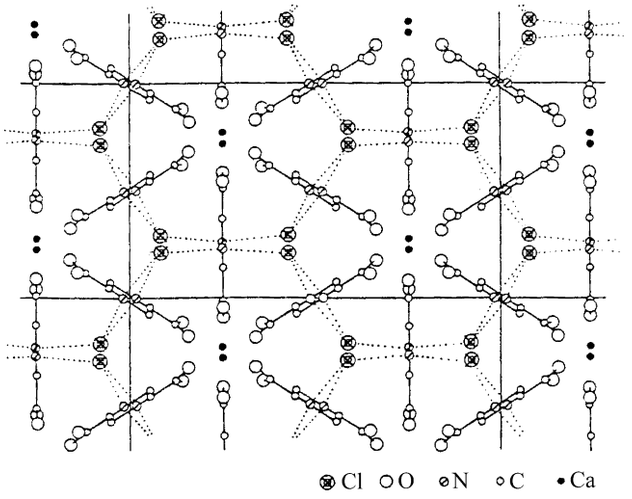

Fig. 3.1.5.14. Structure of tris-sarcosine calcium chloride, $(CH_3NHCH_2COOH)_3CaCl_2$. The hydrogen ion (proton) on the COOH group is relocated in the crystal onto the N atom to form a zwitter ion, forming an H—N—H group that hydrogen bonds to adjacent chlorine ions. Each nitrogen forms two such hydrogen bonds, whereas each chlorine has three, forming a very complex network of hydrogen bonding. The phase transition is actually displacive, involving a rather rigid rolling of whole sarcosine molecules, which stretches the N—H bonds; it is not order–disorder of hydrogen ions in a Cl···H—N double well. (The Cl···H—N wells are apparently too asymmetric for that.)

CH_3NHCH_2COOH in which the hydrogen ion comes off the COOH group and is used to hydrogen bond the nitrogen ion to a nearby chlorine, forming a zwitter ion. As is illustrated in this figure, this results in a relatively complex network of N—H···Cl bonds. The COO^- ion that results at the end group of each sarcosine is ionically bonded to adjacent calcium ions. The resulting structure is highly ionic in character and not at all that of a 'molecular crystal'. The structure at ambient temperatures is *Pnma* (D_{2h}^{16}) with $Z = 4$; below 127 K it distorts to *Pna*2$_1$ (C_{2v}^{9}) with Z still 4.

It had been supposed for some years on the basis of NMR studies of the Cl ions, as well as the conventional wisdom that 'hydrogen-bonded crystals exhibit order–disorder phase transitions', that the kinetics of ferroelectricity at the Curie temperature of 127 K in TSCC involved disorder in the proton positions along the N—H···Cl hydrogen bonds. In fact that is not correct; even the NMR data of Windsch & Volkel (1980), originally interpreted as order–disorder, actually show (Blinc *et al.*, 1970) a continuous, displacive evolution of the H-atom position along the H···Cl bond with temperature, rather than a statistical averaging

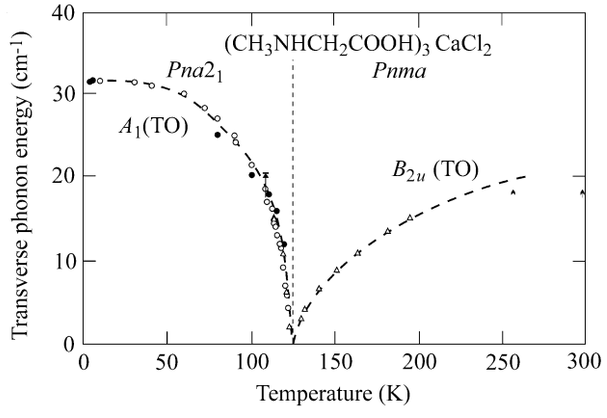

Fig. 3.1.5.15. 'Soft' optical phonon frequencies *versus* temperature in both ferroelectric and paraelectric phases of tris-sarcosine calcium chloride.

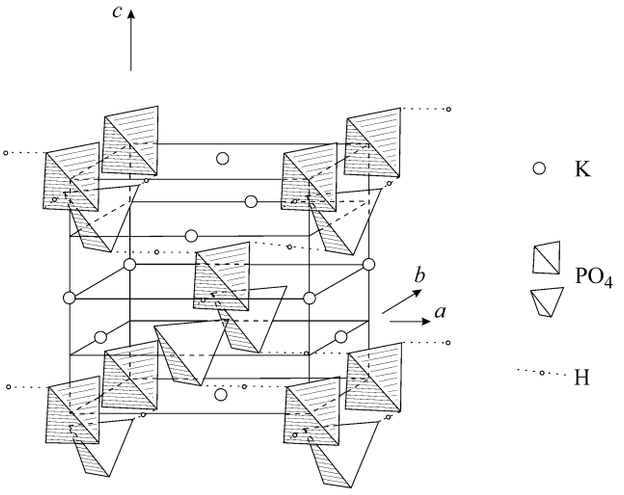

Fig. 3.1.5.16. The structure of potassium dihydrogen phosphate, KH_2PO_4, showing the O···H···O hydrogen bonds.

of two positions, which would characterize order–disorder dynamics. In addition, as shown in Fig. 3.1.5.15, there is (Kozlov *et al.*, 1983) a lightly damped 'soft' phonon branch in both the paraelectric and ferroelectric phases. TSCC is in fact a textbook example of a displacive ferroelectric phase transition. The hydrogen bonds do not exhibit disorder in the paraelectric phase. Rather, the transition approximates a rigid rotation of the sarcosine molecules, which stretches the N—H···Cl bond somewhat (Prokhorova *et al.*, 1980).

3.1.5.2.10. *Potassium dihydrogen phosphate, KH_2PO_4*

Potassium dihydrogen phosphate, colloquially termed 'KDP', has probably been the second most studied ferroelectric after barium titanate. It has been of some practical importance, and the relationship between its hydrogen bonds, shown in Fig. 3.1.5.16, the perpendicular displacement of heavier ions (K and P) and the Curie temperature has fascinated theoretical physicists, who generally employ a 'pseudo-spin model' in which the right and left displacements of the hydrogen ions along symmetric hydrogen bonds (O···H···O) can be described by a fictitious spin with up (+1/2) and down (−1/2) states.

Unlike TSCC, discussed above, KDP has perfectly symmetric hydrogen bonds. Therefore, one might expect that above a sufficiently high temperature the protons can quantum-mechanically tunnel between equivalent potential wells separated by a shallow (and temperature-dependent) barrier. Below T_C the protons order (all to the right or all to the left) in spatial regions that represent ferroelectric domains. This model, initially proposed by Blinc (1960), is correct and accounts for the large isotope shift in the Curie temperature noted for deuterated specimens. The complication is that the spontaneous polarization arises along a direction perpendicular to these proton displacements, so the dipoles do not arise from proton displacements directly. Instead, the proton coupling (largely Coulombic) to the potassium and phosphorus ions causes their displacements along the polar axis. This intricate coupling between protons along hydrogen bonds, which undergo an order–disorder transition, and K and P ions, which undergo purely displacive movements in their equilibrium positions, forms the basis of the theoretical interest in the lattice dynamics of KDP. Following Strukov & Levanyuk (1998), we would say that arguments over whether this transition is displacive or order–disorder are largely semantic; the correct description of KDP is that the thermal change in occupancy of the O···H···O double wells modifies the free energy in such a way that the K and P ions undergo a displacive rearrangement.

Copyright © 2006 International Union of Crystallography