Anomalies of macroscopic quadrupole moment in an incommensurable phase of the crystal adjacent to the nonpolar and polar phases

V. V. Gladkiĭ, S. N. Kallaev, V. A. Kirikov, L. A. Shuvalov, and A. N. Izrailenko
Institute of Crystallography, USSR Academy of Sciences

(Submitted March 20, 1979)

Pis'ma Zh. Eksp. Teor. Fiz. **29**, No. 8, 489–493 (20 April 1979)

The anomalous spontaneous macroscopic quadrupole moment, which corresponds to the spatially modulated polarization, was determined and studied in the incommensurable phase of the $(NH_4)_2BeF_4$ crystal. It is shown that this effect can be used to identify and investigate phases with such a structure.

PACS numbers: 61.60. + m

It has become clear lately that phase transitions in many crystals proceed via the intermediate temperature phase with an incommensurable superstructure whose spacing is not a multiple of the lattice period. If the incommensurable phase is adjacent to a nonpolar or a polar phase, then a spatially modulated polarization should occur in it.

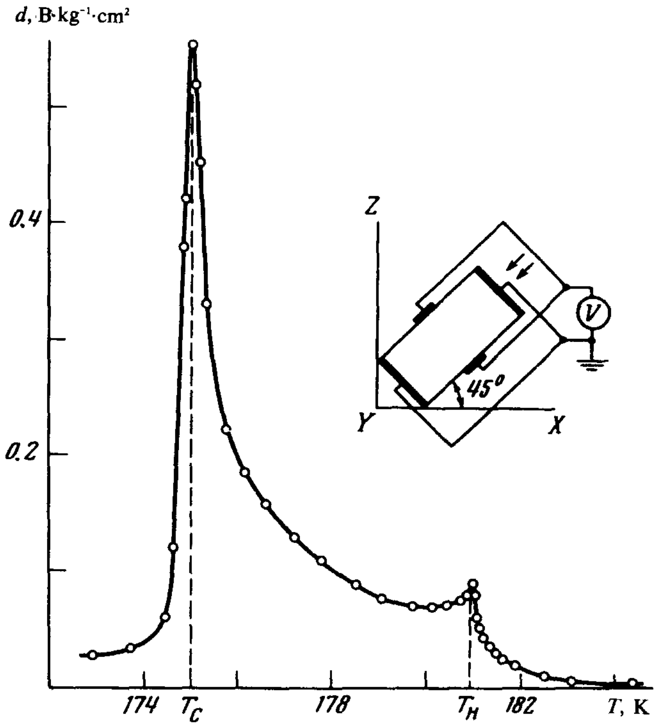

FIG. 1. Temperature dependence of the "pliability" $d = V/\sigma$ in the region of the incommensurable phase of the $(NH_4)_2BeF_4$ crystal ($\sigma = 60$ kg/cm^2). The shape of the crystal and the distribution of the electrodes are show in the inset. The arrows indicate the direction of compression.

The phenomenological theory of such phase transitions, which is based on the Landau theory and is similar to the Dzyaloshinski theory of magnetic materials, was recently developed by Levanyuk and Sannikov.[1]

At present, an intensive search is under way for different methods of identifying and investigating the incommensurable phases. Recently, it was shown that they can be identified by using the method of generation of the second harmonic of light[2] and NQR.[3]

In this paper, using the $(NH_4)_2BeF_4$ crystal (ammonium fluoroberyllate) we identified and measured for the first time the characteristic anomalies of the macroscopic quadrupole moment of an incommensurable phase.

Ammonium fluoroberyllate (AFB) has a nonpolar-incommensurable-polar phase sequence with transition temperatures $T_I = 181$ K and $T_C = 175$ K, respectively. The incommensurable phase was identified by the neutron-scattering method.[4] According to Ref. 1, the components of polarization P in AFB with an accuracy to the second-order of smallness over components of the order parameter η and ξ have the form

$$P_x = P_1 = 0, \quad P_y = P_2 = c_2 \eta \xi, \quad P_z = P_3 = c_3(\eta^2 - \xi^2), \tag{1}$$

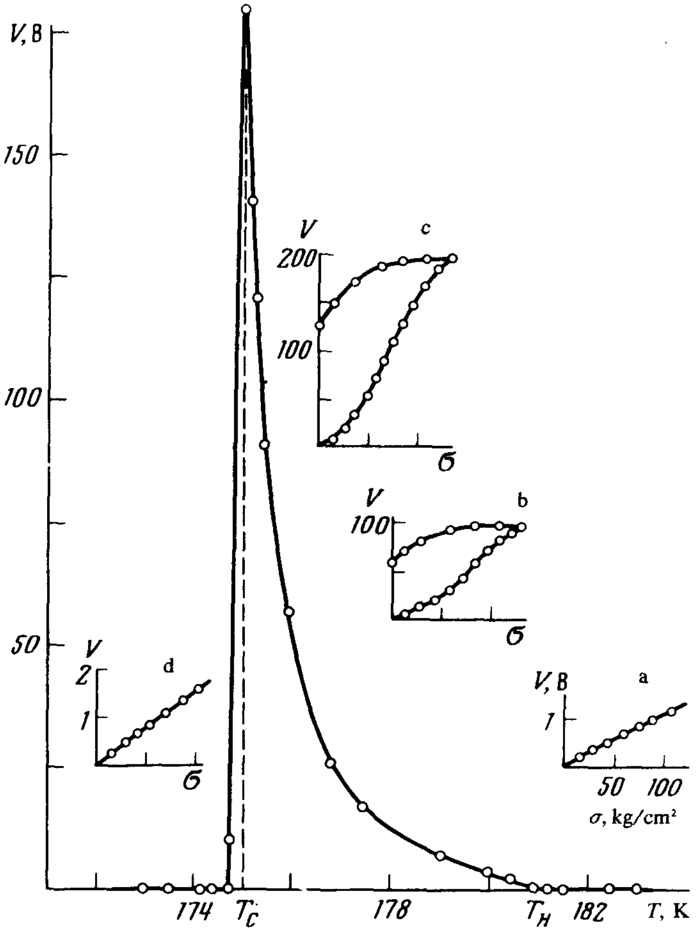

FIG. 2. Temperature dependence of the spontaneous potential V and the dependence of V on the mechanical stress σ for different T of the $(NH_4)_2BeF_4$ crystal: a, $T = 182.8$ K; b, 176.2 K; c, 175.6 K; d, 174.1 K.

