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Pseudo Jahn–Teller origin of ferroelectric instability in $BaTiO_3$ type perovskites: The Green's function approach and beyond

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ABSTRACT

The local origin of dipolar distortions in ABO_3 perovskite crystals is reexamined by means of a novel approach, the Green's function method augmented by DFT computations. The ferroelectric distortions are shown to be induced by the pseudo Jahn–Teller effect (PJTE). The latter involves vibronic hybridization (admixture) of the ground state to same-spin opposite-parity excited electronic bands. Similar to numerous molecular calculations, the PJT approach provides a deeper insight into the nature of chemical bonding in the octahedral cluster $[BO_6]$ and, in particular, reveals the local origin of its polar instability. This allows predicting directly which transition ions can create ferroelectricity. In particular, the necessary conditions are established when an ABO_3 perovskite crystal with an electronic d^n configuration of the complex ion $[BO_6]$ can possess both proper ferroelectric and magnetic properties. Distinguished from the variety of cluster approaches to local properties, the Green's function method includes the influence of the local vibronic-coupling perturbation on the whole crystal via the inter-cell interaction responsible for creation of electronic and vibrational bands. Calculated Green's functions combined with the corresponding numeric estimates for the nine electronic bands, their density of states, and the local adiabatic potential energy surface (APES) confirm the eight-minimum form of this surface and feasibility of the PJT origin of the polar instability in $BaTiO_3$. We show also that multicenter long-range dipole–dipole interactions critically depend on the PJTE largely determining the magnitude of the local dipoles. DFT calculations for the bulk crystal and its clusters confirm that the dipolar distortions are of local origin, but become possible only when their influence on (relaxation of) the whole lattice is taken into account. The results are shown to be in full qualitative and semiquantitative agreement with the experimental data for this crystal.

1. Introduction

For many years cubic perovskites served as a testing ground for different models and theories of ferroelectricity [1–9]. Peculiar features of its most studied representative, $BaTiO_3$, attract increasing attention. Further developments in this field led to the discovery of a new class of substances with coexisting and related (switchable) ferroelectric and magnetic properties called multiferroics. Barium titanate is a cubic perovskite crystal with four temperature dependent structural phases, three of which exhibit ferroelectric properties. There were many attempts to explain the origin of ferroelectricity in these and similar systems beginning with the “classical” theories of Devonshire [1], Ginzburg [2], Cochran [3], Anderson [4], and Landau [5], in which the basic idea is that the ferroelectric distortion of the crystal occurs as a result of the compensation of the local repulsions (resisting dipolar displacements) by long-range dipole–dipole interactions. The history of suggested models and further developments of the theory is well presented in books and reviews (e.g. [6–9]). From more relevant to our paper models involving the details of local interactions we mention here the attempts [10] to deduce dipolar instability of $[TiO_6]^{8-}$ from the estimated ionic radii of Ba^{2+}, Ti^{4+}, and O^{2-} which allow for a relatively large cage for Ti^{4+} providing enough room for its off-center displacements. In other models, the authors *implied* a six-minimum [11] or an eight-minimum [12] potential for the transition metal (Ti) ion. In addition to (and as a consequence of) the rough presentation of the electronic structure these models failed to explain the experimental data and to answer the most important question about the origin of such a potential, and why it is only present in $BaTiO_3$ and absent in other similar crystals, e.g., $BaVO_3$. Another theory suggested p–d orbital hybridization as the driving force of dipolar distortions [13].

Many models of ferroelectricity [3] emphasized the role of long range interactions, a trend that has been confirmed with the

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advent of detailed ab initio calculations and the possibility of atomic control over the growth of ferroelectric thin-films. In particular, the experimental finding of a critical size for ferroelectricity [14] indicates that the displacement of a single center cannot generate the instability of the multicenter system if the other centers are not involved in the relaxation process. This has been confirmed by DFT calculations [15] and is consistent with the results presented here. Much effort has been done to calculate the contribution of dipole–dipole interactions to the force constant using DFT calculations. In particular, presenting the force constant as a sum of long-range dipole–dipole contribution and the short-range contribution, the former was shown [16] to be very large and negative, while the latter was, similarly, very large but positive. When added, both contributions yield a small, negative force constant interpreted as the dominance of long-range contributions to the instability. This reasoning ignores the local negative (PJTE) contribution K_v which, as shown also in this paper, may be larger than the positive (repulsion) K_0 value, thus producing the local dipole distortions.

Quite a number of recent theoretical works (see, e.g. [15–32] and references therein) contribute essentially to the understanding of the origin of ferroelectricity in a variety of its different manifestations. One of these important findings is the confirmation of the large covalent changes occurring during ferroelectric distortions [18] and their influence on the instability [32]. Some of the papers assume a strong anharmonicity in the Hamiltonian of the metal–oxygen interaction which may result in an off-center displacement of the transition metal toward the oxygen atoms when stabilized by the cooperative (dipole–dipole) interaction in the crystal [19]. In fact, anharmonicity is a correct assumption, and its presence in ferroelectrics is confirmed by ab initio calculations (it is of vibronic origin, Section 3). Widely used is the simplified version of the anharmonic cubic potential replaced by its power series expansion up to fourth-order terms [33]. However, the same question was left behind about the origin of this very strong anharmonicity, characteristic for $BaTiO_3$ and absent in other very similar systems.

