

A simulation study of induced failure and recrystallization of a perfect MgO crystal under non-hydrostatic compression: Application to melting in the diamond-anvil cell

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ABSTRACT

Recent experimental studies revealed that the thermal pressure in a diamond-anvil cell with laser heating can be large. Accounting for this pressure is therefore important for treatment of experimental results. In earlier studies, we developed an MgO model that was demonstrated to perform very well for calculations of thermoelastic properties. Here, we study the effect of thermal stress on the behavior of MgO under high pressure and temperature conditions using molecular dynamics and the earlier developed interatomic potential. The simulations show that thermal stress can produce such effects as dynamic recrystallization, which may be interpreted as onset of convective-like motion and which may cause a change in the slope of laser power-temperature curve. Because these two criteria are used for the identification of melting, it is possible that what was interpreted as melting in previous experiments with MgO was in reality recrystallization.

INTRODUCTION

The use of the diamond-anvil cell (DAC) experimental technique with laser heating has generated a significant advance in our knowledge of material properties under extreme pressure (P) and temperature (T) conditions (e.g., Boehler and Chopelas 1991; Jephcoat and Besedin 1996). Simultaneously, advances in computational methods allow us to assess material properties with increasing reliability. Obviously, neither experimental techniques nor computational methods are perfect. It is of crucial importance to examine carefully the reasons for any discrepancy between experiment and theory each time it appears. It helps us to advance both theoretical and experimental methods, and it is especially important when experimental results are either controversial as in the case of MgSiO₃ perovskite melting (e.g., Knittle and Jeanloz 1989; Zerr and Boehler 1993) or are not yet confirmed by alternative experiments, as in the case of MgO melting (Zerr and Boehler 1994).

In this paper, we examine the possible reasons for the discrepancy between existing theoretical predictions (Belonoshko and Dubrovinsky 1996b, 1996c; Cohen and Gong 1994; Cohen and Kluge 1995; Cohen and Weitz 1996; Jackson 1977; Ohtani 1983; Vocadlo and Price 1996) and experimental measurements (Zerr and Boehler 1994) of the melting curve of periclase. As one can see from Figure 1, all the available theoretical predictions provide significantly higher melting temperatures at high pressure than those measured experimentally. Among the eight predictions shown in Figure 1, the melting curve by Cohen and Gong (1994) shows significantly higher temperatures than the other seven. The explanation of these erroneously high melting temperatures was provided by

Belonoshko and Dubrovinsky (1996b). Barring the melting curve of Cohen and Gong (1994), the remaining seven predictions are internally consistent, and the ability of MD simulation to predict correctly the room pressure melting temperature of periclase was also demonstrated by Ferneyhough et al. (1994). Vocadlo and Price (1996) used three interatomic potentials in their simulations and obtained close results. Their melting curves are somewhat higher than that calculated by Belonoshko and Dubrovinsky (1996b, 1996c) at high pressures. This can be explained by the different potentials used, unavoidable overheating in their simulation or both. Cohen and Kluge (1995) calculated the melting curve of periclase, which is somewhat lower than the curve by Cohen and Gong (1994) and is more consistent with the Belonoshko and Dubrovinsky (1996b, 1996c) predictions. Recently, Cohen and Weitz (1996) provided a melting curve that is also generally consistent with the other molecular dynamics predictions.

Therefore, there is a consistent set of theoretical predictions of periclase melting (in fact, the degree of consistency has no precedent in the literature) and an experimental determination, which provides significantly lower melting temperatures at high pressures in relation to the predictions. The difference between experiment and theory amounts to more than 1000 K at 30 GPa. Notwithstanding the fact that temperature measurements in the DAC are subject to some errors owing to the neglect of the dependence of emissivity on temperature and pressure, which can amount up to 300 K at temperature of 4000 K (Shen 1994; Zerr and Boehler 1994), the difference of more than 1000 K cannot be explained solely by that. Of course, one can argue that all the theoretical pre-

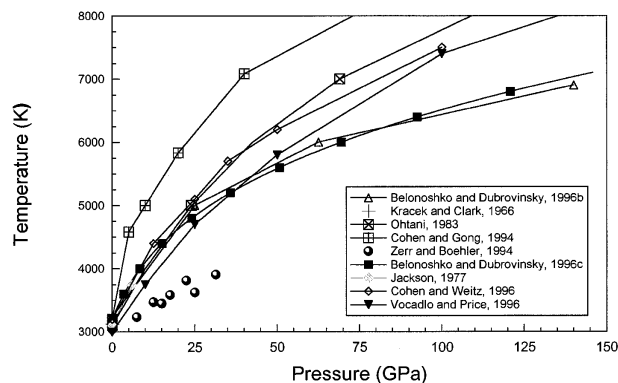


FIGURE 1. The existing data on the melting of periclase. All theoretical predictions are internally consistent up to 30 GPa, except the one by Cohen and Gong (1994), which is likely to be erroneous (Belonoshko and Dubrovinsky 1996b). The predictions by Ohtani (1983) and Belonoshko and Dubrovinsky (1996b) are different above 30 GPa most likely because of Ohtani's (1983) extrapolation of the melting curve by the Simon (1930) equation.

