First-principles study of the electric field gradient at the cubic-tetragonal phase transition in barium titanate

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The question concerning the driving mechanism (displacive or order disorder) of the paraelectric–ferroelectric phase transition in $BaTiO_3$ is investigated by means of the study of the electric field gradient tensor at the Ti site. A comparison of recent NMR results close to the critical temperature T_c versus first-principle calculations of displacive and off-site Ti order–disorder type structures are accomplished. At a temperature just below T_c the calculated V_{zz} for the displacive-type structure describes well the experimental value, while the calculated order–disorder static V_{zz} value is far away from it.

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I. INTRODUCTION

The ferroelectric phase transition $Pm3m \rightarrow P4/mmm$ of $BaTiO_3$ has been widely studied in the last years due to the uncertainty about the nature of the dominant driving mechanism of the transition. On the one hand, this transition can be considered as an order–disorder type phase transition.[1] On the other, it can be associated with a displacive soft-mode transition[2] type, describable by anharmonic lattice dynamics.[3] Most recent studies, both experimental and theoretical, predict a coexistence of these two models or even an occurrence of a crossover from displacive to order–disorder in the neighborhood of the critical temperature (T_c).[4–6] Although there are numerous studies addressing this issue, the actual mechanism of the phase transition remains an open question.

Recently, Zalar *et al.*[7] by means of Nuclear Magnetic Resonance, presented experimental values of the Electric Field Gradient (EFG) at the Ti site, at temperatures very close (above and below) to T_c. The EFG is a very sensitive quantity directly related to changes in the electronic structure and therefore senses the geometric configuration in the neighborhood of the probe. This feature of the EFG makes these new experimental data to be of great interest for the analysis of the nature of the phase transition, because very different EFGs at the Ti site are expected for each of the proposed models.

The aim of this work is to calculate the EFG at the Ti site using structural data taken from experiments at temperatures close to T_c. The different models in question can be compared with the above mentioned new experimental data. For this purpose, very precise results can be obtained by performing state-of-the-art first-principles electronic structure calculations within the Density Functional Theory (DFT).

II. METHOD

The EFG is a symmetric traceless tensor whose components are defined as the

$$V_{ij} =: \left. \frac{\partial^2 V}{\partial x_i \, \partial x_j} \right|_{r=0}$$

second spatial derivatives of the Coulomb potential at a nuclear position.

The Coulomb potential can be calculated from the total electronic and nuclear charge in the crystal by solving the Poisson's equation, once the electronic charge distribution has been determined. After diagonalization of the EFG tensor and rearranging the components according to $|V_{xx}| \leqslant |V_{yy}| \leqslant |V_{zz}|$ the principal component is V_{zz} and is called EFG. The experimentally measured quadrupole coupling constant ν_Q is related with V_{zz} by

$$\nu_Q = \frac{eQV_{zz}}{h},$$

where e stands for the electron charge, Q is the nuclear quadrupole moment and h is the Planck's constant.

For the determination of the electronic structure we used the *ab-initio* full-potential linearized augmented plane wave method (FP-LAPW) in a scalar relativistic version as embodied in the WIEN2K code.[8] This method is one of the most accurate schemes for electronic structure determination in solids. In this framework, the unit cell is divided into nonoverlapping spheres around the nuclei and an interstitial region, where in the former the corresponding wave functions are expressed in atomic like functions but in the latter in plane waves. Also, added to the usual LAPW basis set, local orbitals for high lying core states have been included.[9] No approximation is made for the potential, except for the exchange and correlation effects. For this work the generalized gradient approximation (GGA) of Perdew *et al.*[10] was employed, but several tests were made using the local density approximation (LDA) and other GGA functions (see below). For each structure, a plane wave cut-off corresponding to $RK_{MAX}=8$ and 300 *k-points* in the Brillouin zone were selected after several tests of EFG convergence were performed. Details of the calculation of the EFG within this

code are described in the works of Schwarz and co-workers.[11,12]

