Melting slope of MgO from molecular dynamics and density functional theory

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We combine density functional theory (DFT) with molecular dynamics simulations based on an accurate atomistic force field to calculate the pressure derivative of the melting temperature of magnesium oxide at ambient pressure—a quantity for which a serious disagreement between theory and experiment has existed for almost 15 years. We find reasonable agreement with previous DFT results and with a very recent experimental determination of the slope. We pay particular attention to areas of possible weakness in theoretical calculations and conclude that the long-standing discrepancy with experiment could only be explained by a dramatic failure of existing density functionals or by flaws in the original experiment. © *2009 American Institute of Physics.* [doi:10.1063/1.3238548]

I. INTRODUCTION

MgO is a major component of the Earth's mantle and so its thermodynamic properties at high pressures (P) and temperatures (T) are crucial to our understanding of its composition and evolution. It is arguably the simplest oxide,[1] being stable in the NaCl cubic structure at pressures up to at least 227 GPa at ambient temperature,[2] and its simplicity and abundance make it a natural starting point for attempts to understand and model oxides of geophysical relevance.[3]

Computer simulations based either on quantum mechanics or on atomistic force fields are playing an increasingly important role in geophysical research because the experimental difficulties at the extreme temperatures and pressures relevant to the Earth's mantle are considerable. However, for simulations to be of use, it is important to be able to rely on the accuracy of theoretical descriptions of interactions between atoms and to understand their limitations. When bonding can be described accurately and efficiently, simulations allow many physical properties of materials to be calculated at arbitrary temperatures and pressures. On the other hand, an inability to accurately calculate the properties of an oxide as simple as MgO would cast serious doubt on the suitability of computer simulations for quantitative studies of more complicated oxides such as $(Mg,Fe)SiO_3$ perovskite and $(Mg,Fe)O$ magnesiowüstite, which together make up about 90% of the lower mantle.

Both MgO and $MgSiO_3$ are known to melt at temperatures substantially above the geothermal profile; however, a quantitative determination of their melting temperatures (T_m) at high pressures is a crucial parameter in rheological, geodynamical, and chemical differentiation models of the lower mantle.[4,5] Viscosity models, for example, scale with the "homologous" temperature (T/T_m), T being the actual temperature along the geotherm.[6] Chemical differentiation in the early, partially molten state of the mantle must have occurred at temperatures above the $MgSiO_3/MgO$ solidus, which is in turn determined by T_m of the end members.

Until recently, only one experimental measurement of the melting temperature of MgO at high pressure existed[7] and this extrapolated to a rather low value of 5000 K for the melting temperature of MgO at core-mantle boundary pressures (130 GPa). If correct, this would imply that viscosity in the lower mantle is dominated by atomic diffusion in MgO (Ref. 4) and suggest that partial melting may be the cause of the seismic anomalies at the bottom of the mantle.[5] However, atomistic modeling has consistently yielded a much steeper increase (dT_m/dP) in the melting temperature of MgO with pressure.[3,8–13] The theoretical estimates of dT_m/dP range from 88 K/GPa (Ref. 11) to 270 K/GPa,[8] while Zerr and Boehler found a value of 36 K/GPa.[7]

Because the melting slope is related through the Clapeyron relation ($dT_m/dP = T_m\Delta V/\Delta E$) to fundamental physical properties of the material such as the change in molar volume upon melting (ΔV) and the latent heat ΔE, if the results of Zerr and Boehler were correct, it would point to a dramatic failure of atomistic models. However, even at low pressures, there are considerable difficulties associated with experimental measurements of the MgO melting point.[14] Ronchi and Sheindlin reported a zero pressure melting point of 3250 ± 20 K,[14] which differs significantly from the value of 3040 ± 100 measured by Zerr and Boehler. Further doubt has been cast on Zerr and Boehler's measurements by a very recent experiment in which Zhang and Fei extrapolated a value of $dT_m/dP = 221$ K/GPa from measurements of melting of (Mg,Fe)O solid solutions at high pressure.[15]

Here we combine molecular dynamics simulations with density functional theory (DFT) to determine the melting

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slope of MgO. There have been two previous calculations of the melting slope that relied heavily on DFT—one by Alfé[12] and one by Aguado and Madden.[13] Our calculations are intended to complement these studies and to demonstrate that, relative to the large discrepancy between the calculated melting slope and that measured by Zerr and Boehler, there is agreement between values of the melting slope calculated by different groups using DFT. The calculations are also in better agreement with the work of Zhang and Fei.

