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Phenomenological theory of the phase transition in improper ferroelectric ammonium sulphate

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Abstract. A phenomenological theory accounting for the phase transition in improper ferroelectric ammonium sulphate has been discussed that is based on a molecular distortion-type microscopic mechanism (reported earlier). The theory uses the SO_4^{2-}-ion distortion as an order parameter and considers its linear coupling with the spontaneous polarisation to account for the ferroelectric behaviour. It has been used to account for the temperature dependence of the order parameter and dielectric constants. The dielectric susceptibility and the coefficient of linear coupling between the order parameter and the spontaneous polarisation in the ferroelectric phase are found to be different from those in the para-electric phase. The temperature dependence of the spontaneous polarisation and its possible origin have also been discussed.

1. Introduction

Ammonium sulphate (AS) is a typical example of an improper ferroelectric. This system has been studied extensively both theoretically and experimentally (see e.g., Jain *et al* 1986 and references therein). Following a comprehensive discussion Jain *et al* (1986) have concluded that the mechanism of the phase transition is neither displacive-type (D-type) nor order–disorder-type (OD-type), but a molecular distortion-type (MD-type), wherein SO_4^{2-}-ion distortion (changes in symmetry and structure) triggers the transition. The distortion has been identified as the order parameter. This phenomenological picture is further supported by our spectroscopic studies that (Bajpai and Jain 1987) reveal that the changes in the NH_4^+ ions and the hydrogen bonds in AS at T_c are minor and gradual, while those in the SO_4^{2-} ion are sudden. Also, the model successfully accounts for the observed heat of transition.

In the present paper we extend our conclusion that the SO_4^{2-}-ion distortion acts as the order parameter (η) to discuss the phenomenological theory of the transition by introducing linear coupling of this distortion with the spontaneous polarisation (P_s). The theory accounts for the temperature dependence of the dielectric constants. The temperature dependence of the spontaneous polarisation and its possible origin are discussed.

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2. Theoretical formulation

The phenomenological theory of improper ferroelectrics is based on the coupling between the order parameter and the spontaneous polarisation (see, e.g., Levanyuk and Sannikov 1968, 1970, Dvořák and Petzelt 1971, Dvořák 1970, 1971, 1974, Kobayashi *et al* 1972, Ikeda *et al* 1973). The spontaneous polarisation and the z component of the SO_4^{2-}-ion distortion in AS have the same symmetry; therefore, the lowest-order interaction term in the expansion of the free energy will be linear in both η and P_s. We further note that (i) AS is an improper ferroelectric for which T_c does not change when the electric field is biased and (ii) the order parameter below T_c changes very slowly with temperature (Jain *et al* 1986), while the changes in P_s may be significant. According to Unruh (1970), P_s assumes its maximum value of 0.62 $\mu C\, cm^{-2}$ at 221.5 K and goes to $-0.03\ \mu C\, cm^{-2}$ at 8 K through zero magnitude at 74.5 K. Both of these observations reveal that the coupling between η and P_s is weak.

It may be mentioned here that Ikeda *et al* (1973) have also discussed the phenomenological theory of the transition in AS; however, in their formulation they did not spell out the physical nature of the order parameter and in addition to the linear coupling between η and P_s they also included higher-order coupling terms in their free energy expansion. The inclusion of higher-order coupling may not be justified, particularly when the lowest-order coupling is itself weak. One also observes that, by including higher-order coupling, the calculated x and y components of the dielectric constant exhibit a discontinuity at T_c (Ikeda *et al* 1973), whereas no such behaviour is found experimentally. We therefore believe that if the higher-order coupling exists at all it is negligibly small, and the linear coupling term should be sufficient to understand the phenomenology of the transition in AS. Thus the free energy (G) of the system can be expressed as

