

**MgO phase diagram from first principles in a wide pressure-temperature range**A. B. Belonoshko,<sup>1</sup> S. Arapan,<sup>1</sup> R. Martonak,<sup>2</sup> and A. Rosengren<sup>1</sup><sup>1</sup>*Condensed Matter Theory, Department of Theoretical Physics, Alba Nova University Center, Royal Institute of Technology (KTH), 10691 Stockholm, Sweden*<sup>2</sup>*Department of Experimental Physics, Faculty of Mathematics, Physics and Informatics Comenius University, 842 48 Bratislava, Slovakia*

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Recent laser-initiated strong shockwave measurements at Livermore provide the opportunity for verification of the MgO phase diagram at extreme pressures and temperatures. This calls for a comprehensive study of the MgO phase diagram. The phase diagram is obtained by *ab initio* molecular dynamics (two phase and Z method) and phonon-based thermodynamic calculations. Energies and forces are computed from first principles projector augmented wave method. The B1 transforms to B2 phase at about 490 GPa. Melting temperatures of B1 are consistent with the two-phase melting curve (Alfe, 2005). The triple point B1-B2-liquid is located at about 2.4 Mbar and 9000 K. The melting curve of the B2 phase rises rather steeply from the triple point. The Hugoniot is likely to cross the B1-B2 boundary first and then to cross the melting curve of B2, therefore, the melting curve of periclase is not relevant for the Hugoniot. MgO melts between 11.3 and 12.5 thousand K and 4.3 and 5 Mbar along the Hugoniot from the B2 phase. The two-phase melting curves of B1 computed with various semiempirical potentials are remarkably close to each other and are consistent with the B1 first principles melting curve at low pressure. This suggests the MgO melting temperatures to be in the close proximity of this determination. The search for new phases of MgO by first principles metadynamics has not produced unknown phases. Therefore, the suggested discontinuity of the Hugoniot at 170 GPa and 3000 K remains enigmatic.

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**I. INTRODUCTION**

MgO is one of the most stable oxides. In an experiment, up to the highest pressure of 227 GPa,<sup>1</sup> it was observed exclusively in the B1 structure. It is also one of the most abundant minerals in the Earth's mantle. Surprisingly, despite its seeming simplicity, its thermal stability and, to a lesser extent, pressurewise stability is clouded by a number of controversial results.

The situation is, to a certain extent, explained by the high melting point of MgO already at the pressure ( $P$ ) 1 bar. At this pressure, MgO is known to melt at the temperature ( $T$ ) of 3098 (Ref. 2) to 3250 K,<sup>3</sup> likely from the B1 structure, though another structure was proposed by Aguado and Madden.<sup>4</sup> As one can see, even the ambient pressure melting point is not precisely determined and there are varying opinions<sup>4</sup> about the structure of the solid phase from which MgO melts. Understandably, an increase of melting temperature with increasing pressure makes measurements technically difficult. Therefore, it is perhaps not totally surprising that the slope  $dT_m/dP$  of the MgO melting curve at  $P=1$  bar was determined as 36 K/GPa in one experiment<sup>5</sup> and, recently, as equal to 221 K/GPa in another.<sup>6</sup> The range of theoretical estimates is nearly as large with a certain shift to higher values [88 (Refs. 7 and 8) to 270 K/GPa (Ref. 9)].

Such a wide range of theoretical predictions is explained in part by the different methods applied to compute the MgO melting curve. There are two thermodynamically justified methods for computing melting temperature in atomistic simulations. One is computing the  $PT$  point where the Gibbs free energies of the liquid and solid are equal by the thermodynamic integration method<sup>10</sup> and the other one is the two-

phase approach. While the latter is universal, the former so far has been almost exclusively restricted to one-component systems (there is one exception where melting in a binary system was computed by calculating Gibbs energies in atomistic simulations<sup>11</sup>). This is simply because it is technically too complicated to perform the integration in a multicomponent system. Therefore, the only option left is the two-phase method. This method has been applied to MgO (Ref. 12) and allowed to obtain thermodynamically correct melting temperatures<sup>13,14</sup> for a pair-wise model of interatomic interaction. As has become clear much later,<sup>15</sup> the melting curve obtained by the two-phase method using a pair potential model<sup>12</sup> is in very good agreement with the melting curve obtained by the two-phase method using *ab initio* calculation of forces in the experimental pressure range (0–30 GPa). Apparently, the description of interactions based on an effective pair potential model was reasonably close to the one obtained from first principles. The explanation is simple—both methods correctly describe repulsion, the dominating part of interactions at high pressure. When the character of the bonding in liquid MgO changes significantly compared to the bonding in solid, the two melting curves<sup>12,15</sup> start deviating from each other.

There are several other methods that have been applied to MgO melting. One of these methods allows to us compute the temperature at which the bulk crystalline material loses its stability. Such a method leads to computing the temperature of superheating instead of melting. The method was applied by Voadlo and Price,<sup>16</sup> who obtained a melting curve higher than that obtained by the two-phase method.<sup>12</sup> However, as will be shown below, when a correct method is applied, the two melting curves comes out nearly identical.

