Revisiting the Theory of Crystal Polarization: The Downside of Employing the Periodic Boundary Conditions

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Periodic boundary condition (PBC) is a standard approximation for calculating crystalline materials properties. However, a PBC crystal is not the same as the real macroscopic crystal; therefore, if applied indiscriminately, it can lead to erroneous conclusions. For example, unlike other extensive observables such as total energy, the polarization of a macroscopic crystal cannot always be described by a PBC model, because polarization is inherently nonlocal and strongly dependent on surface terminations, irrespective of crystal size. Moreover, the symmetry of the macroscopic crystal can be altered when the PBC is applied to a macroscopic crystal. We demonstrate in this paper that the polarization of a macroscopic crystal receives contributions from both the repeating bulk units and the crystal surfaces, which must be treated on an equal footing. When the combined system of the bulk and its surfaces is taken into account, materials traditionally classified as nonpolar can, in fact, admit polar symmetry, thus explaining why experimentalists have observed polarization in some nominally "nonpolar" systems. Our study, thus, clarifies that polarization can only exist in polar group systems and that apparent violations of the Neumann's principle reported in some recent works originate from misinterpreting bulk PBC crystal as intrinsic macroscopic crystal, ignoring the contribution from the surfaces. We demonstrate that when the full bulk-plus-surface system is considered, the crystal polarization and symmetry are fully consistent with Neumann's principle.

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The concept of electric dipole moment plays a crucial role in electrostatics, especially in understanding a system's response to electric fields. It is textbook knowledge that the electric dipole moment can only exist along polar directions in a polar crystal with the following ten point groups: C_{6v}, C_6, C_{4v}, C_4, C_{3v}, C_3, C_{2v}, C_2, as well as C_s and C_1. For the first eight groups, the electric dipole moment can only exist along the rotation axis.[1] In the C_s group, the polarization direction can only be parallel to the mirror plane, while in the C_1 group, due to the absence of any symmetry, the electric dipole moment can occur along any direction. Traditional ferroelectricity is often associated with a structural phase transition associated with atomic displacements from an inversion-symmetric non-polar structure to a noncentrosymmetric polar structure (the symmetry of the structure belongs to the ten polar crystal point groups). However, in recent years, some researchers have claimed the discovery of many new ferroelectric materials that do not belong to the ten polar point groups.[2–15] Typically, periodic boundary condition (PBC) is assumed to explain the crystal symmetry, and modern theory of polarization (MTP)[16–22] is used to calculate the polarization of these new ferroelectric materials.

The MTP has undoubtedly been very successful in calculating ferroelectric polarization. Starting from wave functions obtained from first-principles calculations, it rigorously and compactly evaluates the polarization change associated with ferroelectric switching by integrating the Berry phase along a fixed path. Unfortunately, due to their success in practical computations, people have gradually begun to blur the distinction between the properties of PBC systems and those of real systems. As a result, conclusions obtained strictly within a periodic picture are at times treated as intrinsic crystal properties, fostering misconceptions (e.g., that the polarization in a real macroscopic system is "multivalued", as in a PBC system). Moreover, several recent studies have been interpreted as observing finite polarization in nonpolar systems,[4,23–27] thus regarded by many researchers as violations of Neumann's principle. However, once the actual surfaces of real crystals are specified, the symmetry of the relevant bulk-plus-surface system is fully consistent with Neumann's principle,[28] thereby resolving these apparent contradictions.

The controversy can be understood as follows. Due to the PBC imposed, a macroscopic crystal is mimicked by a **periodic** crystal, in which the two ends are connected (top of Fig. 1). However, real macroscopic crystalline materials are inevitably of finite size, with well-defined surfaces, despite the number of repeating cells of the crystal approaching infinitely large (bottom of Fig. 1).

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Fig. 1. The difference between a periodic crystal (top) and a real infinitely large crystal (bottom), illustrated using a one-dimensional charged chain as an example, is that in terms of symmetry, the periodic crystal belongs to the nonpolar symmetry group D_∞, whereas the actual real crystal effectively exhibits polar symmetry group C_∞.

These two systems are equivalent only if the implicit assumption that—as the number of repeating unit cells in a crystal increases to macroscopic scale, the contribution from the surfaces to the crystal's propery **per unit cell** becomes negligible—is correct.

