

## New Insights into the Melting Behavior of MgO from Molecular Dynamics Simulations: The Importance of Premelting Effects

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We provide a plausible resolution of a long-standing controversy relevant to the geophysics community, namely, that the experimental slope of the melting curve  $T_m(P)$  of MgO at low pressures is about 3 times smaller than that obtained from computer simulation of the melting of the normal rock-salt-structured crystal. With increasing temperature at zero pressure, our simulations predict a solid-solid phase transition (from a rock salt to a wurtzite crystalline lattice) to occur just before melting. The coexistence of wurtzite and liquid phases at low pressures is found to be described by a Clapeyron slope which is in much better agreement with the experimental results of Zerr and Boehler [Nature (London) **371**, 506 (1994)] than the calculated melting line for the rock salt structure. We also show that the existence of a certain concentration of lattice defects in the rock salt phase cannot provide an alternative explanation.

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MgO (periclase) is an end member of magnesiowüstite (Mg, Fe)O, one of the main mineral constituents of the Earth's lower mantle. A fundamental understanding of its high-pressure, high-temperature properties is a prerequisite for the correct description of more complex oxides or silicates forming the bulk of the Earth [1]. The comparative simplicity of MgO with respect to other minerals means that it has become the standard test-bed for the evaluation of theoretical methods to calculate such properties. However, a long-standing disagreement exists concerning the melting curve of periclase: the initial slope of the melting curve  $dT_m/dP$ , as predicted by computer simulation [2–6], is approximately a factor of 3 bigger than the experimental slope determined by Zerr and Boehler (ZB) [7] in a diamond anvil cell (DAC). Agreement is much better for the location of the melting point at zero pressure itself [8]. Alfè and co-workers [9] have recently enumerated possible reasons for the discrepancy. For example, the sample might be subjected to nonhydrostatic or thermal stress (leading to crystal failure for  $T < T_m$  [10]) and the method of locating the melting point in a DAC at  $\sim 4000$  K might be questioned. On the other hand, simulation of the melting process is not easy, as a large number of atoms and long simulation times, together with accurate atomic interactions, are needed in order to obtain reliable thermodynamic properties, especially for defective solids. Nevertheless, the discrepancy seems larger than one would expect on the basis of the much better agreement obtained for many other thermoelastic properties [1], and suggests that either simulations or experiment might be missing some essential ingredient.

Here, we analyze molecular dynamics (MD) simulations, performed under strictly hydrostatic pressure conditions, for premelting effects, associated with the thermal

excitation of lattice defects or with temperature-driven solid-solid phase transformations which might be a precursor of the true melting transition.

To describe the interatomic interactions over the requisite range of physical conditions is a substantial problem. *Ab initio* simulation methodologies [9] cannot yet be routinely applied to a problem of this size. Laio *et al.* [11] introduced an *ab initio* “force-matching” procedure in which the interactions are modeled by a parametrized potential, fitted to reproduce *ab initio* values for the interatomic forces and stress tensor for a number of representative atomic configurations. The use of an interaction potential allows for longer, larger simulations than the *ab initio* simulation method. We have recently shown [12–15] that highly transferable models of interactions in simple metal oxides may be generated by applying this procedure to a physically based, analytical expression for the potential, which incorporates many-body features and independently describes all relevant components of the atomic interactions (as extracted from quantum-mechanical perturbation theory [16]). In our recent work [15], we showed that our potential model for MgO is able to mimic the *ab initio* interactions in both bulk, surface and cluster, environments with similar accuracy. A detailed description of the potential model and of the quality of our fitting to *ab initio* results can be found there.

We locate the melting point at zero pressure,  $T_{m,0}$ , by directly simulating the coexistence of solid and liquid phases in the isothermal-isobaric (*NPT*) statistical ensemble. We make use of the thermostat-barostat method of Martyna *et al.* [17] under periodic boundary conditions in which the supercell undergoes arbitrary shape deformations in response to stress tensor fluctuations (even though the average pressure is hydrostatic). This so-called two-

phase simulation method [5] is expected to avoid the superheating effects observed in one-phase simulations. Once  $T_{m,0}$  is known, we generate the whole melting curve by integration of the Clausius-Clapeyron equation ( $dT_m/dP = T_m \Delta V / \Delta H$ ). The changes in volume ( $\Delta V$ ) and enthalpy ( $\Delta H$ ) across the melting transition are calculated by means of a series of (less expensive) one-phase simulations of solid and liquid phases. In order to check the correctness of this integration, we performed additional two-phase simulations at the highest coexistence pressures predicted by these means. The same integration procedure was adopted to study the coexistence of two different crystalline phases. For the two-phase simulations, we employed between 1200 and 1500 atoms and simulation times of the order of 200 ps; for the one-phase simulation, simulation times of 20 ps and supercells of 512 (rock salt), 600 (wurtzite), and 1024 atoms (liquid) were used.