We pay particular attention to analyzing possible sources of error in our calculations and in previous calculations. Our calculations indicate that the rate of increase in the melting temperature with pressure is between three and five times steeper than reported experimentally by Zerr and Boehler. Furthermore, this discrepancy does not appear to be explainable by statistical uncertainties in our calculations or by differences in the description of interatomic forces between the model potentials that we use for efficient statistical sampling and DFT. We are forced to conclude that either the local and generalized-gradient approximations (GGAs) to DFT fail spectacularly for solid and/or liquid MgO or there are problems with the experimental results of Zerr and Boehler. Such a dramatic failure of density functionals for a material as simple as MgO would be very surprising and, to our knowledge, unprecedented. Therefore, given that the experiment of Zhang and Fei casts doubt on the results of Zerr and Boehler, it seems likely that current models of viscosity for the Earth's mantle which rely on these results need to be revised.

II. PREVIOUS CALCULATIONS

Many of the early calculations of the melting slope were performed using empirical atomistic models. These are potential energy functions of the atomic coordinates that were parametrized using low-temperature experimental or DFT data for crystalline MgO. There are several potential problems with these calculations. One potential problem is that many of these atomistic models do not adequately describe electronic effects, such as ionic polarization, that may have a significant impact on thermodynamics. This is of particular concern for pairwise-additive force fields which do not contain any phenomenological representation of the response of electrons on an ion to changes in the ion's environment. A second potential problem is that the data to which these atomistic models were fitted do not relate directly to the relevant thermodynamic (P, T) conditions and do not relate directly to the liquid state. This means that one can be less confident of the models' applicability under these conditions where disorder and changes in volume may alter the electronic structure. Finally, if the quantity of data to which a model is fitted is small it is relatively easy to achieve a good fit. However, one can never be sure that this fit results in a good underlying description of the forces on the ions. For these reasons, it is difficult to assess the reliability of calculations of the melting slope that are based on these purely empirical atomistic models.

Parameter-free (or first-principles) approaches based on DFT and on the full description of the quantum electronic ground state have proven to be much more accurate and reliable than conventional force fields for the calculation of the static and vibrational properties of crystalline MgO at low temperature.[16] A serious drawback of first-principles approaches, however, is their computational expense, which limits simulations to short time and length scales. Therefore, statistical sampling is usually poor and the precision with which thermodynamic properties can be calculated is low. Nevertheless, recent methodological advances and increasing computational resources have allowed the study of high-T thermodynamic properties of minerals in a few cases, including melting[17] and thermoelasticity.[18] To find the reason for the discrepancy between theory and experiment on the melting slope of MgO, we will attempt to rule out as many of the possible reasons for this discrepancy as we can. Because simulations that rely solely on empirical or semiempirical atomistic force fields yield calculated melting slopes that differ by up to a factor of 3 and because their accuracy is very difficult to assess, we must assume, for the sake of the present argument, that they are untrustworthy. Therefore, we consider only the more recent calculations of dT_m/dP that have been performed with substantial help from first-principles calculations.