Meanwhile in a series of recent experiments [34–51] including X-ray diffraction data [38,39], Raman and optical reflective experiments [35–37], ESR with probing ions [40–41], NMR experiments [46,47], EXAFS measurements [42,44], neutron scattering [51], etc., several peculiar features in the ferroelectric properties of this crystal were revealed. Among them the most important ones are the off-center displacements of the Ti ion along the trigonal axis in all the four phases of $BaTiO_3$, ferroelectric and paraelectric, and the phase transition between them includes order–disorder components. These data were interpreted under the assumption that only the lowest in temperature rhombohedral phase is a fully ordered ferroelectric crystal, but in the next three phases that occur consecutively at higher temperatures the crystal is only partially ordered in one, two, or all the three directions, respectively, the latter highest in temperature being thus fully disordered and non-ferroelectric [34]. All these experimental observations [34–51] and other empirical data, *as a pattern*, are consistent with the predicted earlier [52] picture of a special (vibronic) eight-minimum potential at the transition metal site with the ion B locally displaced along one of the eight trigonal [111] type directions that originates from the local pseudo Jahn–Teller effect (PJTE). At $T \sim 100$ K, in the low-temperature phase, these displacements are fully ordered resulting in the observed rhombohedral symmetry. At higher temperatures transitions between the minima result in partial or full disorder providing for a qualitative and semiquantitative explanation of the origin of the phase transitions [52,53] and the other experimental data [34–51].

Obviously, the problem as a whole is complicated and the previous approaches to the vibronic coupling theory are rather approximate, subject to improvements. In particular, for the $BaTiO_3$ crystal the vibronic coupling perturbation that leads to the off-center displacement of the Ti ion was considered in a cluster approximation within the $TiO_6{}^{8-}$ group, leaving beyond the possible strong influence of intercenter interactions (presented in the real crystal by the electronic and vibrational bands) that may challenge the results. Indeed, DFT calculations show (Section 4) that in the cubic lattice with fixed ion positions the equilibrium position of any selected Ti ion is at the center of symmetry and is not displaced. In addition, novel experimental observations were published that should be explained by the theory.

In this paper we fully reexamine the problem employing a more rigorous and accurate approach, based on the Green's function method [54] accompanied by DFT calculations. Distinguished from the previous approaches [52,53] in which the PJT cluster is considered independent of the environment (including the intercenter interactions at a later stage), the Green's function method takes into account the descending influence of the crystal, up to many coordination spheres, on a given Ti center. In this approach only the vibronic coupling operator is of local origin, its perturbation being applied to the whole crystal. DFT calculations confirm the local origin of the polar distortions and allow estimating the density of states required for calculation of observables. We focus here on the origin of ferroelectric instability in perovskite crystal structures at $T = 0$ K leaving the discussion of the nature of ferroelectric phase transitions in $BaTiO_3$, displacive vs. order–disorder, for another publication (see also [53]). Although, as mentioned above, the main idea of the vibronic theory of ferroelectricity was suggested long ago [52], presently available experimental data [34–51] were unknown at the time. A more rigorous up-to-date description allows obtaining more convincing proofs with numerical results, and a comparison with observable properties. Below we give first a brief general qualitative view on the physics of the PJTE applied to local properties in crystals that allows also formulating the necessary condition of dipolar distortions in the presence of unpaired electrons (multiferroicity), followed by detailed (rigorous) Green's function treatment of the influence of the local vibronic coupling on the crystal properties. This reveals the adiabatic potential energy surface (APES) and its extreme properties, and the condition of dipolar distortions. Details of the Green's function calculations of the electronic and vibrational bands are given in Appendix. We show also that the large value of atomic charges in the long-range interactions, as calculated in [8,17,18,22], is, in fact, a consequence of the PJTE.

2. Model and method of calculation

In the cubic perovskites under consideration we can use the lattice-polarizing normal coordinates $\mathbf{Q} = (Q_x, Q_y, Q_z)$ as the order parameters instead of polarization density, $\mathbf{P} = (P_x, P_y, P_z)$. In Landau's theory of phase transitions [5] the Helmholtz free energy Φ is assumed to be a smooth function of $\mathbf{P}$. Since $\mathbf{P}$ is proportional to $\mathbf{Q}$, the free energy can be expanded in terms of $\mathbf{Q}$. In a cubic perovskites ABO_3 the free energy Φ is a scalar of the cubic symmetry group. Therefore the power series does not include odd order terms

$$\Phi = \Phi_0 + A\left(Q_x^2 + Q_y^2 + Q_z^2\right) + B\left(Q_x^2 + Q_y^2 + Q_z^2\right)^2 + C\left(Q_y^2 Q_z^2 + Q_x^2 Q_z^2 + Q_y^2 Q_z^2\right) + \text{higher-order terms} \quad (1)$$

In the ferroelectric phase $A < 0$, and the free energy $\Phi(Q_x, Q_y, Q_z)$ has a maximum at the high-symmetry point $Q_x = Q_y = Q_z = 0$. In