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Phase transition and temperature dependence of the molecular distortion of ions in ammonium sulphate

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Abstract. The temperature dependence of the molecular distortion of ions in ammonium sulphate (AS) is discussed in order to ascertain the correct microscopic mechanism of phase transition (PT) in this crystal. It is reported that the transition in AS is triggered by distortion arising in the structure of the SO_4^{2-} ion. This has been confirmed from a detailed analysis of the crystal structural data available at different temperatures around T_c. It is concluded that the type of transition occurring in AS is different from the well known displacive/order–disorder type and it could be given a name such as molecular distortion type. Such a transition can only take place in crystals having one or more than one kind of molecular unit. It leads to a change mainly in the structure and symmetry of such units, rather than in their location and orientation. Our model is found to be consistent with the phenomenological theory of Ikeda and co-workers which explains reasonably well the temperature variation of dielectric constant, elastic compliances, etc.

1. Introduction

Ammonium sulphate (AS) undergoes a peculiar ferroelectric phase transition (PT) at 223 K. The tetra-molecular unit cell of AS belongs to the D_{2h}^{16} space group in the paraelectric phase and to C_{2v}^{9} in the ferroelectric; it contains two crystallographically different ammonium ions: NH_4^+ (I) and NH_4^+ (II) (Wyckoff 1964, Schlemper and Hamilton 1966). This transition has been the subject of a large number of studies: structural (Schlemper and Hamilton 1966), twin plane motion (Makita *et al* 1976), dielectric (Ikeda *et al* 1973, Yoshihara *et al* 1976, Ohi *et al* 1978, Unruh *et al* 1978), DMR (O'Reilly and Tsang 1967), NMR (Blinc and Levstek 1960), EPR (Abe and Shibata 1977, Barb *et al* 1978, Manjunath and Srinivasan 1978, Ramnathan and Srinivasan 1978, Hirabayashi and Abe 1980, Narayana and Kevan 1981), DTA (Badr and Awad 1984) as well as IR absorption and Raman scattering (Torrie *et al* 1972, Jain *et al* 1973, Jain 1974, Petzelt *et al* 1974, Venkateswarlu *et al* 1975, Iqbal and Christoe 1976. Several semi-theoretical and theoretical studies of the transition are also available (Sawada *et al* 1973, Jain and Bist (1974a, b), Dvořák and Ishibashi 1976, Onodera *et al* 1978, Zinenko *et al* 1980). However, the microscopic mechanism of the transition is yet to be correctly understood. According to O'Reilly and Tsang (1967), the transition is of order–disorder type involving reorientation of distorted ammonium ions, NH_4^+ (I) and NH_4^+ (II), while in the view of Sawada *et al* (1973) it is of displacive type. Jain and co-workers (Jain *et al* 1973, Jain

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and Bist 1974a, b) suggested a new mechanism of the transition on the basis of their observation on the temperature variation of IR absorbance of a few thermosensitive bands and other observations available at that time. Accordingly, the transition is triggered by distortion arising in the structure of the SO_4^{2-} ion and the order parameter coupled with spontaneous polarisation has several components including spontaneous strain in the SO_4^{2-} ion as its major contributor. Although several investigations have since then corroborated this suggestion, at times it has also been suggested that a better understanding of the microscopic mechanism can be obtained from detailed analysis of the structural data of the crystal kept at different temperatures around T_c. In this paper we therefore analyse such data recently reported by Hasebe (1981).

