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ON THE NATURE OF PHASE TRANSITION IN THE POTASSIUM FERROCYANIDE CRYSTAL FAMILY

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A model of arrangement of water molecules in the lattice on the basis of NMR data for homogeneous KRCT crystal is suggested. The influence of twinning on the value and direction of spontaneous polarization is discussed. The ferroelectrical phase transition is connected with the ordering of a part of water molecules in crystal.

The ferroelectric properties of potassium ferrocyanide trihydrate $K_4Fe(CN)_6 \cdot 3H_2O$ (KFCT) crystals have been studied for many years. But so far there is no common conception on the nature of ferroelectricity in these crystals. It is partially due to a very high tendency of KFCT crystals to twinning that greatly influences all crystal properties including ferroelectricity. It gives rise to some difficulties in unequivocal interpretation of experimental results.

It seems that this fact accounts for differences in the determination of proton structure in KFCT crystal.^{1,2} An attempt to avoid the experimental difficulties connected with the crystal twinning was undertaken in Ref. 2. However, as it was shown earlier⁷ the results described in ^{1,2} are likely to be related to the twinned crystals and this fact causes difficulty in their interpretation.

We have found that for the ferroelectric potassium ruthenocyanide $K_4Ru(CN)_6 \cdot 3H_2O$ (KRCT) isomorphous to those of KFCT the crystals of better quality can be obtained and this obtains more accurate experimental data.

Thus a number of KRCT crystals were grown and the technique of determination of the homogeneous, non-twinned crystals was worked out on the basis of NMR spectra analysis.

The spectrum of the KRCT twinned crystal as shown in ^{7,8} can be interpreted as a sum of two doublets of homogeneous crystal folded in the cleaved planes (010) and turned at the angle of 90° around the axis "b". Spectrum of KFCT single crystal is similar to the unresolved spectrum of KRCT twinned crystal.

So, KRCT twinned crystal can be considered to consist of separate rather large blocks of homo-

geneous crystals turned at 90°. In KFCT crystal continuous distribution of blocks at the limits of some atomic layers is observed which leads to the appearance of unresolved nmr spectrum due to diffusion of water molecules between the layers.⁹ Thus, the difficulties of obtaining of KFCT homogeneous crystals can be explained by continuous distribution of blocks.

Analysis of doublet splitting angular dependences of nmr low-temperature spectra in rotation of KRCT non-twinned crystal around some crystallographic axes allowed us to suggest a model for arrangement for p - p vectors of water molecules in KRCT¹⁰ (Figure 1).

As was shown the origination of spontaneous polarization in KRCT non-twinned crystal below T_c is connected with the ordering of water molecules "I" dipole moments which occupy the 4e positions in the structure and this must lead to the macroscopic dipole moment along the [100] direction.

It is worthwhile to mention that this direction differs by 45° from the generally known [101] direction of spontaneous polarization in KFCT crystals.¹¹ And indeed the special macroscopic measurements fulfilled on homogeneous KRCT crystals have shown⁷ that in these crystals the ferroelectric axis is [100]. We consider this to be the most important argument in favour of the suggested model and the leading role of water molecules in the spontaneous polarization mechanism.

There are some additional arguments on water molecule role in phase transition. The polarization value P_0 at 0 K in the mentioned model can be written as

$$P_0 = MN$$

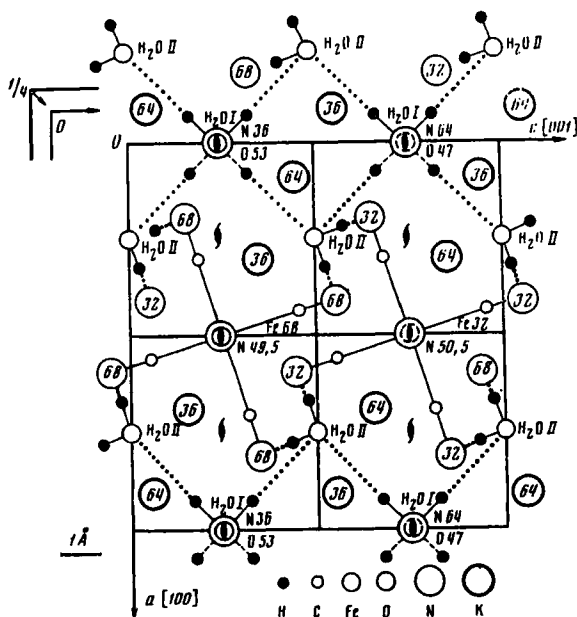


FIGURE 1 The crystal structure of KFCT viewed along (010).

where M is the dipole moment of the water molecule and N the number of water molecules type I in unit volume. (One-third of all water molecules.) The value 1.7 mk/sm^2 is calculated for P_0 . It is in good agreement with earlier data.¹¹

In the temperature range of phase transition the water molecules contributing to polarization possess diffusion and reorientational motions which don't change considerably around T_c .⁹ Nevertheless, the high perturbation of the proton system is observed in this range due to the increase of critical fluctuations. Thus, the effect of anomalous relaxation is caused by this phenomenon. The critical fluctuations

modulate the magnetic dipole-dipole interaction, the correlation in the proton system being better.

Such correlated motion of water molecules can be observed in measuring the orientational dependence of spin-lattice relaxation time T_1 .

In the framework of the suggested model of the water molecules arrangement the correlated intermolecular motion of protons gives the dependence of T_1 on the angle θ between the external magnetic field and the direction of p - p vectors like

$$T_1^{-1} \sim (1 + \cos^2 \theta)$$

Namely, this orientational dependence is observed in KFCT crystal near the ferroelectric transition temperature T_c .⁶

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