BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 52 (3), 941—942 (1979)

Mechanism of the Ferroelectric Phase Transition in $K_4[Fe(CN)_6]\cdot 3H_2O$ and $K_4[Fe(CN)_6]\cdot 3D_2O$

Masaharu OGUNI, Takasuke MATSUO, Hiroshi SUGA, and Syûzô SEKI*
Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka 560

(Received September 4, 1978)

Synopsis. Mechanism of the ferroelectric phase transition in potassium hexacyanoferrate trihydrate is discussed from static and dynamic points of view, and a new model is proposed. The model takes into account four states as accessible for a water trimer, instead of two in the earlier model. If the four states were equally probable in the disordered phase, the predicted transition entropy is R ln 4 compatible with the experimental value. It is expected that a glass transition, if possible, occurs at 50—60 K for the model. Since the anomalous heat capacity in this temperature region is effectively zero, the model is consistent with absence of a glass transition. Occupancy fractions of hydrogen sites are given for the earlier and the present models.

There are three aspects of interest in the property of orientationally disordered crystals. First, what is the molecular unit of disorder in the crystal? Second, is the disorder static or dynamic? and if dynamic, how rapid is the molecular reorientation? And third, at what temperature does the disorder change to order? The first and third are equilibrium aspects and can be studied by structural and thermodynamic methods. The second is the kinetic property and has been studied rather independently of the other two by NMR, dielectric and other spectroscopic methods. However, it has been shown recently that precise measurement of the heat capacity, a typical equilibrium property, can be used for study of molecular motion in a number of orientationally disordered crystals including molecular, ionic and hydrogen-bonded crystals.[1] The principle involved here is simple and may be summarized as follows. A relaxational heat-capacity anomaly occurs at the temperature at which the molecular relaxation time becomes comparable with the time required for a single heat-capacity measurement, typically 10^2—10^5 s. An important proviso for the anomaly, glass transition, to be observed is that orientational heat capacity has to be appreciable at that temperature. When such a situation prevails in a stable (as opposed metastable) crystal, formation of a glassy state is an unescapable result. If one does not find a glass transition in a careful measurement of the heat capacity of a substance, one can conclude that molecular reorientation is sufficiently rapid in the relevant temperature range. In this note we shall supplement the previous paper on the calorimetric study[2] of the phase transition in potassium hexacyanoferrate trihydrate $K_4[Fe(CN)_6]\cdot 3H_2O$ and the deuterate analogue in the light of above argument.

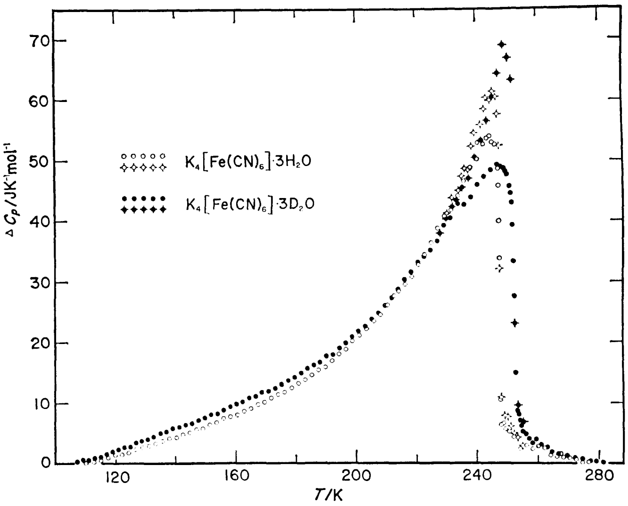

Fig. 1. Anomalous part of heat capacity of $K_4[Fe(CN)_6]\cdot 3H_2O$ and $K_4[Fe(CN)_6]\cdot 3D_2O$.

