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Internal fields and ferroelectric ordering in potassium ferrocyanide trihydrate

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Abstract. On the basis of the existing experimental data it is assumed that the mechanism responsible for the ferroelectric transition of potassium ferrocyanide trihydrate is a rotational reorientation of the water molecules. Accordingly, the electrostatic energy of the water molecules (approximated by three point charges) is calculated as a function of their orientation. The low temperature configuration is obtained by minimising the electrostatic energy. A possible model is then proposed for the ferroelectric to paraelectric transition, consisting in the switching of the water molecules between two energetically equivalent configurations. The results are in good agreement with the experimental data.

1. Introduction

Since its discovery by Waku *et al* (1959) the ferroelectric transition of potassium ferrocyanide trihydrate ($K_4Fe(CN)_6 \cdot 3H_2O$, to be abbreviated as KFCT) has been the object of many investigations using different experimental techniques. In spite of the great amount of information so far obtained, there is no general agreement about a model for the transition. Firstly, while according to most authors the transition is due to a reordering of the water molecules (WM), others (Hazony *et al* 1968, Sastry 1976) believe that it is of the displacive type. Secondly, among the authors favouring the former mechanism there is no agreement about the orientation of the WM. Some of the experimental results appear to contradict each other, while others are difficult to interpret due to the strong tendency of KFCT to twinning.

In this paper we assume a simplified model of the crystal and find the electrostatic energy of the WM as a function of their orientation. By minimising this function we obtain two energetically equivalent configurations. We propose a model according to which in the PE phase the WM are disordered into two positions.

2. Discussion of our model for the KFCT structure

The structural properties of KFCT have been extensively investigated by Toyoda *et al* (1960). KFCT crystallises either in a monoclinic (pseudotetragonal) or a tetragonal modification. Tetragonal crystals transform irreversibly into twinned monoclinic crystals on cooling below -55°C. Only the monoclinic modification undergoes the FE–PE transition. Hereafter we will only consider monoclinic crystals. KFCT has a strong

tendency to twinning: twinned crystals are composed of two monoclinic individuals, rotated by 90° with respect to each other about their common axis y. Twinned crystals have a complicated dielectric behaviour, showing several peaks at different temperatures, with spontaneous polarisation $\boldsymbol{P}_s$ both in the [101] and [10$\bar{1}$] directions (Waku *et al* 1959). On the other hand, single crystals show a unique peak at $T_c = -24°C$, $\boldsymbol{P}_s$ being in the [10$\bar{1}$] direction† (Waku *et al* 1960a, Toyoda *et al* 1960).

According to the x-ray diffraction experiment of Kiriyama *et al* (1964) (to be referred to as KKWNH), the space group of the monoclinic form is $C2/c$, and the lattice constants are $a = 9{\cdot}40$ Å, $b = 16{\cdot}86$ Å, $c = 9{\cdot}41$ Å, $\beta = 90°3'$ in the PE phase, while values very close to the former are obtained in the FE phase. The structure is made of double layers of ions (the $Fe(CN)_6^{4-}$ octahedra and the K^+), parallel to the xz plane, between which layers of WM are inserted. There are three kinds of WM (which will be called 1, 2 and 3) in the FE and two in the PE phase. WM 2 and 3 become equivalent to each other in the PE phase. The unit cell contains four formula units, and the coordinates of all the atoms except the hydrogens have been determined by KKWNH. The positions of the H in the PE phase have been found by neutron diffraction by Taylor *et al* (1970) (to be referred to as TMH). TMH's results, however, can be interpreted in different ways, as will be discussed below.