Another method is built upon calculating the Clausius-Clapeyron slope of the melting transition.<sup>7,17</sup> However, it is important to understand that it is impossible to self-consistently calculate the melting curve within that method because while the derivative is known, the starting point is impossible to determine within the method. Therefore, other considerations have to be applied to figure out an initial point on the curve. Needless to say, this makes the method as such empirical if these considerations originate from experimental information. What happens if the starting point is guessed reasonably close to the true one for the given model? One would expect that the whole curve would be reasonably close to the one computed by a correct method for the given model. The answer is—not necessarily. The problem with this method is that the initial error becomes larger with increasing pressure. This is simply because of the normally different compressibilities and heat capacities of a solid and the liquid. If the starting point is lower than the “true” point of the model, the melting curve will be lower than the melting curve of the model and if the starting point is larger than the true melting point then the melting curve will be larger than the true melting curve of the model. We emphasize here that the starting melting point should be that of the model—any other reference makes the approach *ad hoc* or empirical at best. An incorrect guessing of the starting point leads to increasing error propagating into the calculations because each subsequent point on the curve is subjected to the error increasing with pressure. We will show below what kind of error one might expect when such a method is applied to MgO. However, when a two-phase method is used to determine the initial point on the melting curve and then the Clausius-Clapeyron slope of the melting transition is computed as performed by Aguado and Madden,<sup>4</sup> the method becomes self-consistent and thermodynamically correct.

A useful alternative has recently been introduced.<sup>18</sup> It is not as rigorous as the two-phase method, but it allows to eliminate most of the superheating characteristic of the one-phase melting. In this method the system cools on melting. When the system reaches the limit of superheating it starts to melt spontaneously. If one does not interfere in this process the system ends up at the melting curve. This observation was confirmed for a number of substances including multi-component ones.<sup>19–21</sup>

Alfe *et al.*<sup>22</sup> introduced a very helpful procedure to compute corrections to the melting temperature. Let us say that we have a reasonably precise (in terms of being close to some flavor of *ab initio* approach or to any other model that one considers to be of interest) yet an approximate model and we can get a reliable melting temperature for the approximate model. Then, by computing energies and pressures with the model of interest for the configurations generated with the approximate model one can compute corrections to the approximate model and, in this way, get the melting temperature for the model of interest. There is a restriction that the two models should be sufficiently close—for the definition of “close” we refer the reader to the original paper.<sup>22</sup>

Finally, one can obtain the melting temperature by the two-phase method and the superheating temperature from the approximate model and then apply correction to the superheating of the model of interest. This is how it was done for

perovskite and post perovskite phase.<sup>23</sup> There is nothing wrong with the heat-until-it-melts method as long as one recognizes its limitations and is able to reliably estimate the degree of superheating. What error one can then expect? The superheating at high pressure is normally on the level of 23%<sup>18,19</sup> and never exceeds 30%.<sup>24</sup> Therefore, the correction to be applied to the superheating of the model of interest varies between 20% and 30%. The approximate model allows to improve this estimate even further. Therefore, the corrected temperature comes within a few percent of the temperature that would have been obtained by the rigorous two-phase method. Such a precision is quite tolerable, especially considering that experimental temperatures very often differ by much more than that.

There are two ingredients involved in the calculations of a melting curve in an atomistic simulation. One is the method as elaborated above and the second is the model of the material that allows to us compute forces between atoms. In our introduction, we did not touch upon the latter. We will talk about that below.

This study was in part inspired by the emerging possibility of comparing our computed MgO phase diagram to the results coming from shock wave experiments where extremely powerful shocks are generated.<sup>25</sup> Clearly these measurements will reach very high temperatures and pressures. Therefore, we need the full phase diagram of MgO (not only of the periclase B1 phase). Since the *PT* range is very broad, we need to rely on first principles calculations. Needless to say, the treatment of the *ab initio* model has to be based on a viable method to get phase boundaries of MgO. So far, none of the studies known to us have addressed all these issues within the frame of one study. In what follows, we first describe the model we used to compute energies and forces acting on atoms. Then we explain our procedure for computing the B1-B2 transition. This is followed by the details of our two methods we apply for computing melting temperatures, that is, the two-phase and *Z* methods. We also explain the two-phase procedure of melting/freezing simulations for the Matsui<sup>26</sup> model. The description of methods is followed by a summary of our results that boils down to the MgO phase diagram. The possible errors of this and previous studies are then discussed.

## II. METHOD

### A. *Ab initio* molecular dynamics

The *ab initio* molecular dynamics simulations have been performed using the Vienna *ab initio* software package (VASP).<sup>27</sup> Following the Alfe<sup>15</sup> experience we also performed the simulations within the local density approximation (LDA).<sup>28</sup> However, in our simulations, because of the ambition to explore a much wider pressure and temperature range than in the previous study,<sup>15</sup> we have used a Mg pseudopotential with a core radius of 1.058 Å and an O pseudopotential with a core radius of 0.82 Å. This made our simulations much more computer time consuming. Even though we did not try to compute very large systems and restricted our calculations to 432 atoms at the most, our simulations are considerably more laborious than anything attempted previously.