dictions are incorrect. However, because of the consistency among many theoretical predictions, we decided to examine in detail the experimental technique that might be responsible for the discrepancy.

It is well known that because of the particulars of the experimental technique the sample in a DAC is heated inhomogeneously. It is appreciated that such inhomogeneous heating influences the precision of temperature measurements (Heinz et al. 1994; Boehler and Zerr 1994). This, in our opinion, is not the only consequence of inhomogeneous heating. Indeed, the temperature gradient across the sample is enormous, amounting up to 600 000 K/cm at temperatures near 3000 K (Shen 1994). A gradient of about 200 000 K/cm is quite usual when a sample is heated to about 2000 K (Boehler et al. 1990). Such gradients are likely to have some influence on the measured properties of a sample. Note that the use of a hydrostatic (or rather quasi-hydrostatic) pressurizing medium does not avoid thermal stress. Thermal stress always exists in a solid when heated inhomogeneously. This is an elementary physical fact, which can be proved by inhomogeneous heating of a solid in such a hydrostatic medium as air under ambient conditions. Such arguments as equality of measured values of pressure in the pressurizing medium before and after heating have no bearing on the thermal stress in a sample. The nature of thermal pressure can easily be understood. The outer part of a sample remains essentially cold, and this maintains the same volume of a sample during partial heating (of its part). Naturally, pressure in the heated part of the sample during heating is higher than compared to that before heating because the volume has been maintained constant by the unheated portion of the sample. Some relaxation decreases thermal pressure, but it is not sufficient to release the stress completely because the temperature gradient is maintained by inhomogeneous laser heating.

Thermal pressure (or rather stress, because it is clear that thermal pressure is different in differently heated parts of a sample) was assessed both theoretically (Heinz 1990) and experimentally (Andraut et al. 1996; Fiquet et al. 1996a, 1996b). These studies demonstrated that thermal pressure can be significant; for example, Fiquet et al. (1996a) obtained a thermal pressure of about 15 GPa when an MgO sample was heated to 3500 K. Experimental studies showed that stress in MgO can be significant and amount to up to 15 GPa at pressure of a few dozen GPa (Duffy et al. 1995). Other measurements gave value of stress up to 4 GPa (Weidner et al. 1994) at pressures up to 40 GPa (Meade and Jeanloz 1988).

Thus, there is a gap between theoretical studies of melting under hydrostatic conditions and experimental conditions, which are nonhydrostatic because of either thermal stress even when the pressurizing medium is quasi-hydrostatic or deviatoric stress when the medium is not hydrostatic. This study is aimed at filling this gap and at simulating the behavior of MgO at high temperature and non-hydrostatic stress.

Briefly, the pattern of the paper is as follows. We estimate thermal stress in a sample, making reasonable assumptions based on experimental data about the temperature distribution in the sample during laser heating. This provides us with the conditions for further simulation. We simulated a slab of MgO pressurized by argon and subjected to superimposed stress in the direction parallel to the slab. In the course of simulation under the conditions corresponding to the highest P - T in the Zerr and Boehler (1994) experiment (cold pressure of approximately 35 GPa and temperature of about 4000 K), we observed that when the applied stress is higher than 18 GPa, the slab begins to recrystallize. We calculated how large overestimation of the strength can be by comparing the simulated values of stress necessary for failure of MgO at 1 bar with the experimental data. We discuss further what impact recrystallization might have on visual observation and the power-temperature curve. We come to the conclusion that it is possible that the simulated process can be realized under experimental conditions and such phenomena might be interpreted as onset of melting.