Figure 1 reproduces the anomalous heat capacity of $K_4[Fe(CN)_6]\cdot 3H_2O$ and $K_4[Fe(CN)_6]\cdot 3D_2O$. The anomaly extends from the transition temperature (250 K (H_2O), 255 K (D_2O)) down to 110 K. The entropy of transition is 12.4 J K^{-1} mol^{-1} (H_2O) and 14.3 J K^{-1} mol^{-1} (D_2O) ($\approx R\ln 4$ or more). According to the neutron diffraction,[3] the crystal contains trimers of water molecules. The trimer itself is polar as shown in Fig. 2. It has been suggested that the ferroelectricity originated from the parallel alignment of the polar trimer. This model leads to the transition entropy of $R\ln 2$ ($=5.76$ J K^{-1} mol^{-1}) because there are two orientations for each of the trimer as shown schematically in Figs. 2(a) and (d). The predicted entropy is too small to account for the experimental value.

An alternative model proposed here assumes four states per water trimer. The two states (b) and (c) of Fig. 2 are assumed in addition to the states (a) and (d). The state (a) is symmetry-related to (d) and (b) to (c), but states (a), (d) are not equivalent to (b) or (c). However, all of hydrogen atoms are engaged in hydrogen bonding in any of the four arrangements. Therefore we may neglect difference in their energy for the moment. The transition entropy is Rln4 for this model in agreement with the experiment.

The kinetic aspect of the model is considered next. Clearly the rearrangement from one state to the other proceeds through the reorientation of water molecules, and as such it is related to librational mode of water molecule. The relaxation time of such rearrangement is usually described by Arrhenius expression $\tau=\tau_0\exp(\Delta H_a/RT)$. The pre-exponential factor τ_0 will be of the order of magnitude 10^{-14}—10^{-15} s, since it may be equated to $1/(2\pi\nu)$ where ν is the vibrational frequency of the librational mode. Similar situations were found to be adequate for relaxation times in the glass transitions of orthoboric acid and stannous chloride

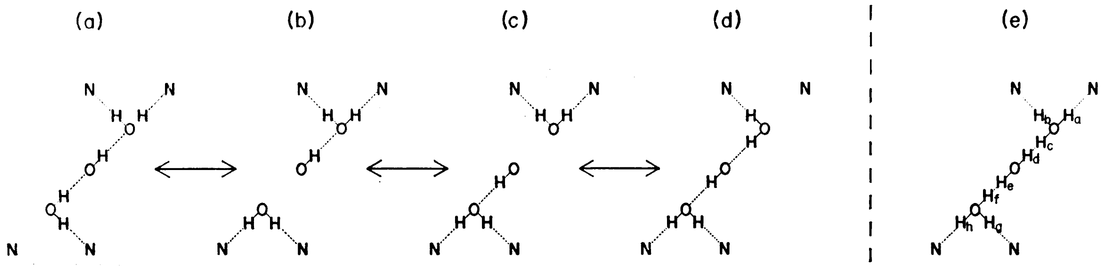

Fig. 2. Arrangements of hydrogen atoms in the hydrogen-bonded system composed of three water molecules and the surrounding nitrogen atoms.

dihydrate crystals.[4,5] The activation enthalpy may be equated to the order of the energy for breaking of the hydrogen bond. The energy of relatively long hydrogen bonds is 15—25 kJ mol^{-1}.[6] Waldstein *et al.*[7] estimated 15 kJ mol^{-1} per bond for the potential barrier hindering the reorientational motion of the molecule in ice. The same value was also found from the thermodynamic study of the glass transition in orthoboric acid crystal.[4] Therefore the activation enthalpy per bond is estimated to be 15—20 kJ mol^{-1} for the present crystals.

If the rearrangement from (a) to (d) in Fig. 2 proceeded through the simultaneous reorientation of three water molecules, then the activation enthalpy for the process would be estimated to be 45—60 kJ mol^{-1}. Since the glass transition takes place when the relaxation time becomes the order of 1 ks, this activation enthalpy corresponds to the glass transition temperature of 140—190 K. Here we took $\tau_0=8\times10^{-15}$ s from experimental value for $SnCl_2\cdot2H_2O$. If this were really the case, the glass transition would have been observed because the configurational contribution to the heat capacity is large enough in this temperature region as shown in Fig. 1. The glass transition, however, was not observed in the actual calorimetric measurement.[2] This indicates that the process assumed above is incorrect.