The LDA was chosen because it was observed that the general gradient approximation leads to incorrect melting temperatures. A plane-wave energy cutoff of 400 eV (at some  $P$  and  $T$  we used 500 eV) and gamma point sampling were used. The time step, because of comparably small masses of atoms and high  $P$  and  $T$ , was kept at 0.5 femtoseconds and in some cases at 0.25 and even 0.1 femtoseconds, depending on pressure and temperature. In the cases where we needed to maintain constant temperature, we used the default option in VASP that is the Nose thermostat with the period of oscillation around 40 timesteps. Most of our simulations were performed in the microcanonical  $NVE$  ensemble ( $N$ —number of particles,  $V$ —volume, and  $E$ —energy). A typical number of atoms in our simulations was 216 for simulations of B1 structure (supercell obtained by  $3 \times 3 \times 3$  translation of the unit cell with eight atoms) and 250 atoms in simulations of the B2 structure (supercell obtained by  $5 \times 5 \times 5$  translation of the unit cell with two atoms). The performance of our set up was tested against the experimental  $PV$  relation at room temperature<sup>1</sup> and we obtained a very reasonable agreement between the measured and computed equations of state.

## B. Phase transitions

There are three known phases of MgO, two solid—B1 (NaCl), B2 (CsCl), and liquid. The B2 phase has so far not been observed in experiments, but there are a number of theoretical studies<sup>7,12,29–38</sup> suggesting its existence. The pressure range of the predicted B1-B2 transitions is large—from 205<sup>30</sup> to 1050<sup>29</sup> GPa at low temperature. Therefore, it is hypothetically possible that the discontinuity on the plot of the velocity of the shockwave front as a function of the velocity of projectile in the range 180 GPa and estimated temperature of 3400 K,<sup>39</sup> might be due to the B1-B2 transition. Clearly, to establish the full phase diagram one needs to compute the B1-liquid and B2-liquid transitions. Besides, in view of possible solid-solid transitions beyond the B1-B2, an investigation of such a transition is warranted. We explored this by the metadynamic approach.<sup>40</sup>

### 1. B1-B2 phase boundary from quasiharmonic phonon calculations

We performed *ab initio* lattice dynamics simulations to determine the B1-B2 phase boundary from the free energy calculations. Calculations were done by using VASP (Ref. 27) and PHON (Ref. 41) codes. In the quasiharmonic approximation, the Helmholtz free energy of the electron-ion system can be calculated as

$$F(V, T) = E_0(V) + F_{ph}(V, T), \quad (1)$$

where  $E_0$  is the energy of the electronic subsystem in the ideal static lattice (we neglected the contribution of the electronic entropy) and  $F_{ph}$  is the phonon free energy. The Helmholtz free energy of phonons  $F_{ph}$  is given by

$$F_{ph} = k_B T \sum_{\mathbf{q}s} \ln[2 \sinh(\hbar \omega_{\mathbf{q}s} / 2k_B T)], \quad (2)$$

where  $\omega_{\mathbf{q}s}$  is the frequency of the vibrational mode  $s$  at wave vector  $\mathbf{q}$ . In a crystal the sum can be replaced by an integral

and evaluated through the phonon density of states  $g(\omega)$  as

$$F_{ph} = k_B T \int_0^\infty d\omega g(\omega) \ln[2 \sinh(\hbar \omega / 2k_B T)], \quad (3)$$

where  $g(\omega)$  is normalized to the number of phonon branches. The Helmholtz free energy was calculated for a set of 20 volumes within a pressure range corresponding to 200–500 GPa. The phonon density of states and free energy were calculated via the small displacement method for a  $4 \times 4 \times 4$  supercell with 128 atoms. The ground-state energy  $E_0$  and forces were calculated within the LDA approximation of the DFT, with a 800 eV cutoff and a  $3 \times 3 \times 3$   $k$  mesh in the reciprocal space.

We determined the B1-B2 phase boundary  $P=P(T)$  as the solution of the equation

$$G_1(P, T) = G_2(P, T), \quad (4)$$

where the Gibbs free energy  $G(P, T)$  was calculated from the Helmholtz free energy  $F(V, T)$  as

$$G(P, T) = F(V, T) - V[\partial F(V, T) / \partial V]_T \quad (5)$$

by fitting  $F(V, T)$  at each temperature to a third order Birch-Murnaghan EOS.

### 2. Two-phase/coexistence *ab initio* simulations

The two-phase<sup>13</sup> and coexistence<sup>42</sup> simulations are sometimes mistaken as identical. In fact, there is a significant difference that becomes especially relevant when systems are small, as is the case in most *ab initio* molecular dynamics simulations.

The coexistence approach was first applied for a generic material by Ladd and Woodcock.<sup>42</sup> In this approach half of the computational cell is occupied by liquid and the other half by solid. The simulation is performed in the  $NVE$  ensemble and the temperature is self regulated by the heat of fusion/solidification, converging to the temperature of melting. It is essential that when the temperature has converged and is averaged over a certain period of time, both phases are present. The relative amounts of liquid and solid phases in the cell are also important. If the amount of one of the phases is too small, surface effects might be significant. Another problematic issue is that in the cell where half of the material is melted and the other half remains solid, pressure becomes strongly nonhydrostatic. Therefore, one needs to adjust the initial shape to accommodate for the volume change on melting. Unfortunately, this is not quite enough, because during the evolution (freezing/melting) of the material in the cell the ratio of solid and liquid volumes changes and nonhydrostaticity becomes an issue again. These problems led Ladd and Woodcock<sup>42</sup> to conclude that the approach can be applied only under the condition when one knows the equations of state well both for liquid and solid phases of the material in question. This is rather laborious, especially for an *ab initio* treatment. In 1977, when the study was performed, even for simple interaction models it was a rather difficult task. Therefore, the approach was abandoned for some time.