NMR experiments (Lundin *et al* 1961, Blinc *et al* 1961, KKWNH, Lundin and Zeer 1965, Tsang and O'Reilly 1965) show that when the temperature is increased from $-140°C$ the mobility of the protons increases. This, together with the already mentioned existence of two positions for the hydrogens, suggests that the FE to PE transition should be due to the disordering of the WM. This disorder is unlikely to be due to the motions of the protons in a double-well potential, as in ferroelectrics of the KH_2PO_4 (KDP) type. In fact, according to the theory, (p 134 of Blinc 1974) the tunnelling probability of a proton in a double well is very different from that of a deuteron, so that the Curie temperature of KDP-type order–disorder ferroelectrics is greatly affected by deuteration. Now, while the Curie temperature for KD_2PO_4 is about 70% higher than that of KH_2PO_4, for KFCT the difference is only about 2% (Waku *et al* 1960a, 1960b). Furthermore, a KDP-type transition requires the existence of quite strong H bonds, which is not the case for KFCT (see below).

In this paper we study the electrostatic energy associated with the orientation of the WM, in order to find the most favourable configuration. We do this using a model introduced by Baur (1965), who applied it to several (non-ferroelectric) hydrated crystals for which the hydrogen positions had been previously determined by neutron diffraction. In Baur's model the ions are considered as point charges, whose values are estimated from the ion electronegativities, and the WM are taken as three point charges rigidly attached to each other. The O–H distance is taken as $d = 0{\cdot}97$ Å and the H–O–H angle as $\alpha = 109{\cdot}5°$. The charge of the hydrogens (q_H) is adjusted so as to give the best agreement with the experimental data for the $BaCl_2 \cdot 2H_2O$ structure: this occurs for $q_H = 0{\cdot}5e$. The polarisabilities of all the ions and WM are neglected. The positions of the oxygens are kept fixed, and the WM are rotated as rigid bodies until the configuration with the least electrostatic energy is found. In spite of its extreme simplicity, Baur's model has been remarkably successful in predicting the positions of the hydrogens of many hydrated crystals, some of them with bent or bifurcated bonds (Baur 1965 and references contained in Baur 1972). The application of this model to KFCT can be justified by the following considerations.

† According to Lundin *et al* (1969), $\boldsymbol{P}_s$ is in the [100] direction in untwinned crystals (see § 4)

The authors who explain the phase transition of KFCT in terms of an ordering of the WM discuss the possible orientations of these primarily in terms of the H bonds that can be formed in the crystal, and pay less attention to the electrostatic interactions of the water dipole moments with each other and with the ions of the structure (Blinc *et al* 1961, KKWNH, TMH, Habuda *et al* 1970). However, H bonds in KFCT are relatively weak: in fact two of them, corresponding to the oxygen of WM 1, have a length of $\approx 2{\cdot}83$ Å, while the others are longer than 3 Å; the intramolecular O–H distance for WM 1 is approximately equal to 0·9 Å (TMH†). A comparison of these values with figure 13.1 and § 13.2 of Megaw (1973) shows that all the H bonds in KFCT are quite weak. This conclusion is also supported by the following facts: (*a*) IR spectra obtained by Blinc *et al* (1961) indicate that most H bonds in KFCT are weak and that the barrier to rotations of the WM is low, at least in the PE phase; (*b*) the rotations of the WM are less hindered in KFCT than in liquid water (Rush *et al* 1966); (*c*) KFCT shows a strong tendency to dehydrate. A rough comparison between the energy of a weak H bond (0·1 or 0·2 eV; see p 303 of Coulson 1960 or p 126 of Kittel 1971) and the electrostatic contributions ($\boldsymbol{p}.\boldsymbol{E} \approx 0{\cdot}6$ eV for $p \approx 2$ D, $\boldsymbol{E}$ corresponding to a K^+ at 3 Å) indicates that the latter are more important in KFCT. On the other hand, a hydrogen bond can be considered as partially electrostatic in nature, its electrostatic character being dominant when the bond is long (p 305 of Coulson 1960).

All the previous considerations suggest that one can try to explain the orientation of the WM in KFCT by means of purely electrostatic forces.