We first determined the temperature for the coexistence of rock salt (*B1*) and liquid phases at zero pressure. This is the same coexistence considered in previous simulations [2–6]. Table I compares our results with previous simulations and experiments [7,8]. In line with previous MD studies, our results for  $dT_m/dP$  are in serious disagreement with the DAC experiments. The fact that our potential reproduces very well several thermoelastic properties of bulk MgO, as well as a number of properties of MgO surfaces and clusters [12–15], together with the observation that a large number of different MD simulations agree with each other, seems to support the validity of the MD results.

Alfè *et al.* [18] have questioned the reliability of potential models derived from force matching, as errors in the relative *energies* of solid and liquid phases (which are not included in the fitting procedure) might result in unacceptable errors in the melting temperature. We explicitly analyzed this by evaluating *ab initio* density-functional theory energies for ten solid and ten liquid statistically independent atomic configurations, extracted from MD runs at the

melting temperature. The calculations were performed with the SIESTA code [19], employing norm-conserving Troullier-Martins pseudopotentials [20] and the generalized gradient approximation for exchange and correlation [21]. Our model potential was found to reproduce SIESTA values for the energy difference between solid and liquid configurations with an accuracy of better than 2%, meaning that we are properly describing energetics. Although not providing an explicit demonstration, these results strongly suggest that an *ab initio* evaluation of the *B1* melting curve would lead to a similar disagreement with experiment.

Next, we considered the possible influence of thermally activated lattice defects. In recent work [15], we have shown that our potential is able to give correct defect energetics. Because of the dense ionic packing in MgO, Frenkel disorder can be excluded from the present analysis [22]. The atomic fraction of Schottky defects,  $N_S$ , at temperatures close to the melting point, is expected to be between approximately  $10^{-2}$  and  $10^{-7}$  [22]. We show in Table I results for a much higher defect concentration,  $N_S = 10^{-1}$ , generated by randomly removing  $Mg^{2+}$  and  $O^{2-}$  ions from a rock salt lattice. Although  $dT_m/dP$  decreases, thus approaching the experimental slope, the effect is quite small; moreover,  $T_{m,0}$  itself also decreases, resulting in a worse agreement with both experiment and previous simulations. We also studied how planar extended defects in the stacking sequence of atoms affects melting behavior. To this end, we introduced two evenly spaced stacking faults in the supercell, ten atomic layers apart, thus changing the stacking sequence along the (111) crystallographic direction from  $abcab\gamma abcab\gamma\dots$  (where Latin and Greek letters denote anion and cation sublattices, respectively) to  $abcab\gamma\gamma abc\beta a\gamma\dots$ . The results in Table I show that stacking faults have a similar effect on melting properties to Schottky disorder. Although we have not explicitly considered other defects, like dislocations or grain boundaries, it seems clear to us from these results that

TABLE I. Values of melting temperature (in K) and slope of melting curve (in  $K GPa^{-1}$ ) at zero pressure, as predicted by several representative MD computer simulations and experiment.

	$T_{m,0}$	$dT_m/dP(P=0)$	Reference
Lewis-Catlow shell model	$3250 \pm 200$	...	[3]
Stoneham-Snagster shell model	$3950 \pm 200$	...	[3]
Potential induced breathing	$3200 \pm 500$	$\approx 115$	[1]
Rigid ion model	$3175 \pm 75$	$\approx 115$	[6]
Fluctuating charge model	$3100 \pm 50$	88.5	[7]
Melting from rock salt ( <i>B1</i> )	$2950 \pm 20$	125	This work
<i>B1</i> with 10% Schottky vacancies	$2890 \pm 20$	102	This work
<i>B1</i> with stacking faults	$2910 \pm 20$	110	This work
Melting from wurtzite ( <i>B4</i> )	$3050 \pm 20$	40	This work
Experiment	$3040 \pm 100$	36	[8]
Experiment	$3250 \pm 20$	...	[9]

the quantitative discrepancy with experiment cannot be explained by a rock salt lattice with a reasonable concentration of defects.