Alfé calculated the melting slope of MgO without any reliance on atomistic force fields by performing first-principles molecular dynamics. He found a value for the melting slope of 102 ± 5 K/GPa.[12] However, we cannot rule out the possibility that his results are affected by uncertainties arising from short equilibration times and production runs. Aguado and Madden, on the other hand, substantially reduced the probability of poor equilibration and substantially increased the precision with which thermodynamic properties are calculated by using a highly accurate atomistic potential that has been parametrized using DFT.[13] Equilibration and statistical sampling have been performed with this relatively efficient force field and they used DFT to check the accuracy of the calculated energy differences between solid and liquid. They found a melting slope of 125 K/GPa. Although the force field that they used is very good, the configurations that they generated to calculate energy and volume differences cannot be trusted as much as those that would be calculated if dynamics had been performed on the DFT potential energy surface. For example, they parametrized their potential by fitting to DFT calculations of configurations from a number of different solid phases. There is no guarantee that their force field would be transferable to the liquid if the liquid structure differed strongly from these crystals.

In this work, we calculate the melting slope using a similar approach to that of Aguado and Madden. We minimize finite-size effects and maximize the lengths of equilibration and production simulations by performing molecular dynamics with a highly accurate and sophisticated atomistic force field.[19] We use perturbation theory to correct the small differences between our force field's description of the potential energy surface and that of DFT. We also take precautions to ensure that the configurations generated by our force field are very close to those that would be generated directly from the

DFT potential energy surface: We parametrize this model by fitting to DFT forces, stresses, and energies calculated on the hot solid *and the liquid*; we also perform a first-principles molecular dynamics simulation of liquid MgO to verify that we get a liquid structure that is very similar to that produced by our force field.

An important conclusion of the present work is that, on the scale of the discrepancy between theory and experiment, there is relative agreement between calculations of the DFT melting slope. It is important to note that there have been DFT-based calculations whose results differ strongly from those of Alfé, Aguado and Madden, and us. However, we draw a distinction between DFT-based calculations that simply use models that rely to some extent on DFT and calculations of the DFT melting slope. The latter are calculations which arrive at a close approximation of the melting slope that would be obtained from large scale molecular dynamics simulations on the DFT potential energy surface. As an example of the former kind of calculation we consider the study by Strachan *et al.* who calculated the melting curve using a model that was fitted to the DFT equations of state (equilibrium volumes, bulk moduli, etc.) of the B1 and the high pressure B2 phases of MgO as well as the shear stresses along the transformation path between them. Therefore, this fit was to a very small amount of *zero temperature* DFT data and the resulting force field was used directly to compute the melting line.

The fit of our models is to high-temperature solid and liquid DFT data and we converge this fit with respect to the quantity of DFT data (~5000 numbers are typically required).[19] The closeness of the fit[19] and the effectively infinite amount of data used in the fit allows us to be confident that the force field provides a very accurate description of the forces on the ions. However, the crucial point, as explained below, is that the role of our model is only to provide us with realistic statistically independent hot solid and liquid configurations. The melting slope is computed by performing DFT calculations directly on these configurations so that, by first-order perturbation theory, we arrive at a close approximation to the DFT melting slope. Furthermore, we estimate the closeness of this approximation below. So, despite the fact that we have a very accurate DFT-parametrized model, our goal is not to calculate this model's melting slope but to use it as a stepping stone to calculate the DFT melting slope.

Semiempirical DFT calculations were performed by Cohen and Gong;[8] however, their potential-induced-breathing model imposes unphysical constraints on the density. For example, it is known that oxygen ions are highly polarizable but, within their approach, they remain spherically symmetric. This results, among other effects, in a vast overestimation of longitudinal optical phonon frequencies.[20] It is not known how oxygen polarization affects the structure of liquid MgO, for example, but it is clear both from our classical and from our *ab initio* molecular dynamics simulations that oxygen ions acquire large dipoles in the disordered solid and in the liquid.

III. CALCULATIONS

We determine the melting slope dT_m/dP of MgO at zero pressure by using the Clapeyron relation. We calculate ΔV and ΔE with classical molecular dynamics and apply corrections to them using DFT.

DFT calculations were carried out within the local density approximation (LDA) using norm-conserving pseudopotentials with and without core corrections[21] for Mg and O, respectively, and a plane wave basis set with 120 Ry energy cutoff. Simulation cells contained 64 atoms and the Brillouin zone was sampled with the Γ-point. Tests with eight k-points yielded negligible ($<1\%$) differences on solid-liquid energy differences with respect to Γ-point sampling.