JUSTIFICATION OF THE CONDITIONS FOR MD SIMULATIONS

We have to make some assumptions to calculate thermal stresses to which a sample in DAC is subjected. These assumptions actually reduce somewhat the values of calculated stresses. The periclase sample in the Zerr and Boehler (1994) experiment is approximately rectangular in shape with the dimensions $100 \times 100 \times <15$ μm . We neglect stress (and temperature gradient) in the direction perpendicular to the sample surface and assume that the sample has cylindrical shape [accounting for rectangular shape will lead to increase of resulting stress (Timoshenko and Goodier 1951)]. We neglect the perpendicular gradient not because we think it is not important, but simply because there is no experimental data on tem-

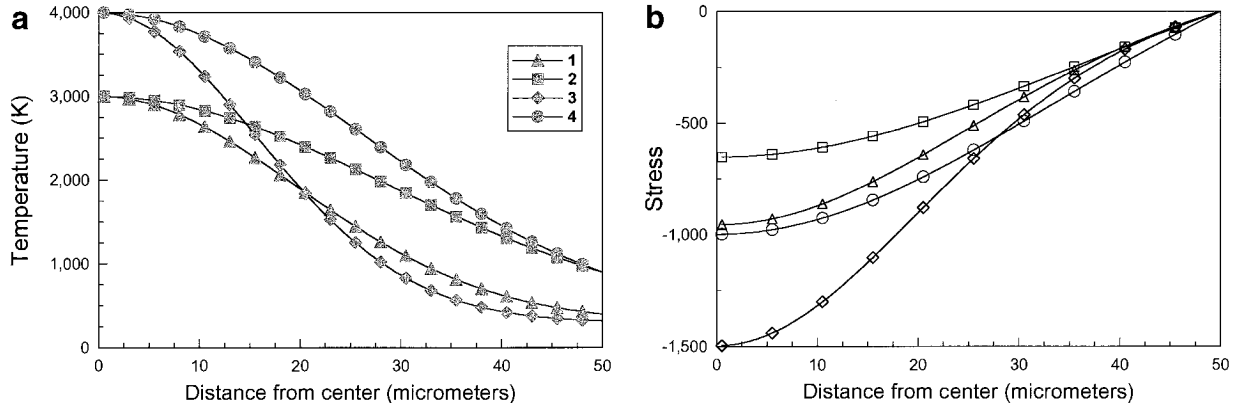


FIGURE 2. Assumed radially symmetric temperature distributions (a) on the surface of the sample in a DAC heated by a laser and corresponding values of the radial component of thermal stresses (b) as a function of distance from the center of a round sample, given in α Units; αE is equal to 7.3 bar/K at 3000 K and 1 bar and to 22.5 bar/K at 4000 K and 30 GPa, therefore, the approximate estimate of thermal stress ranges from 0.5 GPa at 3000 K and 1 bar to 3.3 GPa at 4000 K and 30 GPa in the range of Zerr and Boehler (1994) experimental conditions. Shape of symbols in (b) corresponds to the temperature distributions shown in (a).

perature gradient in the direction perpendicular to the surface of a sample. Accounting for the vertical temperature gradient would probably increase the total magnitude of the stress. If temperature $T(r)$ as a function of distance r from the center of sample is known, the radial (σ_r) and tangential (σ_θ) thermal stresses can be calculated as follows (Timoshenko and Goodier 1951):

$$\begin{aligned}\sigma_r &= \alpha E \left(\frac{1}{b^2} \int_0^b T r dr - \frac{1}{r^2} \int_0^r T r dr \right) \\ \sigma_\theta &= \alpha E \left(-T + \frac{1}{b^2} \int_0^b T r dr + \frac{1}{r^2} \int_0^r T r dr \right)\end{aligned}\quad (1)$$

where α is the thermal expansivity, E is the Young modulus, and b is the radius of the sample. Note that radial stress vanishes at the border of sample; therefore the requirement of mechanical equilibrium is fulfilled.

Boehler et al. (1990), Lazor et al. (1993), and Shen (1994) have shown that the temperature distribution across the sample can be described by Gaussian function. Indeed, such a distribution is justified by solving the heat transfer equation when a laser is the source of heat (Karlo et al. 1995). Therefore, for describing the temperature profile as a function of distance from the center of the hot spot, the following expression has been used

$$T(r) = (T_0 - 300) \exp\left(-\frac{r^2}{r_0^2}\right) + 300 \quad (2)$$

where T_0 is the value of temperature measured in the center of hot spot and r_0 is an adjustable parameter that can be determined either by assuming certain temperature at the border of the sample [slightly higher than room temperature (A. Zerr, personal communication)] or from reported values of temperature gradients (Boehler et al. 1990; Boehler and Zerr 1994; Heinz et al. 1994; Shen 1994).