The smaller slope for  $T_m(P)$  found in the experiments suggests, qualitatively, that solid and liquid phases coexisting at  $T_{m,0}$  are more similar than inferred from simulation. We show radial distribution functions (RDF) for  $B1$  and liquid at  $T = T_{m,0}$  in Fig. 1. The average coordination number  $N_C$  is 6 and 4 for solid and liquid, respectively. We also show the RDF for the four-coordinate wurtzite phase at the same temperature; it is much more similar to that of the liquid than the  $B1$  RDF. Melting from a solid phase with  $N_C = 4$  would be expected to have a smaller Clapeyron slope.

Melting from a solid phase other than rock salt is a simple idea which has not been quantitatively tested yet. The relative stability of  $B1$ ,  $B3$  (sphalerite or zinc blende) and  $B4$  phases at zero Kelvin was studied with SIESTA calculations. These predicted that  $B1$  transforms to  $B4$  at a tensile pressure of between  $-6$  and  $-8$  GPa, depending on details of the basis set, convergence parameters, etc.  $B3$  is never the most stable phase in the pressure range considered ( $P \geq -20$  GPa). Our model potential locates the transition pressure at  $-8.5$  GPa ( $B1 \rightarrow B4$ ), again in very good agreement with the *ab initio* prediction. The full  $B1$ - $B4$  coexistence line, generated by following the approach of Strachan *et al.* [6], is shown in Fig. 2. A solid-solid phase transformation is observed at zero pressure, with the wurtzite phase being thermodynamically more stable beyond a critical temperature  $T_c = 2920$  K, below the rock salt melting temperature. At zero pressure, MgO is therefore predicted to melt from a wurtzite crystalline lattice. By means of the two-phase simulation method, we obtain  $T_{m,0} = 3050$  K from  $B4$ , in much better agreement with experiment than from  $B1$  (see Table I). The initial slope of the melting curve is also in fair agreement with experiment. The whole melting curve is displayed in Fig. 2. It shows a slope discontinuity at  $P \approx 10$  GPa,

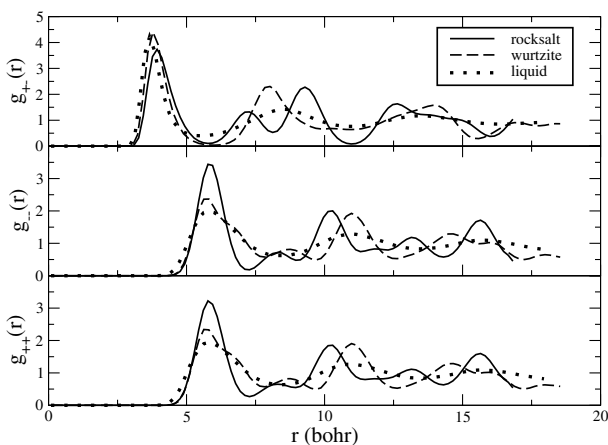


FIG. 1. MD simulations for the pair distribution functions of MgO at 3050 K in its rock salt, wurtzite, and liquid phases.

because at that pressure the wurtzite phase reconverts to rock salt. Given the error bars of the DAC experiments [7], our MD results are seen to be fully consistent with the experimental findings.

An important point here is that simulation of the  $B1$ -liquid interface is representing a metastable thermodynamic state, yet we do not observe nucleation of the wurtzite phase in the time scale of our simulations. This is a warning against overconfidence in the two-phase simulation method. It may be free from superheating effects, but only if we know in advance which solid phase coexists with the liquid. The problem is not solved by cooling the liquid in one-phase MD simulations. We have tried this and always observed that the liquid crystallizes into a rock salt lattice (with some defect concentration, due to the kinetics of the process). As  $T_{m,0}$  and  $T_c$  are quite close in MgO, and substantial supercooling is required in the MD simulations to make the liquid crystallize, this brings the temperature lower than  $T_c$  and therefore in the region of rock salt thermodynamic stability.