III. RESULTS

The structural data for the tetragonal phase of $BaTiO_3$ is described in the work of Kwei *et al.*[13] and references therein. In the displacive model, the ferroelectric distortion appears due to the Ti's and the O's statically displaced from their high symmetry position in the [011] direction. In the eight-sites model, the displacement are actually in the [111] direction and the ions jump between four of the eight equivalent sites. Independent of the transition mechanism, it is expected that V_{zz} strongly decreases as the temperature T approaches T_c (from below) while the tetragonal distortion tends to zero. Thus, the precise determination of the structural parameters in the neighborhood of T_c would be crucial for the comparison of the calculated and the experimental EFG. Unfortunately, in the work of Zalar *et al.* this information is not available. Moreover, the authors report a value of T_c that is higher than the generally accepted values (Zalar *et al.*;[7] T_c = 415 K; Kanert *et al.*;[14] T_c = 415 K; Kwei *et al.*;[13] T_c = 393 K). It is possible that the high purity of the sample used in that work favors the stabilization of the tetragonal structure at a higher temperature. For this reason the lattice constants and the internal atomic parameters, which are used in the present work, were extrapolated to 415 K from the work of Kwei.[13] The following values were used: $a=b$ = 4.0 *Å*, c = 4.035 *Å* for the lattice constants and $\Delta\mathrm{Ti}=0.018$, $\Delta\mathrm{O1}=-0.0265$ and $\Delta\mathrm{O2}=-0.012$ for the ferroelectric distortion (the latter expressed as fraction of the c lattice constant). With these values two distinct tetragonal cells were built: One with the ferroelectric distortion pointing in the [001] direction and the other in the [111] direction. For each structure we calculated V_{zz} as a function of the parameter δ, which represents the percentage of the extrapolated values $\Delta\mathrm{Ti}, \Delta\mathrm{O1}$ and $\Delta\mathrm{O2}$ of the ferroelectric distortion mentioned above. In Fig. 1(a) the obtained V_{zz} values as a function of δ are shown, together with the experimental value ($\pm 0.30\ 10^{21}$ V/m^2). The double sign indicates that experimentally the sign of the EFG cannot be resolved. For the [001] distortion the EFG is a decreasing function of δ. The calculated and the experimental values coincide for δ=90%. Figure 1(b) shows the total energy dependence on δ for both tetragonal structures. The theoretical equilibrium ferroelectric distortion is obtained with δ=90% for the structure with the displacements along the [001] direction, just the same δ value for which theoretical and experimental data of EFGs coincide. For the [111] distortion the EFG grows with δ, beginning with a value double the experimental for δ=20% and ending with a value six times higher for δ=100%. The equilibrium structure is obtained with δ=74% with a corresponding EFG three times higher than that measured.

In the work of Zalar *et al.*[7] it is concluded that above T_c there is a coexistence of order–disorder and displacive type transition, with a dynamic tetragonal distortion of the unit cell ($c/a \neq 1$). Below T_c, the tetragonal distortion augments and turns static, freezing the displacive mode. The result obtained in the present work gives quantitative support to the last affirmation, in virtue of the good agreement between the calculated V_{zz} value for the [001] (frozen) distortion and the experimental result.

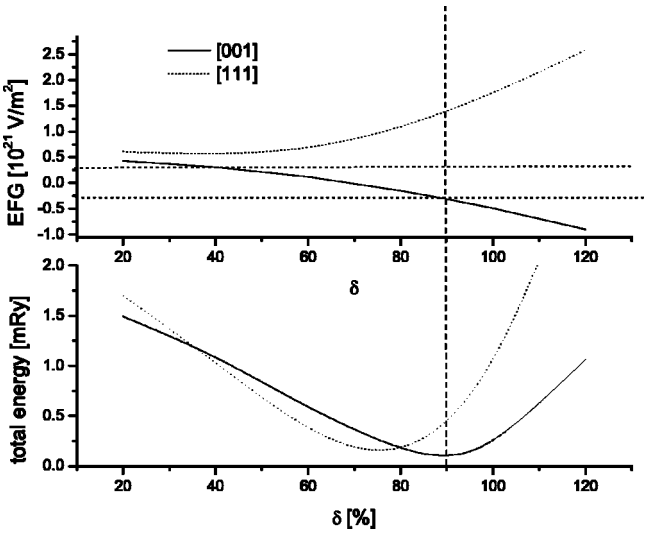

FIG. 1. (a) EFG as a function of the δ parameter. The short-dashed lines indicate the two possible values of the experimental EFG: $\pm 0.30 \times 10^{21}$ V/m^2. (b) Total energy as a function of δ. The vertical dashed line connects the [001] minimum with the upper figure.

