Proc. JSSF-2, Kyoto, 1980
J. Phys. Soc. Jpn. **49** (1980) Suppl. B, pp. 83–85.

Macroscopic Electrical Properties of Incommensurate Phases of Ferroelectrics

V. V. Gladkii, S. N. Kallayev, V. A. Kirikov, A. P. Levanyuk and L. A. Shuvalov

Institute of Crystallography, Academy of Sciences of the USSR,
Leninsky pr. 59, Moscow 117333, USSR

The macroscopic quadrupole moment related to space modulated polarization is shown to be a characteristic of incommensurate phases of ferroelectrics. The moment is forbidden by the crystal point group but allowed by the symmetry group of the limited sample of crystal. Anomalies of the quadrupole moment for the ammonium fluoberyllate, potassium selenate, rubidium trihydrogen selenite crystals were found and studied experimentally in the vicinity of transitions to incommensurate phase.

Recently,[1] the macroscopic quadrupole moment (MQM) related to space modulated polarization was shown to be as much a characteristic property for incommensurate phases (IF) of ferroelectrics as the dipole moment for polar ones. This report presents some results of study of MQM of various ferroelectrics in the temperature region of parent nonpolar phase, IF and polar one.

We furnish at first with some results of the phenomenological analysis of such phase transitions. According to refs. 2–5 one of the spontaneous polarization components P_k has to exhibit the following alteration. In the parent phase $P_k=0$, in the IF it depends periodically on coordinates and in the polar phase a homogeneous P_k arises in the crystal. In the IF near the temperature $T_{\rm i}$ of the transition from parent phase P_k takes the form

$$P_k=b\sin\left(m\frac{2\pi}{L}x_1+\varphi\right) \qquad (1)$$

where L is the superstructure period, m is an integer, b depends on temperature, φ is an arbitrary quantity. On moving away from $T_{\rm i}$ and approaching to the temperature $T_{\rm c}$ of the transition to the polar phase L increases and higher harmonics appear in Eq. (1):

$$P_k=\sum_{n=0}^{\infty} b_n\sin\left[(2n+1)\frac{2\pi}{L}mx_1+\varphi\right]. \qquad (2)$$

The quantities in Eqs. (1) and (2) depend on the thermodynamic potential coefficients and the values of b_n and m depend on the symmetries of parent and polar phases.[2-5)]

Let us show now that a limited crystal sample in IF may have different from zero spontaneous components of MQM,

$$q^{\rm i}_{kl}=q^{\rm i}_{lk}=\frac{1}{2v}\int(P_kx_l+P_lx_k)\,\mathrm{d}v, \qquad (3)$$

being due to the periodical space change in P_k. Substituting (1) and (2) into (3) one can obtain near $T=T_{\rm i}$

$$q^{\rm i}_{kl}=\frac{b}{4\pi m}L\cos\varphi \qquad (4)$$

and far from $T=T_{\rm i}$

$$q^{\rm i}_{kl}=\frac{1}{4\pi m}\sum_{n=0}^{\infty}\frac{b_n}{(2n+1)}L\cos\varphi. \qquad (5)$$

The value of $q^{\rm i}_{kl}$ in Eqs. (4) and (5) depends on φ, i.e. on the value of P_k at the sample boundaries. Suppose, for simplicity, that there is a whole number of the "frozen" polarization wave lengths in the sample. If $P_k=0$ on the boundaries $q^{\rm i}_{kl}$ is maximum. The values of φ may change also within the sample because of defects i.e. there may exist in the sample submacroscopic regions different in φ and hence in $q^{\rm i}_{kl}$. The mechanical stress σ_{kl} must equalize the values of φ, and thus $q^{\rm i}_{kl}$ in the regions, so that the dependence of q_{kl} on σ_{kl} may be expected to have a form of hysteresis loop.[1)]

The ferroelectrics $(NH_4)_2BeF_4$ (AFB), K_2SeO_4 (PS), $RbH_3(SeO_3)_2$ (RHS) were studied. The symmetry changes in the crystals at the transition from parent phase to polar one are respectively $D^{18}_{2h}\to C^{17}_{2v}$, the unit cell doubled along the axis $X_1\|a$ and the spontaneous polarization $P_s\|X_2\|b$, $D^{16}_{2h}\to C^{9}_{2v}$, the cell tripled along $X_1\|a$ and $P_s\|X_3\|c$, $D^4_2\to C^2_2$, the cell doubled along $X_3\|c$ and $P_s\|X_2\|a$. The quantities in Eqs. (1) and (2) can be shown to equal: $P_k = P_2$, $m=2$, $b_n \sim \varrho_0^2$ for AFB,[2,3] $P_k = P_3$, $m=3$, $b_n \sim \varrho_0^3$ for PS[4,5] and $P_k = P_1$ or $P_k = P_2$, $m=2$, $b_n \sim \varrho_0^2$ for RHS,[6] where $\varrho_0 \sim (T_i - T/T_i)^{1/2}$ is the order parameter. The IFs were found recently by neutron scattering studies in the deuterated AFB,[7] PS,[8] deuterated RHS.[9]

According to Eqs. (4), (5) there are expected to exist in the IF of the crystals anomalies of MQM, namely of the components q_{12}^i for AFB, q_{13}^i for PS, q_{13}^i and q_{23}^i for RHS.

