On the possibility of observing macroscopic properties in a finite crystal that are forbidden by the symmetry point group

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The difference between the symmetry group of a finite crystal and its point group is examined. These differences account for the point-group-forbidden components of the quadrupole moment, which are especially large in crystals with an incommensurable superlattice. The possibility of observing other macroscopic properties, which are forbidden by the point group, is discussed.

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The appearance of additional components of the macroscopic quadrupole moment tensor as a result of transition of a crystal to an incommensurable phase was observed in Ref. 1. The authors, however, did not point out the fact that the point group of the incommensurable phase, which is identical to the group of the high-temperature phase, forbids these components. The observation in Ref. 1, therefore, does not agree with the well-known hypothesis of macroscopic crystal physics, according to which the symmetry of the tensor properties of the crystal is determined by its point group.[2,3]

We wish to draw attention to the fact that this observation can be accounted for by the difference in the symmetry groups of finite and infinite crystals. A symmetry breakdown due to sample finiteness would appear to lead only to weak surface effects that are vanishingly small for macroscopic samples. However, as will be shown below, these symmetry breakdowns are the controlling factor for the quadrupole moment, are noticeable for the dipole moment, and lead to very small corrections for the other properties, which are very difficult to detect.

The quadrupole moment of a crystal is described by a second-rank symmetrical tensor q_{ij} with a trace equal to zero. Any component of q_{ij} for a homogeneous crystal sample can be calculated by two methods: by summing over all unit cells, or by considering the q_{ij} of the sample as the result of a presence of spontaneously polarized faces. Therefore, in searching for the q_{ij} components different from zero, it is necessary

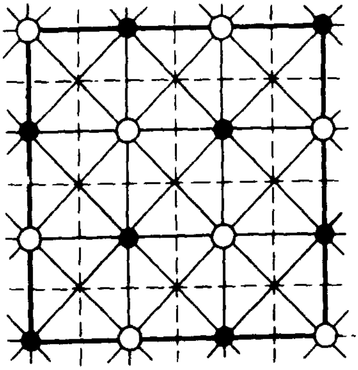

FIG. 1. Two-dimensional A^+B^--type crystal. The crystal point group is 4 *mm*. The symmetry group of the example is *mm*.

to consider the symmetry group of the samples faces, rather than the point group of the crystal.

In this case the elements of the crystal space group such as the screw axes and slip reflection planes perpendicular to the face are not included in the symmetry elements of the face and hence in the sample, since they do not coincide with the face. In addition, because of the finiteness of the face, the rotation axes perpendicular to it and the mirror reflection planes that pass through a row of identical atoms of the face also are not included, since a presence of such elements would significantly perturb its electrical neutrality condition.

We shall examine the examples that illustrate the reduction of symmetry due to crystal finiteness. The first example is an electrically neutral sample of a A^+B^-type, two-dimensional square crystal (Fig. 1). The "faces" of this crystal have a dipole moment, and, in view of the above-stated reasons, the sample loses the fourth-order axis and the planes perpendicular to the "faces." As a result, the sample has a forbidden quadrupole moment. The second example, a crystal with an incommensurable superlattice (Fig. 2), can be treated as a crystal with very large unit cells that contain an integral number of "frozen polarization waves." Generally, an arbitrary, fractional

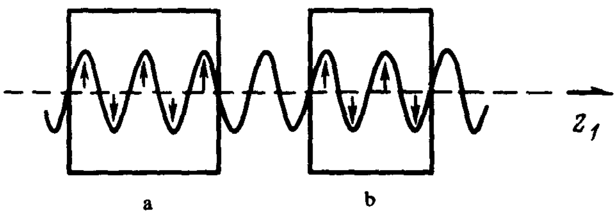

FIG. 2. A crystal with an incommensuarble superlattice: a, odd number; b, even number of polarization half-waves in the sample. The crystal point group includes the second-order axis and the symmetry plane whose projection is denoted by a dashed line. The symmetry group of the samples does not have these elements.

number of "waves" can be fitted into a sample. The screw axis and the slip reflection plane of an infinite crystal apparently are not symmetry elements of the faces perpendicular to them. As a result, both a dipole moment (a) and a quadrupole moment (b), which are forbidden by the symmetry of the infinite crystal, can appear in the sample.