In spite of their lower accuracy, model potentials can speed up considerably the task of calculating ΔV and ΔE from first principles if they are used as a "reference" model for the first-principles potential.[22] The model potential is used to generate statistically significant atomic configurations at the P-T conditions of interest and the first-principles values of ΔV and ΔE are then obtained by performing DFT calculations on those configurations only. We will show that, thanks to the quality of the model potential used in this work, the errors introduced by this procedure are significantly smaller than those intrinsic to the standard approximations to DFT, which therefore remains the main source of uncertainty in our calculations. In order to achieve such a level of precision we use a model potential for MgO recently developed by us, which accounts for arbitrary aspherical distortions of the oxygen valence shell.[19] Its parameters are obtained by best fit to DFT forces, stresses, and energy in atomic configurations which are representative of the physical conditions of interest.[23] For this study we have used one potential (Φ_l) which was optimized in the liquid at 3000 K and P =0 GPa and another (Φ_s) which was optimized at the same P-T conditions in the solid. Average energies were set to be identical to the DFT values (this can trivially be imposed through an arbitrary additive constant). For both potentials, phonons, thermal expansion, and equations of state across a wide range of temperatures and pressures are in very good agreement with experiments and with independent DFT calculations.[19]

Figure 1 shows ΔV and ΔE as extracted from long (~100 ps) molecular dynamics simulations of the solid (with Φ_s) and the liquid (with Φ_l) in a range of temperatures close to the experimental values for T_m [3040 ± 100 K (Ref. 7) or 3250 ± 20 K (Ref. 14)]. Simulations were performed in cells containing 512 atoms under periodic boundary conditions. We verified that finite-size effects on volume, compressibility, and thermal expansivity were negligible with this cell size.

The first-principles values of ΔV and ΔE can be obtained by series expansion in the difference between the reference potential and the first-principles potential.[22] The first-principles energy can be obtained as

$$E_{fp} = \langle \Phi_{fp} \rangle_{fp}$$
$$= \langle \Phi_{mp} \rangle_{mp} + \langle \Phi_{fp} - \Phi_{mp} \rangle_{mp} + \beta$$
$$\times \langle (\Phi_{fp} - \langle \Phi_{fp} \rangle_{mp})(\Phi_{fp} - \Phi_{mp}) \rangle_{mp} + O(\beta^2),$$
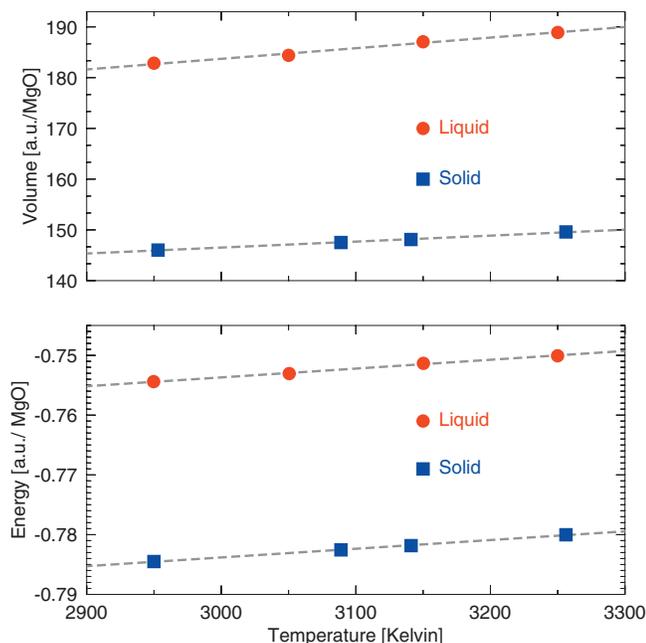
FIG. 1. Energy and volume of liquid and solid MgO as a function of temperature from molecular dynamics simulations.

