First-Principles Study of the Temperature-Pressure Phase Diagram of $BaTiO_3$

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We investigate the temperature-pressure phase diagram of $BaTiO_3$ using a first-principles effective-Hamiltonian approach. We find that the zero-point motion of the ions affects the form of the phase diagram dramatically. Specifically, when the zero-point fluctuations are included in the calculations, all the polar (tetragonal, orthorhombic, and rhombohedral) phases of $BaTiO_3$ survive down to 0 K, while only the rhombohedral phase does otherwise. We provide a simple explanation for this behavior. Our results confirm the essential correctness of the phase diagram proposed by Ishidate *et al.* (Phys. Rev. Lett. **78**, 2397 (1997)).

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$BaTiO_3$ is a paradigmatic example of a ferroelectric material [1]. Over the years it has been extensively studied from both the experimental and theoretical points of view. It is thus surprising to discover that its temperature-pressure phase diagram remains very poorly investigated. Actually, even the qualitative form of the phase diagram is still controversial.

Figure 1a illustrates the results of early experimental studies of the phase diagram of $BaTiO_3$ [2, 3], which were confined to pressures up to $\sim$3 GPa only. In this pressure range the system retains its zero-pressure transition sequence with decreasing temperature. That is, it progresses from the high-temeperature paraelectric cubic phase to ferroelectric tetragonal, then ferroelectric orthorhombic, and finally ferroelectric rhombohedral phases. It was proposed that the diagram should be completed as shown in Fig. 1a [2] (or with a modification in which the critical points labeled '1' and '2' meet at a multicritical point [4]). This kind of scenario has been generally accepted ever since. On the other hand, in 1997 Ishidate *et al.* [5] published the first (and, up to now, the only) experimental study extending high enough in pressure to reveal the actual form of the entire phase diagram. Surprisingly, these authors found that all the polar phases of $BaTiO_3$ survive down to 0 K as sketched in Fig. 1b.

Ishidate *et al.* attributed this remarkable result to the zero-point motion of the ions, which they argued should be significant up to temperatures as high as 200 K. This explanation may appear difficult to accept, given that no atom lighter than oxygen is present in $BaTiO_3$. Indeed, it may be tempting to dismiss the phase diagram of Ishidate *et al.* on the basis of technical concerns. In particular, it is not easy to find a pressure-transmitting medium that remains fluid (i.e., isotropic) at the low temperature and high pressure required for this study [3]. This is a crucial issue because anisotropies in the applied pressure could easily upset the delicate balance of stabilities of the polar phases of $BaTiO_3$ and lead to incorrect results. In view of these doubts, there is clearly a pressing need for a fresh approach to this problem.

In this work, we use a first-principles effective-Hamiltonian approach [6, 7] to carry out a theoretical study of the pressure-temperature phase diagram of $BaTiO_3$. First-principles methods have been used extensively since the early 1990s in many successful studies of ferroelectric perovskites [8]. Our approach is well suited to the present problem because it enables us (i) to calculate the thermodynamic properties of $BaTiO_3$ in the presence of *perfectly hydrostatic* pressures, and (ii) to switch on and off the zero-point motion of the ions at will. Surprisingly, our results corroborate the scenario proposed by Ishidate et al. [5]. We confirm that quantum fluctuations completely change the high-pressure structure of the phase diagram and allow all three ferroelectric phases to survive down to zero temperature, as sketched in Fig. 1b. We discuss these results and provide a simple explanation for the predicted form of the phase diagram.

For this study we have made use of the effective-Hamiltonian approach proposed for $BaTiO_3$ by Zhong *et al.* [6, 7]. The effective Hamiltonian is a Taylor-series expansion of the potential energy of the system around a high-symmetry phase, written in terms of a set of relevant degrees of freedom. For $BaTiO_3$, the relevant variables are the local polar modes (that add up to produce the spontaneous polarization of the system) and the homogeneous strains, and the reference struc-