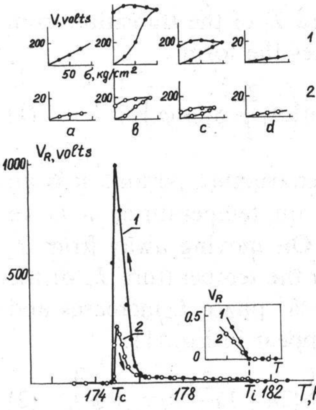
It should be emphasized that these MQM components are forbidden by the point group of IF and the fact that they occur can be explained by the difference between the symmetries of unbounded and bounded crystals. In particular, glide planes and screw axes are not symmetry elements for the sample.[10] Taking into account this observation we consider an AFB crystal. Its point group in the IF as well as in the parent phase is D_{2h} and an occurrence of the superstructure leads only to a change in translational symmetry.[2] However the symmetry group of the sample in the parent phase is C_{2h} as there is only one rotational axis *2* and one mirror plane in the crystal space group being respectively parallel and perpendicular to the axis X_3. In the IF, generally speaking, the sample may contain any number (including fractional number) of polarization wave lengths. Therefore the symmetry group of the sample depends on the boundary values of modulated polarization component P_2 and, as it could be shown, may be C_{2h}, C_{2v} or C_s. As a result there has to exist in the parent phase and in the IF a nondiagonal spontaneous component q_{12} forbidden by the point group but permitted by the symmetry group of the sample. It is obvious now that q_{kl}^i in Eqs. (4) and (5) for AFB is an additional part of q_{kl} related to the modulated polarization of IF. The change in q_{kl} was registered by measuring the voltage V between two points on the sample surface. For the definite sample orientation and deposition of sample electrodes V is proportional to the change in the definite component q_{kl}, $V \sim q_{kl}$.[11] Measurements of V were carried out by means of an electrometer method. The samples were $3 \times 3 \times 5$ mm rectangular bars.

The results obtained experimentally coincide well with those expected theoretically. Actually for all the crystals the quadrupole effects being a mere consequence of the existence of spontaneous q_{kl}^i are observed, namely hysteresis dependences of the voltages $V \sim q_{12}$ on σ_{12} for AFB (Fig. 1), $V \sim q_{13}$ on σ_{13} for PS,[12] $V \sim q_{13}$ on σ_{13} and $V \sim q_{23}$ on σ_{23} for RHS[13] (Fig. 2), temperature dependences of the coefficients d $= V/\sigma$ being a "compliance" of the crystal electrical structure to the externally applied stresses σ (Fig. 3).

The most pronounced anomalies of MQM are found of AFB. The anomalies for PS are less than those for AFB and could be revealed only near $T = T_c$. This fact is in agreement with the theory[2-5] as due to relations $V^{KS} \sim q_{13}^i \sim b_n \sim \varrho_0^3$ for PS and $V^{AFB} \sim q_{12}^i \sim b_n \sim \varrho_0^2$ for AFB the inequality $V^{KS} < V^{AFB}$ has to be valid.

In addition to the component q_{12}^i the second component q_{13}^i is observed in the IF of AFB (Fig. 1). This means apparently that according to Eq. (3) there exist in AFB besides the modulated P_2 the the second modulated component P_3, i.e. the polarization of IF in AFB as well as in RHS is a spiral twisted along the axis X_1. Therefore the parent phase of AFB seems to have not the symmetry group treated by the theory[2,3] but another space group permitting an existence of the two modulated polarization components.

In distinction from AFB and PS the crystal RHS as well as ammonium Rochele salt[14,15] seems to be an example of the occurrence of



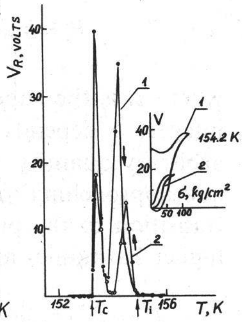


Fig. 1 **Fig. 2**

Fig. 1. Voltage $V \sim q_{kl}$ vs. shear stress δ and remanent voltage V_R vs. temperature for $(NH_4)_2BeF_4$.
1 – $V \sim q_{12}$, $\delta = \delta_{12}$; 2 – $V \sim q_{13}$; a – 174.1; b – 175.3; c – 176.2; d – 182.8 K.

Fig. 2. Voltage $V \sim q_{kl}$ vs. shear stress δ and remanent voltage V_R vs. temperature for $RbH_3(SeO_3)_2$.
1 – $V \sim q_{23}$, $\delta = \delta_{23}$; 2 – $V \sim q_{13}$, $\delta = \delta_{13}$.

