\mu} = [3(A-1)/A^3]^{1/2} \quad (8)$$

which gives a simple relation between  $P_s$  and  $A$ .

Assuming that the applied electric field  $E$  is equal to  $E_0 e^{i\omega t}$  and  $P_d = P_s + P_0 e^{i\omega t}$ , with  $P_s$  satisfying Eq. (8), then the time varying polarization  $P_0$  is given by:

$$P_0 = \frac{\left(\frac{A}{\beta}\right) \left[ 1 - \left(\frac{P_s}{N\mu}\right)^2 \right] E_0}{1 - A \left[ \left(\frac{P_s}{N\mu}\right)^2 \right] + i\omega\tau_0 \exp \left( \frac{\Delta U}{kT} \right) / \cosh \left( \frac{AP_s}{N\mu} \right)} \quad (9)$$

Under the assumption inherent in Eq. (4) the electric displacement  $\tilde{D}$  is given by:

$$\tilde{D} = 4 \pi \tilde{P}_0 + 4 \pi \tilde{P}_E + \tilde{E} = \tilde{E} \quad (10)$$

Substituting Eq. (9) into Eq. (10) one obtains for the dielectric constant, Mason's expression:

$$= \varepsilon' + \frac{\frac{4\pi A}{\beta} \left[ 1 - \left(\frac{P_s}{N\mu}\right)^2 \right]}{1 - A \left[ 1 - \left(\frac{P_s}{N\mu}\right)^2 \right] + \frac{i\omega\tau_0 \exp \left( \frac{\Delta U}{kT} \right)}{\cosh \frac{AP_s}{N\mu}}} \quad (11)$$

### Conclusions

Equation (11) can be used to describe the behavior of three kinds of crystals.

1. *A non-ferroelectric order crystal.* In this case  $P_s = 0$  and  $\Delta U = 0$  and hence  $\delta = 0$ . From relation (6) it is seen that  $A = 0$ . Then the second term in Eq. (11) vanishes and the dielectric behavior is determined only by the first term  $\epsilon'$ .

2. *A ferroelectric order-disorder crystal.* An example is  $NaNO_2$ . This crystal has an orthorhombic symmetry. It is generally accepted that the nitrogen atoms of the  $NO_2^-$  ions can assume two equivalent positions along the  $b$ -axis. We can easily identify the main characteristics of  $NaNO_2$  with the basic assumptions given in Mason's theory. In this case the  $x$ -direction is the  $b$  axis direction of the crystal. The jumping particle is the nitrogen atom taking equivalent positions separated by  $\delta$  either at the right or at the left of the  $ac$  crystallographic plane. The spontaneous polarization, which is known to be parallel to the  $b$  axis, will satisfy Eq. (8). (For details of how Eq. (12) explains the behavior of  $\epsilon$  vs  $T$  for  $NaNO_2$  see ref. [3].) A similar explanation for  $K_4Fe(CN)_6 \cdot 3H_2O$  was proposed by Andrade and Porto [3] for its tetragonal ferroelectric phase.

3. *A non-ferroelectric order-disorder crystal.* At room temperature  $K_4Fe(CN)_6 \cdot 3H_2O$  has a monoclinic symmetry and it is para-electric. R. Kiriya et al. [8] have carried out X-ray and NMR experiments and found that its crystal structure shows a double-layered group of octahedrally co-ordinated  $Fe(CN)_6$  complex ions and surrounding  $K^+$  ions. Between these double layers is inserted a layer of water molecules. The shortest distance is 2.86 Å indicating the existence of a normal OH-N hydrogen bond. There are two different site symmetries for the water molecules at room temperature:  $2H_2O$  at 8 ( $f$ ) (Whyckoff notation) and  $1H_2O$  at 4 ( $l$ ). NMR experiments show that the water molecules exhibit rapid orientation around more than one axis. There is no difference in behavior between the two kinds of water molecules. Both are rotating around two or more axes with frequencies higher than  $10^5$  cps.