However, unlike total energy and other local extensive material properties, the unit polarization of a macroscopic crystal often cannot be described by that of a periodic crystal, even when the number of repeating cells increases to infinity. This is because the application of PBC neglects the contribution from the surface, but the effect of the surface on the polarization is of the same order of magnitude as that of the interior repeating unit cell no matter how large the system is. More seriously, applying PBC often gives wrong crystal symmetry, which leads to unphysical conceptions. Therefore, in this paper, we show that in a macroscopic crystal C, the unit polarization $\boldsymbol{P}$ originates from two parts: the unit polarization of the repeating unit cell $\boldsymbol{P}_{\rm U}$ and the contribution of the remaining part of C after removing the repeating unit cells, which we denote as the surface polarization contribution $\boldsymbol{P}_{\rm S}$. Our argument demonstrates that for neutral macroscopic solids, The unit polarization $\boldsymbol{P}$ of a macroscopic crystal is a single-valued and well-defined quantity for a specific surface condition, that is independent of the choice of unit cell. Consequently, $\Delta\boldsymbol{P}$ is a state function, depending only on the initial and final states. In considering the symmetry of a macroscopic crystal, the symmetry of the repeating unit cell and the surface must be taken into account together to determine the correct overall symmetry, which is essential for a proper analysis and interpretation of the physical properties. This global (bulk-plus-surface) symmetry also explains why materials traditionally labeled as "nonpolar" can exhibit an observable, "unexpected" macroscopic polarization.

In the ionic limit, the dipole moment $\boldsymbol{d}$ of a neutral crystal with a collection of charges q_i at positions $\boldsymbol{r}_i$ is defined as

$$\boldsymbol{d} = \sum_i q_i \boldsymbol{r}_i, \tag{1}$$

for the case of a continuous charge distribution with density $n(\boldsymbol{r})$, this expression is straightforwardly extended to

$$\boldsymbol{d} = \int n(\boldsymbol{r})\boldsymbol{r}\,\mathrm{d}\boldsymbol{r}. \tag{2}$$

For a macroscopic neutral crystal, this is a well-defined single value quantity. In general, for macroscopic crystal C, we can choose a unit cell U and divide the crystal C into two parts: a repeating part $n \cdot U$ composed of U, and the remaining part as surface S.

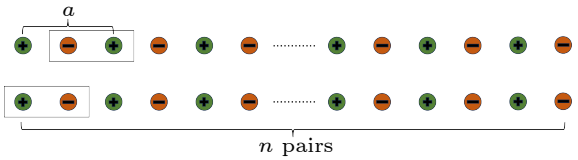

Fig. 2. One-dimensional charge chain. The top box and the bottom box represent different choices of neutral unit cells (without losing generality, we choose charge $q = 1$).

$$C = n \cdot U + S, \quad S = C \bmod U. \tag{3}$$

For the per unit polarization $\boldsymbol{P}$ of a crystal C,

$$\begin{aligned}\boldsymbol{P} &= \frac{\mathbf{d}}{V_{\rm tot}} = \frac{\sum^n \boldsymbol{d}_U + \boldsymbol{d}_S}{V_{\rm tot}} \\ &= \frac{V_U}{V_{\rm tot}} \sum^n \boldsymbol{P}_U + \frac{\boldsymbol{d}_S}{V_{\rm tot}} \\ &= \frac{nV_U}{V_{\rm tot}} \boldsymbol{P}_U + \boldsymbol{P}_S. \end{aligned} \tag{4}$$

For macroscopic solids $n \to \infty$,

$$\boldsymbol{P} = \boldsymbol{P}_U + \boldsymbol{P}_S, \tag{5}$$

where $\boldsymbol{P}_U = \boldsymbol{d}_U/V_U$ represents the contribution from the polarization within the unit cell, where V_U denotes the volume of the unit cell. $\boldsymbol{P}_S = \boldsymbol{d}_S/V_{\rm tot}$ represents the contribution of polarization from the surface, where $V_{\rm tot}$ is the total volume of the macroscopic crystal. In the following discussion, for simplicity and better readability, we map the real quantum system onto an effective point-charge model. We emphasize that this point-charge representation is not an excessive simplification of the underlying quantum system; on the contrary, its equivalence to the full description of the real system can be rigorously established via Wannier or Boys orbitals.[20,29,30]