2. Analysis of structural data

Hasebe (1981) has published crystallographic data of AS at 233, 224.5, 219.5, 209, 183 and 133 K. In order to make a fruitful analysis of these data, dipolar distortion (δr) in SO_4^{2-}, NH_4^+ (I) and NH_4^+ (II) ions has been calculated; δr is given (Jain and Bist 1974a, b) by

$$\delta r = \sum_{i=1}^{3} \sum_{r=1}^{4} (B_i^r - A_i) \qquad (1)$$

where A_i and B_i^r are the ith components of the position vectors respectively of the A atom and the rth B atom of the $AB_4^{\mp n}$ tetrahedron. The calculated values of $|\delta r|$ are given in table 1 and are plotted in figure 1 to depict the nature of their temperature variation. A critical examination of these plots reveals the following:

(a) The distortion in the SO_4^{2-} ion is less in the para-electric than in the ferroelectric phase; on cooling the crystal, it increases slowly and smoothly, except at T_c, where it suddenly increases by a factor of 2.0. The theory of distortion induced IR and Raman intensity of the forbidden modes of molecular units, developed by Jain and Bhattacharjee (1985) has shown that this observation is in close agreement with what formed the basis of the conclusions of Jain and co-workers (Jain *et al* 1973, Jain and Bist 1974a, b).

(b) The exact amount of change in distortion of ammonium ions at T_c could not be estimated from the curves (figure 1) because the structural data pertaining to these ions in para-electric AS at temperature near T_c are not available. However, it is clear that the changes in the distortion of NH_4^+ ions do not occur only at T_c (if they do at all) but also

Table 1. Calculated value of distortion in NH_4^+ (I), NH_4^+ (II) and SO_4^{2-} ions in $(NH_4)_2SO_4$.

Temperature (K)	Distortion ($\lvert\delta r\rvert$) (Å)		
	SO_4^{2-}	NH_4^+ (I)	NH_4^+ (II)
233.0	0.018801		
224.5	0.021463		
219.5	0.044621	0.15611	0.15389
209.0	0.049009	0.14456	0.18035
183.0	0.052002	0.20250	0.03106
133.0	0.054663	0.11519	0.18863

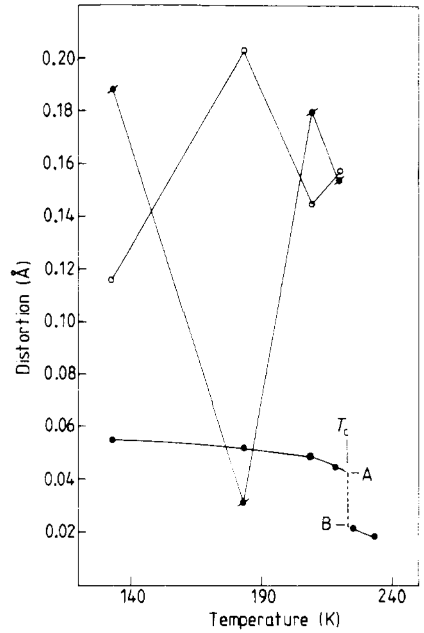

Figure 1. Plot of temperature dependence of the distortion in NH_4^+(I) (○), NH_4^+(II) (✱) and SO_4^{2-} (●) ions. (A) $\delta r^-(T_c) = 0.044$; (B) $\delta r^-(T_c) = 0.022$.

at other temperatures, e.g. at about 183 K where no PT is known to occur. In addition, several investigations conclude beyond any doubt that the structural and dynamical changes associated with NH_4^+ ions are not commensurate with the first-order nature of the transition. For example: (i) NH_4^+ ions in the para-electric phase oscillate with large amplitudes which continue in the ferroelectric phase; the NH_4^+ (I) ion freezes at ~160 K, while NH_4^+ (II) continues moderate oscillations even up to ~90 K (Kydon *et al* 1967), (ii) O'Reilly and Tsang (1967) showed that the order-disorder phenomenon can be consistent with the first-order phase transition in $(NH_4)_2SO_4$ if the transition involves the cooperative re-orientation of NH_4^+ ions at T_c which however does not occur according to the well discussed study of NMR data by Miller *et al* (1962). (iii) No change in NMR line-width takes place at T_c (Blinc and Levstek 1960), (iv) T_c is not affected by deuteration (Hoshino *et al* 1958) or is negligibly affected (Unruh and Rüdiger 1972). (v) The intensity of the thermosensitive IR band at 3303 cm^{-1} associated with NH_4^+ ions changes slowly (Jain and Bist 1974a).

