Towards a Quantum Theory of Polarization in Ferroelectrics: The Case of $KNbO_3$

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The spontaneous macroscopic polarization of perovskite $KNbO_3$ is calculated as a Berry's phase using the Bloch functions of the tetragonal crystal. The result $P = 0.35$ C/m^2 supports the measured value 0.37 C/m^2 and implies that earlier data from hysteresis loops are too low. The polarization is linear in the ferroelectric distortion; the Born effective charges show strong variations from nominal ionic values and a large inequivalence of the O ions. Linearity *a posteriori* demonstrates that the polarization of perovskites at finite temperature can be safely predicted assuming the ions frozen in their time-averaged positions.

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The basic quantity in ferroelectrics is the spontaneous macroscopic polarization P, which results, e.g., upon application of an electric field, and persists at null field in two (or more) enantiomorphous metastable states of the crystal; experiments measure, via hysteresis cycles, the difference ΔP between these states [1]. Well known ferroelectrics are the perovskite oxides, having a cubic prototype phase above the Curie temperature, and displaying a series of structural transitions to low-symmetry ferroelectric phases when temperature is lowered. Typically, the first transition is to a tetragonal phase, which is characterized by a small uniaxial macroscopic strain, accompanied by microscopic displacements of the ions out of their high-symmetry sites: the latter distortion determines a preferred polarity of the tetragonal axis, and is responsible, upon symmetry grounds, for the occurrence of P. Although several microscopic models have been postulated over the years, little is known about any *quantitative* correlation between ionic displacements and electronic polarization. In this Letter we propose a quantum approach to the macroscopic polarization of ferroelectrics, which includes all orders in the internal strain, and provides novel insight at the microscopic level into the basic physics of ferroelectricity. Results are given for a paradigmatic ferroelectric: tetragonal $KNbO_3$, which is one of the most studied perovskites.

Classical models [2, 3] introduce *ad hoc* microscopic polarizable dipoles as responsible for the occurrence of P; but no genuine insight into the phenomenon can be reached without a quantum description of the electronic system, particularly in materials with delocalized electrons. First-principles charge-density maps are available for some perovskite oxides [4, 5]: although providing microscopic data relevant for the ferroelectric instability, such maps cannot carry any information about P, since the macroscopic polarization of a periodic charge distribution is ill defined [6]. In fact, no quantum-mechanical calculation of the spontaneous polarization of a crystal existed until the work of Ref. [7] on pyroelectric BeO, where the bulk polarization was obtained from the charge density of finite thickness slabs. The procedure of Ref. [7] is not easily implementable—at the first-principles level—to more complex crystals such as the perovskites. There has been therefore a search for new methods to derive the spontaneous polarization. They are based on the electronic *wave functions*—as opposed to the charge density—of the periodic polarized crystal in a null field. In fact, the use of wave functions allows one to write the macroscopic polarization of a *finite* piece of insulating matter as a boundary-insensitive expression whose thermodynamic limit is uniquely defined. Such a procedure has been demonstrated—at least in principle—in Ref. [8]; subsequently, King-Smith and Vanderbilt (KSV) [9] provided an equivalent and alternative approach which is elegant and more appealing for practical computations. We have tested the KSV approach using the existing results on BeO as a benchmark

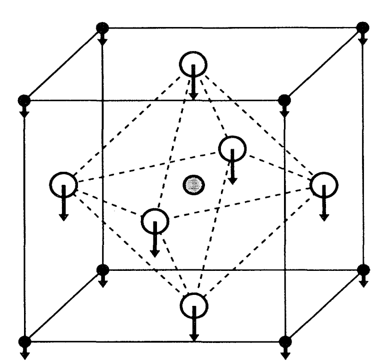

FIG. 1. Ideal tetragonal structure of $KNbO_3$, with $c/a = 1.017$. Solid, shaded, and empty circles represent K, Nb, and O atoms, respectively. Internal displacements (indicated by arrows, and magnified by a factor of 4) transform the ideal structure into the experimental one at 270 °C. Top and bottom O ions will be called O1, while the four O ions in the basal plane of the octahedron will be called O2 and O3.

[7]. The success in reproducing [10] the results of Ref. [7] with reduced computational load prompted us to undertake the first-principles investigation of the macroscopic spontaneous polarization in much more relevant materials like the ferroelectric perovskites.

$KNbO_3$ is stable in the tetragonal phase between 225 and 418 °C. Its spontaneous polarization is known to be rather high. Early direct measurements [11] gave $P = 0.30$ C/m^2, while more recent data [12, 13] suggest the higher value 0.37 C/m^2. We perform our study assuming a "frozen" ionic configuration, corresponding to the structural parameters measured [14] at 270 °C. Our sample has $a = 3.997$ Å and $c = 4.063$ Å; considering such macroscopic strain only, the cubic perovskite structure is transformed into a nonpolar centrosymmetric tetragonal phase (Fig. 1), which will be called "ideal." A further internal strain—consisting of ionic displacements u_s along the tetragonal axis—transforms the ideal structure into the experimental one. We choose $u_{\rm Nb} = 0$, and the remaining displacements are then [14], in units of c: −0.023 (K), −0.040 (O1), and −0.042 (O2,O3). The internal strain therefore leaves the oxygen cage almost undistorted, while the two cation sublattices undergo different displacements relative to it. We calculate the polarization difference ΔP between the polar ($\lambda = 1$) and the ideal ($\lambda = 0$) tetragonal structures assuming a continuous adiabatic transformation which consists in scaling the internal strain with the parameter λ ($0 \le \lambda \le 1$). Since the polarization of the ideal structure vanishes by symmetry, ΔP coincides with the spontaneous polarization P of the distorted phase.