The two-phase approach does not require that in the end the computational cell contains both liquid and solid. Nor-

mally, the simulation is performed in the  $NPT$  ensemble starting from a configuration where solid and liquid are present. By performing a number of simulations at varying  $P$  and  $T$ , one can make observations on stability of solid and liquid at particular conditions and, in this way, bracket the melting curve.

Both methods become practically identical when the number of atoms is large. This, however, is not always the case in first principles simulations.

We applied *ab initio* molecular dynamics (MD) to determine melting of B1. To perform these simulations one needs first to prepare the two-phase computational cell. For that purpose the computational cell was obtained by a  $3 \times 3 \times 6$  translation of a B1 unit cell with 8 atoms. The unit cell parameter was chosen as 4 Å, that is, 16 Å<sup>3</sup>/f.u. At  $T = 0$  K this volume corresponds to 20 GPa. Then half of the atoms (216 atoms) was frozen and high temperature (8000 K) was applied to melt the other half. The resulting configuration was subjected to high nonhydrostatic stress. To bring the configuration to hydrostatic conditions, the liquid part was elongated 8.5%. This was sufficient to get approximately hydrostatic pressure. However, when the system is simulated starting from a number of initial temperatures between 6000 and 7000 K, pressure becomes strongly nonhydrostatic varying between  $\sim 50$  GPa along the interface and  $\sim 70$  GPa across the interface. We made the conclusion that such simulations require larger numbers of atoms to decrease the uncertainty in the computed melting temperature. We performed another two runs for the  $NVT$  ensemble at  $T = 6000$  and 7000 K. We observed that at 6000 K and  $\sim 50$  GPa the system became crystalline (with atomic planes severely strained by nonhydrostatic stress) and at 7000 K and  $\sim 60$  GPa the system melted. These simulations were short (2000 timesteps). The results are consistent with the melting curve obtained by Alfe.<sup>15</sup> Considering that these simulations are extremely expensive (about 60 times more expensive than those performed earlier<sup>15</sup> for the systems of the same size), it would be impractical to apply it for computing melting temperatures within, say, 5% error. Therefore, we relied mostly on the Z method as explained below.

### 3. Z method

The Z method received its name because of the characteristic shape of the isochore crossing the melting curve on gradual increase of the kinetic energy ( $K$ ) assigned to atoms at the beginning of the simulation.<sup>18,19,43</sup> When the initial  $K$  (kinetic energy) is low, the system of interacting atoms equilibrates while remaining in the solid structure. The temperature converges to that corresponding to approximately half of the  $K$  due to equipartition (if the system is dynamically stable at  $T = 0$  K). On further increase of  $K$ , the system crosses the melting curve while remaining in the solid state and enters the regime of superheating. That is, the system now metastably preserves the solid state. All these points on the  $PT$  plane form approximately a straight line that constitutes the upper cap of the letter Z. Eventually the magnitude of  $K$  exceeds a critical value that is called the limit of superheating. If  $K$  is very close to the critical value, the computed  $P$  and  $T$  might belong to the line, connecting the upper and

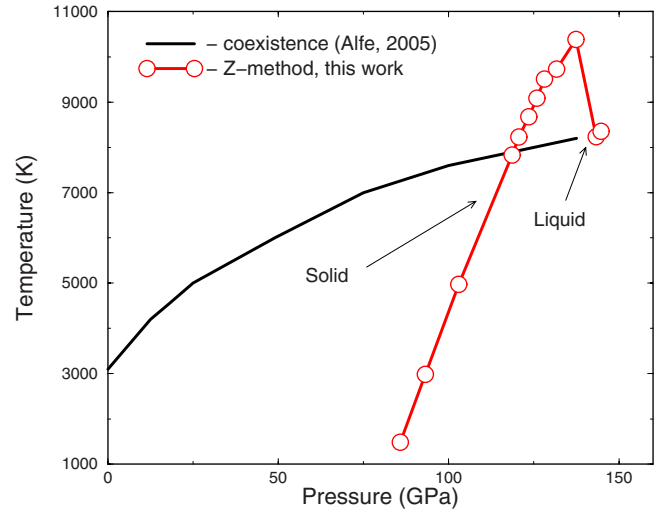


FIG. 1. (Color online) Comparison of the melting curve obtained by coexistence method (Ref. 16) and Z method (Ref. 19). The melting point is located right on the melting curve when the temperature drops down on melting. The points on the isochore are obtained by AIMD for  $V = 13.72$  Å<sup>3</sup>/f.u.

lower caps of the letter Z. Eventually, the points will belong to the lower cap of the Z letter. The point, where the lower cap is at its lowest  $T$ , belongs to the melting curve within the error bars. The physical explanation is that when the total energy of the system is large enough to move on to the liquid branch of the isochore, the only way to increase the configuration energy of the system is by lowering the  $K$  (and, thus,  $T$  as well). This is because the total energy  $E = K + U$  ( $U$ —configuration energy also known as potential energy) is constant. This exchange of kinetic and potential energy in a closed system leads to melting. For a detailed description and demonstration of the abilities of the method see Refs. 18–21, 43, and 44.