The stresses were calculated with the use of temperature distributions shown in Figure 2a. These distributions

$[T(r)]$ were calculated assuming $T(0)$ as 3000 and 4000 K [approximately the lowest and the highest temperatures of periclase melting measured by Zerr and Boehler (1994)] and corresponding (Fig. 2a) values at the sample border; there are four combinations of $T(0)$ and $T(R)$ which were composed from high and low values in the center and at the border of a sample. Maximum temperature gradients are well within the limits of those measured in DAC (Lazor et al. 1993; Shen 1994; Shen et al. 1993). Using these $T(r)$, thermal stresses were calculated (Fig. 2b).

The analysis above shows that thermal stress can be significant, ranging from 0.5 to 4 GPa, depending on temperature distribution, and therefore needs serious consideration. The estimated values of thermal stress are in reasonable agreement with the values provided by Heinz (1990), which is not surprising because we used the same analytical procedure.

MOLECULAR DYNAMICS SIMULATION

The consideration of the thermal stress given above shows that previous simulations of the melting of MgO are not adequate for the conditions in the diamond anvil cell. We maintained hydrostatic conditions during a two-phase simulation (Belonoshko 1993; Belonoshko and Dubrovinsky 1996b, 1996c). Consideration of the thermal stress in DAC suggests that to make direct comparison between measured and simulated melting curves one has to carry out simulation under non-hydrostatic conditions. The goal of the present MD simulations is to study the behavior of MgO subjected not only to confining hydrostatic pressure but also to superimposed non-hydrostatic stress, which inevitably exists as a result of inhomogeneous laser heating.

It is well known that the theoretical approach provides significantly higher values of yield strength in comparison with experimental values (Selinger et al. 1993; Lynden-

Bell 1995). Several obvious reasons for that result include neglect of polycrystallinity, defects, particular orientation, and a very high pace of loading. To estimate the magnitude of overestimation of the strength of MgO, we decided first to calculate the impact of stress on MgO at low pressure where experimental data exist (Weidner et al. 1994) and then to proceed with simulations at 4000 K and 35 GPa, approximately the highest P - T conditions in the experiment of Zerr and Boehler (1994). The purpose of these simulations is to determine whether we can observe any drastic changes in MgO when we apply non-hydrostatic stress instead of hydrostatic pressure and what is the value of stress necessary to initiate such changes.

Computational cells at 1 bar and 35 GPa

To simulate the effect of stress on the behavior of a sample at 1 bar, we arranged computational cell in the way shown in Figure 3a. The cell consists of $8 \times 8 \times 4$ MgO unit cells with each unit cell containing 4 MgO formula units and contains 2048 atoms overall. The upper half of the cell remained empty. The vertical size was kept constant. Constant pressure (stress) was applied in X and Y directions.

The cell was arranged in a similar way to study the impact of stress at 35 GPa. In addition, we used 400 Ar atoms as the pressurizing medium placed above (in Z direction) the MgO part (Fig. 3b). The MgO part of the cell consisted of $6 \times 6 \times 6$ MgO unit cells with each unit cell containing 4 MgO formula units and with 1728 Mg and O atoms overall. The size in Z direction was chosen to correspond to initial pressure of 35 GPa and was kept constant during simulations. An additional (on top of the 35 GPa) stress was applied in the X and Y directions. Periodic boundary conditions have been applied in both cases as usual.

Interatomic interaction

The Mg-Mg, Mg-O, and O-O interactions have been calculated using the interaction potential (IP) described by Belonoshko and Dubrovinsky (1996b). The Ar-Ar IP was the same as applied for modeling Ar melting (Belonoshko 1992). The Ar-Mg and Ar-O interactions were calculated using the Ar-Ar IP. The variation of Ar-Mg and Ar-O interaction parameters within the range typical for fluids (Belonoshko and Saxena 1992) did not influence the obtained results.

Technical details of the simulations

The molecular dynamics simulations were carried out using the Parrinello-Rahman (1981) method. Temperature was maintained constant using the Nose-Hoover algorithm (Allen and Tildesley 1989; Hoover 1985; Nose 1984). Coulomb interactions were calculated using the Ewald technique. The time step ranged from 1 to 2 fs. Calculations were continued up to 20 000 time steps (up to 40 ps) if no drastic changes in moving averages were observed and for about 2000 time steps if such changes were observed. Such long computational experiments

with considerable number of atoms (more than two thousand) were possible with the use of IBM SP2 massively parallel computers (Maui and Stockholm High-Performance Computing Centers).

Simulations at 1 bar

The simulations at 1 bar were done to see how significantly we overestimate the yield strength of MgO. The stress in X and Y directions (in the plane of slab) have been gradually increased. At 300 K and up to 28 GPa no drastic changes were observed. At 32 GPa the slab failed and the resulting configuration was similar to the one shown in Figure 3c.