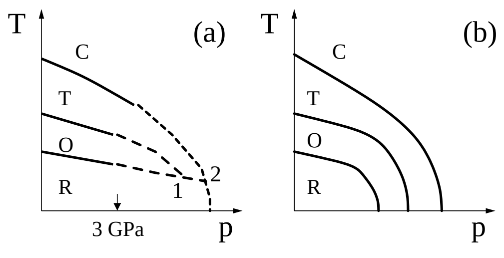

FIG. 1: (a) Sketch of phase diagram of $BaTiO_3$ as discussed in Refs. [2, 3, 4]. Phases are cubic (C), tetragonal (T), orthorhombic (O), and rhombohedral (R). Solid and dashed lines represent measured data and suggested hypothetical completion, respectively. (Alternatively, critical points '1' and '2' were suggested to coincide in Ref. [4]). (b) Sketch of phase diagram of $BaTiO_3$ as measured by Ishidate *et al.* [5].

ture is the paraelectric cubic phase. The parameters in this expansion are obtained from first-principles density-functional calculations [9]. Zhong *et al.* [6] performed classical Monte Carlo (MC) simulations on the basis of such an effective Hamiltonian and demonstrated that it correctly reproduces the non-trivial phase transiton sequence of $BaTiO_3$ along the *zero*-pressure isobar [10]. Indeed, after this initial achievement, the first-principles effective-Hamiltonian method has been successfully applied over the years to situations of increasing complexity [11].

However, one should bear in mind that the quantitative accuracy of this approach is still limited. The approximations involved in the effective-Hamiltonian construction, including those related to the first-principles methods used, result in some calculated quantities (especially transition temperatures) that are not in very good quantitative agreement with experiment. Of particular relevance for us is the well-known understimation of the equilibrium volumes given by the local-density approximation, which brings about a systematic error in the location of our zero of pressure [10]. For these reasons, the results of the present calculations are to be regarded as reliable only at the qualitative level.

Classical theory.— We first calculated the phase diagram of $BaTiO_3$ at a classical level by performing standard Monte Carlo simulations for a number of temperatures and external hydrostatic pressures. We simulated a $12 \times 12 \times 12$ supercell with periodic boundary conditions, and typically did 30,000 MC sweeps to thermalize the system and another 30,000 sweeps to calculate averages. Our classical calculation is essentially a repeat of the one reported in Fig. 4 of Ref. [7], except that we have taken special pains to resolve the high-pressure part of the phase diagram as carefully as possible.

Our result, depicted with open circles in Fig. 2, is topologically identical to the one shown in Fig. 1a. The interesting action occurs in a small region of low temperature and high pressure where the different phases meet. In this region the free-energy landscape of the system is extremely isotropic and it is difficult to locate the phase boundaries precisely. We can say with some confidence that the rhombohedral and cubic phases meet along a phase boundary that extends from about 12.5 GPA at T=0 K to about 11.5 GPa at about 10 K. Whether all phases then meet at a multicritical point, or whether there are two separate critical points as illustrated in Fig. 1a, is difficult to decide (although we tentatively favor the latter possibility). A more reliable calculation adopting an approach such as that of Ref. [12], which allows for a detailed exploration of the free-energy landscape, would probably be needed to decide for certain.

The key conclusion we extract from our classical calculations is that, provided the zero-point motion of the ions is not considered, only the cubic and rhombohedral phases can survive down to zero temperature, i.e., can be true ground states of the system. To be certain that this conclusion is not an artifact of any approxima-

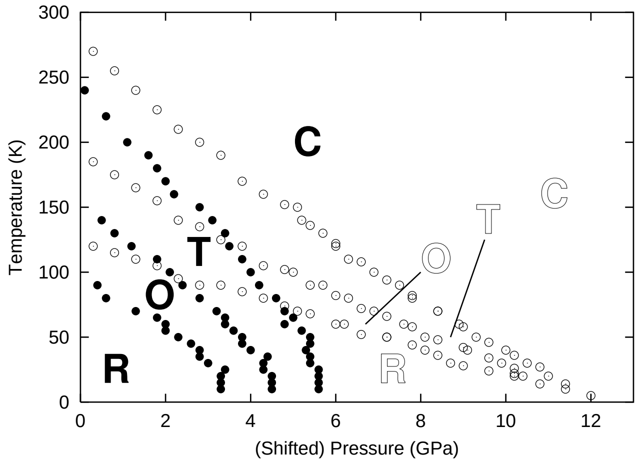

FIG. 2: Phase diagram of $BaTiO_3$ calculated at the classical level (open circles and labels) and including quantum fluctuations (solid circles and labels). Theoretical pressures are corrected (shifted) following Zhong *et al.* [10].

tions made in connection with the effective-Hamiltonian method, a careful check was carried out using zero-temperature density-functional calculations directly [13]. These tests confirm the presence of a second-order transition directly from the ferroelectric rhombohedral to the paraelectric cubic phase with increasing pressure along the zero-temperature isotherm.

