Comment on "*Ab Initio* Study of the Spontaneous Polarization of Pyroelectric BeO"

Recently, Posternak, Baldereschi, Catellani, and Resta (PBCR) [1] reported on a method of *ab initio* calculation of the spontaneous polarization and its variation in pyroelectrics. I believe that their results are disputable in several aspects.

Spontaneous polarization.—PBCR reported that they had calculated the spontaneous polarization of a periodical structure corresponding to a linear pyroelectric (nonferroelectric) stressing that they had found the bulk characteristic of the structure. The following arguments can be put forward against this statement.

(i) In general, there exists no such bulk characteristic of a pyroelectric as the spontaneous polarization (only in the case of ferroelectrics can this quantity be unambiguously introduced, using some additional arguments). In fact, one can ascribe any value to the permanent polarization of any infinite periodical distribution of charge density. (A most straightforward proof of this statement can be found in Refs. [2,3].) Therefore, if one ascribes by means of some procedure a definite value of the permanent polarization to a specified infinite periodical structure then this value appears as a characteristic of the procedure rather than one of the structure.

(ii) However, it is possible to define the permanent polarization of a given structure "with respect to another nonpolar structure," i.e., to ascribe to the former the polarization equal to the polarization arising in the course of continuous conversion of the latter into the former. The quantity introduced above may be single valued because the variation of polarization may be unambiguously introduced. Applying this definition to a ferroelectric one can unambiguously define the permanent polarization of the ferroelectric phase with respect to the paraelectric one, which is called spontaneous polarization of the ferroelectric. PBCR tried to extend this definition to the case of a linear pyroelectric (nonferroelectric), calculating the polarization of the wurtzite (W) structure with respect to the zinc-blende (ZB) one. I believe that their analysis of the interface between W and ZB may yield the W polarization with respect to the ZB nonpolar structure. However, the result of such an analysis should be interpreted not as a bulk property of W but rather as a property of the pair of materials chosen (W and ZB). The point is that the permanent polarization of a specified structure with respect to another nonpolar one, in general, should be different for a different choice of the nonpolar structure. This statement can be easily seen from the proof of indeterminacy of the permanent polarization presented in Refs. [2,3].

Variation of polarization.—PBCR applied their method to calculate the polarization variation for a pyroelectric. Generally speaking, that may be done in the framework of the approach used in Ref. [1]. However, I believe that PBCR's method cannot yield the correct value of the common piezoelectric constants. The point is that the piezoelectric constants describe the linear response of the polarization in the absence of a macroscopic electric field, whereas the consideration in Ref. [1] deals with the pyroelectric substance layer which is under the action of a strong macroscopic electric field.

The relation between the common bulk piezoelectric constant λ_{ijk} and $\partial P_i/\partial u_{jk}$ calculated by PBCR in Ref. [1], in general, is not easy to find. However, one can easily obtain this relation for the case where the layer of piezoelectric is embedded in a nonpolar matrix and no macroscopic electric field outside the layer is present. In this case, the variation of the polarization of the layer induced by the application of strain u_{ik} is [4]

$$\delta P_i = P_j^{(0)} u_{ij} - P_i^{(0)} u_{jj} + \lambda_{ijk}(E^{(0)}) u_{jk} + \chi_{ij} \delta E_j , \qquad (1)$$

where $P_i^{(0)}$ is the average dipole moment density of the layer before the application of the strain, $\delta E_i = -4\pi \delta P_i$, $E_i^{(0)} = -4\pi P_j^{(0)}$, and χ_{ij} is the clamped dielectric susceptibility. Here only the third right-hand term is related to the bulk piezoelectric response [5]; $\lambda_{ijk}(E^{(0)})$ stands for the value of the bulk piezoelectric constant in the presence of the electric field $E^{(0)}$. In the linear approximation this quantity is connected with the piezoelectric constant by the relation $\lambda_{ijk}(E^{(0)}) \simeq \lambda_{ijk} + \partial \lambda_{ijk}/\partial E_m E_m^{(0)}$. Then, using (1) and the thermodynamic identity $4\pi \partial \lambda_{ijk}/\partial E_m = \partial \epsilon_{im}/\partial u_{jk}$, where $\epsilon_{ij} = 1 + 4\pi \chi_{ij}$, one can obtain the following relation between the piezoelectric constant λ_{ijk} and calculated quantity $\partial P_i/\partial u_{jk}$:

$$\lambda_{ijk} = \epsilon_{im} \partial P_m/\partial u_{jk} + (\partial \epsilon_{im}/\partial u_{jk} - \delta_{mk}\delta_{ij} + \delta_{kj}\delta_{im}) P_m^{(0)} . \qquad (2)$$

For the case considered by PBCR, some formula more general than (2) should be used, because in that case the electric field and the polarization outside the W region, E_{ZB} and P_{ZB}, are to be taken into account also. However, for $E_{ZB} = 0$ and $P_{ZB} = 0$, this general formula should transform into (2). I believe that the correction procedure proposed by Posternak, Resta, and Baldereschi [6] that takes into account, in fact, only the first right-hand term of (2) does not suffice.

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