Equation (5) shows that for a real solid C, the polarization $\boldsymbol{P}$ consists of two parts: $\boldsymbol{P}_U$ and $\boldsymbol{P}_S$. Although selecting different unit cells U leads to different $\boldsymbol{P}_U$, the corresponding $\boldsymbol{P}_S$ also changes such that the total polarization $\boldsymbol{P}$ of the crystal remains invariant. Taking the one-dimensional chain shown in Fig. 2 as an example and letting $n \to \infty$, when we select the unit cell shown at the top of Fig. 2, we obtain $\boldsymbol{P}_U = 1/2$ and $\boldsymbol{P}_S = -1$, so

$$\boldsymbol{P} = \boldsymbol{P}_U + \boldsymbol{P}_S = \frac{1}{2} - 1 = -\frac{1}{2}.$$

Note that $\boldsymbol{P}_S$ is finite and does not vanish even as $n \to \infty$. When we select the unit cell shown at the bottom of Fig. 2, we obtain

$$\boldsymbol{P} = \boldsymbol{P}_U + \boldsymbol{P}_S = -\frac{1}{2} + 0 = -\frac{1}{2}.$$

So, the polarization is independent of how one chooses the unit cell, as one would expect. Note that $\boldsymbol{P} = \boldsymbol{P}_U$ only when the unit cell is chosen appropriately to make the surface contribution vanish. However, if we apply PBC to this one-dimensional chain, the chains in Fig. 2 are forced to change from polarized chains to a non-polar system with inversion symmetry, and the polarization becomes multi-valued: $\boldsymbol{P} = 1/2$ for the top unit cell choice and $\boldsymbol{P} = -1/2$

for the bottom unit cell choice. In general, under PBC, the polarization $\boldsymbol{P}$ is given by

$$\boldsymbol{P} = \boldsymbol{P}_U + m\boldsymbol{P}_q. \tag{6}$$

Here, m is an integer, $\boldsymbol{P}_q$ is the polarization value resulting from the displacement of an ion with charge q by one lattice vector, i.e., a constant polarization quantum.

This simple example illustrates the essential difference between a periodic crystal and a macroscopic crystal: the polarization $\boldsymbol{P}$ of a macroscopic crystal is well-defined, single valued for a specific surface, and observable. Imposing PBC on a macroscopic crystal disregards the surface termination, but the influence of the surface S on polarization cannot be ignored.

We want to emphasize here that from a symmetry perspective, as show in Fig. 1, a periodic one-dimensional pair chain has center inversion symmetry, and its symmetry group is D_∞, which is a non-polar point group. In contrast, an infinite repeating pair chain has symmetry C_∞, where the rotation axis is the one-dimensional chain, making it a polar point group. The difference in symmetry indicates that symmetry imposed by a PBC may not be correct to describe the polarization of a real macroscopic crystals, therefore, one may obtain wrong conclusions by enforcing PBC, such as one can obtain polarization in a "nonpolar" crystal.

When considering the change in polarization $\Delta\boldsymbol{P}$ during ferroelectric switching, according to Eq. (5),

$$\Delta\boldsymbol{P} = \Delta\boldsymbol{P}_U + \Delta\boldsymbol{P}_S. \tag{7}$$

According to Eq. (6) under PBC, we can obtain another form

$$\Delta\boldsymbol{P} = \Delta\boldsymbol{P}_U + \Delta m\boldsymbol{P}_q. \tag{8}$$

The latter term in Eq. (8) arises from the additional indeterminacy introduced by the PBC assumption; in order to obtain the correct $\Delta\boldsymbol{P}$, Δm must be determined via the specific surface variation $\Delta\boldsymbol{P}_S$. Equation (7) implies that we need to consider the $\Delta\boldsymbol{P}_S$ induced by surface charge variations.[31] In conventional ferroelectric materials, ionic displacements during the ferroelectric phase transition usually occur within a single unit cell, so that $\Delta\boldsymbol{P}_S = 0$. Therefore, neglecting the surface contribution does not cause serious issues in calculating $\Delta\boldsymbol{P}$.[32] However, for cases where the surface conditions change before and after a ferroelectric phase transition, this contribution must be properly accounted for. As an example, when we move all the anion by half a lattice unit in the 1D chain, from Fig. 3(a) to Fig. 3(b),

$$\Delta\boldsymbol{P}_U = 0, \tag{9}$$

$$\Delta\boldsymbol{P}_S = -1. \tag{10}$$

This demonstrate that both $\boldsymbol{P}_S$ and $\Delta\boldsymbol{P}_S$ cannot be neglected in general.