Quantum-mechanical theory.— The ionic zero-point motion can be included in our calculations by carrying out the thermodynamic simulations using the path-integral quantum Monte Carlo (PI-QMC) technique [14] in place of the classical Monte Carlo. The same effective Hamiltonian is used in both cases. A preliminary study of this kind, but limited to zero pressure and small Trotter numbers, was initiated by Zhong and Vanderbilt [15], who showed that the transition temperatures are indeed significantly affected by the quantum-mechanical fluctuations. For instance, the rhombohedral to orthorhombic transition, classically calculated to occur at 200 K, was found to fall to 150 K. Not only is this effect quite large, but it is also present at surprisingly high temperatures.

The technical details of the PI-QMC calculations are as follows. A careful convergence analysis of simulations at 10 K led us to take a Trotter number $P = 64$ as a good compromise between accuracy and computational feasibility. (Note that the size of the simulated system is proportional to P.) For consistency, we kept the quantity $1/TP$, which determines the degree of convergence of the PI-QMC results, constant throughout the studied temperature range. In order to obtain a thermalized configuration for a given P, we find it convenient to increase P from smaller values in a stepwise manner. For example, if our target is $P = 12$, we consider $P = 1 \to 3 \to 6 \to 12$, feeding every new calculation with the thermalized configuration obtained in the previous one. We typically performed 30,000 and 70,000 MC sweeps for thermaliza-

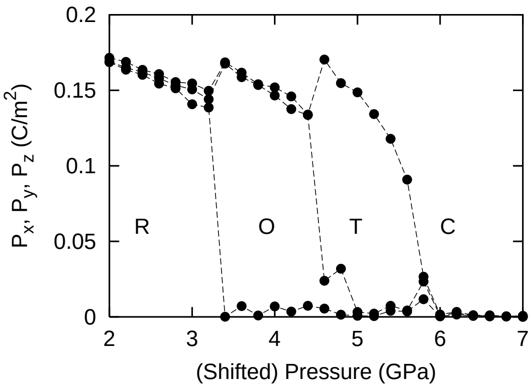

FIG. 3: Calculated (quantum) phase transition sequence of $BaTiO_3$ along the 10 K isotherm, showing equilibrium polarization (P_x, P_y, P_z) as a function of pressure. Theoretical pressures are corrected (shifted) following Zhong *et al.* [10].

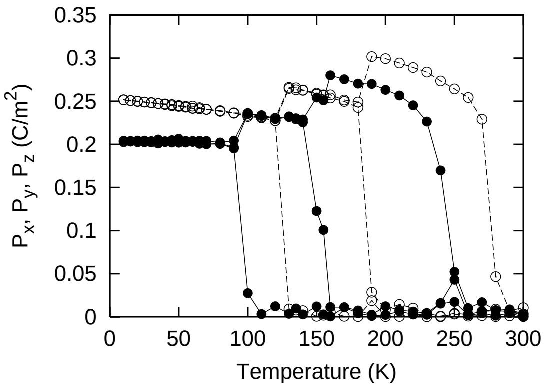

FIG. 4: Phase transition sequence of $BaTiO_3$ along the zero-pressure isobar, calculated at the classical (empty circles) and quantum-mechanical (filled circles) level, showing equilibrium polarization (P_x, P_y, P_z) as a function of temperature. In both cases, the transition sequence with decreasing temperature is C→T→O→R.

tion and averages respectively, using a $10 \times 10 \times 10$ supercell. We checked that these choices led to well-converged results.

Our result is depicted with filled circles in Fig. 2. We find, in perfect qualitative agreement with Ishidate *et al.*, that all the polar phases of $BaTiO_3$ survive down to 0 K! Note the dramatic *bending* of the transition lines, which pass from following the classical law $T_c \propto (p_0 - p)$ at high temperatures to following the quantum-mechanical law $T_c \propto (p_c - p)^{1/2}$ [16] at lower, but still relatively high, temperatures. This is exactly the crossover that Ishidate *et al.* observed and which led them to attribute the occurrence of the orthorhombic and tetragonal phases at 0 K to the zero-point motion of the ions in the system. Our result clearly shows that such an interpretation is correct.