3. Calculation of the electrostatic energy

In order to calculate the electrostatic energy per molecule of KFCT we need to describe its unit cell. As we have already said, KFCT has monoclinic (pseudotetragonal symmetry, with the ions and the WM arranged on alternating layers perpendicular to the y axis. Six of the WM contained in the unit cell are located on or near the plane $y = 0$, the other six being on or near the plane $y = 0{\cdot}5$. We characterise the position of a WM by that of its oxygen; the atomic coordinates of the latter are given in table 1. O_1, O_2 and O_3 refer to the three kinds of non-equivalent (in the FE phase) WM. In the last two columns of table 1 we have indicated how vectors (such as dipole moments) associated with a site transform from one site to another according to the crystal symmetry in both phases. It is easily seen that the net polarisation must lie in the xz plane. It is important to notice that the ionic environment (i.e. the environment one would have if the WM were absent) of an $O_{2,i}$ site is related to that of an $O_{3,i}$ by inversion; also, the ionic environment of $O_{\alpha,i}$ is related to that of $O_{\alpha,ii}$ by a reflexion in the xz plane ($\alpha = 1, 2, 3$).

In the present calculation we approximate the structure by taking $a = c$ and $\beta = 90°$, while the WM of type 1 are taken as lying on the same planes as those of types 2 and 3 (i.e. we set $y = 0{\cdot}0$ for WM 1 and 4 and $y = 0{\cdot}5$ for WM 7 and 10 of the unit cell; see table 1). These approximations are justifiable if one considers that the assumed model for the WM is itself a very crude one. About this, let us notice that up to now there exist considerable discrepancies among the estimated values for the dipole moment of a WM in a crystal. For instance, for the value of p_{H_2O} in ice Crowe and Santry (1973) found the same value as in the water vapour, i.e. 1·86 D, while Coulson and Eisenberg (1966)

† The data of TMH refer to deuterated KFCT, but H bonds are very little affected by deuteration (p 346 of Megaw 1973).

Table 1. Coordinates of the oxygen atoms of the unit cell. Transformation properties of vectors associated with the WM sites. The last two columns must be interpreted according to the following example. Let (x_2, y_2, z_2) be a vector associated with site 2, such as the O–H vector of one of the hydrogens of the WM at that site. The corresponding vector associated with site 3 is given as follows: in the FE phase it may take any value (x_3, y_3, z_3), being totally unrelated to the vector at site 2, while in the PE phase it must be equal to $(-x_2, -y_2, -z_2)$. The transformation properties refer to average values. For instance the O–H vectors of WM 1 in the PE phase are not oriented in the y direction (which of course would be impossible for both of them simultaneously), but are disordered in such a way that their x and z components average to zero.

Water molecule		x	y	z	FE phase	PE phase
O_1	1 *i*	50	03	25	(x_1, y_1, z_1)	$(0, y_1, 0)$
	4 *ii*	50	97	75	$(x_1, -y_1, z_1)$	$(0, -y_1, 0)$
	7 *i*	00	53	25	(x_1, y_1, z_1)	$(0, y_1, 0)$
	10 *ii*	00	47	75	$(x_1, -y_1, z_1)$	$(0, -y_1, 0)$
O_2	2 *i*	75	00	00	(x_2, y_2, z_2)	(x_2, y_2, z_2)
	5 *ii*	75	00	50	$(x_2, -y_2, z_2)$	$(x_2, -y_2, z_2)$
	8 *i*	25	50	00	(x_2, y_2, z_2)	(x_2, y_2, z_2)
	11 *ii*	25	50	50	$(x_2, -y_2, z_2)$	$(x_2, -y_2, z_2)$
O_3	3 *i*	25	00	00	(x_3, y_3, z_3)	$(-x_2, -y_2, -z_2)$
	6 *ii*	25	00	50	$(x_3, -y_3, z_3)$	$(-x_2, y_2, -z_2)$
	9 *i*	75	50	00	(x_3, y_3, z_3)	$(-x_2, -y_2, -z_2)$
	12 *ii*	75	50	50	$(x_3, -y_3, z_3)$	$(-x_2, y_2, -z_2)$

obtained 2·6 D and Onsager and Dupuis (1962) 3·8 D. In Baur's model with $q_H = 0{\cdot}5e$ the water dipole moment is 2·69 D.