$$G = \tfrac{1}{2}\alpha\eta^2 + \tfrac{1}{4}\gamma\eta^4 + \tfrac{1}{6}\delta\eta^6 + f\eta P_z + \tfrac{1}{2}\chi_{xx}^{-1}P_x^2 + \tfrac{1}{2}\chi_{yy}^{-1}P_y^2 + \tfrac{1}{2}\chi_{zz}^{-1}P_z^2 \tag{1}$$

where $\alpha = \beta(T - T\eta)$ and the terms $\tfrac{1}{2}\chi_{ii}^{-1}P_i^2$ $(i = x, y, z)$ give the dielectric response of the system in an external applied field. Here f gives the strength of the coupling between the order parameter (η) and the spontaneous polarisation (P_z). As the total polarisation results from the dipoles associated with the SO_4^{2-} ion as well as the NH_4^+(I) and NH_4^+(II) ions, the energy of the coupling, $f\eta P_z$, may be given by

$$f\eta P_z = f_1\eta P_z^{s} + f_2\eta P_z^{n_1} + f_3\eta P_z^{n_2} \tag{2}$$

where P_z^s, $P_z^{n_1}$ and $P_z^{n_2}$ are the polarisations due to SO_4^{2-}, NH_4^+(I) and NH_4^+(II), respectively. In writing equation (2) we have considered the fact that the dielectric behaviour can equally be affected by changes in the structure and dynamics of the NH_4^+ ions, although the transition is triggered by the SO_4^{2-}-ion distortion. However, since the SO_4^{2-}-ion distortion remains fairly constant and P_z changes significantly with temperature (we discuss this in § 3), it is reasonable to argue that the temperature dependence of P_z is mainly due to the continuous reorientation of the NH_4^+ dipoles and the weak coupling betwen the order parameter and the NH_4^+ dipoles. Obviously the coupling between η and P_z is largely governed by $f_1\eta P_z$.

Using G (equation (1)) in the equilibrium condition $\partial G/\partial\eta = 0$, we obtain

$$\alpha + \gamma\eta^3 + \delta\eta^5 + fP_z = 0. \tag{3}$$

In this expression the higher terms in η may be neglected to deduce the dielectric response for the para-electric phase:

$$\eta = -(f/\alpha)P_z \tag{4}$$

where P_z is the polarisation produced in the lattice by subjecting the crystal to an electric field E_z. The expressions for the dielectric constants may be obtained by using $\varepsilon_i = 1 + P_i/\varepsilon_0 E_i$ with equation (4) and $\partial G/\partial P_i = E_i$ (E_i being the applied electric field). The result is

$$\varepsilon_x^P = 1 + \chi_{xx}/\varepsilon_0 \tag{5}$$

$$\varepsilon_y^P = 1 + \chi_{yy}/\varepsilon_0 \tag{6}$$

$$\varepsilon_z^P = \varepsilon_z^0 + C/(T - T_0) \tag{7}$$

where $\varepsilon_z^0 = 1 + (1/\varepsilon_0)\chi_{zz}$, with the Curie constant $C = (\varepsilon f^2/\beta)(\chi_{zz}/\varepsilon_0)(\chi_{zz}/\varepsilon_0)$. Here $T_0 = T + (f^2/\beta)\chi_{zz}$ is the temperature at which ε_z tends to infinity.

For the ferroelectric phase in the absence of any electric field or stress, we have

$$\left.\frac{\partial G}{\partial \eta}\right|_{\eta = \eta_s P = P_s} = 0 \qquad \left.\frac{\partial G}{\partial P}\right|_{P = {}_s \eta = \eta_s} = 0 \tag{8}$$

where η_s and P_s are the spontaneous values of the order parameter and the polarisation, respectively. Using equations (1) and (8), we obtain

$$\alpha\eta_s + \gamma\eta_s^3 + \delta\eta_s^5 + fP_s = 0 \tag{9}$$

$$P_s/\chi_{zz} + f\eta_s = 0. \tag{10}$$

In the presence of the external applied field, the values of η_s and P_s will change and a new equilibrium will be obtained for

$$\begin{aligned} \eta &= \eta_s' = \eta_s + \Delta\eta \\ P &= P_s' = P_s + \Delta P. \end{aligned} \tag{11}$$