The same simulations were done at 3000 K. The maximum value of stress that the slab was able to sustain is about 8 GPa (Fig. 4). When the slab fails the a and b sizes decrease because the atoms begin to move into the empty half of the computational cell. The resulting configuration is liquidlike (Fig. 5) in full agreement with the results by Lynden and Bell (1995), who also noticed appearance of a liquidlike structure when crystal failed.

Since the yield strength measured by Weidner et al. (1994) is about 3 GPa at 300 K and decreases with increasing temperature, we can conclude that we overestimate the value of strength by about an order of magnitude as a result of the neglect of dislocations, vacancies, polycrystallinity, and the very high speed of loading.

Simulations at 35 GPa and 4000 K

The pressure and temperature conditions of these simulations were the highest melting P - T of the Zerr and Boehler (1994) MgO melting curve, approximately 4000 K and 35 GPa. The initial configuration was prepared in the following way. The size of MgO part was calculated using the equation of state (Belonoshko and Dubrovinsky 1996a, 1996b) at 4000 K and 35 GPa. This gave us the size of MgO cube equal to 24.24 Å. The argon part of computational cell was prepared by melting an fcc crystal of Ar at 4000 K and 35 GPa, maintaining the pressure in Z direction constant and the size in X and Y directions equal to 24.24 Å. Then the MgO and Ar parts of the cell were put together in the configuration shown in Figure 3b.

To model the impact of thermal pressure on the behavior of the sample, we kept the size in Z direction constant and applied cold pressure plus stress in X and Y directions. We chose cold pressure equal to 35 GPa and varied value of stress from 0 to 28 GPa. Simulations under hydrostatic pressure of 35 GPa at temperature 4000 K showed that the size and shape of the cell did not change. Only a slight change of Z size was observed because of the adjustment of Ar and MgO parts to each other to form the interface.

When the imposed pressure in X and Y directions became higher than 53 GPa (stress of 18 GPa), drastic changes in the behavior of the computational cell were observed (none of these changes was observed below 53 GPa). The MgO part of the sample started to recrystallize