where Φ_{mp} is the model potential (Φ_s or Φ_l), Φ_{fp} is the first-principles potential, $\beta = 1/k_B T$ (k_B is the Boltzmann constant), and statistical averages on the model or first-principles potential are indicated with $\langle \cdots \rangle_{mp}$ and $\langle \cdots \rangle_{fp}$, respectively. Similarly, for the first-principles value of the molar volume we have, to lowest order in β and ΔV: $V_{fp} \simeq V_{mp} + V_{mp} K_T \langle P_{mp} - P_{fp} \rangle_{mp}$, where $P_{fp,mp}$ is the pressure calculated from first principles or with the model potential and K_T is the isothermal compressibility. The first-principles value of ΔE (ΔV) is then obtained as the difference between the values of E_{fp} (V_{fp}) in the liquid and in the solid.

We computed E_{fp} and V_{fp} at 3070 K and $P = 0$ GPa both in the liquid and in the solid by using 20 statistically independent configurations extracted from a long molecular dynamics run with the model potential. Each configuration was separated from the previous one by tens of picoseconds. Because the potentials have been arbitrarily given an energy offset so that $\langle \Phi_{fp} - \Phi_{mp} \rangle_{mp} = 0$ at 3000 K, the first significant term of the series expansion for the energy is the linear term in β. We verified that this term is indeed very small (-4.3 K in the liquid and -2.6 K in the solid), which implies that higher terms can be safely neglected.

The same holds true for the volume, where we find that $\langle P_{fp} - P_{mp} \rangle_{mp} = 0.06$ GPa, with a mean square deviation of 0.4 GPa, which means that uncertainties in the determination of the first-principles volumes are of the order of 1%.

The very good performance of our model potential on the thermal expansion for the solid phase[19] suggests that the agreement on ΔV between DFT and the potentials in Fig. 1 can be extended to all temperatures in the vicinity of 3070 K. A similar conclusion can be reached for the energy difference based on the fact that energy fluctuations, and therefore heat capacities,[24] are correct to within 10%.[19] We can summarize the above considerations by saying that the data of Fig. 1 represent the first-principles values of ΔE within 10% and of ΔV within 2%.

What is clear from Fig. 1 is that neither ΔV nor ΔE is strongly temperature dependent and that the melting slope, therefore, depends approximately linearly on the melting temperature. The uncertainty in T_m (and therefore dT_m/dP) is of the order of $\sim 10\%$ which is much less than the discrepancy with experiment on dT_m/dP ($>300\%$) which we want to address in this work. Fits of straight lines to the data of Fig. 1 yield

$$\Delta E = 0.0295 + 1.97 \times 10^{-7} T,$$

$$\Delta V = 9.71 + 9.16 \times 10^{-3} T. \tag{1}$$

From this we can calculate melting slopes ranging from $dT_m/dP = 130$ K/GPa if $T_m = 3050$ K to $dT_m/dP = 145$ if $T_m = 3250$ K.

For the sake of completeness, we have attempted a determination of T_m. This was achieved by first calculating the melting temperature of Φ_l by means of the two-phase method[9] and then correcting the results using perturbation theory.[22] A simulation cell containing 1024 atoms was used for the two-phase method. Previous investigations[9,10] have concluded that the finite-size effects are negligible with this size. We find that $T_m = 3010 \pm 50$ K for Φ_l, the error reflecting only statistical uncertainties related to the two-phase method and not other systematic errors due to the optimization procedure or to approximations to DFT. However, we caution that, in this simulation, potential Φ_l is used to describe both the liquid and the solid phases, at variance with the calculations of ΔV and ΔE where two different potentials were employed to describe the liquid and the solid and which therefore resulted in a much more accurate calculation. From Eq. (1), therefore, we find that the value of the melting slope calculated with our model potential, before DFT corrections have been applied, is 127 K/GPa. We can calculate DFT corrections to the Gibbs free energy difference between solid and liquid using the method described in Ref. 22. If we do so, we find that the DFT Gibbs free energy differences are 17% larger than those calculated with the model potential, indicating that the model potential overstabilizes the liquid with respect to the DFT potential. This brings about a similar correction for T_m,[22] so that the "DFT" value of T_m is estimated to be about 3500 K and the melting slope 156 K/GPa.

