Macroscopic quadrupole moment of a crystal in the region of a structural phase transition

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An electric method is proposed for the investigation of the structural changes occuring in phase transitions in nonpolar crystals. The method is based on recording the changes of the potential ϕ of the electrostatic field produced by the macroscopic quadrupole moment. The possibilities of the method and its effectiveness are illustrated by an example consisting of a measurement of the nonlinear dependences of ϕ on the temperature and on the mechanical stress in an NH_4Br crystal in the region of the transition from the cubic to the tetragonal phase.

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It is known[1] that the potential of the field excited by a crystal of nonpolar class is equal to

$$\phi = \int_V q_{ij} \frac{\partial^2 (r^{-1})}{\partial x_i \partial x_j} dV, \qquad (i, j = 1, 2, 3), \tag{1}$$

where q_{ij} is the quadrupole-moment density and is a symmetrical second-rank tensor, while r is the distance from the element dV to the point of observation of ϕ.

If q_{ij} is the same over the entire volume of the crystal, then in the coordinate system in which the matrix q_{ij} is diagonal we can represent the potential in the form

$$\phi = \int_S q_{ii}\, n_i \frac{\partial (r^{-1})}{\partial x_i} dS, \tag{2}$$

where S is the surface of the crystal and n_i are the projections of the outward normal to S.

Using (2), we can obtain ϕ for each concrete case. For all the cubic crystals we have $q_{11}=q_{22}=q_{33}$ and $\phi=0$ everywhere, while for crystals having a symmetry axis of more than twofold order ($q_{11}=q_{22}\neq q_{33}$), we have

$$\phi = k(q_{33} - q_{11}), \tag{3}$$

where $k=\int_S n_3[\partial(r^{-1})/\partial x_3]\,dS$ depends on the shape of the crystal and on the point of observation of ϕ.

If we change the value of q_{ij} by some external action, then it is possible to measure the resultant potential difference $\Delta\phi$ between two points on the crystal surface. An experimental estimate of $\Delta\phi$ in different centrosymmetric crystals of noncubic classes was made in[2] for a varying temperature and a varying mechanical stress.

According to (2) and (3), the change of ϕ can serve as a measure of the dis-

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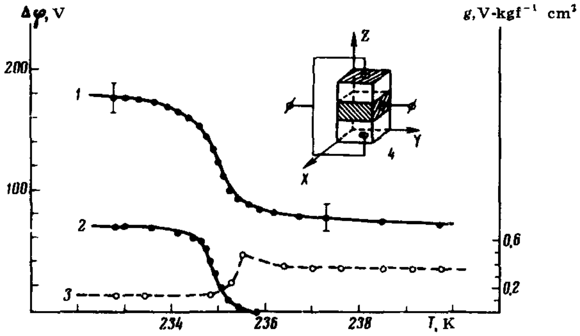

FIG. 1. Temperature dependences: 1) of the potential difference $\Delta\phi$, which is proportional to the change of the quadrupole moment of the crystal NH_4Br, under a compression stress $\sigma_{zz}=200$ kg/cm^2; 2) of the residual $\Delta\phi$ at $\sigma_{zz}=0$; 3) of the piezoelectric coefficient $g=\Delta\phi/\sigma_{zz}$ at $\sigma_{zz}=50$ kg/cm^2. Insert 4 shows the shape of the crystal and of the electrodes.

tortion of the crystal symmetry. This raises the question of whether the measurements of $\Delta\phi$ can be used to investigate nonferroelectric phase transitions. Indeed, the strain component u_{ij} that arises spontaneously in the transition should be accompanied by a spontaneous change of the component q_{ij}, which transforms exactly like u_{ij}, and by a change of the field ϕ. In this case, measurement of the dependences of $\Delta\phi$ on the mechanical stress σ_{ij} conjugate to u_{ij} and on the temperature T could yield the same information on the thermodynamic properties of the transition as the measurements of the polarization on the electric field and on T in ferroelectrics.