We take $q_K = e$, and for the charge distribution in the $Fe(CN)_6^{4-}$ group we use a result of Alexander and Gray (1967), according to which the charge on the Fe is $0{\cdot}42e$. So we take a point charge $0{\cdot}42e$ at the Fe site and twelve point charges of $-4{\cdot}42e/12$ at each of the C and N sites†. The atomic coordinates of all the WM and ions in the unit cell are obtained from KKWNH by using the symmetry operations of the $C2/c$ group (p 101 of the Int Tables for X-Ray Crystallography, Vol I, 1952).

The electrostatic energy of a point charge in a crystal as a function of its position is given by a lattice sum which has an extremely slow convergence. Methods avoiding such a problem give more or less complicated expressions (see Appendix B of Tosi 1964). Now, the function we have to minimise depends on nine independent variables (the Euler angles of the three non-equivalent WM), so that calculating the lattice sums at every step of the minimisation program would take a very long computation time. We prefer to perform the lattice summation once and for all by proceeding as follows.

We start by considering the WM as point dipoles of magnitude $p = 2q_H d \cos\frac{1}{2}\alpha$. The parameters q_H, d and α are taken as in Baur (1965) (see above). The interaction energy per molecule of KFCT (i.e. of three non-equivalent WM) of the dipoles with each other

† We also made an alternative calculation, taking six point charges each equal to $-4{\cdot}42e/6$ at the middle points of the C–N vectors. The results obtained in this case are approximately the same as in the previous one. This shows that the field at the O sites is largely insensitive to the exact charge distribution in the CN group, provided this is not asymmetric. From Alexander and Gray (1967) it can be seen that the orbitals centred on C and N have indeed very similar weight to each other in the ferrocyanide ion.

and with the ions can then be expressed in terms of coefficients that are independent of the dipole orientation:

$$W^{(0)} = \tfrac{1}{4}W^{(0)}_{\text{cell}} = W^{(0)}_{pp} + W^{(0)}_{pq}$$
$$= \sum_{\alpha,\beta}\sum_{k,h} a_{\alpha\beta,kh}e_{\alpha,k}e_{\beta,h} - \sum_{\alpha}\sum_{k} b_{\alpha,k}e_{\alpha,k}. \tag{1}$$

(for the derivation and the values of the coefficients see below). Here, $e_\alpha \equiv \boldsymbol{p}_\alpha/p_\alpha$ (the Greek indices refer to the 1, 2 and 3 sublattices and the Latin indices to the Cartesian components).

The value so obtained is then corrected by subtracting the interaction energy of each WM with the nearest ions and WM (where all the WM are taken as point dipoles) and adding the interaction energy of the WM with the same ions and WM (using now Baur's three-point-charges model):

$$W = W^{(0)}_{pp} - \sum_{\alpha}\sum_{\beta,\lambda}[W_{\alpha\beta,\lambda}(p;p) - W_{\alpha\beta,\lambda}(3q;3q)] +$$
$$+ W^{(0)}_{pq} - \sum_{\alpha}\sum_{\kappa,\lambda}[W_{\alpha\kappa,\lambda}(p;q) - W_{\alpha\kappa,\lambda}(3q;q)]. \tag{2}$$

Here, α and β label WM sublattices, κ labels ion sublattices and λ stands for three indices denoting the cell to which the interacting WM or ion belongs. If a sufficient number of neighbours are included into the summation, expression (2) converges to the value given by the three-point-charges model. The convergence of (2) is much more rapid than that of the series one would have obtained by simply considering the Baur terms:

$$W = \sum_{\alpha}\left[\sum_{\beta,\lambda} W_{\alpha\beta,\lambda}(3q;3q) + \sum_{\kappa,\lambda} W_{\alpha\kappa,\lambda}(3q;q)\right]. \tag{2'}$$

This of course is why we performed the calculation in the above-described way.

