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.

Surprisingly, these authors found that all the polar 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)).

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. [5]). (b) Sketch of phase diagram of BaTiO$_3$ as measured by Ishidate et al. [6]
tecture is the paraelectric cubic phase. The parameters in this expansion are obtained from first-principles density-functional calculations. Zhong et al. performed classical Monte Carlo (MC) simulations on the basis of such an effective Hamiltonian and demonstrated that it correctly reproduces the non-trivial phase transition sequence of BaTiO$_3$ along the zero-pressure isobar. Indeed, after this initial achievement, the first-principles effective-Hamiltonian method has been successfully applied over the years to situations of increasing complexity.

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 underestimation of the equilibrium volumes given by the local-density approximation, which brings about a systematic error in the location of our zero of pressure. 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. [1], 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. 1. 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. 1, is difficult to decide (although we tentatively favor the latter possibility). A more reliable calculation adopting an approach such as that of Ref. [2], 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 approximations made in connection with the effective-Hamiltonian method, a careful check was carried out using zero-temperature density-functional calculations directly [3]. 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 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 [5], 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 $P = 1 \rightarrow 3 \rightarrow 6 \rightarrow 12$, 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].

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 $T_c \propto (p_o - p)$ at high temperatures to following the quantum-mechanical law $T_c \propto (p_o - p)^{1/2}$ [14] 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 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. [14] in the context of structural phase transitions. Following Ref. [10], 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
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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