Using the relations

$$\left.\frac{\partial G}{\partial \eta}\right|_{\eta = \eta_s' P = P_s'} = 0$$

and

$$\left.\frac{\partial G}{\partial P_i}\right|_{\eta = \eta_s' P = P_s'} = E_i$$

we can express E_i in terms of P_i to yield

$$\varepsilon_x^f = 1 + \frac{\chi_{xx}}{\varepsilon_0} \tag{12}$$

$$\varepsilon_y^f = 1 + \frac{\chi_{yy}}{\varepsilon_0} \tag{13}$$

$$\varepsilon_z^f = 1 + \frac{\chi_{zz}}{\varepsilon_0}\left(1 + \frac{f^2\chi_{zz}}{a - f^2\chi_{zz}}\right) \tag{14}$$

where

$$a = \alpha + 3\gamma\eta_s^2 + 5\delta\eta_s^4. \tag{15}$$

To investigate the temperature dependence of η and the dielectric constants we introduce the parameter y, the relative distortion of the SO_4^{2-} ion, defined by

$$y = \eta(T)/\eta(T_c) \tag{16}$$

where $\eta(T)$ represents the value of the order parameter at a given temperature T and $\eta(T_c)$ is that at T_c. Of the three (x, y and z) components of the dielectric constant, only the expression for the z component shows an explicit temperature dependence, through $\alpha = \beta(T - T\eta)$. Expression (14) may now be rewritten as

$$\varepsilon_z^f = 1 + \frac{\chi_{zz}}{\varepsilon_0}\left(1 - \frac{A}{Py^2/2 + Qy^4}\right) \tag{17}$$

$$P = \gamma\eta_c^2/\beta(T_c - T_0) \tag{18}$$

$$Q = \delta\eta_c^4/\beta(T_c - T_0) \tag{19}$$

and

$$A = \chi_{zz} f^2/4\beta(T_c - T_0). \tag{20}$$

Using equations (16), (19) and (20), the equilibrium condition

$$\left.\frac{\partial G}{\partial \eta}\right|_{\eta=\eta_s P=P_s} = 0$$

can be rearranged to

$$t + Py^2 + Qy^4 = 0 \tag{21}$$

where

$$t = (T - T_0)/(T_c - T_0). \tag{22}$$

Clearly, equation (21) provides the temperature dependence of the relative order parameter y.

3. Results and discussion

The SO_4^{2-}-ion distortion that we have concluded to be the order parameter has been described in detail previously (Jain *et al* 1986). In brief, it represents the changes in S–O bond lengths and O–S–O bond angles from the values that are compatible with a tetrahedral structure. In other words, it is a measure of the departure from the non-polar tetrahedral structure to a polar structure. In the present case the polar structure of the SO_4^{2-} ion has C_s symmetry in the para-electric phase, changing to C_1 in the ferroelectric phase. It has been shown (Bajpai and Jain 1987) that changes in the S–O bond lengths as a result of freezing the asymmetric ν_3 (S–O stretch) polar mode present a reasonably accurate account of the observed heat of transition, revealing that the structural change responsible for the transition mainly involves the change in interatomic separation between the S and O atoms of the SO_4^{2-} ion. In figure 1 we plot the temperature variation of the relative distortion of the SO_4^{2-} ion (Δ_{rel}) deduced from structural data (Hasebe