We have used DFT to correct the values of ΔV and ΔE obtained with our model potential and, as a result, can be confident that we have calculated the free energy difference between the solid and the liquid generated from Φ_l with very close to DFT accuracy. However, there remains the possibility that the structure of the liquid generated by Φ_l is not realistic. Given the accuracy of this potential and that it has been parametrized from DFT calculations of the liquid, this possibility would appear to require a liquid-liquid phase transformation that involves changes in the electronic structure of the ions that cannot be captured by our model's phenomenological representation of the electrons. It is important to consider this possibility; therefore, we have performed Car–Parrinello molecular dynamics (CPMD) simulations[25] of 64 atoms of liquid MgO at 3050 K. These simulations were performed at zero pressure using variable cell dynamics.[26] A small fictitious mass of $\mu = 100$ a.u. was used
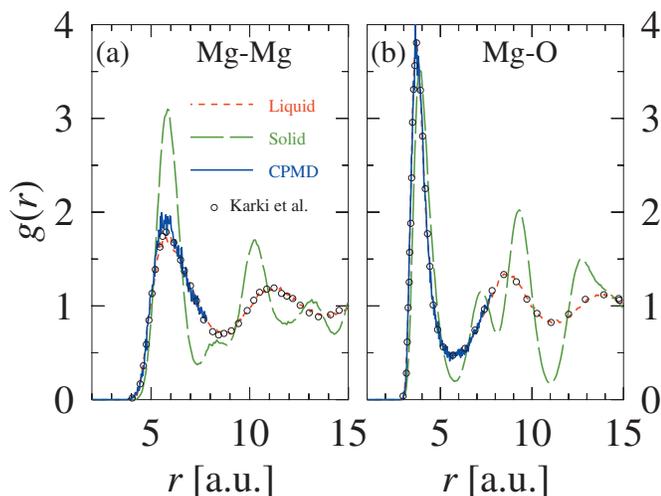
FIG. 2. Pair correlation functions of solid and liquid MgO at ~3100 K from molecular dynamics using a model potential compared to the results of first-principles molecular dynamics of the liquid. Both our CPMD simulations and Born–Oppenheimer molecular dynamics simulations by Karki *et al.* (Ref. 28) are presented.

and temperature and pressure were corrected as described in Ref. 27. The CPMD simulation was a continuation of a very long simulation using potential Φ_l. After 2 ps of equilibration with CPMD, a 1.5 ps production run was used to compute the radial distribution functions of the liquid. The results are plotted in Fig. 2 and compared with the results of Born–Oppenheimer molecular dynamics simulations carried out by Karki *et al.*[28] There is near-perfect agreement on the pair-distribution functions between the two independent first-principles simulations and our simulations of a 512-atom supercell using our model potential Φ_l. The agreement between the first-principles simulations seems to rule out major structural artifacts of the starting configuration in both simulations. The agreement with the structure of the liquid generated with Φ_l confirms the reliability of this potential and also appears to rule out large finite-size effects on the pair-distribution functions. The results presented in Fig. 2 are strong evidence that realistic liquid structures have been used to calculate DFT corrections to ΔV and ΔE and, therefore, that we have calculated these quantities with very close to DFT accuracy.

It is important to note at this point that our reported DFT results have been obtained within the LDA, as this approximation has proven to be very accurate in describing low-temperature properties. However, nonlocal corrections to the LDA, such as those contained in GGA theories, are known to have a significant effect on melting temperatures.[12,29] Therefore, as a test of the importance of exchange and correlation effects we repeated the analysis of energy differences with a GGA functional.[30] We find that average GGA energy fluctuations at 3000 K are within 12% of those calculated with the model potential. Moreover, we find that the correction to the Gibbs liquid-solid free energy difference is only 2.7%, which implies a value for the GGA T_m of 3090 K. This improves dramatically the agreement of T_m with experiment with respect to the LDA and confirms that exchange and correlation effects are indeed important in the determination of T_m. We

caution, however, that the potential was constructed by fitting LDA quantities, so it is possible that the atomic configurations chosen for the comparison were not fully representative of the GGA potential. We did not attempt a determination of ΔV with GGA as this would require a very expensive equilibration with the GGA functional. ΔV would have to be an order of magnitude larger than the LDA value to resolve the discrepancy with experiment on the melting slope, which is highly unlikely.