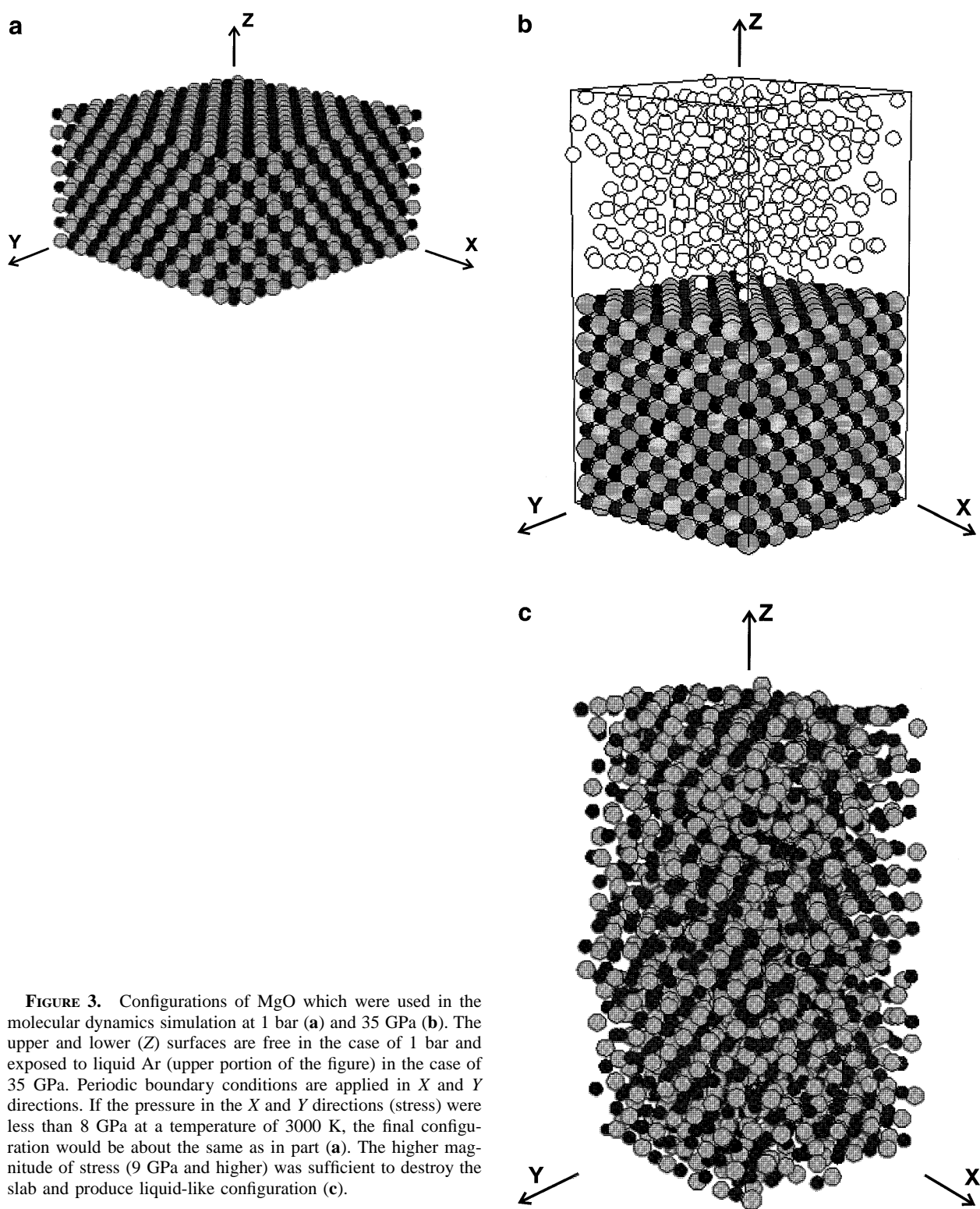


FIGURE 3. Configurations of MgO which were used in the molecular dynamics simulation at 1 bar (a) and 35 GPa (b). The upper and lower (Z) surfaces are free in the case of 1 bar and exposed to liquid Ar (upper portion of the figure) in the case of 35 GPa. Periodic boundary conditions are applied in X and Y directions. If the pressure in the X and Y directions (stress) were less than 8 GPa at a temperature of 3000 K, the final configuration would be about the same as in part (a). The higher magnitude of stress (9 GPa and higher) was sufficient to destroy the slab and produce liquid-like configuration (c).

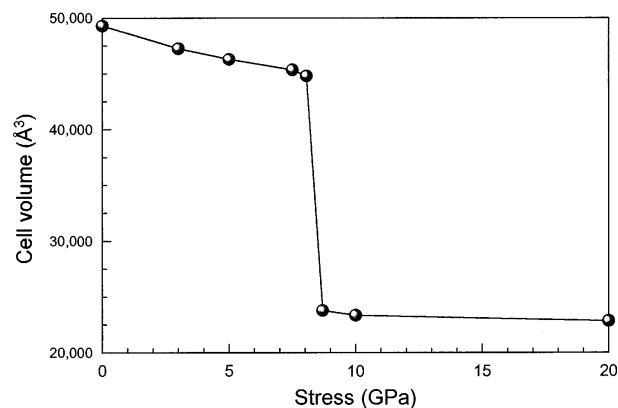


FIGURE 4. Dependence of size of computational cell at 3000 K containing 2048 Mg and O atoms on the applied in X and Y directions stress. Resulting pressure in the Z direction is 0 below approximately 8 GPa and becomes equal to stress in XY direction if the stress is above 8 GPa.

(Fig. 6a–e) forming finally (Fig. 6e) a crystal of $10 \times 12 \times 14$ layers instead of the initial (Fig. 6a) $12 \times 12 \times 12$ atomic layers. The incommensurate “rest” of atoms formed incomplete layers at the top of MgO part. The mechanism of the observed recrystallization is glide of two parts of crystal along the (110) surface (Fig. 6d). Because of recrystallization, a larger portion of the cell in Z direction is occupied by MgO atoms. Because the size in the Z direction was kept constant, the Z component of pressure increased but still remained lower than 53 GPa (pressure in X and Y directions), the value of stress decreased, and the process of recrystallization stopped. The observed change of cell size is illustrated in Figure 7.

The recrystallization is accompanied by changes of structure. Figure 8 shows Mg-O radial distribution function (RDF) during the simulation. One can see how the RDF goes through stages of distortion, broadening of peaks, and finally back to the RDF typical of cubic oxide.