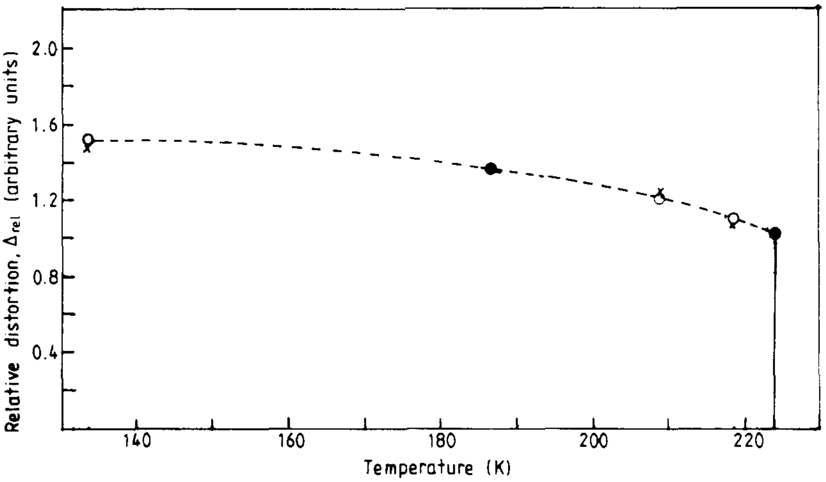

Figure 1. The temperature variation of a typical order parameter for the first-order phase transition (broken curve) and the relative distortion of SO_4^{2-} ion recognised as the order parameter for AS (circles). These points match with equation (21) for $P = -5.46$ and $Q = 4.46$ (crosses).

1981) using the relation

$$\Delta_{rel} = \frac{(|\delta^- r(T)| - |\delta^+ r(T_c)|)}{(|\delta^- r(T_c)| - |\delta^+ r(T_c)|)} \tag{23}$$

where the positive and negative signs signify the values of the distortion $|\delta r|$ above and below T_c, respectively, at the temperature given in parentheses. Here δr is defined by

$$\delta r = \sum_{i=1}^{3} \sum_{r=1}^{4} (A_i - B_i^r) \tag{24}$$

where A_i and B_i are the ith position coordinates of the A atom and rth B atom in an AB_4 tetrahedron.

It may be mentioned that even in the para-electric phase SO_4^{2-} has finite distortion and therefore, to evaluate the relative distortion as an exact synonym of the relative order parameters y (equation (16)), we substract $|\delta^+ r(T_c)|$ from $|\delta^- r(T_c)|$ in equation (23). Here $|\delta^+ r(T_c)|$ serves as a threshold distortion at which the transition commences.

It is found that the temperature variation of the experimentally observed Δr_{rel} agrees well with equation (21) for $P = -5.46$ and $Q = 4.46$, and this fixes the values of these parameters to be used in equation (17) to evaluate the temperature variation of ε_z^f. If the polarisability of the ions does not change when the system goes from the para-electric to the ferroelectric phase, one may use $\varepsilon_0 \chi_{zz}^{-1}$ and $A = C\varepsilon_0\chi_{zz}/4(T_c - T_0)$ obtained by matching the para-electric experimental values with equation (7) in the evaluation of the z components of the dielectric constant in the ferroelectric phase (equation (17)). However, the theoretical results so evaluated do not agree with the experimental values (see figure 2). It appears that the above-stated condition concerning the polarisability of the ions is not valid for AS.

It should be noted that the microscopic mechanism of the transition in AS envisages changes in the structure and symmetry of the microscopic units, i.e. SO_4^{2-}, NH_4^+ (I) and