3. Discussion

In view of the above analysis, the crystallographic data of Hasebe (1981) confirm the observations of Jain and co-workers (Jain *et al* 1973, Jain and Bist 1974a, b) and obviously corroborate their inferences. One may also note that these observations and inferences are also corroborated by recent studies. For example, Iqbal and Christoe (1976) and Hirabayashi and Abe (1980) have also observed that the phase transition in AS is accompanied by deformation of the SO_4^{2-} ion. Badr and Awad (1984) and Abe and

Shibata (1977) have inferred that the SO_4^{2-} is responsible for the spontaneous polarisation and it plays a vital role in the process of transition. Manjunath and Srinivasan (1978) reiterate exactly what has been concluded by Jain and Bist (1974a, b). Zinenko *et al* (1980) believe that the unusual behaviour of P_s in AS may be due to the fact that the phase transition is not associated with the ordering of NH_4^+ ions as suggested in their model but with the ordering of the SO_4^{2-} ion. We also note that: (i) Hasebe and Tanisaki (1977) could not explain x-ray diffuse scattering which they had observed in terms of order–disorder of NH_4^+ ions. The results are rather understood in terms of the librational motion of the SO_4^{2-} ion. (ii) Neutron diffraction data, which are obviously considered to be more accurate and reliable than x-ray diffraction data for determining the positions of H atoms, do not reveal order–disorder mechanism (Schlemper and Hamilton 1966). Evidently, the order–disorder mechanism involving NH_4^+ ions (as envisaged by Hasebe) is not supported by several investigators.

It may be mentioned that Hasebe (1981) reports that the positional parameters of sulphur change slightly but those of oxygen atoms change drastically with temperature below T_c. He suggests that the configuration of the SO_4^{2-} ion below T_c can be derived from that above T_c (−40° C) by a small amount of translation followed by a rotation through a certain angle about an axis passing through sulphur. But this cannot be true in general because one cannot exclude the possibility of structural distortion of the SO_4^{2-} ion. Our calculations (table 1) evidently show that distortion in the SO_4^{2-} ion does occur. Thus Hasebe did not interpret his data correctly and consequently made an erroneous conclusion that the structure of the SO_4^{2-} ion even in the ferroelectric phase resembles the regular tetrahedron.

In view of these facts, revealed from several experimental observations, we believe that the phase transition in AS should have the following microscopic mechanism. It may be noted that the crystal structure of AS with respect to the positions of NH_4^+(I), NH_4^+(II) and SO_4^{2-} is mainly decided by inter-ionic forces, while the structure of individual NH_4^+(I), NH_4^+(II) and SO_4^{2-} ions is decided mainly by intra-ionic forces (covalent in nature). Since the inter-ionic forces are more anharmonic than covalent forces, thermal contraction (with decreasing temperature) in the size of individual ion is less than that in the volume available for these ions in the crystal cell. Consequently with decreasing temperature, ions experience a force that tends to squeeze and deform them. This force should obviously be resisted by the intra-ionic forces trying to retain their original shape and size. In the process, the stress on the ions increases. At T_c, this stress becomes sufficient to force the ions (and the crystal as a whole) to assume a structure and symmetry different from what they had above T_c. Guided by the fact that T_c remains unaffected by deuteration (Hoshino *et al* 1958, Unruh and Rudiger 1972), we infer that the main driving force for the transition is centred around the SO_4^{2-} ion; the NH_4^+ ions simply follow the change that is forced on them. The change in the strength of H bonding is also a secondary effect. As a result of increased deformation, the SO_4^{2-} ion acquires significant magnitude of electric dipole moment and this additional dipole appears between the two already existing NH_4^+ dipoles. This reduces the effective distance between the dipoles. Consequently, the distortion of the SO_4^{2-} ion is followed by its re-orientation immediately to acquire the new configuration of minimum free energy; the NH_4^+ ions continue their large amplitude oscillation (through the transition point) which freezes only at temperatures as low as ~160 K for NH_4^+(I) and ~90 K for NH_4^+(II) (Kydon *et al* 1967).