The possibility of investigating phase transitions by recording $\Delta\phi$ was verified by us on crystalline NH_4Br, which undergoes at $T\approx 235$ K a transition from the centrosymmetric cubic phase $Pm3m$ into the centrosymmetric tetragonal phase $P4/nmm$, with a doubling of the unit cell[3] The sample was a rectangular parallepiped measuring $3\times3\times5$ mm. The potential difference was measured with a UT-6801A electrometer between two electrodes, one of which was de-

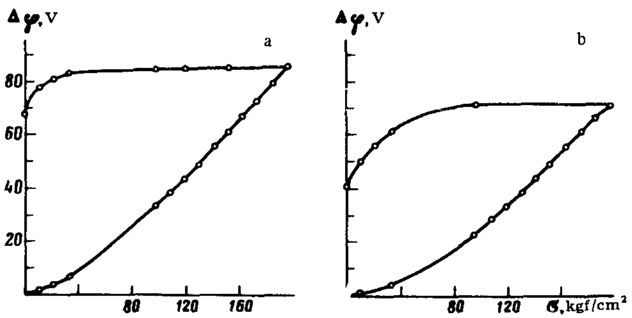

FIG. 2. Dependence of the potential difference $\Delta\phi$ on the compression stress σ_{zz} in the noncentrosymmetric phase of NH_4Br at temperatures 234.3 K (a) and 234.9 K (b).

posited on the face perpendicular to the z axis, and the other was a strip 1.5 mm wide deposited on the lateral faces (Fig. 1). The capacitance of the sample was $C_0 = 0.07$ pF, and the input capacitance of the electrometer and of the conducting contacts was $C_e = 200$ pF. A mechanical compression stress σ was transmitted along the z axis of the sample. Calculation in accordance with formula (3) yields for this sample and electrode geometry the value $\Delta\phi \approx 3\pi(q_{33} - q_{11})$.

Measurements of the dependences of $\Delta\phi$ on σ and on T have shown that in the cubic phase of the crystal the spontaneous $\Delta\phi = 0$, while the induced $\Delta\phi = g\sigma$ with $g = 10^{-9}$ cgs esu. In the tetragonal phase there appears a spontaneous $\Delta\phi$, and the $\Delta\phi(\sigma)$ dependence takes the form of loops analogous to the dielectric-hysteresis loops in ferroelectrics. Observation of the induced $\Delta\phi$ in the cubic phase is a demonstration of a unique piezoelectric effect in a centrosymmetric cubic crystal, in which no ordinary piezoeffect takes place.

Figure 1 shows the temperature dependences of $\Delta\phi$ at $\sigma = 200$ kg/cm^2 and of the residual difference $\Delta\phi$ at $\sigma = 0$, measured while the sample was continuously heated (for 20 minutes) after its cooling under a load $\sigma = 200$ kg/cm^2; Fig. 1 shows also the temperature dependence of the piezoelectric coefficient $\Delta\phi/\sigma$ at $\sigma = 50$ kg/cm^2. The saturation of the loops is insufficiently pronounced because of the high coercive stress σ (Fig. 2).

Let us estimate the minimal deformation of NH_4Br that can be registered with the aid of the measurement of $\Delta\phi$. Assuming $(\Delta\phi)_{min} = 2 \times 10^{-5}$ V (sensitivity of the electrometer) and a compliance $s_{33} = 3 \times 10^{-12}$ cgs esu,[3] we obtain $(u_{33})_{min} = s_{33}(C_e/C_0)[(\Delta\phi)_{min}/g] = 4 \times 10^{-7}$, which agrees in order of magnitude with the sensitivity of dilatometric methods.

The presented estimate of $(u_{33})_{min}$ is not the limit, since modern electrometric measurement means make it possible to increase the voltage sensitivity by at least one more order of magnitude.

In NH_4Br crystals, the quantities u_{ij} and q_{ij} are not parameters of the phase transitions, and small spontaneous u_{ij} and q_{ij} are the results of a more complicated realignment of the structure, and are apparently second-order effects.[3] It is natural to expect the change of $\Delta\phi$ to be much larger in the case of phase transitions for which u_{ij} (or q_{ij}) plays the role of a parameter.

The change of the quadrupole moment of a nonpolar crystal can be registered while simultaneously measuring other physical quantities, for example the heat capacity; this is an advantage of the proposed method in the case of comprehensive investigation of structural phase transitions.

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