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Molecular dynamics simulation of phase transitions and melting in $MgSiO_3$ with the perovskite structure—Comment

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Chaplot et al. (1998) purport to simulate $MgSiO_3$-perovskite melting. Instead, the paper contains simulations of a thermal instability.

One can define thermal instability of a crystal lattice as a mechanical instability induced by temperature. The temperature of thermal instability can be found by gradual increase of temperature until the sudden change of properties appears. This is exactly what was performed by Chaplot et al. The temperatures of thermal instability of the ideal lattice were high compare to experimental. Recognizing the possibility of overheating, Chaplot et al. carried out simulations to determine temperatures of thermal instability of the lattice containing 1% vacancies. The lattice with defects is less stable than the ideal lattice, therefore, the temperature of thermal instability for defect structure was lower than for the ideal lattice. Still, neither the simulation of ideal nor defect structures answered the question: What is the melting temperature of the $MgSiO_3$-perovskite with the accepted model of interatomic interaction?

Melting and thermal instability are different phenomena. Temperature of melting (T_{melt}) is defined as the temperature where Gibbs free energies of crystal and liquid phases are equal. Morris et al. (1994) showed that calculating T_{melt} by calculating Gibbs energies is equivalent to finding T_{melt} from two-phase simulations. The question is how much melting temperatures could differ from temperatures of thermal instability calculated by Chaplot et al. for ideal lattice? An exact answer could be provided by the direct comparison of two methods, as was done by Belonoshko (1998) for melting of corundum. In absence of this comparison, we can refer to other studies to obtain an approximate values of overheating in Chaplot et al. calculations.

Matsui and Price (1991) and Belonoshko (1994) have studied the melting of perovskite. Matsui and Price (1991) has calculated T_{inst}, whereas Belonoshko (1994) applied the two-phase method to calculate T_{melt}. Interesting, an application of correct method allows to reach good agreement with experiment (Fig. 1). The same model of interatomic interaction was applied in both studies. From the comparison it follows that T_{inst} is higher than T_{melt} by about 1500 K at the pressure of 25 GPa. Because overheating increases with pressure (Belonoshko 1998), the value of 1500 K is likely to be a lower bound for overheating. The potential applied by Chaplot et al. is different from that applied by Matsui and Price (1991) and Belonoshko (1994). However, the common thing about both potentials is that they do reproduce experimental properties in good agreement with experiment (Belonoshko and Dubrovinsky 1996c). Belonoshko and Dubrovinsky (1996b) has demonstrated that a different potential may produce about the same melting curve if experimental data is reproduced. Therefore, we can rather safely accept the estimate of 2000 K for overheating in calculations by Chaplot et al. when the ideal structure was studied. As for temperatures of thermal instability of defect lattice, it is not clear how much they differ from true melting temperatures (true with respect to correctly calculated for the accepted model). In fact, T_{inst} of defect structure can be higher or lower than T_{melt}. It is possible to determine how many atoms should be taken out from an ideal structure to make it collapse at, e.g., room tem-

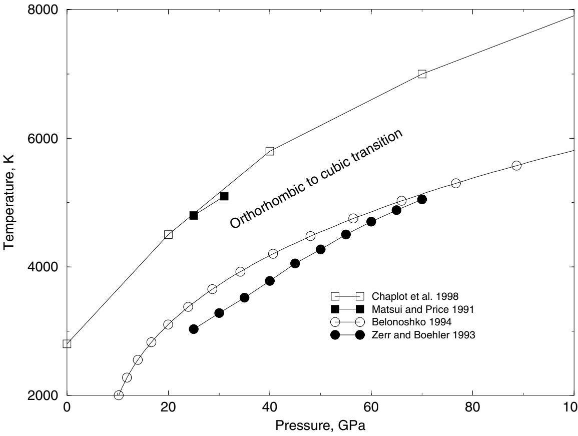

FIGURE 1. Pressure dependence of melting temperatures of $MgSiO_3$-perovskite as suggested in the studies indicated on the legend. Matsui and Price (1991) and Chaplot et al. (1998) calculated curves provide temperatures of thermal instability, not melting temperatures, as purported. The 2-phase simulations by Belonoshko (1994) for the Matsui and Price (1991) model produces melting temperatures in close agreement with experimental data. The curve shown is a digitization of the curve used by Zerr and Boehler (1993) to represent their experimental data. The text "orthorhombic to cubic transition" is placed as close as possible to the range where it was calculated by Matsui and Price (1991) and Chaplot et al. (1998).

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perature.

From the Figure 1 the pressure-T_{inst} curve is higher than experimental melting curve by about 2000 K, depending on pressure. It is likely, that if Chaplot and co-authors would use two-phase simulation method (e.g., Belonoshko and Dubrovinsky 1996a) then their melting curve would match experimental curve closely, as is the case with the simulation by Belonoshko (1994).

The orthorhombic to cubic perovskite transition found by Chaplot et al. occurs at the temperatures close to T_{inst}. It is likely that the transition is above the melting temperature and should be regarded as an artifact of erroneous simulation of melting. The same transition was observed by Matsui and Price (1991). Again, above the melting temperature (Belonoshko 1994). Chaplot et al. observed that the orthorhombic to cubic perovskite transition is accompanied by melting of the oxygen sublattice. A similar feature was observed by Belonoshko (1998). However, because Belonoshko (1994), in contrast to Chaplot et al., has calculated melting temperature, he was able to distinguish that phenomena as an artifact. Similar high ionic diffusion was found by Zhou et al. (1997) when conducting MD simulation of neighborite in the close vicinity of "melting" (as we now understand, possibly above T_{melt} but below T_{inst}). Zhou et al. (1997) wrote that the phenomena was similar to what was observed by Matsui and Price (1991)—and now we know that that was an artifact.

The major point of this comment is that one has to model melting correctly. Otherwise it is not clear if results of simulation are meaningful or rather concerned with phenomena in the metastably overheated range. Several studies calculated melting in the style of Chaplot et al., known also under the name HUIY (heat-until-it-yields). Using HUIY method, MD simulated "melting" was reported in a number of studies (e.g., Boehler et al. 1997; Cavazzoni et al. 1999; Matsui and Price 1991; Vocadlo and Price 1996; Zhou et al. 1997).

A huge variation in melting temperatures exists in part because some studies claim to calculate melting (e.g., Chaplot et al. 1998), but instead provide calculations of instability whereas others indeed simulate melting (e.g., Belonoshko 1994).

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