Ferroelectricity in AS is accounted for by the permanent dipole moment of distorted ions in the crystal (Jain and Bist 1974a, b). The kind of distortion that results in a permanent dipole moment comes into existence obviously when the structure of the ions becomes frozen with non-zero amplitude of IR active internal modes, ν_3 and ν_4. Rotation of the tetrahedral ion on the other hand does not lead to a structure that can have ferroelectricity unless the ion is distorted. Thus distortion is the prerequisite of the coupling between the rotation of ions and polarisation of the crystal. Further, the rotation cannot account for the change in the internal structure of the ions. It should be noted that the rotation does not belong to the IR active F_2 species of T_d point group. Hence, the freezing of tetrahedral ion, only with finite rotation, as suggested by Hasebe (1981), about any axis cannot lead to a structure with permanent dipole moment. As a regular tetrahedron, the SO_4^{2-} ion does not have even a quadrupole moment. Consequently, even the quadrupole–dipole type weak interaction should be absent between the librating SO_4^{2-} ion (if it has T_d structure) and pseudo-spins (NH_4^+ ions). Obviously Hasebe's observation that the SO_4^{2-} ion retains its regular tetrahedral structure and his proposed coupling between librating SO_4^{2-} ion and pseudo-spins are not in line with each other. However, the fact remains that the SO_4^{2-} ion acquires increased distortion and electric dipole moment at T_c. Therefore, the possibility of the said coupling can be rationalised in terms of a dipole–dipole interaction. But it should be remembered that this coupling comes into play only after the SO_4^{2-} ion acquires distortion. This explains how re-orientation of the NH_4^+ ions (or their disordering, as Hasebe puts it) follows as an after-effect of SO_4^{2-} ion distortion. In view of these facts the importance of SO_4^{2-} ion distortion as an essential component of the order parameter is rightly emphasised; the rotation of the ion could be an additional component. This is further supported by the fact that the point charge model calculations reveal that the antiparallel NH_4^+ ions at -53.5 °C contribute only 0.13 $\mu C\ cm^{-2}$ to P_s against 0.40 $\mu C\ cm^{-2}$ as claimed by Hasebe (1981).

The soft mode, which fits in our model, should obviously be a mixed mode of internal vibration and libration of the SO_4^{2-} ion. This falls well in agreement with the observation of Ramanathan and Srinivasan (1978) Fujimoto *et al* (1977), Hasebe and Tanisaki (1977) and other workers (Narayana and Kevan 1981, Badr and Awad 1984). Because of the strong interaction of the SO_4^{2-} ion with its surroundings, both components of this soft mode should be fast relaxing. Note, that Petzelt *et al* (1974) and Fujimoto *et al* (1977) have argued that the soft mode may not be observed if it relaxes fast. This could be the reason that the soft mode responsible for the transition in AS has not been observed in the far infrared (Torrie *et al* 1972, and Petzelt *et al* 1974) and low-frequency Raman (Torrie *et al* 1972 and Jain 1974) spectra studied up to as low as 30 cm^{-1} phonon frequency. We also notice that the librational mode of tetrahedral ion is forbidden both in IR and Raman spectra. Consequently, this mode of the SO_4^{2-} ion having almost tetrahedral structure in para-electric phase of AS may not gain observable intensity. Even in the ferroelectric phase it may only gain low intensity. This could be another reason why the librational component of the soft mode has not been detected.