$W^{(0)}$ was calculated using the formulae of the 'planewise summation method' (see de Wette and Schacher, 1965 for $W^{(0)}_{pp}$ and Massidda, 1976 for $W^{(0)}_{pq}$†:

$$W^{(0)}_{pp} = -\lambda^2\{[-0{\cdot}00185(e^2_{1,x} + e^2_{2,x} + e^2_{3,x})$$
$$+ 0{\cdot}02480e_{1,x}(e_{2,x} + e_{3,x}) + 0{\cdot}03080e_{2,x}e^2_{3,x})$$
$$+ [0{\cdot}00569(e^2_{1,y} + e^2_{2,y} + e^2_{3,y}) - 0{\cdot}00402e_{2,y}e_{3,y}]$$
$$+ [0{\cdot}01443(e^2_{1,z} + e^2_{2,z} + e^2_{3,z})$$
$$+ 0{\cdot}02480e_{1,z}(e_{2,z} + e_{3,z}) - 0{\cdot}00175e_{2,z}e_{3,z}]\}\ \text{eV}. \tag{3}$$

$$W^{(0)}_{pq} = -\lambda[-0{\cdot}1943e_{1,y} + 0{\cdot}3999(e_{2,x} - e_{3,x})$$
$$+ 0{\cdot}0008(e_{2,y} - e_{3,y}) + 0{\cdot}1013(e_{2,z} - e_{3,z})]\ \text{eV}. \tag{4}$$

Here, the dipole moment of the WM has been written as $\boldsymbol{p}_\alpha = (\lambda/3)\,10^{-29}\,\boldsymbol{e}_\alpha$ Cm, where λ gives the value of p_α in debyes. In the present calculation $\lambda = 2{\cdot}69$.

The calculation of the minima of W was carried out with the CERN program MINUIT, which finds the relative minima of functions of up to 15 independent variables. The results are presented and discussed in the next section.

† We considered a specimen with $N_x = N_y = N_z = 0$. This corresponds to a short-circuited slab in a standard experimental arrangement (see de Wette and Schacher 1965 and pp 450–9 of Kittel 1971).

4. Results and comparison with previous models

The electrostatic energy is found to be a minimum for two configurations of the WM, which are equivalent to each other due to the crystal symmetry. They are characterised by giving the positions of the hydrogens relative to their oxygens ($\boldsymbol{r}_{\alpha,1}$ and $\boldsymbol{r}_{\alpha,2}$) for all the WM ($\alpha = 1, 2, 3$). The values obtained by us for one equilibrium configuration are

Table 2. Positions of the hydrogens with respect to the oxygens of their WM (in Å) and directions of the water dipoles according to the present paper and to TMH's data interpreted in agreement with model (*b*) of KKWNH.

Molecule	Vector	Present result			TMH (model (*b*))		
		x	y	z	x	y	z
1	$\boldsymbol{r}_{1,1}$	−0·19	−0·94	0·13	−0·20	−0·87	0·00
	$\boldsymbol{r}_{1,2}$	0·69	0·10	−0·68	0·71	0·07	−0·54
	$\boldsymbol{e}_1$	0·45	−0·75	−0·49	0·47	−0·73	−0·50
2	$\boldsymbol{r}_{2,1}$	0·50	0·45	0·71	0·52	0·10	0·71
	$\boldsymbol{r}_{2,2}$	0·61	−0·49	−0·57	0·59	−0·36	−0·77
	$\boldsymbol{e}_2$	0·99	−0·04	0·12	0·97	−0·23	−0·05
3	$\boldsymbol{r}_{3,1}$	−0·34	−0·43	−0·80	−0·52	−0·10	−0·71
	$\boldsymbol{r}_{3,2}$	−0·73	0·45	0·46	−0·59	0·36	0·77
	$\boldsymbol{e}_3$	−0·95	0·01	−0·30	−0·97	0·23	0·05