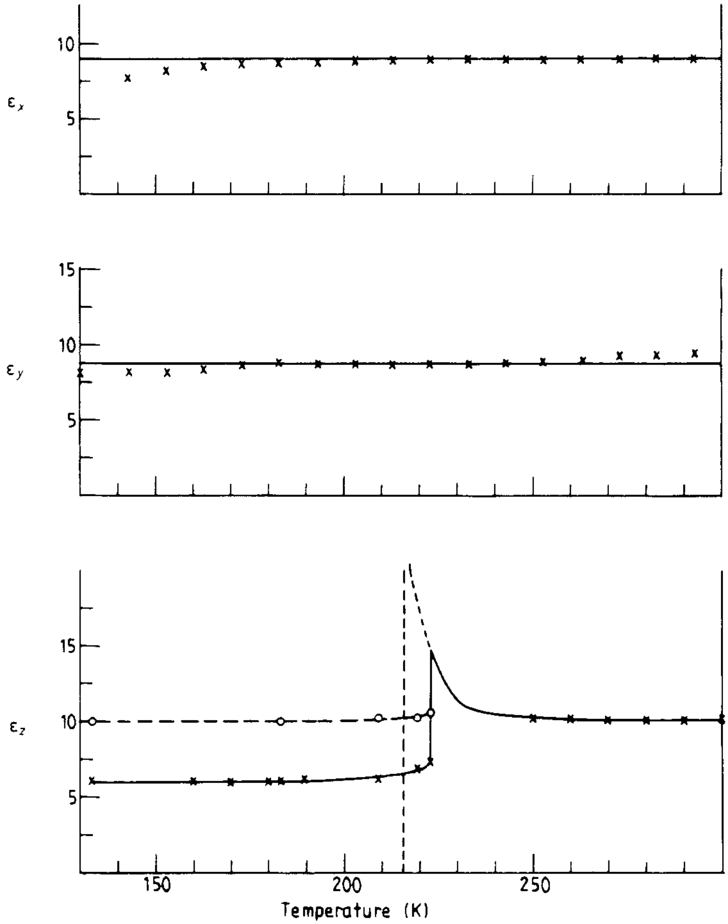

Figure 2. A comparison of the temperature dependence of the dielectric constants ε_x, ε_y and ε_z between the present theory (full curve) and the experimental values (crosses) (Ikeda *et al* 1973). For ε_z in the para-electric phase two results match for $\varepsilon_0\chi_{zz}^{-1} = 0.11$ and $A = 0.091$; however, for these values ε_z in the ferroelectric phase calculated from equation (17) (circles) does not match the experimental values. Agreement is obtained for $\varepsilon_0\chi_{zz}^{-1} = 0.206$ and $A = 0.53$.

NH_4^+ (II), and these ions acquire different magnitudes of the dipole moments below T_c. The magnitude also changes with changes in the temperature. Consequently AS, as a system of electric dipoles, that are the microscopic bases of the dielectric properties to a larger extent, is different in the ferroelectric phase and in the para-electric phase. Obviously, $\varepsilon_0\chi_{zz}^{-1}$ and A, to be used in equation (17) for evaluating ε_z^f, are expected to differ from those values obtained from the agreement between the experimentally measured ε_z^p and equation (7). Moreover, the increased SO_4^{2-}-ion electric dipole is located between the two NH_4^+ dipoles, the strength of the coupling of the SO_4^{2-}-ion distortion with other dipoles and thereby with the macroscopic polarisation P_z also increases.

In the light of the above discussion, we consider a set of changed values of A and $\varepsilon_0\chi_{zz}^{-1}$ to account for the observed temperature dependence of ε_z^f below T_c. The best agreement between the calculated results and the experimentally observed values (cf figure 2) is obtained for $A = 0.53$ and $\varepsilon_0 \chi_{zz}^{-1} = 0.206$.

The ferroelectric transition is the result of long-range cooperation between the molecular units. If there is no change in the polarisabilities of the ions and the strength of the dipole moments associated with them, the permittivity is expected to revert to its para-electric value below T_c. However, in the present system there is a marked change in the dipole moments associated with the ions and this should obviously change the coupling between η and P_s. With the values of $A = 0.53$ and $\varepsilon_0 \chi_{zz}^{-1} = 0.206$ obtained as the best fit to account for the observed temperature variation of ε_z^f (equation (17)), the coupling constant f is found to be 2.4 times that of the para-electric value.