Next, the alternative model including states (b) and (c) is examined. The process (a)↔(b), (b)↔(c), or (c)↔(d) may be interpreted as the transfer of a Bjerrum L defect. In this case the activation enthaply will be 15—20 kJ mol^{-1} because it involves disruption of only one hydrogen bond. Using the same τ_0 as above one obtains 50—60 K for the glass transition temperature. The glass transition will not be observed in this case because the configurational heat capacity is practically zero at this temperature. This agrees with the experimental result that the glass transition does not occur in this crystal.

At the same time, the assumption that the four states (a)—(d) occur equally probably in the high temperature disordered phase would be reasonable because they all involve one L defect in common. Thus, by allowing the intermediate states (b) and (c) as well as the states (a) and (d) in the disordered phase, one can interpret consistently both the observed entropy of transition and absence of glass transition in this compound. A direct test of the model proposed here, including the validity of the energetical equivalence of the four arrangements, may be obtained from precise determination of the occupancy fraction of the hydrogen sites at different temperatures by neutron diffraction. The symbols H_a, $H_b\cdots$ in Fig. 2(e) represent hydrogen sites in a water trimer. Now let α, β, γ, δ, ε, ζ, η, and θ denote the occupancy fraction for H_a, H_b, H_c, H_d, H_e, H_f, H_g, and H_h, respectively. If the energy of states (b) and (c) in Fig. 2 were higher in the disordered phase by E than that of (a) and (d), the fraction would be given as follows; $\alpha=\theta=(1/2)[1+2\exp(-E/RT)]\cdot[1+\exp(-E/RT)]^{-1}$, $\beta=\eta=1$, $\gamma=\zeta=(1/2)[1+\exp(-E/RT)]^{-1}$, and $\delta=\varepsilon=1/2$. In the earlier model taking only the states (a) and (d) as accessible into account, $\alpha=\theta=1/2$, $\beta=\eta=1$, $\gamma=\zeta=1/2$, and $\delta=\varepsilon=1/2$ in the disordered phase. In the limiting case of $E=0$, where the four states (a)-(d) in Fig. 2 are allowed equally probably, we obtain $\alpha=\theta=3/4$, $\beta=\eta=1$, $\gamma=\zeta=1/4$, and $\delta=\varepsilon=1/2$. Thus the two models predict different occupation fractions of proton or deuteron in each site. The earlier neutron diffraction data have been analysed *a priori* with $\alpha=\theta=1/2$, $\beta=\eta=1$, $\gamma=\zeta=1/2$, and $\delta=\varepsilon=1/2$. New diffraction experiment as well as reinvestigation of the earlier neutron diffraction data will be interesting because the proposed model is a modification of the half-hydrogen model of hydrogen bonding that has been used so extensively.

References

1) H. Suga and S. Seki, *J. Non-Cryst. Solids*, **16**, 171 (1974).

2) M. Oguni, T. Matsuo, H. Suga, and S. Seki, *Bull. Chem. Soc. Jpn.*, **48**, 379 (1975).

3) J. C. Taylor, M. H. Mueller, and R. H. Hitterman, *Acta Crystallogr., Sect. A*, **26**, 559 (1970).

4) M. Oguni, T. Matsuo, H. Suga, and S. Seki, *Bull. Chem. Soc. Jpn.*, **50**, 825 (1977).

5) T. Matsuo, M. Oguni, H. Suga, and S. Seki, *Bull. Chem. Soc. Jpn.*, **47**, 57 (1974).

6) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Company, San Francisco, (1960) p. 213.

7) P. Waldstein, S. W. Rabideau, and J. A. Jackson, *J. Chem. Phys.*, **41**, 3407 (1964).

Note added in proof

Helwig, Klöpperpieper, and Müser measured recently the spontaneous polarization and heat capacity of $K_4[Fe(CN)_6]\cdot3H_2O$ in a limited temperature range covering the transition point) (*Ferroelectrics*, **18**, 257 (1978)). Their data support our conclusion on a phenomenological level.