Another important comment is that the triple point for the coexistence of  $B1$ ,  $B4$ , and liquid phases is located at  $\approx 10$  GPa because the  $B1$ - $B4$  coexistence line exhibits an appreciable curvature. For the rock salt lattice, we observe that the equilibrium volume always increases when the pressure is raised from  $-8.5$  to 0 GPa along the coexistence curve, which means that the thermal expansion effect is dominant. The wurtzite lattice, on the contrary, is much more compressible and shows a continuous volume decrease from  $-7.8$  to 0 GPa; that is, the pressure effect dominates. Despite this volume decrease, the entropy of the wurtzite phase increases faster with temperature along the coexistence curve, as compared to the rock salt entropy.

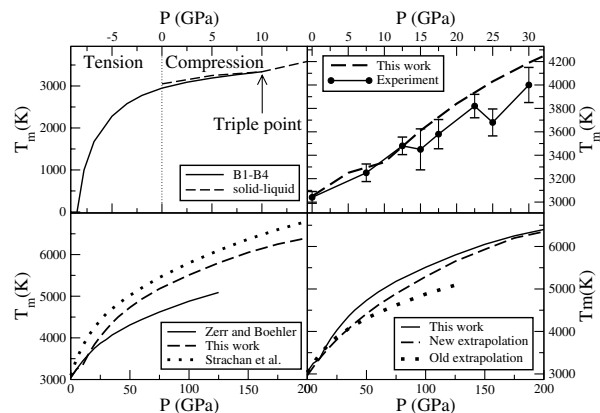


FIG. 2. Phase diagram of MgO as obtained from our first-principles force field. In the upper left part,  $B1$ - $B4$ ,  $B4$ -liquid, and  $B1$ -liquid coexistence curves are shown; upper right: comparison to experimental [7] melting results; lower left: comparison to experimental extrapolation [7] and other theoretical results [6]; lower right: comparison with a new extrapolation, derived here by employing only  $B1$ -liquid coexistence data (see text).

Both effects act to reduce the slope of the coexistence curve by approximately 70% in the range of tensile pressures, thus enlarging the stability range of the wurtzite phase for positive pressures more than could have been anticipated, given the proximity of  $T_c$  to the rock salt melting temperature. Finally, we stress that, for pressures larger than 50 GPa, liquid simulations employing 216-atom supercells show crystallization at the corresponding coexistence temperatures, implying the existence of strong finite size effects. Similar effects have been observed in simulations of molten silica [23]. This is to be expected from the quite long-ranged spatial correlations for molten MgO observable in the partial distribution functions of Fig. 1.

The presence of a slope discontinuity in  $T_m(P)$  implies, in principle, that the extrapolation procedure employed by ZB [7] to predict melting temperatures of MgO at lower-mantle pressure conditions is not justified. In Fig. 2, we compare ZB's extrapolation with that obtained by exchanging the experimental results for  $P \leq 10$  GPa with our simulated results for B1-liquid coexistence, in an attempt to avoid any discontinuity. This new extrapolation is even more consistent with our results. We obtain  $T_m(130 \text{ GPa}) = 5850 \text{ K}$ , which is 700 K higher than the ZB prediction, and significantly higher than the estimated temperature for the core-mantle boundary (CMB) of  $\sim 4000 \text{ K}$ . Recent work [24] strongly indicates that  $\text{MgSiO}_3$  undergoes a similar solid-solid transition at thermodynamic conditions close to those of the CMB. Such a transition could introduce another slope discontinuity in the melting curve of  $\text{MgSiO}_3$ , which would not be reproduced by an extrapolation procedure. Therefore, it is still too soon to decide whether the geophysically relevant conclusion advanced by ZB [7], namely, that  $\text{MgSiO}_3$  perovskite is not the low melting phase in the MgO-SiO<sub>2</sub> system at high pressure, is valid.

The main message to be extracted from this study is that melting may be a complicated process even for a relatively simple mineral such as periclase. We emphasize, in closing, that present results provide only one plausible explanation for the existing discrepancies regarding the melting curve of periclase. We have not considered the free surface of the material, or the effect of nonhydrostaticity, and there might well be alternative explanations for these differences. Also, as mentioned in the introduction, the method

for identification of the melting point in the experiments might be questioned.

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