given in table 2, where the directions of the WM dipole moments, $\boldsymbol{e}_\alpha = \boldsymbol{p}_\alpha/p_\alpha = q_H(\boldsymbol{r}_{\alpha,1} + \boldsymbol{r}_{\alpha,2})/p_\alpha$, are also given. The other equilibrium configuration is given by

$$(r_x, r_y, r_z)'_1 = (-r_x, r_y, -r_z)_1$$
$$(r_x, r_y, r_z)'_2 = (-r_x, -r_y, -r_z)_3$$
$$(r_x, r_y, r_z)'_3 = (-r_x, -r_y, -r_z)_2$$

for both $\boldsymbol{r}_{\alpha,1}$ and $\boldsymbol{r}_{\alpha,2}$. The orientation of the WM according to our results is shown in figure 1.

The existence of two energetically equivalent configurations suggests that at low temperature the WM order into either of them, while at high temperature they are disordered into both of them. This situation is the same as in two models proposed by previous authors, who however disagree with us and with each other about the orientation of the WM (see below). In the equilibrium configurations found by us the orientations of WM 2 and 3 are nearly opposite to each other. This reflects the fact that the ionic environments of the two sites are related to each other by inversion and that the interaction with the ions is what mainly dictates the orientation of the WM. So, in the absence of any intermolecular interaction WM 2 and 3 would be exactly opposite to each other; the actual interaction is not strong enough to radically alter this situation. Also, the orientation of WM 2 is nearly the same in both equilibrium configurations; the same holds for WM 3. For these reasons the spontaneous polarisation $\boldsymbol{P}_s$ receives very small contributions from WM 2 and 3, and is mainly due to WM 1. The ionic charges do not contribute to $\boldsymbol{P}_s$ due to the crystal symmetry.

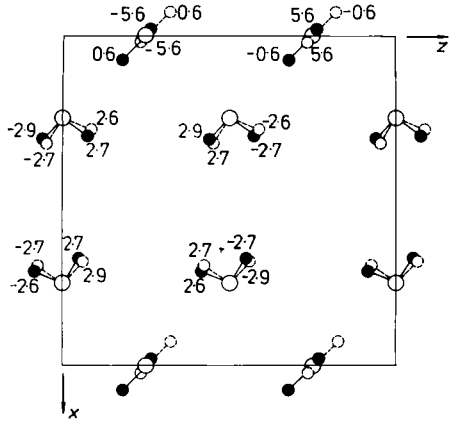

Figure 1. Orientations of the water molecules of the $y = 0{\cdot}5$ layer according to the results of the present paper. The figures indicate the y parameters of the hydrogens relative to that plane.

The spontaneous polarisation obtained by us ($\boldsymbol{P}_s$ at 0 K) is

$$\boldsymbol{P}_s = (1{\cdot}16\boldsymbol{i} - 1{\cdot}62\boldsymbol{k})\,\mu\mathrm{C\,cm^{-2}}.$$

Its projection in the $[10\bar{1}]$ direction is $1{\cdot}97\,\mu\mathrm{C\,cm^{-2}}$, in reasonable agreement with experimental values (1·4 at −80°C (Waku *et al* 1961a), 1·6 at −70°C (O'Reilly and Schacher 1965)). The deviation from the $[10\bar{1}]$ direction is about 14°.