The total polarization change can be decomposed into its electronic and ionic terms:

$$\Delta P = \Delta P_{\rm el} - \frac{e}{\Omega}\sum_s Z_s u_s, \tag{1}$$

where Ω is the cell volume, $-eZ_s$ are the bare charges of the ionic cores which do not polarize, and $\Delta P_{\rm el}$ refers to valence electrons only. Following KSV, the latter can be calculated as

$$\Delta P_{\rm el} = -\frac{2e}{(2\pi)^3}\int dk_x\, dk_y \int dk_z\, \frac{\partial}{\partial k'_z}[\varphi_1(\mathbf{k},\mathbf{k}') - \varphi_0(\mathbf{k},\mathbf{k}')]\bigg|_{\mathbf{k}'=\mathbf{k}}, \tag{2}$$

where z is along the polarization axis, the integrals are over the whole Brillouin zone, the k_z integral has the properties of a Berry's phase [15] given that

$$\varphi_\lambda(\mathbf{k},\mathbf{k}') = {\rm Im}\,\{\ln \det S^{(\lambda)}(\mathbf{k},\mathbf{k}')\} \tag{3}$$

is the phase of the determinant of the overlap matrix $S^{(\lambda)}(\mathbf{k},\mathbf{k}')$ between the *periodic parts* $\chi^{(\lambda)}$ of the occupied Bloch states at $\mathbf{k}$ and $\mathbf{k}'$, i.e., the matrix whose elements are

$$S^{(\lambda)}_{mn}(\mathbf{k},\mathbf{k}') = \langle \chi^{(\lambda)}_m(\mathbf{k})|\chi^{(\lambda)}_n(\mathbf{k}')\rangle, \tag{4}$$

m and n being the occupied valence-band indices. All band-structure calculations are performed within the local-density approximation to density-functional theory; the Kohn-Sham wave functions [16] are obtained from the full-potential linearized augmented-plane-wave (FLAPW) method [17]. The gradients and the integrations occurring in Eq. (2) have been performed numerically on a discrete mesh [18].

The calculation yields $P = 0.35$ C/m^2, supporting the higher experimental value [12, 13]. Since the Berry's phase is defined modulo 2π, the value of ΔP is only defined modulo the "quantum" $2ec/\Omega = 1.99$ C/m^2. Therefore, the calculated value of P is unambiguously defined—as a function only of the two structures $\lambda = 0$ and 1—since $|\Delta P|$ is much smaller than the quantum. We further notice that while ΔP is independent of the convention $u_{\rm Nb} = 0$ in Eq. (1), its electronic and ionic terms separately *do* actually depend on it. We have explicitly verified that a rigid translation of the whole crystal induces a vanishing ΔP: the cancellation of the two terms in Eq. (1) holds to five significant figures.

The good agreement between the calculated value of P and experimental data demonstrates that the crystal wave functions in the frozen ferroelectric structure convey the essential physics of the spontaneous polarization in real materials. This finding opens the way to investigating a number of issues where no insight was previously possible. The first such issue is whether P is linear in the internal strain: to this aim, we have calculated the polarization change between $\lambda = 0$ and $\lambda = 1/4$. We get $P = 0.095$ C/m^2, which is very close to 1/4 of the full value. Given its rather high P (and internal strain) values, $KNbO_3$ is a stringent test case, and we therefore argue that linearity is a general feature of ferroelectric perovskites. This result is by no means trivial, since ferroelectricity is essentially a nonlinear phenomenon. Furthermore, it is worth quoting that the Born theory of the pyroelectric effect [19] crucially depends on the assumption that P is *nonlinear* in the ionic displacements.

The explicit verification of linearity proves the soundness of the phenomenological expression

$$P = \frac{|e|}{\Omega}\sum_s Z^*_s u_s, \tag{5}$$

where $|e|Z^*_s$ are the Born (or transverse) effective charges, defined as the linear term in the polarization change due to a unit displacement of the sth ion, keeping all the other ions *and* the macroscopic field fixed [20]. We calculate them directly from their definition and in the ideal structure, since—due to linearity—it is irrelevant whether they are evaluated in the ideal or the experimental geometry. The results are 0.82 (K), 9.13 (Nb), −6.58