Figure 3 shows the calculated sequence of phase transitions along the 10 K isotherm. It is apparent that, in spite of the difficulties involved in our PI-QMC calculations, we are able to identify the phase transitions unambiguously. The calculated pressure range of stability of both the orthorhombic and tetragonal phases at low temperatures is around 1 GPa, while in Ref. [5] ranges of about 0.6 GPa are reported. Also, we obtain a value of approximately 6 GPa for the critical pressure p_c at which ferroelectricity disappears, in rough agreement with the value of 6.5 GPa obtained by Ishidate *et al.* Of course, given the limitations of our method, this level of agreement may be partly fortuitous.

Discussion.— This quantum phase diagram can be rationalized in the following way. It is natural to assume that in $BaTiO_3$ the lattice-dynamical fluctuations, *either thermal or quantum mechanical in character*, tend to favor the paraelectric cubic phase, followed respectively by the tetragonal, orthorhombic, and finally rhombohedral ferroelectric phases. On the other hand, we know from our first-principles calculations on $BaTiO_3$ that the potential-energy preference follows just the reverse order (for any pressure $p < p_c$). We can thus view the phase transition sequence of this material along the zero-pressure isobar as the result of the competition between these two tendencies. Now let us turn to the case of the zero-temperature isotherm, in which no thermal fluctuations are present. At small pressures the rhombohedral phase is the ground state because the potential energy contribution dominates over the ion zero-point energy. However, as we compress the system, the potential-energy differences between the different phases of $BaTiO_3$ decrease, as a direct consequence of the weakening of the ferroelectric instability, and thus the *relative* importance of the quantum-mechanical fluctuations grows accordingly. Hence the phase transition sequence can occur in a similar way along both the zero-pressure isobar and the zero-temperature isotherm.

Figure 4 shows the calculated polarization along the zero-pressure isobar, for both the classical and quantum cases. Classically the polarization reaches 0 K with a finite slope, while the slope is zero quantum mechanically. This is the expected quantum saturation of the order parameter that has been discussed by Salje *et al.* [16] in the context of structural phase transitions. Following Ref. [16], the quantum-saturation effects in $BaTiO_3$ can be predicted to be significant up to several hundred Kelvin, such high temperatures being a consequence of the shallowness of the potential-energy wells associated with the ferroelectric instabilities of the system. Indeed, in the pressure range from about 3 GPa to about 6 GPa, this strong quantum saturation can be regarded as inhibiting additional phase transitions to lower potential-energy phases, thus allowing for the occurrence of orthorhombic and tetragonal ground states.

It is important to note that the classical and quantum phase diagrams depicted in Fig. 2 cannot be related by the approximate quantum-mechanical correction that is most common in the context of Landau theories of phase transitions [16]. As shown in Ref. [12], the classical free-energy landscape of $BaTiO_3$ at low temperatures is described by a fourth-order expansion in the polarization, sixth-order terms being identically zero at 0 K. On the other hand, some features of the quantum-mechanical phase diagram at low temperatures, e.g. the existence of an orthorhombic ground state, are strictly sixth-order in character. Since the usual quantum-mechanical correction of the classical Landau potential only involves a modified temperature dependence of the quadratic term [16], it could never account for such features. Hence, the variety of accessible phases in $BaTiO_3$ results in non-trivial quantum corrections and considerably hampers analytical treatment of the problem, costly numerical solutions being required.

In summary, we have made use of the first-principles effective-Hamiltonian method of Zhong *et al.* to study in detail the temperature-pressure phase diagram of $BaTiO_3$. We have gone beyond the usual approach and considered the zero-point motion of the ions in our calculations by means of the path-integral quantum Monte Carlo method. We find that the quantum fluctuations make a dramatic difference with respect to the classical result. In the quantum-mechanical case, all the polar phases of the system (rhombohedral, orthorhombic, and tetragonal) survive down to 0 K, while at the classical level only the rhombohedral phase does. Our result is in essential agreement with the experimental work of Ishidate *et al.*, thus giving strong support to the conclusions of these authors.

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[10] Zhong *et al.* constructed their effective Hamiltonian for $BaTiO_3$ within the local-density approximation, which is well-known to underestimate equilibrium volumes. Accordingly, these authors estimated −4.8 GPa to be their *theoretical*zero pressure [7]. We adopt the same approach throughout this Letter. Consequently, the pressure scale is shifted in Figs. 2 and 3, etc.
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