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THE FERROELECTRIC TRANSITION OF (NH₄)₂SO₄

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Résumé. — A l'aide de raisonnements de thermodynamique, on montre que les fonctions diélectriques $D(E)$, propres à l'état paraélectrique et à l'état ferroélectrique du sulfate d'ammonium ne se déduisent pas l'une de l'autre de façon continue.

En conséquence, on suppose que la transition de phase à 223 K n'est pas une transition diélectrique. Pour expliquer la dépendance avec la température de la polarisation spontanée de ce cristal et du composé deutéron correspondant, on suppose une distribution du type ferroélectrique des moments dipolaires.

Abstract. — By thermodynamical arguments it is shown that the dielectric functions $D(E)$, appropriate to the paraelectric and to the ferroelectric state of ammonium sulfate do not transform into one another continuously. The phase transition at 223 K is supposed to be not a dielectric one, therefore. It is suggested to explain the temperature dependence of the spontaneous polarization of this crystal and the respective deuterated compound by the assumption of a ferroelectric array of dipole moments.

The thermodynamic theory of ferroelectrics is based on the assumption that the properties of the crystals may be derived from a series expansion of a thermodynamic potential in powers of the appropriate independent variables. It is supposed further that the coefficients of higher order terms describing the dielectric nonlinearity are the same for the paraelectric and for the ferroelectric states. However, the spontaneous polarization does not represent always the decisive order parameter. For example, this has been shown for gadolinium molybdate [1]. Some other ferroelectrics with very small dielectric anomalies in the transition region may belong to this group, the instabilities of which are not dielectric ones primarily, and we suppose ammonium sulfate (AS) to be another example.

From proton and deuteron magnetic resonance measurements O’reilly and Tsang [2]-[4] concluded that the nature of the ferroelectric transition of AS is of the order-disorder type. This view was supported by the neutron scattering study of Dahlborg et al. [5], whereas Schlemper and Hamilton [6] gathered from their neutron diffraction work that structural changes are essential features of this transition.

Recently we found by pyroelectric measurements that the spontaneous polarization of AS shows a continuous decrease with decreasing temperature, so that even the sign of $P_s$ is reversed when cooling to below 85 K [7]. From additional investigations on this point it can be excluded that another transition is responsible for the observed behaviour. We assumed that $P_s$ cannot be correlated with the transition directly. This was confirmed by the results of Anistratov and Martynov [8], who pointed out that the spontaneous deformation of AS is not determined by the electrostrictive effect.

The differences between the functions of state of the paraelectric and the ferroelectric crystal at given temperature are seen by measurements of the dielectric displacement $D$ versus electric field $E$ within the region of thermal hysteresis: We found that AS is dielectrically linear in the paraelectric state up to at least $E = 1.5 \times 10^7 \text{ Vm}^{-1}$. In the ferroelectric state, at the same temperature, the usual dielectric hysteresis loops appeared with coercive fields of about $10^7 \text{ Vm}^{-1}$. Double loops have not been observed at all, although we have been looking for them carefully. From these experiments we conclude that the cubic term of the expression $E = \beta_0 D + \xi D^3 + \zeta D^5$ is much smaller than the linear one up to fields of about $10^7 \text{ Vm}^{-1}$. Assuming $|\xi|D^3 < 0.1 \beta_0 D$ and

$$\beta_0^{-1} = 13.3 \times 8.85 \times 10^{-12} \text{ CV}^{-1} \text{ m}^{-1} [7]$$

one has $|\xi| < 3.5 \times 10^{14} \text{ Vm}^5 \text{ C}^{-3}$. On the other hand from the thermodynamic theory we know the critical field strength $E_c$, which has to be applied at the critical temperature in order to reach the critical displacement $D_c$ [9]. This point is defined by

$$(\partial E/\partial D) = \beta = 0 \text{ and } (\partial^2 E/\partial D^2) = 0.$$ 

Using $D_c = \sqrt{-\xi/\zeta} \approx 6 \times 10^{-3} \text{ Cm}^{-2}$ and the value of $\xi$ estimated above, the evaluation of

$$E_c = 0.24(0.3 |\xi|^{5/2} \zeta^{-3/2})$$

yields $E_c < 1 \times 10^7 \text{ Vm}^{-1}$. This clearly contradicts the observed linear behaviour of the function $D(E)$. So no continuous transition can exist between the
two dielectric functions which is supposed in the molecular field approximation [3] and in the thermodynamical approach, however.

Besides the determination of the correct order parameter of the transition, an explanation of the temperature dependence of \( P_s \) is required. Therefore, we measured \( P_s(T) \) of deuterated ammonium sulfate (DAS) too. The samples were cut from crystals grown from aqueous solution. The degree of deuteration is estimated to be about 90%. The result is shown in figure 1.

![Figure 1](image1.png)

**Fig. 1.** Temperature dependence of the spontaneous polarization of ammonium sulfate (AS) and deuterated ammonium sulfate (DAS) from static pyroelectric measurements.

The isotopic effect on the transition temperature is rather small (about \( 0.6 \pm 0.1 \) K). The behaviour of \( P_s(T) \) is almost the same as in the case of AS. Especially it has been proved that the maxima just below the transition temperatures refer to the homogeneous crystals. At about 125 K \( P_s \) of DAS is zero and tends to \(-0.1 \mu \text{C cm}^{-2}\) at low temperatures. First of all we learn from these results that the hydrogen bonds do not play an essential role in the ferroelectric effect of AS. From the crystal structure it is known that ammonium and sulfate groups form slightly distorted tetrahedra [2], [6]. So each group will carry a dipole moment which may depend on temperature. However, the absolute values of these moments may be assumed to be largely independent of the state of polarization. The problem of constructing the energy expression can be treated, therefore, by the formalism introduced by Bertaut [10].

There are four formula units \((\text{NH}_4)_2\text{SO}_4\) in each elementary cell. One unit projected onto the \(b, c\)-plane is shown in figure 2. According to the symmetry conditions of the space group \(Pna_2\), the components of a definite type of dipoles, say of the four ammonium-

![Figure 2](image2.png)

**Fig. 2.** Projection of one formula unit ammonium sulfate onto the \(b, c\)-plane in the paraelectric state, space group \(Pnam\), and in the ferroelectric state, space group \(Pna_{21}\) [6]: \(\circ S; \bullet N1; \bullet N2; (\text{NH}_4)_2\text{SO}_4\).

L-groups, must be arranged parallel or antiparallel. From the character table of the irreducible representations of this symmetry group it can be shown that a ferroelectric array with a moment \(F_e\) is possible only in the \(c\)-direction. In \(a\)- and \(b\)-directions different antiferroelectric structures will occur generally [10]. The dipole moment of the sulfate group is assumed to be small because the distortion of this ion seems to be negligible [6]. Therefore, the macroscopic polarizations of AS and DAS are interpreted in terms of the ammonium group contributions \(F_{ei}^1\) and \(F_{ei}^{11}\). The behaviour of \(P_s(T)\) demands \(F_{ei}^1\) and \(F_{ei}^{11}\) to be antiparallel, so that a ferrielectric structure exists with respect to these dipole components. The results of the magnetic resonance measurements indicate that the ammonium groups freeze out at different temperatures [2]. This is reflected by the \(P_s(T)\)-curve. In a quantitative description it would be necessary to take into consideration the temperature dependence of the situation shown in the lower part of figure 2 with respect to the positions and distortions of the various groups.

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**References**