

## Rapid Communications

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### Role of covalent bonding in the polarization of perovskite oxides: The case of $\text{KNbO}_3$

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In ferroelectric perovskites, the strong spontaneous polarization is due to giant values of the Born effective charges, which are much larger than predicted on the basis of the nominal ionicity: we investigate the physical origin of such charges, which by definition measure the current traversing the sample during polarization reversal. Our first-principles calculations for  $\text{KNbO}_3$  identify unambiguously the dominant mechanism with the presence of covalent bonding. The giant charges are reduced to their nominal values in a computational experiment performed on a fake material, where covalence has been artificially suppressed.

The perovskite oxides are materials which display large values of the spontaneous polarization:<sup>1</sup> owing to this fact, and to their simple crystal structure, they are among the most studied ferroelectrics. Their formula unit is  $\text{ABO}_3$ , where  $A$  is a monovalent or divalent metal, and  $B$  is a pentavalent or tetravalent metal in the transition series: they have a cubic prototype phase above the Curie temperature, and display a series of structural transitions to low-symmetry 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 is responsible for the phenomenon of ferroelectricity. The peculiar electrical and structural behavior of these materials has its microscopic origin into some unusual features of the valence electrons. Because of this, the electronic properties of the ferroelectric perovskites have been theoretically investigated using a wide spectrum of tools, from simple models<sup>2,3</sup> to first-principles quantum calculations.<sup>4-12</sup> To the latter class belong papers dealing with structural instability, lattice dynamics, microscopic charge distribution, electronic density of states, and—last but not least—spontaneous polarization. Several of these papers have addressed a long-standing dilemma: ionicity versus covalence. Despite the deep insight into the electronic states provided by first-principles approaches, there is no common consensus so far on this very basic issue.<sup>13</sup> The concepts of ionicity and covalence—though being affected by some arbitrariness—are nonetheless of overwhelming importance in identifying the dominant electronic mechanisms: on their basis, for instance, one could understand which microscopic features make the behavior of perovskite oxides so much different from that of simple oxides like  $\text{MgO}$  or  $\text{CaO}$ . In this paper we address the above unsettled issues from a different viewpoint: we will show that investigating the electronic origin of the dynamical (or Born) effective charges leads to a definite

and unbiased answer to the ionicity and/or covalence dilemma, and explains several peculiarities of the ferroelectric perovskites.

We choose as a paradigmatic case study the perovskite  $\text{KNbO}_3$ , for which several physical properties have been previously investigated from first principles.<sup>7-10</sup> Its tetragonal phase is stable between 225 and 418 °C and we perform our study assuming a “frozen” ionic configuration corresponding to the structural parameters measured<sup>14</sup> at 270 °C. Despite the fact that the real material is rather far from this schematized picture,<sup>15,16</sup> the frozen-ion approximation is indeed a sound one for studying any property related to polarization, as demonstrated in Ref. 8. Considering the macroscopic strain only, the cubic perovskite structure is transformed into a nonpolar centrosymmetric tetragonal phase which we have previously called “ideal”:<sup>8</sup> the macroscopic lattice parameters are  $a = 3.997 \text{ \AA}$ , and  $c = 4.063 \text{ \AA}$ . A further internal strain—consisting of ionic displacements  $u$ , along the tetragonal axis—transforms the ideal structure into the experimental one: keeping the origin at the Nb site, their actual values—in units of  $c$ —are  $u_K = -0.0023$ ,  $u_{O1} = -0.040$ , and  $u_{O2} = -0.042$  (there are two nonequivalent oxygen sites: those which are vertically above and below Nb along the tetragonal axis are called O1, while the side ones are called O2).

The electronic states are calculated using the same technical ingredients as in Refs. 8 and 9, to which we refer for computational details. We report in Fig. 1(a) the band structure of both the ideal and the experimental structures, in a neighborhood of the fundamental gap. The nine valence bands shown in the figure will be called O  $2p$  in the following, and in fact they would be purely O  $2p$  within a completely ionic model, where six electrons are transferred to the three  $\text{O}^{2-}$  ions, one coming from K, and the remaining five from Nb. However, since the transfer is not complete, these crystalline states will indeed have some admixture with the

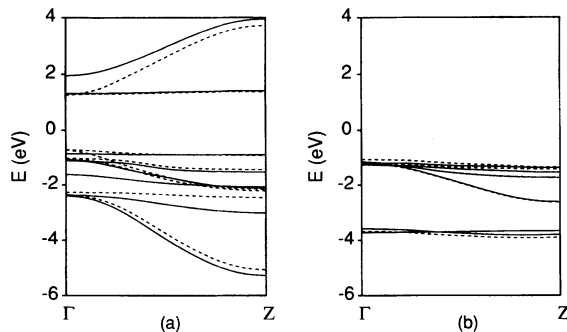


FIG. 1. Energy-band dispersion of  $\text{KNbO}_3$  near the fundamental gap, along the  $\Gamma$ -Z vertical line, and measured from the top of the valence band at point A (not shown here). Bands for both the experimental (solid) and the ideal (dashed) tetragonal structures are shown. (a) Realistic calculation; (b) calculation for the fake material (see text).