We now apply the foregoing mathematical reasoning to one of the most classic crystal structures—the zinc-blende (ZB) structure—which is normally considered as non-polar material with T_d symmetry when PBC is applied. As shown in Fig. 4, we can view the ZB crystal in terms of its primitive unit cell L and its conventional unit cell H. In Fig. 4(a), the primitive ZB cell consists of one positive charge and one negative charge. The movement from configuration L_1 to configuration L_2 results in a change in polarization $\Delta\boldsymbol{P}$,

$$\begin{aligned}\Delta\boldsymbol{P}_{U_L} &= -\frac{1}{V_0}[(3/4,3/4,3/4) - (1/4,1/4,1/4)] \\ &= -\frac{1}{V_0}(1/2,1/2,1/2),\end{aligned} \tag{11}$$

where V_0 represents the volume of the primitive cell. However, in Fig. 4(b), the change in polarization $\Delta\boldsymbol{P}_{U_H}$ between configurations H_1 and H_2 is given by

$$\begin{aligned}\Delta\boldsymbol{P}_{U_H} = -\frac{1}{4V_0}[&(1/4,1/4,3/4) - (1/4,1/4,1/4) \\ &+(1/4,3/4,1/4) - (1/4,3/4,3/4) \\ &+(3/4,1/4,1/4) - (3/4,1/4,3/4) \\ &+(3/4,3/4,3/4) - (3/4,3/4,1/4)] \\ = 0.&\end{aligned} \tag{12}$$

Note that when PBC is applied to both cases in Fig. 4, L_1 is equivalent to H_1 and L_2 is equivalent to H_2. This implies that neglecting the surface effects prevents unique determination of $\Delta\boldsymbol{P}$ from the initial to final states, further suggesting that PBC are unsuitable for this system.

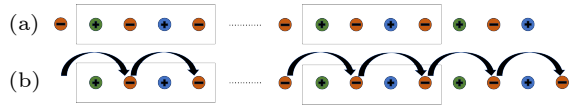

Fig. 3. A one-dimensional chain with the black square representing the unit cell. When the anion moves by half a lattice vector along the black arrow, the chain changes from (a) to (b).

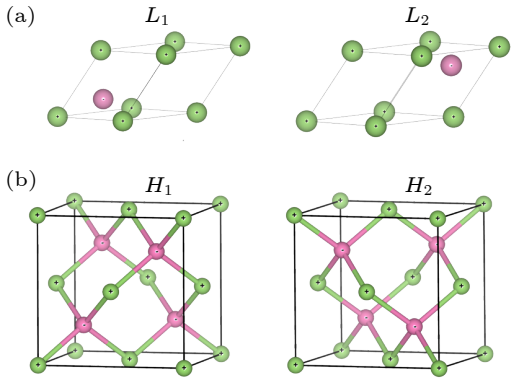

Fig. 4. (a) The primitive cell L of the ZB structure. The configuration on the left is denoted as L_1. By moving the anion along the [111] direction by $(1/2, 1/2, 1/2)$, we obtain the configuration on the right, denoted as L_2. (b) The conventional cell H of the ZB structure. The left configuration is denoted as H_1 and the right as H_2. In the figure, green spheres represent positive charge centers, and pink spheres represent the negative charge centers.

The origin of the above-observed polarization in a "non-polar" system becomes clear if we treat the above example as macroscopic crystals and take into account the contribution of surface. The unit cell choices in Figs. 4(a) and 4(b) correspond to different macroscopic crystals when the surface is taking into account. For macroscopic crystals, the corresponding symmetries of L_1 and L_2 are C_{3v}, which is polar and can have non-zero polarization, while H_1 and H_2 belong to T_d, a non-polar point group, which requires $\boldsymbol{P}_{U_{H_1}} = \boldsymbol{P}_{U_{H_2}} = 0$. Imposing 3D periodicity can lead to the misconception that L and H are identical,[4] both exhibiting T_d symmetry, which in turn leads to the unphysical conclusion that non-polar crystals can have polarization and be ferroelectric.