DISCUSSION

Real vs. ideal

In fact, after we finished this study, we felt that we are trying to prove what is already self evident, namely, that MgO cannot sustain some sufficiently high stress and that some changes will be inevitably noticed if stress is higher than some critical value. It is possibly fortuitous that the value of the stress at which the drastic changes are observed is close to the value of thermal pressure because our simulated system, even being closer to a real one than ever simulated, still is very far from the real situation. A real sample has defects, whereas the simulated one does not. A real sample is polycrystalline, whereas the simulated one is a single oriented crystal. It is possible to name other reasons, such as rate of loading, for example. However, these differences act in opposite way, canceling effects. On the one hand, a real sample is more capable of relaxing the stress due to defects and different orien-

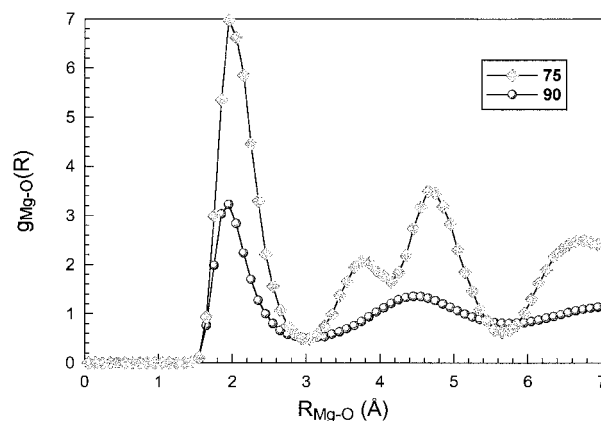


FIGURE 5. Radial Mg-O distribution functions at stresses of 7.5 (diamonds) and 9 (spheres) GPa and 3000 K. The RDF at 7.5 GPa is typical for solid and the RDF at 9.0 GPa is typical for liquid state.

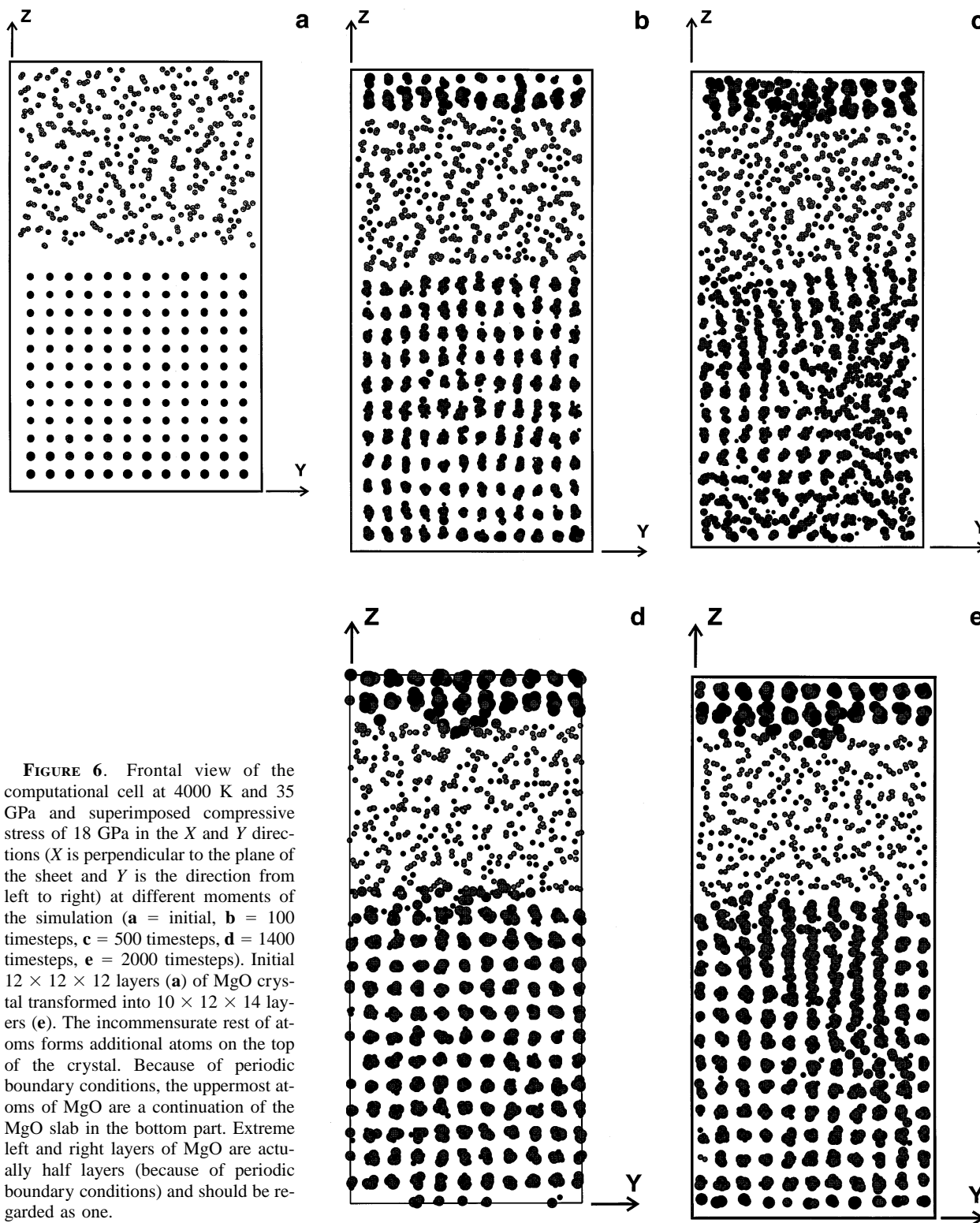
tation of crystallites. On the other hand, the same defects and polycrystallinity is likely to decrease strength of a sample in about the same degree as they are capable of stress relaxation. The value of the thermal pressure (18 GPa) that we use as a thermal stress is likely not the value of thermal stress in a sample. However, it is likely that a real sample has lower strength compared with that of an ideal crystal. It is also of interest to note that Fiquet et al. (1996a, 1996b) measured thermal pressure in MgO about 15 GPa and were puzzled how a powder sample can sustain such a high stress.