Alfé pointed out[12,31] that, because the energy gap between occupied and unoccupied electronic states is significantly smaller in the liquid than in the solid, it is more appropriate to perform DFT calculations with a finite electronic temperature. This results in a lowering of T_m by approximately 500 K. Consideration of this correction brings our LDA and GGA values of T_m into very good agreement with those of Alfé. Alfé reported that the correction to ΔE from this effect is almost 0.0036 a.u. per molecular unit. Because energy gaps calculated within LDA are generally too small (by as much as ~50%), the error incurred in ΔE is likely to be significantly smaller than this. In any case, for a fixed value of T_m, the reduction of ΔE by inclusion of the electronic entropy contribution to the free energy should *increase* the calculated melting slope, thereby bringing the calculated value even further from the experimental value of Zerr and Boehler.

IV. CONCLUSIONS

To summarize, we find that that the DFT/LDA value for the melting slope of MgO ranges from ~130 to ~150 K/GPa, depending primarily on the value chosen for T_m and with an overall uncertainty of about 10%–15% due to the model potential and to statistical sampling. We can safely conclude that the DFT/LDA result is a factor of 3–4 larger than the value of 36 K/GPa found in Zerr and Boehler's experiment.

There remains a small difference in the melting slopes calculated here and by Alfé. The source of this difference is unknown but may be due to differences in the details of the DFT calculations such as our different pseudopotential representations of the inert core electrons. The important point is that this difference is substantially smaller than the discrepancy with the experimental results of Zerr and Boehler. The present work, when taken together with the results of Alfé and Aguado and Madden, shows that on the scale of the discrepancy between calculations and experiment, there appears now to be a convergence of the results of calculations of the melting slope. The only major source of error that would affect all of these calculations is the approximation to the exchange-correlation energy. However, tests with a GGA exchange-correlation functional show that, although the choice of functional changes the values of T_m and dT_m/dP, these changes are relatively small. Therefore it seems highly unlikely that inadequacies of the DFT approximations used can fully explain the historical discrepancy between theory and experiment.

The possibility of problems with the experiment of Zerr and Boehler[7] has previously been suggested[3,9,32] and the fact

that there is a large disagreement between experimental measurements of both the melting temperature[7,14] and the melting slope[7,15] suggests that more experimental work is necessary. A determination of the density change and latent heat at zero pressure is crucial to resolve the issue. The disagreement between *our* DFT results and experiment could also be explained by assuming that the slope of the melting curve is initially very steep, but that it flattens out very quickly, perhaps due to a liquid structure which changes rapidly under pressure to being much more similar to the solid. However, this explanation would not be compatible with the findings of Alfé or Aguado and Madden, who explicitly computed the melting temperature at high pressures. Therefore, we must discount this possibility.

We note that the suggestion by Aguado and Madden that the discrepancy between theory and experiment can be explained by the existence of a solid phase with a lower free energy than the rocksalt structure cannot be correct. This is because, among possible solid phases, the one with the lowest Gibbs free energy has the highest melting temperature. Therefore, the melting curve for a more stable solid phase should lie above the rocksalt melting curve, i.e., it should have a higher T_m at every pressure P.

The geophysical implications of a steep melting slope for MgO are manifold.[12,15] A steep melting slope implies that the melting temperature of (Mg,Fe)O, of which MgO is an end member, is likely to be substantially higher than the geotherm and comparable to the melting temperature of $(Mg,Fe)SiO_3$ at lower mantle conditions. This suggests, among other consequences, that large scale melting may never have occurred in the mantle.[5]

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