We performed Z-method simulations of MgO melting with *ab initio* MD for B1 (for two volumes, 13.72 Å<sup>3</sup>/f.u. and 10.72 Å<sup>3</sup>/f.u., where f.u. is a formula unit, that is MgO) and B2 (for one volume, 9.26 Å<sup>3</sup>/f.u.). The first volume was chosen in the range where Alfe has computed coexistence of liquid and solid (B1) MgO to check the performance of the Z method for MgO. Two other volumes are chosen to check the range of very high pressures, at or higher than the pressure of the B1-B2 transition.

### 4. Two-phase classical molecular dynamics simulations

The Fig. 1 in the paper by Alfe<sup>15</sup> is misleading. The melting curves by Belonoshko and Dubrovinsky<sup>12</sup> and Strachan *et al.*<sup>8</sup> are substituted for each other, giving the impression that the melting curves obtained from pair potentials<sup>12,16</sup> are completely different and that the Belonoshko curve is close to experiment.<sup>5</sup> In fact, it is not. It is notable, that the melting curve obtained from the *ab initio* coexistence MD simulations by Alfe<sup>15</sup> is extremely close to the one obtained by Vocadlo and Price<sup>16</sup> for the pair potential model developed by Matsui.<sup>26</sup> The melting curve by Vocadlo and Price is obtained by the so called heat-until-it-yields (HUIY) method.<sup>45</sup>

This method provides temperatures of superheating as described earlier, substantially overestimating the melting temperature. The peculiar proximity of the *ab initio* and pair potential melting curves is likely due to mutual cancellation of the errors in Ref. 16 related to the poor performance of the model (that underestimates the melting temperature) and the method HUIY (Ref. 45) that by definition overestimates the melting temperature. To test, whether this is indeed so we performed two-phase simulations with the Matsui<sup>26</sup> pairwise model.

Molecular dynamics simulations were performed by using the DL\_POLY\_2 code (version 2.20). The interaction between ions was approximated by a short-range pairwise Buckingham potential with the Matsui parameters for the Mg-Mg, Mg-O, and O-O interactions.<sup>26</sup> In order to simulate the melting of MgO we used a  $10 \times 10 \times 20$  supercell comprising 16 000 ions for the B1 phase, and a  $16 \times 16 \times 32$  supercell with 16 384 ions for the B2 phase. At each pressure the calculation of melting temperature was performed in three stages of simulation. In all calculations a simulation time step of 1 fs was used and the run time was 10 ps for each calculation within the first of the two stages of simulation (preparing the two-phases system), and 60–120 ps in the final stage of calculations (determining the melting temperature). Within the first stage we used the Berendsen thermostat and barostat (*NPT* ensemble) to equilibrate the system at given  $P$  and  $T$ , and at fixed  $P$  the simulation temperature was gradually raised from the ambient temperature until melting occurred. To identify melting we analyzed the radial distribution function (RDF) as well as the dependence of volume and three-dimensional diffusion coefficients as a function of temperature. Since we simulated an ideal periodic system, the melting occurred at temperature much higher than the melting temperature  $T_m$ . A configuration of the crystalline system at equilibrium with temperature below that at which melting occurred was used to prepare the two-phase system, that is, a supercell with one half of the ions in the solid state and another half in the liquid phase. At the second stage we performed simulations similar to the first stage, but with half of the atoms frozen. Temperature was gradually raised until the subsystem of the free-to-move ions melted. At each temperature the system was brought to equilibrium via the Berendsen *NPT* ensemble and the equilibrated configuration at  $T$  served as an input for simulation at  $T + \Delta T$ . Finally, we used the system with half of the atoms frozen in a crystalline phase at finite temperature and the other half of the atoms in a liquid phase to simulate the two-phase melting. In the third stage all atoms were allowed to move and the two-phase system was equilibrated for a set of temperature values via the Hoover *NPT* ensemble. In the end of simulations, the systems with equilibrium temperature lower than the melting one,  $T_s < T_m$  solidified, while systems with equilibrium temperature higher than the melting one,  $T_l > T_m$ , melted. Thus, the melting temperature is located between  $\max(T_s)$  and  $\min(T_l)$ . In our simulations this interval is 100 K wide.

### III. RESULTS

Applying the  $Z$  method at the  $V = 13.72 \text{ \AA}^3/\text{f.u.}$  we tested the performance of our method by comparing to the melting

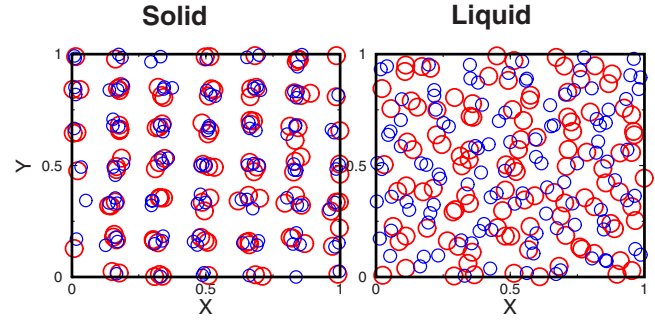


FIG. 2. (Color online) Snapshots of the structures in the AIMD simulations. Solid, left—when isochore crosses the melting curve on temperature increase. Liquid, right—the structure on the spontaneous drop of the temperature on melting. Even though this is an instantaneous structure (small circles are oxygens, large circles are Mg atoms) the difference of structures is obvious.