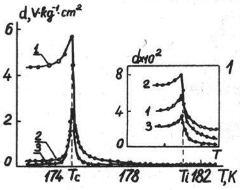


Fig. 3

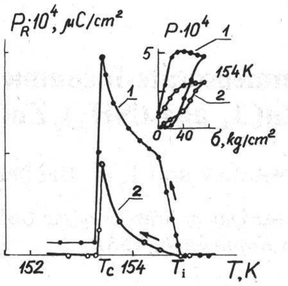


Fig. 4

Fig. 3. "Compliance" coefficients $d = V/\delta$ for $(NH_4)_2BeF_4$.
$1 - V{\sim}q_{12}$, $\delta = \delta_{12}$: $2 - V{\sim}Q_{13}$, $\delta = \delta_{13}$: $3 - V{\sim}q_{23}$, $\delta = \delta_{23}$.

Fig. 4. Homogeneous polarization P vs. shear stress δ and remanent P_R vs. temperature for $RbH_3(SeO_3)_2$.
$1 - P = P_2$, $\delta = \delta_{13}$; $2 - P = P_1$, $\delta = \delta_{23}$.

polar IF. In the temperature region delimited by the two phase transitions[16,17] besides q^{i}_{13} and q^{i}_{23} the spontaneous homogeneous components P_1 and P_2 exist in this crystal. The hysteresis loops of the dependences of P_1 on σ_{23}, of P_2 on σ_{13} and the temperature dependences of remanent P_1 and P_2 obtained from the loops are shown in Fig. 4.

It should be noted that one succeeded to reveal the nonlinear dependences of q_{kl} on σ_{kl} for all the crystals and of P_1, P_2 on σ_{23}, σ_{13} for RHS in the IF only upon changing temperature in the definite direction shown in figs. by arrows. Unfortunately this phenomenon is not explained yet.

The results obtained show that the measurement of MQM is a method of discovering and investigation the IF in ferroelectrics. The method in distinction from the recently proposed microscopic NQR,[18] second harmonic generation[19] and EPR[20] methods allows the peculiarities of macroscopic electrical structure of such a phase to be revealed.

The authors are grateful to A. N. Izrailenko, R. F. Fedosyuk and B. Březina for single crystal growing and participating in the work.

References

1) V. V. Gladkii, S. N. Kallayev, V. A. Kirikov, L. A. Shuvalov, A. N. Izrailenko: Sov. Phys.-JETP (Letters) **29** (1979) 489.
2) A. P. Levanyuk, D. G. Sannikov: Sov. Phys.-Solid State **18** (1976) 423.
3) Y. Ishibashi, V. Dvořak: J. Phys. Soc. Jpn. **44** (1978) 32.
4) M. Iizumi, J. D. Axe, G. Shirane, K. Shimaoka: Phys. Rev. **B15** (1977) 4392.
5) D. G. Sannikov, A. P. Levanyuk: Sov. Phys.-Solid State **20** (1978) 1005.
6) D. G. Sannikov, A. P. Levanyuk: Sov. Phys.-Solid State **19** (1977) 118.
7) M. Iizumi, K. Gesi: Solid State Commun. **22** (1977) 37.
8) M. Iizumi, A. D. Axe, G. Shirane, K. Shimaoka: Bull. Am. Phys. Soc. **21** (1976) 292.
9) K. Gesi, M. Iizumi: J. Phys. Soc. Jpn. **48** (1980) 697.
10) A. P. Levanyuk, V. V. Gladkii: Sov. Phys.-JETP (Lett.) **31** (1980) 651.
11) W. Voigt: Lehrbuch der Kristallphysik, B. G. Teubner, (1928) p. 299.
12) V. V. Gladkii, S. N. Kallayev, V. A. Kirikov, L. A. Shuvalov, B. Březina: Sov. Phys.-Solid State, to be published.
13) V. V. Gladkii, S. N. Kallayev, V. A. Kirikov, L. A. Shuvalov: Sov. Phys. Solid State **21** (1979) 3732.
14) M. Iizumi, K. Gesi: J. Phys. Soc. Jpn. **45** (1978) 711.
15) V. V. Gladkii, S. N. Kallayev, V. A. Kirikov: Sov. Phys.-Solid State **22** (1980) 904.
16) V. V. Gladkii, V. A. Kirikov, V. K. Magataev, L. A. Shuvalov: Sov. Phys.-Solid State **19** (1977) 291.
17) V. V. Gladkii, V. A. Kirikov, V. K. Magataev, R. M. Fedosyuk, L. A. Shuvalov: Ferroelectrics **21** (1978) 511.
18) A. K. Moskalev, I. A. Belobrova, I. S. Aleksandrova: Sov. Phys.-Solid State **20** (1978) 3288.
19) A. N. Vtyurin, V. F. Shabanov, K. S. Aleksandrov: Sov. Phys.-JETP **77** (1979) 2358.
20) S. Waplak, L. A. Shuvalov, J. Stankovski: to be published.