To further demonstrate the contribution from the surfaces, we show in Fig. 5 two different phase transition pathways from H_1 to H_2,

$$\boldsymbol{P}_{C_\mathrm{i}} = \boldsymbol{P}_{U_{H_1}} = 0, \tag{13}$$

$$\boldsymbol{P}_{C_\mathrm{f}} = \boldsymbol{P}_{U_{H_2}} = 0, \tag{14}$$

$$\begin{aligned}\boldsymbol{P}_{C'_\mathrm{f}} &= \boldsymbol{P}_{U_{H_2}} + \boldsymbol{P}_S = 0 + \frac{-1}{2V_0}(0,0,1) \\ &= -\frac{1}{2V_0}(0,0,1),\end{aligned} \tag{15}$$

then

$$\Delta\boldsymbol{P}_{\mathrm{Path1}} = \boldsymbol{P}_{C_\mathrm{f}} - \boldsymbol{P}_{C_\mathrm{i}} = 0, \tag{16}$$

$$\Delta\boldsymbol{P}_{\mathrm{Path2}} = \boldsymbol{P}_{C'_\mathrm{f}} - \boldsymbol{P}_{C_\mathrm{i}} = -\frac{1}{2V_0}(0,0,1). \tag{17}$$

For periodic systems, we cannot distinguish between C_f and C'_f; however, for macroscopic systems, C_f and C'_f have distinct differences: C_f is entirely composed of H_2, while C'_f has a new surface S due to the overall upward shift of the anions. It is this newly formed surface that causes $\Delta\boldsymbol{P}_{\mathrm{Path2}}$ to be non-zero. In fact, compared to the small changes in $\Delta\boldsymbol{P}$ that occur during traditional ferroelectric phase transitions, the large fractional $\Delta\boldsymbol{P}$ in the ZB structure corresponding to the space group $F\bar{4}3m$ results from the movement of atoms from the 4*c* to the 4*d* Wyckoff positions. The underlying physical reason is that the movement of atoms between Wyckoff positions leads to a change in the surfaces, which causes a large $\Delta\boldsymbol{P}_S$.[13,33] This implies that crystals forced into non-polar groups by imposed PBC, and thus regarded as incapable of ferroelectric switching, actually exhibit polar symmetry once surfaces are considered and represent potential new types of ferroelectric materials.[4,23]

Based on the above discussion, we present the following general conclusions: (i) The polarization $\boldsymbol{P}$ of a macroscopic crystal consists of two parts: $\boldsymbol{P}_U$ and $\boldsymbol{P}_S$. Regardless of the number of repeating cells in the solid, both $\boldsymbol{P}_U$ and $\boldsymbol{P}_S$ are equally important and, in general, cannot be neglected. (ii) Although $\boldsymbol{P}_U$ and $\boldsymbol{P}_S$ depend on the choice of repeating unit cell, the total polarization $\boldsymbol{P} = \boldsymbol{P}_U + \boldsymbol{P}_S$ of a macroscopic crystal is independent of the choice of unit cell and is a well-defined, single-valued quantity. (iii) $\Delta\boldsymbol{P}_U$ and $\Delta\boldsymbol{P}_S$ are equally important,

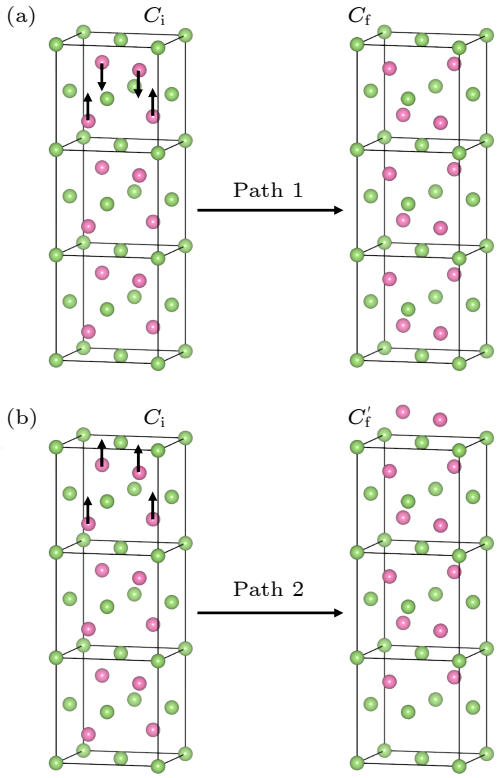

Fig. 5. Two different phase transition pathways from H_1 to H_2. The black arrows indicate the direction of anion movement. C_i represents the macroscopic crystal corresponding to H_1. (a) The final state obtained from C_i moving along Path 1 is C_f; (b) the final state obtained from C_i moving along Path 2 is C'_f.

and $\Delta\boldsymbol{P}_S$ is not always negligible. Furthermore, the above discussions suggest that (iv) for crystals of any space group, by properly choosing the unit cell and displacement path and repeating the unit cell, one could, in principle, tailor the combined bulk-plus-surface system to belong to a polar point group, thereby enabling a broad new class of materials with polarization or even being ferroelectricity.