curve computed by the *ab initio* molecular dynamics (AIMD) coexistence method.<sup>15</sup> Figure 1 shows the comparison of melting data obtained by the two methods. The agreement is very reasonable and justifies application of the  $Z$  method. Figure 2 shows structure of MgO along the isochore at melting  $P$  and  $T$  conditions. It is clearly seen that after the temperature drop (Fig. 1) the structure is completely molten. The energy spent to bring the low energy solid structure toward the high energy liquid structure (Fig. 2, right) is taken from the kinetic energy and, thus, results in bringing the temperature down to the MgO melting curve.

The B1-B2 curve is obtained as described above and shown in Fig. 3. Figure 3 also summarizes the data on MgO melting as obtained previously by AIMD.<sup>15</sup> Even though we obtained just three melting points for MgO (Fig. 3) and a

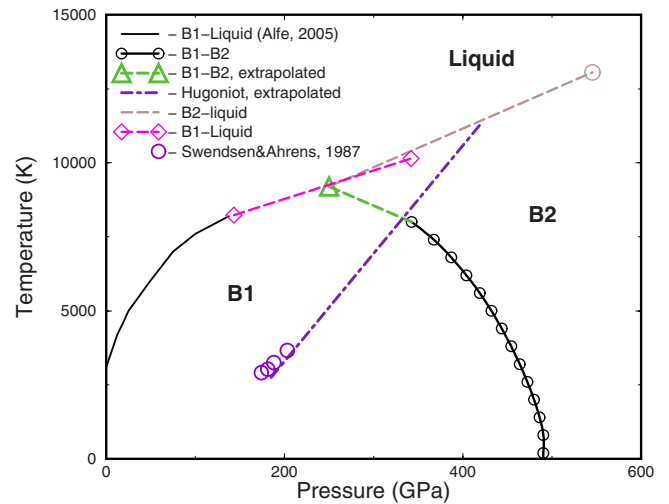


FIG. 3. (Color online) Phase diagram of MgO. The B1-liquid boundary consists of the low-pressure melting curve [solid curve (Ref. 16)] and long-dashed line with diamonds. The triple point (large triangle) B1-B2-liquid is obtained by extrapolation of the B1-B2 boundary (solid curve with circles). The long-dashed line with circle is the B2-liquid boundary. The dot-dashed line is the Hugoniot estimated previously (Ref. 18). The circles represent the shock wave data (Ref. 46).

continuous curve B1-B2, it is sufficient to provide a reasonably precise MgO phase diagram. We judged that further significant computational effort resulting in comparably small improvements of the MgO phase diagram is hardly justified. We did not compute the B1-B2 transition at very high temperatures being warned by Wu *et al.*<sup>38</sup> that the quasiharmonic approximation at these temperatures becomes imprecise. Rather, we extrapolated the B1-B2 boundary from lower temperatures. The pressure of the B1-B2 transition at zero temperature is slightly lower than 500 GPa. This is in good agreement with the studies by Oganov *et al.*,<sup>36</sup> Alfe,<sup>15</sup> and Wu *et al.*<sup>38</sup>

The triple point is obtained by extrapolation of the B1-B2 boundary and the melting curve of the B1 phase approximated by the straight line connecting our two computed B1 melting points. This approximation is reasonably precise because at the high pressure melting temperature changes slowly. The B2 melting curve is approximated by the straight line connecting the triple point and the computed B2 melting point at around 5 mbar.

The melting of MgO in a shock wave experiment can be estimated from the  $PT$  locus of Hugoniot experimental points by Svendsen and Ahrens<sup>47</sup> and their extrapolation by Koker and Stixrude.<sup>17</sup> We assume that when the Hugoniot crosses the B1-B2 transition (Fig. 3) the  $PT$  locus does not change too much. In principle, since the Clapeyron  $dT/dP$  slope of the B1-B2 transition is negative, the Hugoniot will be shifted to higher pressures and the temperature of the melting at the Hugoniot conditions will occur at a higher temperature. We note that even though the Hugoniot temperatures, measured in experiment and estimated from the data on MgO are consistent with each other,<sup>47</sup> there are alternative estimates of temperatures (e.g., Ref. 46). One can see that the Hugoniot crosses the MgO melting curve at a pressure around 430 GPa and the temperature of 11 300 K. Then the Hugoniot will follow the melting curve of MgO and take off from the melting curve at pressures around 500 GPa (given the estimate provided by Koker and Stixrude).<sup>17</sup> At this pressure the melting temperature will be around 12 500 K. Therefore the range of melting temperatures along the Hugoniot can be rather reliably estimated between 11 and 12.5 thousands K and pressures between 430 and 500 GPa. MgO melts from B2 phase along the Hugoniot.