Our model allows a rough estimation of the transition specific heat. Let $(\phi_{\alpha 0}, \theta_{\alpha 0}, \psi_{\alpha 0})$ and $(\phi'_{\alpha 0}, \theta'_{\alpha 0}, \psi'_{\alpha 0})$ ($\alpha = 1, 2, 3$) be the values of the Euler angles of the WM at the two equilibrium positions and let us assume that during the switching from one configuration to the other all the angular coordinates change in such a way that the variation of each of them can be described by one and the same parameter (η):

$$u_\mu(\eta) = (u'_{\mu 0} - u_{\mu 0})\eta + u_{\mu 0} \qquad 0 \leqslant \eta \leqslant 1$$

(the u's are the Euler angles: $\mu = 1, 2, \ldots, 9$). We calculated the electrostatic energy per molecule (equation 2) as a function of η obtaining, as expected, a curve with a double well. The average value of the energy inside each well is approximately −3·54 eV, while the average over all the values of η is $\approx -3{\cdot}52$ eV Therefore, the difference due to the disordering is of about 0·02 eV. This value is of course affected by a large estimation error (not less than 50%). Anyway, it is encouraging to notice that this estimation is in good agreement with the values of Malcolm *et al* (1973) and of Matsuo *et al* (1973) (0·018 and 0·022 eV per molecule respectively).

Let us now compare our model with those proposed by previous authors and with their experimental results.

The first model for the FE–PE transition of KFCT was proposed by KKWNH, on the basis of their NMR data. The interpretation of these data was not easy because the experiment was performed with a twinned crystal. KKWNH discussed two possible cases, which can be described in terms of the following configurations (see figure 2):

Configuration a—solid lines for all the WM
Configuration $\bar{a}$—broken lines for all the WM
Configuration b—solid lines for WM 1 and 2, broken lines for 3
Configuration $\bar{b}$—broken lines for WM 1 and 3, solid lines for 2.

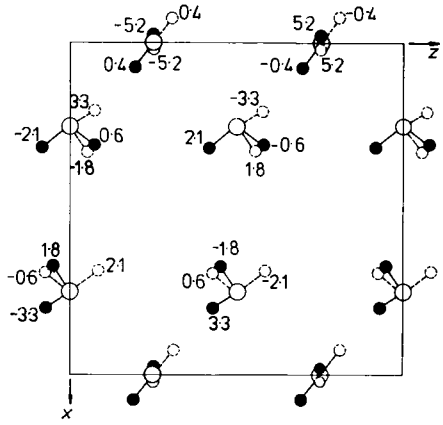

Figure 2. Orientations of the water molecules of the $y = 0{\cdot}5$ layer according to KKWNH's models. The figures indicate the y parameters of the hydrogens relative to that plane

Configurations a and $\bar{a}$ are equivalent to each other and the same holds for b and $\bar{b}$, so that the choice is actually restricted to the two following cases: (*a*) in the PE phase the WM are switching between configurations a and $\bar{a}$; in the FE phase they are 'frozen' in one of the former sets of positions; (*b*) same as above, but for b and $\bar{b}$.

KKWNH concluded that model (*a*) is preferable to (*b*). Later on, O'Reilly and Tsang (1967) and TMH supported model (*a*), even though their data were also compatible with (*b*), as they too worked with twinned crystals†. This can be clearly seen in TMH's neutron diffraction experiment, which is of particular interest because it is the only direct determination of the hydrogen positions so far performed. TMH observed two positions for each one of the WM 1, 2 and 3. The positions observed for WM 2 are related to each other by a 90° rotation about the y axis; the same holds for WM 3. The two positions observed for WM 1, however, are related by a 180° rotation about the y axis. Therefore, the presence of two positions in the same specimen for WM 2 and 3 can be attributed to the 90° twinning occurring in KFCT, while for WM 1 we conclude that both positions must coexist in each twin (i.e. they would appear even in a single crystal).