(O1), −1.68 (O2,O3). The acoustic sum rule $\sum_s Z_s^* = 0$ is fulfilled to within 0.02, which is a remarkable performance even when compared to pseudopotential calculations for simple semiconductors [21]. A global check of these values is provided by the measured [13] longitudinal (LO) and transverse (TO) optical phonon frequencies ω_j, which are related to the effective charges by the exact sum rule

$$\varepsilon_\infty \sum_j [\,\omega_j^2(\mathrm{LO}) - \omega_j^2(\mathrm{TO})\,] = \frac{4\pi e^2}{\Omega} \sum_s \frac{(Z_s^*)^2}{M_s}, \quad (6)$$

where M_s are the ionic masses. Equation (6) can be derived from the trace of the dynamical matrix [20], under the hypothesis of *harmonicity*. The left-hand side member, when evaluated with the experimental data of Refs. [12,13], yields 2.41×10^6 cm^{-2}, while the theoretical value of the right-hand member is 2.97×10^6 cm^{-2}. The discrepancy could derive from the strong anharmonicity of the adiabatic energy surfaces in perovskite oxides [4]. It should also be considered that phonon frequencies have been measured at 312 °C, i.e., a 42 °C higher temperature than that of the measurement of the structural parameters used in this work.

The most conspicuous features of the effective-charge values are the strong inequivalence of the O ions, and the large absolute values of Z_{Nb}^* and Z_{O1}^*. The former was to be expected on symmetry grounds and on the basis of model calculations [2], but no reliable figure was available so far for the ratio $Z_{\mathrm{O1}}^*/Z_{\mathrm{O2}}^*$. The values of Z_{Nb}^* and Z_{O1}^* are much larger than the nominal ionic charges: The Born effective charge is indeed a *macroscopic* concept [6,20], involving the polarization of valence electrons as a whole, while the charge "belonging" to a given ion is an ill-defined concept. The high Z^* values indicate that relative displacements of neighboring O1 and Nb ions against each other trigger highly polarizable O $2p$ electrons: Roughly speaking, a large amount of nonrigid, delocalized charge is responsible for both Z_{Nb}^* and Z_{O1}^*. The sensitivity of the $2p$ oxygen orbitals to the relative displacement of Nb is explicitly demonstrated by the density of states given in Fig. 2. The top panel shows that, as a result of band splittings produced by the tetragonal strain, the O $2p$ lowest band edge is purely O1, while the highest edge is purely O2 (and O3). More generally, O1 contributes more than O2 and O3 to the O $2p$ density of states in the low-energy region, which is the significant one for the interaction with Nb (middle panel; see also Ref. [22]).

Finally we have verified that, as far as the macroscopic polarization is concerned, the ferroelectric distortion of $KNbO_3$ can be modeled assuming a simple cubic perovskite unit cell, whose volume is equal to that of the tetragonal one, and an internal strain whose unique displacement is $u_{\mathrm{Nb}} = 0.041$ (in units of the lattice constant) against the rigid frame of all the remaining ions. With

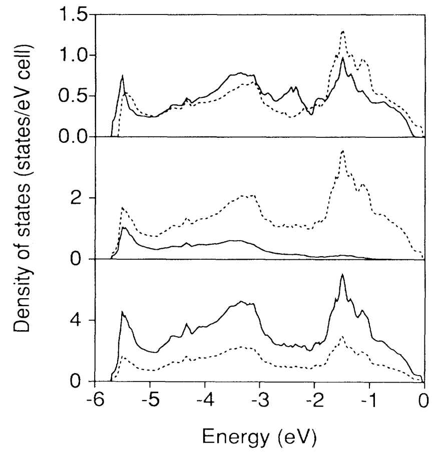

FIG. 2. Density of states of the topmost nine occupied bands (the so-called O $2p$ bands) of $KNbO_3$ in the experimental tetragonal structure. Bottom panel: total density (solid) and its fraction in the interstitial region (dashed). Middle panel: d projection in the Nb sphere (solid) and total p projection in all O spheres (dashed). Top panel: the O $2p$ projection into the O1 (solid) and O2 (or O3, dashed) spheres. The density-of-states decompositions depend on the atomic spheres, whose radii in our case are 2.9, 2.2, and 1.3 a.u. for K, Nb, and O, respectively.

respect to the complex distortion pattern of the experimental structure studied so far, the model neglects (i) the small macroscopic tetragonal strain, (ii) the small deformation of the O cage, and (iii) the displacement of K, given its low effective charge. Within this simplified scenario we obtain $P = 0.33$ C/m^2, which demonstrates that the polarization is essentially due to the displacement of Nb out of the center of the O octahedron. All structural features neglected by the model—though important for the stability of the tetragonal phase [5]—are irrelevant for its macroscopic polarization.

The major result of this work is that in ferroelectric perovskites the Born effective charges are independent of the ionic displacements, i.e., the macroscopic polarization is linear with the internal strain. This nontrivial feature—besides being relevant in its own—demonstrates that the finite-temperature polarization of perovskites can be safely calculated assuming the ions frozen in their time-averaged position. The validity of this approximation guarantees the soundness of the approach proposed in this work for predicting the spontaneous macroscopic polarization of solids, and opens the way to a quantum treatment of pyroelectricity as well.

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