It may be mentioned that the measured dielectric constants reported in the literature (Hoshino *et al* 1958, Kaniyoshi and Miyamoto 1954, Unruh 1965, Koptsik *et al* 1960, Oshima and Nakamura 1966, Ikeda *et al* 1973) are in some disagreement, as pointed out by Anistratov and Martinov (1970). However, the latest data of Ikeda *et al* agree with most of the results reported previously. We have therefore considered these data to be the most reliable for our discussion. It may be mentioned that, according to equations (12) and (13), ε_x and ε_y are expected to remain constant with temperature. This is consistent with experimental observations (figure 2). Minor differences can easily be understood in terms of the minute microscopic changes that occur in the system. These changes are not supposed to be accounted for in such a phenomenological theory.

At this point some comment about the temperature dependence of the spontaneous polarisation (P_s) would be in order. In the present theoretical framework P_s is related to the order parameter η_s through the constant f and the susceptibility χ_{zz} (equation (10)). As χ_{zz} is fairly constant below T_c, the spontaneous polarisation is expected to exhibit a temperature dependence similar to that of η_s, which increases slowly below T_c (see figure 1). This result seems to be in line with the experimental finding that P_s is independent of temperature by Hoshino *et al* (1958) and Ikeda *et al* (1973). However, it may be mentioned that the experimental situation regarding the temperature dependence of P_s is not quite conclusive. Measurements by others reveal that: (i) P_s changes with temperature smoothly in magnitude as well as in direction (Unruh 1970) and (ii) the growth conditions of the crystal greatly influence the results, so that one can observe P_s to be dependent on temperature for one crystal and independent of temperature for another (Zaitseva and Rozhnova 1975). We make the following observations in this context.

(i) All the ions in the crystal (i.e. SO_4^{2-}, NH_4^+ (I) and NH_4^+ (II) contribute to P_s (Jain and Bist 1974) and we can have

$$P_s = n[p^s \cos(\hat{p}^s, \hat{z}) + p^{n_1} \cos(\hat{p}^{n_1}, \hat{z}) + p^{n_2} \cos(\hat{p}^{n_2}, \hat{z})]. \tag{25}$$

Here n is the number density of the dipoles in SO_4^{2-} (p^s), NH_4^+ (I) (p^{n_1}) and NH_4^+ (II) (p^{n_2}). Clearly, continuous orientation of the dipoles accompanying the changes in temperature will introduce a temperature-dependent change in P_s through the cosine factors in equation (25), even if the magnitudes of the different dipoles remain temperature-invariant. The fact that all three dipoles continuously reorientate with temperature has already been concluded on the basis of the analysis of crystallographic data (Bajpai and Jain 1987) and NMR data (O'Reilly and Tsang 1967).

(ii) In the present approach we introduce the interaction of the order parameter η with the spontaneous polarisation due to individual ions, including NH_4^+ ions, through equation (2). In principle, this interaction should reveal the nature of P_s as the temperature changes. However, the interaction coefficients f_1, f_2 and f_3 characterise the weak coupling between η and P_s and the orientations of the dipoles are governed by relatively stronger dipole–dipole interactions. Consequently the continuous reorientation of the dipoles and hence the temperature dependence of P_s cannot be strictly connected with the temperature dependence of the order parameter η_s.

(iii) We also see that equation (10) is derived from the stability conditions using the free-energy expansion, equation (1). In a strict sense this expansion is valid near T_c only. Obviously, changes in a physical property of the crystal at a temperature away from T_c cannot be traced accurately in the framework of a phenomenological theory such as this. This should be particularly true when the order parameter interacts only weakly with the polarisation.

In conclusion, the linear coupling between the order parameter and the polarisation is sufficient to explain the ferroelectric transition in AS and its dielectric behaviour. The SO_4^{2-}-ion distortion acts as the order parameter. The analysis clearly confirms the molecular distortion-type (MD-type) mechanism in this system. A qualitative explanation of the temperature dependence of the spontaneous polarisation and a clear picture of its microscopic origin have been presented.

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