#### IV. DISCUSSION

Practically all existing calculations predict high melting temperatures of MgO as recently described in the paper by Tangney and Scandolo.<sup>48</sup> This is in striking contrast with the temperatures measured by Zerr and Boehler.<sup>5</sup> Comparably recently, new experiments<sup>6</sup> suggested that the contrast might be not entirely due to complete failure of all theoretical methods but rather due to experimental errors in the Zerr and Boehler experiments. Indeed, a number of melting curves obtained in a diamond anvil cell are extremely low (particularly for such transition metals as Fe, Mo, Ta, and W) as compared to the most precise theoretical assessments and shock wave measurements.<sup>43</sup> Belonoshko and co-authors suggested a generic scenario for such systematically low

measured temperatures.<sup>49,50</sup> According to this scenario,<sup>50</sup> if the melting temperature of a material is high and resistance to shear is low, the material yields to the stress and macroscopic flow might be observed and mistakenly be identified as melting. Stress is always present in diamond anvil cell (DAC) (one does not need high stress if the yield strength is low). Such a flow will have impact on the x-ray measurements as well. An experimental solution to this problem could be the application of impulse heating of the sample in DAC. This technique is looks very promising.<sup>51</sup> An application of this technique, provided that structural measurements are performed very fast, will allow to distinguish between phase transitions and stress-induced flow. The kinetic of phase transitions is fast, in metals it is on the order of microseconds and less, while the flow is restricted to the velocity of the material transfer and is, thus, much slower. Indeed, in shock wave experiments shear stress is likely larger than in DAC experiments, still shock wave melting temperatures for transition metals are in very good agreement with theoretical calculations. The explanation is that during shock wave experiments the time of measurement is extremely short and the shear simply has no time to interfere in the process of a phase transition. Therefore, the impulse heating technique along with very fast structure measurements seems to be the cure.

Another confirmation of our suggestion has recently been provided by Wu *et al.*<sup>52</sup> They simulated the impact of shear on Ta. The melting temperature of Ta was high, much higher than experimental DAC data (in agreement with shock wave data).<sup>53</sup> When Wu *et al.*<sup>52</sup> applied shear to their sample, they observed structure disordering exactly at the same  $PT$  conditions where it was observed in the DAC experiment. Based on this finding such an 'urban legend' as the "liquid glass" was proposed.<sup>54</sup> We note that glass is an undercooled liquid, and therefore it is either liquid or glass but not both at the same time. Thus, Wu *et al.*<sup>52</sup> reproduced both curves—melting, at high temperature under hydrostatic conditions and flow, at low temperature, under nonhydrostatic conditions. Ta does not become an exotic material because of such behavior. In fact, it is quite a common behavior of a system under nonhydrostatic stress explained a long time ago.<sup>55</sup> According to the authors,<sup>55</sup> a system subjected to the impact of "ultrahigh pressure+shear," splits into two subsystems—one with the atoms located close to their crystallographic positions and another with the atoms traveling across the barriers. As temperature increases, the barriers become lower due to increasing amplitude of thermal motion. An increasingly large fraction of atoms moves to the activated subsystem giving the impression of melting and changing the x-ray pattern. This process might be enhanced if the material approaches temperature induced solid-solid phase transition.<sup>43,56-58</sup>

Even though all theoretical methods provide melting temperatures of MgO considerably higher than the DAC (Ref. 5) melting curve, the range of the theoretical curves is also significant. Analysis of early attempts to compute MgO melting was provided in Ref. 12 and recently Tangney and Scandolo<sup>48</sup> gave an overview of more recent papers. Here we address two melting curves<sup>7,16</sup> computed for MgO in B1 phase. As described above the Vocadlo<sup>16</sup> melting curve is in

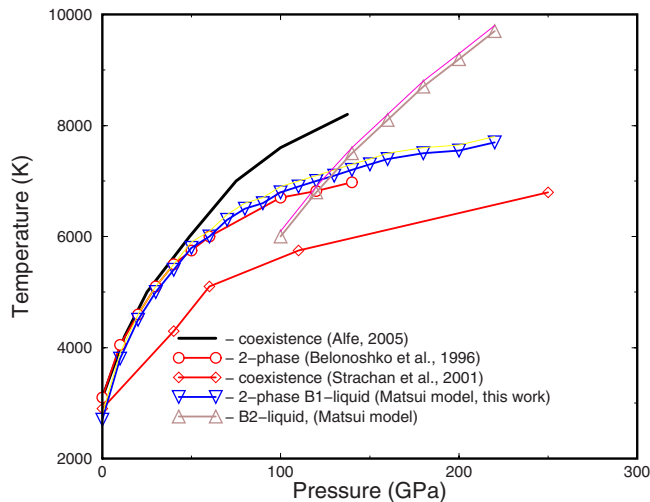


FIG. 4. (Color online) Comparison of the MgO B1 melting curve computed by Alfe (Ref. 16) to the B1 melting curves obtained by Belonoshko (Ref. 12), Strachan (Ref. 8), and the melting curve computed for the Matsui pairwise model (Ref. 27). It is interesting to note, that Alfe (Ref. 16) showed excellent agreement between his melting curve and the one computed by Vocadlo (Ref. 17) using the same Matsui pairwise model (Ref. 27). The only difference in Vocadlo calculations was that they used the incorrect method HUIY (Ref. 47) and therefore obtained superheating temperatures instead of melting ones. The melting curve of the B2 phase computed for the Matsui model is shown for completeness.