The fact that inter-ionic force is more anharmonic than intra-ionic force, as mentioned by us, should not imply that the forces governing the internal modes of the SO_4^{2-} ion are not anharmonic. In fact the internal modes of the SO_4^{2-} ion in AS are governed by intra-ionic potential as well as inter-ionic potential and the anharmonic component of both these potentials influences these modes. Thus our conclusion regarding the nature of the soft mode is very much in line with the fact that the mode softening occurs due to anharmonicity. The frequencies of the internal modes ($\nu_1 = 976$, $\nu_2 = 450$, $\nu_3 = 1087$ and $\nu_4 = 618$ cm^{-1} (Venkateswarlu *et al* 1975)) of the SO_4^{2-} ion in AS do not differ by more than a few wavenumbers from those ($\nu_1 = 981$, $\nu_2 = 451$, $\nu_3 = 1104$

and $\nu_4 = 613\ \mathrm{cm}^{-1}$ (Herzberg 1945)) in its free state. Therefore, it should not be difficult to believe that the internal modes of the ion retain their identity in the crystal.

In order to examine how the mechanism of transition in AS as proposed in this report is different from displacive/order–disorder type, we consider the transition as an operator, which forces some set(s) of atom(s)/molecule(s) to change their position(s)/ posture/ internal-structure through freezing of their translational/rotational/internal modes with non-zero amplitude. In this framework the displacive type transition is the result of the freezing of translatory modes (for example, the transition in $BaTiO_3$), while the order–disorder type may arise due to freezing of translatory/rotatory modes of the unit (e.g. transition in KH_2PO_4, NH_4Cl, etc.). However, a transition resulting from the freezing of internal modes of the unit cannot be fitted into the class of displacive/order–disorder type; such a transition should obviously be named differently. Perhaps it could be known as molecular distortion type since this leads to some distortion in the structure of molecular unit(s) rather than causing a change in their position and/or posture. Normally, a transition arises due to freezing of a mixed mode having different amplitude of translatory/rotary/internal modes. However, the nature of the mode with maximum amplitude may be chosen to decide whether the transition is of the displacive/order–disorder/molecular distortion type. It may be remarked that the distortional type transition may only occur in crystals having molecular unit(s). If we examine the transition in AS in the framework of this kind of classification, it may easily be seen to be the molecular distortion type.

Ikeda *et al* (1973) developed a theory of phase transition in AS which explains reasonably well the temperature variation of dielectric constant, spontaneous polarisation, elastic compliance, etc. They introduced an order parameter (η) of undefined physical nature and its coupling with spontaneous polarisation ($P_S = P_3$) and stress (X), in the free energy formulation, expressed by

$$G = \tfrac{1}{2}\beta(T - T_\eta)\eta^2 + \tfrac{1}{4}\gamma\eta^4 + \tfrac{1}{6}\delta\eta^6 + f\eta P_3 + \ldots \tag{2}$$

Many terms of G formulated by Ikeda *et al* (1973) are not reproduced here as they are unimportant for our discussion. Notations β, T_η, δ, etc., have their usual meaning; f is the measure of coupling between η and P_3. Ikeda *et al* conclude that temperature variation of the relative order parameter satisfies

$$(T - T_0)/(T_c - T_0) + Py^2 + Qy^4 + n(1 - FJ + g_3y^2F^2) = 0 \tag{3}$$

where

$$y = \eta(T)/\eta(T_c) = \frac{\text{Spontaneous } \eta \text{ at } T < T_c}{\text{Spontaneous } \eta \text{ at } T = T_c}$$

$$F = (1 + dy^2 + ey^4)/(1 + g_3y^2)$$

$$J = 1 + 3dy^2 + 5ey^4.$$

They evaluated the values of all relevant parameters e.g. $T_0 = 216.5$, $P = -4.33$; $Q = 3.12$, $n = 0.39$, $d = -0.06$, $e = 0.01$, etc, from a variety of experimental results such as temperature variation of dielectric constants, polarisability, elastic compliances, etc., and used these values in equation (3) to obtain the y against T curve reproduced in figure 2. In this figure we also mark the temperature variation of relative distortion of the SO_4^{2-} ion (Δ_{rel}) deduced from structural data (Hasebe 1981) and distortion induced IR absorbance (I) (Jain 1974) of ν_1 of SO_4^{2-}, using the relation (Jain and Bhattacharjee 1985) $I = K|\delta r|^2$ (K is constant).