If a component of the order–disorder type exists below T_c, the experimental V_{zz} should not be compared straight forwardly to that calculated for a [111] distortion, but should include some dynamical averaging over the four occupied directions. Another observation is related to the periodic boundary conditions imposed in the calculations. Once a specific [111] ferroelectric distortion is chosen, all other cells are assumed to have the distortion in the same direction. But, according to the eight-sites model, the ions jump between equivalent positions, thus having a disordered arrangement. We expect that the influence of the disorder in the neighboring cells be very small for the EFG value at a fixed Ti site due to the long distances involved and the tiny displacements of the ferroelectric distortion.

The method employed to analyze what occurs below T_c cannot be applied for a comparative analysis with the experimental values above T_c. This is due to the fact that the detected V_{zz} above T_c is of the order of 10^{18} V/m^2. This low value is far below the precision of our method of calculation ($\approx 10^{19}$ V/m^2). The choice for the exchange-correlation potential and several convergence parameters can vary the prediction of the EFG by the same order of magnitude. For a perfect cubic structure, the EFG at the Ti site should be zero by symmetry.

Another remark must be made concerning the selection of the exchange correlation potential. In the work of Singh and references therein,[15] the validity of the LDA vs GGA approximation for $BaTiO_3$ is analyzed by determining the equilibrium lattice constant and bulk modulus for the paraelectric cubic structure of $BaTiO_3$ and for the NaCl structure of BaO. The exchange correlation potential for the GGA used in that work[16] leads to much larger lattice constants and thus over-

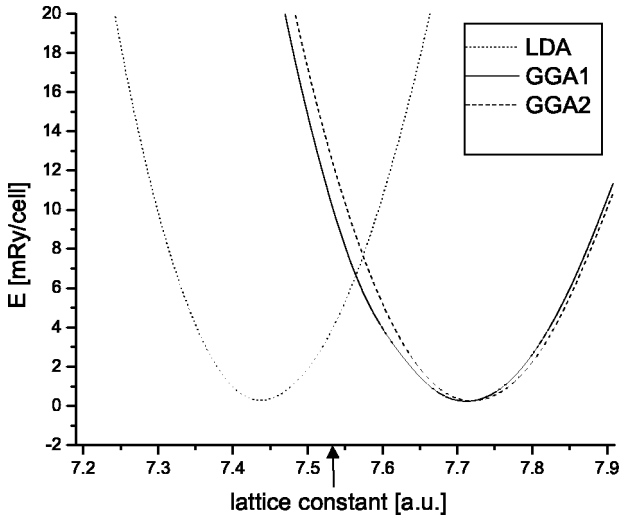

FIG. 2. The total energy as a function of the lattice parameter for cubic $BaTiO_3$. GGA1 and GGA2 are related to the exchange correlation potential of Refs. 10, 16, respectively. The arrow indicates the experimental value of the lattice constant.

corrects the normal underestimation of the LDA lattice constant. Since a newer GGA version was used in the present work,[10] Singh's calculation of the equilibrium lattice constant was repeated adding a third curve to his results shown in Fig. 2. It can be seen that both GGA potentials predict the same minimum position for the total energy as a function of the cubic lattice constant. In view of the fact that both GGA approximations do not improve the agreement with experiment with respect to LDA, the curves of Figs. 1(a) and 1(b) were calculated again using the LDA. The positions of the energy minima with respect to δ are not altered with this change. The LDA EFG values are 0.24×10^{21} V/m^2 for the [001] distortion and δ=90% and 1.90×10^{21} V/m^2 for δ =100% for the [111] distortion. The first one falls 20% within the experimental value 0.30×10^{21} V/m^2 and the second one lies farther away than the GGA previously obtained. Thus, the same conclusions are obtained using the LDA.

IV. CONCLUSIONS

In the present paper we present first principles electronic structure calculations for the tetragonal $BaTiO_3$ structure in order to calculate the EFG at the Ti site. Two distinct types of structures were constructed: one having the ferroelectric distortion along the [001] direction corresponding to the displacive soft-phonon phase transition, and the other with the distortion along the [111] direction, corresponding to the eight-sites model. Below T_c, the EFG calculated with the [001] distortion matches with the recently obtained experimental value, while for other distortios the calculated EFG is three times bigger. These results give a quantitative support to some of the conclusions given in the recent experimental paper of Zalar *et al.*[7]

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