It should be emphasized that our above analysis and arguments concerning the physical properties of real systems do not imply that the MTP is incorrect in calculating ferroelectric polarization. On the contrary, the MTP and our discussion are not in conflict but are fully consistent. When we actually calculate the polarization of a real solid, it is difficult to compute $\boldsymbol{P}_S$ directly from Eq. (2) because of the complexity of effects such as surface reconstruction. However, according to the surface theorem,[20,29,30] one can show that the contributions from the finite displacements of ions and from the electronic cloud induced by surface reconstruction vanish in the macroscopic limit ($n \to \infty$). This implies that the magnitude of $\boldsymbol{P}_S$ defined in this work is strictly equal to $m\boldsymbol{P}_q$, where the integer m is completely determined by the net charge on a single surface. For example, if the left surface carries a charge of $5e$, then, due to overall charge neutrality, the right surface must carry $-5e$, and thus $m = 5$. This means that we only need to count the static charge on the chosen surface in order to obtain the exact value of $\boldsymbol{P}_S$.

For the unit polarization $\boldsymbol{P}_U$, we can follow the stan-

dard procedure of the MTP by first idealize the real crystal as an infinite periodic system. Using first-principles band-structure calculations with PBC, the usual output is the cell-periodic electronic Bloch function $|u_{n\boldsymbol{k}}\rangle$. It is then convenient to compute the unit polarization $\boldsymbol{P}_U$ using the Berry-phase/Wannier-center formulation[22,34–38] as follows:

$$\boldsymbol{P}_U = \frac{1}{V}\left(\sum_i (q_i \boldsymbol{r}_i)^{\text{ions}} + \sum_n^{\text{occ}} (q_n \bar{\boldsymbol{r}}_n)^{\text{WFs}}\right). \tag{18}$$

$$\bar{\boldsymbol{r}}_n = \mathrm{i}\frac{\Omega}{(2\pi)^3}\int_{\text{BZ}} \mathrm{d}^3k\, \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}}\left\langle u_{nk}\middle|\frac{\partial u_{nk}}{\partial \boldsymbol{k}}\right\rangle. \tag{19}$$

Because of the multivalued nature of $\bar{\boldsymbol{r}}_n$ under PBC, the $\boldsymbol{P}_U$ obtained from the above formulas is likewise multivalued. The next step is to "cut" the real system of interest out of this idealized periodic crystal, i.e., to introduce surfaces. It is crucial at this stage to choose surfaces that are consistent with those of the actual system. This requirement also removes the arbitrariness in the choice of unit cell, so that $\boldsymbol{P}_U$ is no longer multivalued but collapses onto a specific branch of the polarization lattice determined by the chosen surfaces. After carrying out these steps, we obtain the polarization of the real macroscopic crystal. We emphasize once again that, although the polarization of the purely periodic PBC system is multivalued, the polarization of the real, cut-out system, $\boldsymbol{P} = \boldsymbol{P}_U + \boldsymbol{P}_S$, is single-valued and well-defined.

In summary, we have used one-dimensional chains and ZB structures as examples to show the importance of the surface contribution to the description of polarization in macroscopic crystals. Neither $\boldsymbol{P}_S$ nor $\Delta\boldsymbol{P}_S$ can be neglected, no matter how large the crystal size is. This indicate that, in general, PBC—which ignores the true surface contribution—is not sufficient to describe the polarization of a real crystal. To put it another way, a macroscopic crystal is not a periodic crystal when polarization is concerned. We have shown that, with the correct treatment of surface, the polarization is independent of the choice of the unit cell and is single-valued for a specific surface configuration. For macroscopic crystals, symmetry classification should account for both bulk and surface conditions. The symmetry of polarized crystals must still belong to polar point groups, whereas the polarization of crystals belonging to non-polar point groups must be zero. Crystals that were traditionally misclassified as non-polar under imposed PBC actually exhibit polar symmetry once surfaces are considered, thereby revealing their potential as new types of ferroelectric materials. These insights not only reveal the inapplicability of PBC to nonlocal physical quantities such as polarization but also highlight the important role of surfaces in ferroelectric phenomena and further enable the realization of a new class of ferroelectric materials through surface-engineered switching.

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