It is clear from the above description that there is a very similar behavior between the nitrogen ion motion in  $NaNO_2$  and the water molecules in  $K_4Fe(CN)_6 \cdot 3H_2O$ .

If we assume that the equivalence between these two kinds of water molecules persists up to the temperature of the decomposition, the behavior of the  $\epsilon$  vs  $T$  curve between 20° and 105° can be explained as follows:

In Eq. (11) let us put  $P_s = 0$ , so

$$\epsilon = \epsilon' + \frac{4\pi A}{\beta} \frac{1}{1 - A + i\omega\tau_0 \exp\left(\frac{\Delta U}{kT}\right)}$$

In this case the difference,  $1 - A$ , in the denominator is responsible for the increase of the dielectric constant, because from Mason's theory  $A = 1$  at the transition temperature. The sudden drop on the  $\epsilon$  vs  $T$  curve above 105° means that the anhydrous compound is an ordered crystal. This behavior above the

transition temperature is very different from the  $NaNO_2$  case. In that case there is a relaxation behavior above the ferroelectric-para-electric transition.

It is important to emphasize the advantage of the combined approach — the thermal and dielectric constant measurements. By use of the combined thermal method one can get informations about the nature of the transition — endothermic, exothermic, with mass loss, etc. The dielectric constant will give information about the “velocity” of the reaction; in the case of water molecules the release could be a very fast process like that in  $CuSO_4 \cdot 5H_2O$  [1] or they may require some “time” to evolve within the crystal as in  $K_4Fe(CN)_6 \cdot 3H_2O$ . The  $\epsilon$  vs  $T$  curves are completely different for these two cases. Also, the dielectric constant could be used as complementary tool for NMR experiments to detect internal molecular motions in crystals.

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RÉSUMÉ — Etude de  $K_4Fe(CN)_6 \cdot 3H_2O$  à l'aide d'un «Derivatograph» entre  $+20$  et  $+300^\circ$  mesure de la constante diélectrique ( $\epsilon$ ) entre  $-80$  et  $+150^\circ$ . La perte des trois molécules d'eau a lieu à  $105^\circ$  et la courbe  $\epsilon$  en fonction de  $T$  montre un comportement de relaxation Debye. D'après la théorie de Mason, il est possible de classer  $K_4Fe(CN)_6 \cdot 3H_2O$  comme cristal para-électrique ordre-désordre entre  $-25$  et  $+100^\circ$ .

ZUSAMMENFASSUNG —  $K_4[Fe(CN)_6] \cdot 3H_2O$  wurde mit dem Derivatograph im Temperaturbereich von  $+20^\circ$  bis  $+300^\circ$  untersucht und die dielektrische Konstante ( $\epsilon$ ) im Bereich von  $-80^\circ$  und  $+150^\circ$  gemessen. Die Abspaltung der drei Wassermoleküle erfolgt bei  $105^\circ$ . Die Kurve von  $\epsilon$  als Funktion von  $T$  zeigt ein Relaxationsverhalten nach Debye. Bei Anwendung der Theorie von Mason gelang es  $K_4[Fe(CN)_6] \cdot 3H_2O$  im Temperaturbereich von  $-25^\circ$  bis  $100^\circ$  als para-elektrischen, geordneten-ungeordneten Kristall einzuordnen.

Резюме — С помощью дериватографа была изучена соль  $K_4[Fe(CN)_6] \cdot 3H_2O$  в области температур от  $+20^\circ$  до  $+300^\circ$  и для которой была измерена диэлектрическая константа в области температур от  $-80^\circ$  до  $+150^\circ$ . Потеря трех молекул воды происходит при  $105^\circ$ , а кривая в координатах  $\epsilon$ - $T$  показывает дебаевское релаксационное поведение. Представилось возможным, используя теорию Масона, классифицировать  $K_4[Fe(CN)_6] \cdot 3H_2O$  в области температур от  $-25^\circ$  до  $+100^\circ$  как параэлектрический упорядоченно-разориентированный кристалл.