very good agreement with the one obtained recently by Alfe. Examples of similar mutual cancellation of errors are known in the literature (for details see Ref. 50). We computed the melting curve using the same Matsui model as applied by Vocadlo and Price (Fig. 4). However, instead of the HUIY method<sup>49</sup> applied by Vocadlo and Price we applied the correct two-phase method. We see (Fig. 4) that the agreement between Vocadlo and Alfe has vanished. Instead, the correctly computed melting curve is in very close agreement with the one computed by Belonoshko<sup>12</sup> (Fig. 4). Indeed, both models are parameterized using essentially the same experimental data even though they are somewhat functionally different. The curve is in agreement with the one computed by Alfe at moderate pressures and deviates when pressure increases beyond 50 GPa. This is expected, because at these pressures and temperatures liquid MgO becomes a metal.<sup>34</sup> The pairwise covalent model cannot account for such a transformation of electronic structure and a melting curve computed for pair models deviate from the one computed from first principles, where such changes are naturally taken into account. Figure 4 also shows the melting curve for MgO in the B2 phase computed for the same Matsui model. While quantitatively not correct, the qualitative behavior is similar to the one computed by us from first principles (Fig. 3). Thus, sometimes the differences between melting curves are illusory—as soon as correctly computed, the melting curves might become identical. Therefore, to compare melting curves where one is computed by a correct method and another by an incorrect is meaningless. Before a comparison is performed, one needs to compute the melting temperatures correctly for the same model.

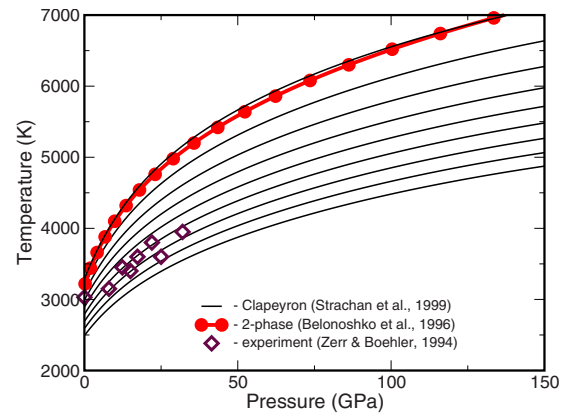


FIG. 5. (Color online) A set of “melting curves” of B1 MgO computed using the data on Clapeyron slope from Ref. 7 and assuming a number of ‘fixed’ points at ambient pressure. The obtained melting curves can be in agreement with experimental data (Ref. 5) and in agreement with the Belonoshko melting curve (Ref. 12), depending on the guessed initial melting point at pressure 1 bar. The Clapeyron method is, therefore, inconclusive.

Another method is based on computing the Clapeyron slope. Figure 5 shows the curve computed by coexistence simulations<sup>8</sup> and claimed to be in agreement with the one computed from the Clapeyron slope *assuming* the initial melting point at 1 bar. Neither details of the coexistence simulations nor a description of the potential were provided in the papers.<sup>7,8</sup> Therefore, we cannot verify the result ourselves. However, we can compute the melting curve assuming initial melting points and using the analytical expression for the MgO B1 Clapeyron slope (Fig. 5). One can see that the range of melting curves, obtained by assuming the initial melting points within reasonable distance from experiment is very large, more than 2000 K at the rather low pressure of 1.3 Mbar. Interesting, if one assumes the initial temperature to be equal to the experimental melting temperature at ambient pressure (3250 K),<sup>3</sup> the melting curve according to Strachan *et al.*<sup>7</sup> practically coincides with the curve computed by Belonoshko<sup>12</sup> (Fig. 5). The melting curve for B1 MgO obtained by Koker and Stixrude<sup>17</sup> with the Clapeyron slope method by assuming initial “fixed” point might change dramatically if another fixed point is assumed.

In order to investigate the possibility of other solid phases, different from B1 and B2, we applied the method of metadynamics.<sup>40</sup> With the Matsui pairwise model we reproduced the B1-B2 transition but did not see any other solid phases. In some runs, B1(B2) transformed into the same structure just with different cell shapes. Metadynamics runs with *ab initio* computation of forces proved to be exceptionally expensive and have not been performed to the extent sufficient to make definite conclusions on the possibility of other solid phases. Therefore, the question about the nature of the discontinuity in the shockwave experiments<sup>39</sup> remains open.

## V. CONCLUSIONS

In this paper we provided phase boundaries between three phases known for MgO. They are computed from first prin-

ciples by the reasonably precise (error 5% or less) *Z* method in the case of melting and in quasiharmonic approximation for the B1-B2 transition. Along the Hugoniot MgO melts from the B2 phase in the temperature range between 11.3 and 12.5 thousand K and in the pressure range between 430 and 500 GPa. The Hugoniot might show a subtle discontinuity when crossing the B1-B2 transition (Fig. 3). The discontinuity along the Hugoniot at about 170 GPa and 3000 K remains enigmatic. The diversity of the melting curves might shrink considerably if a correct method is applied. There is little

doubt that early DAC experiments on MgO melting are erroneous.

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