atomic states which have been emptied. The O  $2p$  crystal states are the only relevant ones to the purposes of the present study, while the lower ones (not shown in Fig. 1) are inert, thus effectively behaving as rigid core states. When ions are displaced in the cell, a macroscopic electric current flows across the sample: the lower states carry a neutral current when their share of nuclear charge is considered altogether.<sup>9</sup>

In order to investigate ionicity, the first thing to do is to analyze the electronic charge distribution, as different authors have previously done.<sup>5</sup> We prefer to simplify the landscape, by plotting only the charge density of the so-called O  $2p$  states, displayed in Fig. 2 in the plane defined by O and Nb atoms; the analogue for the ideal centrosymmetric structure is also shown for comparison. Qualitatively, we identify a dominant ionic picture, with some Nb-O1 hybridization which reduces the static charge on O below its nominal ionic value. Quantitatively, one would like to give a measure of the electronic charge associated with the O ions. This is a rather ill-defined issue, based on arbitrary charge partitioning: some authors<sup>7</sup> have even extracted from a first-principles calculation *positive* values for the oxygen charge. Within a tight-binding model,<sup>17</sup> the O static charges (usually called Mulliken charges) are unambiguously defined, and assume reasonable values, ranging from  $-1.7$  to  $-1.5$  in perov-

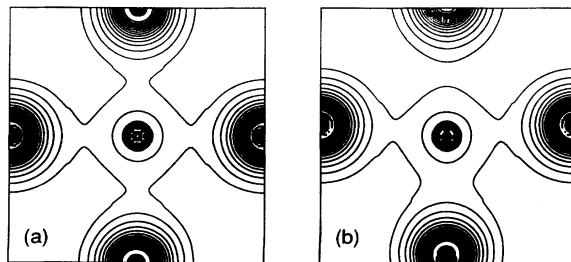


FIG. 2. Electronic charge density for the highest group of valence bands (so-called O  $2p$ ) in the vertical plane passing through Nb (figure center), O1 (top and bottom sides), and O2 (left and right sides). (a) Centrosymmetric ideal structure; (b) ferroelectric experimental structure.

skites. In a recent first-principles calculation<sup>5</sup> for  $\text{BaTiO}_3$ , a best fit of the self-consistent crystal charge to that of overlapping ions has provided the values  $-1.63$  (O) and  $+2.89$  (Ti) for the static charges.

The quantity which is well defined in a model-independent way is the *dynamical* charge, which measures the macroscopic current flowing across the sample while the ions are adiabatically displaced. Such currents are responsible for building up the spontaneous polarization, when ions are continuously displaced from the centrosymmetric structure to the ferroelectric one,<sup>18–20</sup> and are directly observed when measuring polarization via hysteresis cycles. The current *cannot* be visualized in Fig. 2: it is in fact mainly a property of the *phase* of the wave functions, while the drawing carries information about their modulus only. The modern theory of macroscopic polarization<sup>18–20</sup> allows the calculation of such currents as Berry's phases. The dynamical Born effective-charge tensor  $Z_s^*$  of a given ion measures by definition the total macroscopic current adiabatically transported by the ion moving with unit velocity, while all the other ions and the macroscopic field are kept fixed.<sup>21</sup> It has been shown<sup>8,11</sup> that the effective-charge tensors are almost constant along the path connecting the two structures, which implies that the spontaneous polarization is simply expressed in terms of the internal-strain displacements  $u_s$  as

$$P_s \approx \frac{|e|}{\Omega} \sum_s Z_s^* u_s, \quad (1)$$

where  $\Omega$  is the cell volume, and  $Z_s^*$  are the diagonal components of the effective-charge tensors along the tetragonal axis.