$$\Delta_{rel} = (|\delta^- r(T)| - |\delta^+ r(T_c)|)/(|\delta^- r(T_c)| - |\delta^+ r(T_c)|) \ldots \quad (4)$$

where positive and negative signs respectively signify the values of distortion $|\delta r|$, above and below T_c at the temperature given in parentheses. It is interesting to note that within the error limits the two curves match closely. This not only supports the theory of Ikeda *et al*, but also corroborates our conclusion that SO_4^{2-} ion distortion is the basic component of the order parameter. In addition, it identifies the physical nature of the order parameter which was not spelled out by Ikeda *et al* and hence clarifies the physical details of the microscopic mechanism of PT. For example, the applied electric field (E) induces lattice polarisation mainly by disturbing the electron charge density, orientation of permanent dipoles and the inter-ionic separation such as r (SO_4^{2-} − NH_4^+). However, E does not affect the inter-atomic separation in the structure of the ions such as SO_4^{2-}, NH_4^+, etc, unless its strength is as high as the crystal fields. This implies that ordinary E and its conjugate parameter, P (the electric polarisation) can hardly affect the magnitude of $\delta r(SO_4^{2-})$, the order parameter. In view of this we can easily understand the weak coupling between $\delta r(SO_4^{2-})$ and P_3 (as considered by Ikeda *et al*) and also the fact that T_c is not affected by applied electric field bias (Hoshino *et al* 1958).

4. Conclusion

The temperature dependence of distortion of ions in AS calculated from x-ray crystallographic data reveals that the centre of triggering force for the transition lies in the SO_4^{2-} ion; changes in the structure of NH_4^+ ions occur as a follow-up process. The change in the strength of H bonding is also a secondary effect. The soft mode of the transition is the mixed mode of internal vibrations and libration of the SO_4^{2-} ion. All these

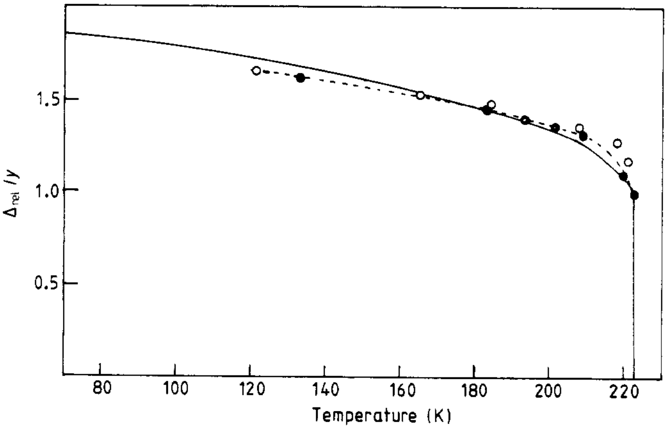

Figure 2. Comparison of the temperature dependence of the order parameter (y) used in the thermodynamic theory of transition by Ikeda *et al* (1973) and the experimental values of relative distortion in the SO_4^{2-} ion deduced from crystal structural data (●) and also from IR absorption intensity (○) of the distortion induced transition associated with the ν_1 mode of the ion.

conclusions are found to be consistent with the theory of this transition developed by Ikeda *et al* which explains reasonably well the several experimental observations. The order parameter of the transition is the distortion of the SO_4^{2-} ion. The microscopic mechanism is suggested to be molecular distortion type.

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