We emphasize that, although we have been concerned primarily with the quadrupole moment, the fact of the matter is that the symmetry of all properties in a finite crystal is lower than that in an infinite medium. In fact, in an unshorted sample a quadrupole moment with a density q should create an electric field E that is nonuniform within the sample and has a gradient $\nabla E \sim q/L^2$ (L is the sample dimension),[2] which, in turn, can give rise[4] to a spontaneous, homogeneous deformation component $u = D\nabla E$ and a birefringence $\Delta n \sim u$.

We give estimates of the possible magnitudes of these effects. Let us assume that there is a dipole moment P of the order of atomic value in a surface layer of thickness d. Thus, the average polarization of the sample is $P_0 \sim (e/a)(d/a)(1/L)$, and $q \sim (e/a)(d/a)$, where a is the unit cell parameter, and e is the electron charge. The coefficient D can be estimated if we assume that $E \sim e/a^2$, $\nabla E \sim e/a^3$, $u \sim 1$, where $D \sim a^3/e$. For u and Δn we now have $u \sim \Delta n \sim D\nabla E \sim (a/L)^2(d/a)$.

We can see from these estimates that only the quadrupole moment q is independent of the sample dimension L, and the forbidden component of q is of the same order of magnitude as that allowed by the point group, i.e., in this sense q is a volume effect, whereas the forbidden components of P_0, u, and Δn are purely surface effects.

The layer thickness d is included in all the formulas. Therefore, all the effects in the crystals with an incommensurable superlattice and a period $l \gg a (d \sim l)$ are much larger than those in the ordinary crystals, where $d \sim a$.

For the ordinary crystals we have: $q \sim 10^{-2}$ CGS unit, a potential difference of $V \sim 3\pi q \sim 30$ V between two points on the sample face[2] and an average polarization of the sample $P_0 \sim ed/a^2L \sim 10^{-6}\ \mu C/cm^2$ (for $L \sim 1$ cm). For crystals with an incommensurable superlattice ($d \sim l \sim 10^2 a$): $q \sim 1$ CGS unit, $V \sim 3 \times 10^3$ V, $P_0 \sim 10^{-4}\ \mu C/cm^2$. The potential difference[1] V for an incommensurable phase of ammonium fluoroberyllate crystals is of this order of magnitude. At the same time, the values u and Δn are very small. Even for the most "favorable" experimental conditions, when, for example, the crystal has an incommensurable superlattice with a period $l \sim 10^2 a$ and $P \sim 10^{-3}(e/a^2)$, and the sample is very small ($L \sim l \sim d$), the linear expansion is $\Delta L \sim uL \sim 5 \times 10^{-3}$ Å, and the birefringence or the phase difference recorded in the experiment is $\Delta\phi = (2\pi/\lambda) \Delta n L \sim 3 \times 10^{-5}$ (for $\lambda = 10^3$ Å).

It follows from the given estimates that the detection of values such as u and Δn apparently is at the limit of the capabilities of present-day experimental methods. At the same time, the forbidden components q and P_0 can be observed both in the crystals with an incommensurable superlattice and also in the ordinary crystals.

We note that the possibility for the appearance of a dipole moment in crystals with a NaCl type nonpolar point group was discussed by Larmor[5] as far back as 1921. This can occur if the crystal is 'cut" in such a way that its faces are charged (comprised of ions of one sign). We examined above a different case in which the faces of the sample are not charged.

In conclusion, we note that a measurement of the temperature dependences of the components of the quadrupole and dipole moments, which are forbidden by the point group of the crystal, provides a convenient method of studying the variation of the crystal structure as a result of phase transitions. The method is especially effective when incommensurable superlattices are formed.

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