In simple, high-symmetry oxides, the oxygen  $Z^*$  tensor is isotropic: its diagonal value can be determined<sup>22</sup> accurately, and is close to 2. The task is less easy in perovskites,<sup>16,23</sup> where simple models<sup>2</sup> hint at nontrivial values of  $Z^*$ . Because of site symmetry,  $Z_K^*$  and  $Z_{\text{Nb}}^*$  are isotropic, while O sits at a noncubic site and  $Z_O^*$  has two independent components: one for displacements pointing towards the Nb ion, and the other for displacements in the orthogonal plane (see the ions O1 and O2 in Fig. 2). Our calculation for  $\text{KNbO}_3$  provided the values 0.8 (K), 9.1 (Nb),  $-6.6$  (O1),  $-1.7$  (O2). Similar giant values for the transition element and for O1 ions have been later confirmed using quite different technical ingredients and/or for other perovskite oxides.<sup>11,12</sup> Therefore, the K and O2 ions look like closed-shell ions, each carrying an effective charge close to its nominal ionic value, in a rigid-ion picture. On the contrary, a large amount of nonrigid, delocalized charge flows across the sample during a relative displacement of the Nb and O1 ions, as in Fig. 2. We anticipate here our main message, stating that this is definitely a covalence effect, dominated by the hybridization of the so-called O  $2p$  bands with Nb  $4d$  states.

In order to get insight into the main microscopic mechanisms, it is quite common in computational physics to blow up physical effects by simulating unusual, pathological, and even completely unrealistic situations. In this spirit, we performed calculations where the possible hybridization between O  $2p$  and Nb  $4d$  states is artificially suppressed. Technically, within our computational scheme it is quite easy to

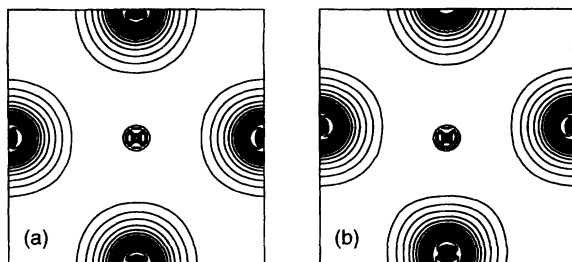


FIG. 3. Same as Fig. 2 but for the fake perovskite crystal (see text).

add a fake repulsive potential, confined to a spherical region around the Nb site (of radius 2.2 a.u.), and acting only on the  $d$ -like component of the electronic states.<sup>24</sup> The effect of the fake potential on the band structure [shown in Fig. 1(b)] is quite dramatic. As expected, the original lowest empty bands—mainly Nb  $4d$  in character—are repelled to higher energies: actually the gap is brought to  $\approx 5$  eV, and the states at the conduction-band minimum are now mostly a mixing of K  $4s$ , K  $4d$ , and O  $3s$ . But the main message of Fig. 1 is that even the highest occupied bands are modified both in width and shape: were the latter bands purely O  $2p$ , they should hardly be affected at all by the fake potential. Further insight is found looking at the effect of internal strain in Fig. 1 (solid vs dashed lines): it is evident that the ferroelectric distortion strongly modifies the O  $2p$  bands in the real material, while its effect is hardly noticeable in the fake material.

Another quantity of interest is the charge density of the O  $2p$  bands in the fake crystal which is shown in Fig. 3. The picture shows a superposition of almost spherical charges, whose shape is largely unaffected by the ferroelectric distortion. Comparison with Fig. 2 confirms that the interstitial charges in the real material are indeed indicative of O  $2p$  Nb  $4d$  hybridization; we also notice in Fig. 2 that the amount of such hybridization looks qualitatively much affected by the ferroelectric distortion.

The Born effective charges assume the following values when the hybridization is suppressed: 0.9 (K), 4.3 (Nb),  $-1.9$  (O1), and  $-1.7$  (O2). It results that our fake perovskite behaves much like simple oxides, where the current associated with any ionic displacement is close to the appropriate rigid-ion value, and is of course almost isotropic for oxygen ions. It is worth pointing out that a previous structural study of BaTiO<sub>3</sub> demonstrates<sup>5</sup> that switching the hybridization off suppresses the ferroelectric instability as well. The microscopic mechanism for the giant effective charges which we previously discovered in this material,<sup>8</sup> and which was later confirmed in other perovskites,<sup>11,12</sup> is therefore unambiguously identified. The effects of the O  $2p$  Nb  $4d$  hybridization on the electronic states are definitely far from negligible at a given structural configuration, while they are even further enhanced when the Nb-O bond lengths are varied, being thus responsible for the flow of giant currents during the ferroelectric distortion. This enhancement can be understood within a simple tight-binding model, if one just postulates some modulation of the hopping integral between O  $2p$  and Nb  $4d$  states induced by the bond-length variations. In fact, using the simple tight-binding parametrization of Harrison,<sup>17</sup> one finds giant effective charges in semiquantitative agreement with the present first-principles values. Our work therefore demonstrates that the simple tight-binding scheme of Harrison—where the perovskite oxides display a large amount of covalence—is quite correct insofar as effective charges and polarization are concerned.

As a conclusion, and from a more general viewpoint, the present study is in agreement with other works where the covalence issue in ferroelectric perovskites has been emphasized on different grounds,<sup>5,10</sup> while it questions the relevance of possible alternative mechanisms, claimed by some authors.<sup>13</sup>

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