where c_2 and c_3 are constant coefficients. In the region of the incommensurable phase η and ξ depend on the x coordinate and near T_I

$$\eta = \rho\cos(kx + \phi), \quad \xi = \rho\sin(kx + \phi), \tag{2}$$

and $\rho^2 \sim T_\text{I} - T$. As we move away from T_I the modulation period $L = 2\pi/k$ increases and higher harmonics appear in expression (2). It can be seen from Eqs. (1) and (2) that the P vector in the incommensurable phase must be twisted into a helix along the X axis (a axis). The thermodynamic potential is independent of ϕ, i.e., ϕ is not fixed. The crystal, therefore, must have macroscopic regions ("domains") which differ in ϕ. At $T = T_\text{C}$ the crystal abruptly goes over to the commensurable polar phase with doubling of the cell parameter along the X axis and the spontaneous P_s along $Y(b)$.

Note the $P_s = 0$ in the incommensurable phase, but there must be a spontaneous quadrupole moment with components $q_{ij} = 1/v\int P_i x_j dv (i \neq j)$. Integrating and taking into account Eqs. (1) and (2), we can show that

$$q_{21} = ac_2\rho^2 L\cos\phi, \qquad q_{31} = ac_2\rho^2 L\sin\phi, \qquad q_{23} = q_{11} = q_{22} = q_{33} = 0, \tag{3}$$

where $a = 1/4\,\pi$ near T_I and $a \sim 1/4$ near T_C because of the higher harmonics in Eq. (2).

It can be seen from Eq. (3) that the domains in the incommensurable phase must have different values $q_{ij} \sim \sin\phi$. Therefore, the external action, the conjugate q_{ij}, must convert the crystal to a single-domain state. According to the expression for the energy $W = -q_{ij}\,\mathrm{grad}_i E_j = g_{ijkl} q_{ij} \sigma_{kl}$ such a force can be either the nonuniform electric field E or mechanical stress σ_{kl}. We took into account here that in the crystal samples of any symmetry $\mathrm{grad}_i E_j = g_{ijkl}\sigma_{kl}$, where the values g_{ijkl} depend on the size and shape of the sample.

We used $3 \times 3 \times 5$-mm^3 samples of different orientation to test the aformementioned assumptions. An uniaxial compression was used as the external force. The variation of q_{ij} was recorded by an electrometer by measuring the potential V corresponding to q_{ij}.[5] Figures 1 and 2 show the result of testing one of the samples. The compression stress σ is equivalent to a simultaneous application of force $\sigma_{11} = \sigma_{33} = \sigma_{31} = \sigma/2$. The induced potential $V = b_1\Delta q_{31} + b_2(\Delta q_{11} - 1/2\Delta q_{22} - 1/\Delta q_{33})$, where b_1 and b_2 depend on the ratio of the dimension of the sample's edges.[5]

The dependence of V on T and σ in the incommensurable AFB phase qualitatively resembles the dependences of P on T and E in ferroelectrics. The "pliability" $d = V/\sigma$ has pronounced λ anomalies at $T = T_I$ and $T = T_C$ (Fig. 1), V is spontaneous in the entire region $T_C < T < T_I$, and the $V(\sigma)$ dependence has the form of hysteresis loops (Fig. 2), which indicates that the domain boundaries move and the sample is converted to a single-domain state under the influence of σ.

The measurement of samples of other orientations showed that the potential corresponding to Δq_{21} behaves analogously and that Δq_{23}, Δq_{11}, Δq_{22}, and Δq_{33} contribute little to the anomalies of V. The results of the study confirm the conclusions of the theory[1] on the direction of the axis of the helix P in AFB.

Thus, on the basis of the quadrupole effects we can conclude unambiguously that the crystal has a structure with a spatially modulated polarization and determine (be measuring the anisotropy of the effects) the direction of the axis of the helix, its pitch, or its amplitude. The measurement of the effects can be considered a macroscopic method of searching and investigating the phases with such structures.

We thank D.G. Sannikov and A.P. Levanyuk for discussion of results.

---

[1] A.P. Levanyuk and D.G. Sannikov, Fiz. Tverd. Tela **18**, 423 (1976) [Sov. Phys. Solid State **18**, 423 (1976)].
[2] K.S. Aleksandrov, A.N. Vtyurin, and V.F. Shabanov, Pis'ma Zh. Eksp. Teor. Fiz. **28**, 153 (1978) [JETP Lett. **28**, 143 (1978)].

[3] A.K. Moskalev, I.A. Belobrova, and I.S. Aleksandrova, Fiz. Tverd. Tela **20**, 3288 (1978) [Sov. Phys. Solid State **20**, 1896 (1978)].

[4] M. Iizumi and K. Gesi, Solid St. Comm. **22**, 37 (1977).

[5] W. Voigt, Lehrbuch der Kristallphysik, Leipzig-Berlin, B.G. Teubner, 1928.