A quite different model has been proposed by Lundin *et al* (1969) (to be referred to as LGZ; see also Habuda *et al* 1970), who worked with a KRuCT single crystal (KRuCT shows much less tendency to twinning than KFCT, to which it is isomorphous). According to them, WM 2 and 3 have opposite orientations and remain fixed in the PE phase. This agrees with our result and with KKWNH's model (*b*) (there is, however, some discrepancy about the orientation of each WM). On the other hand, WM 1 switch, in the PE phase between two opposite positions lying on the xz plane, while in the FE phase they align parallel to each other in one of the former positions, with their dipole moments in the [100] (or the [$\bar{1}$00]) direction. For the KRuCT crystal used by LGZ the measured $\boldsymbol{P}_s$ was indeed found to be in the [100] direction.

This of course contradicts the work of the Japanese authors (Waku *et al* 1960a, Toyoda *et al* 1960), according to which the polarisation direction is [10$\bar{1}$] for KFCT and KRuCT single crystals. LGZ argue that the Japanese authors must have been working with twinned specimens, but this explanation is hardly acceptable because (*a*) Toyoda *et al* (1960) are very careful in distinguishing between twinned and untwinned crystals

† The experiment of the former authors is described in Tsang and O'Reilly (1965).

and (*b*) if the polarisation direction in single crystals were [100], then whenever polarisation in the [10$\bar{1}$] direction is observed in a given specimen, it should also be observed in the [101] direction: this is contrary to the experimental results of Waku *et al* (1960a and b), Toyoda *et al* (1960) and Tsang and O'Reilly (1965).

It can be seen that our results are in marked disagreement with both model (*a*) of KKWNH and LGZ's model. On the contrary, they are in very good agreement with model (*b*) of KKWNH: this can be seen by comparing our values for the hydrogen coordinates with those obtained by interpreting TMH's data according to model (*b*) (table 2).

Due to their mutual agreement, our model and the previously discussed model (*b*) support each other, so that one can confidently believe that they give a good description of the physical situation. According to this, the FE–PE transition should essentially consist in the disordering of the WM into two configurations such as those we found in this paper. Notice that the two high temperature configurations are not necessarily identical with the low temperature ones (we shall call the latter A and B and the former A′ and B′). In fact, the orientation of each WM is dictated by its interactions with the ions (which are fixed) and with the other WM. In other words, the exact shape of the double well in which each WM moves depends, to some extent, on the orientation of the other WM. The orientations corresponding to configurations A and B have been obtained with all the WM in an ordered arrangement.

If the disordering process took place in a random way, then the field at each WM site would not be the same in the PE as in the FE phase, because the contributions from the intermolecular interactions would be different in both phases. Therefore, A′ and B′ should be different from A and B respectively.

Another possibility is that in the PE phase all the WM switch cooperatively between the two positions A′ and B′, which in this case would be identical with A and B. This could explain why the disordering occurring at T_c was not detected in the inelastic neutron scattering experiment of Rush *et al* (1966). It is interesting to notice that such a cooperative motion of the WM would be a phenomenon of the same kind as the 'dipole plasmon' whose existence in a dipole liquid (CH_3–NO_2) has been detected by Ascarelli (1976). In fact, the force causing the WM to move cooperatively is, in a first approximation, an electrostatic dipole–dipole interaction. In the present case we might speak of a 'dipole phonon' becoming soft at the transition temperature.

A way of choosing between both disordering processes could be a determination of the hydrogen positions at low temperature by neutron diffraction (provided, of course, that the difference between the H positions in the two phases was large enough to be detected), in order to compare them with TMH's values, which were obtained at high temperature.

5. Conclusion

The orientations of the WM of the KFCT structure in the low temperature phase are found assuming that the WM are only subject to electrostatic interactions. The results are in good agreement with experiment. This allows one to conclude that the simplified model assumed in this paper is a reasonable one, and can be used for further studies about the FE–PE transition of KFCT.

The existence of a double-well potential in which the WM switch in the PE phase suggests that the transition is of the order–disorder type, via an orientational switching

of the WM in the PE phase, such as in $NaNO_2$ (§ 15.20 of Megaw 1973). This process is quite unlike the reordering of protons in the double well of an X–H–Y bond.

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