The overestimation of yield strength of MgO is about an order of magnitude, as the comparison of the simulated value at 1 bar (30 GPa) with experimental data (3 GPa) demonstrates. It is possible that the critical value of stress equal to 18 GPa is also higher by approximately an order of magnitude in comparison with the real one. If so, then the magnitude of calculated thermal stress (0.5 to 4 GPa; see above) is quite sufficient to initiate the simulated changes at 4000 K and 35 GPa. Of course, it is possible that the magnitude of the thermal stress in a sample remains below the critical value. In this case none of the observed phenomena would be developed. However, in the case of thermal stress of about 4 GPa the overestimation could be below a factor of five.

Impact of recrystallization on indication of melt

The decision about the appearance of melt in the DAC with laser heating is based mainly on two criteria (we consider here the technique employed by Boehler and coworkers).

One criterion is visual observation. In earlier papers, “convective motion” or “vigorous convection” or “fluid-like movement” (Boehler et al. 1990; Boehler 1992; Shen et al. 1993) were reported. Jeanloz and Kavner (1996) argued that it cannot be “convective motion,” moreover “vigorous convection.” Nevertheless, it is evident that movement of material is indeed observed. What



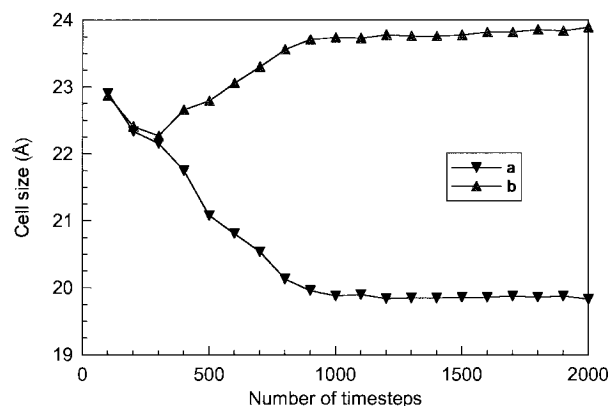


FIGURE 7. Change of a and b size of computational cell as a function of simulation time at 4000 K and 35 GPa and superimposed stress in $X(a)$ and $Y(b)$ directions of 18 GPa. Values of a and b are averages calculated over 100 preceding timesteps. During initial 300 timesteps change of a and b follows a compression pattern. After that the recrystallization process leads to diverging behavior. At about 1000 timesteps an initially symmetric crystal forms 12×10 layers in the XY plane (interlayer separation is about 2 Å).

kinds of motion are possible? First, it is possible that the observed motion is indeed an indication of melting may be convection, for example, movement of melting and solidification fronts. The second possibility is the process of dynamic recrystallization simulated in this study. Because the different crystallites are subjected to different stresses due to temperature gradient and different orientation, the recrystallization would occur not simultaneously, but rather in chaotic regime, possibly giving the impression of convection. Jeanloz and Kavner (1996) described other possibilities.

The second criterion for indication of melting in DAC experiments is the change of the slope in the laser power-temperature curve. Recrystallization is likely to cause the change for several reasons. First, the texture is likely to change. Second, release of thermal stress leads to Joule-Thompson effect. When pressure on a substance is adiabatically released, temperature drops by approximately $V\Delta P/C_p$, where V is volume (if we neglect its change, the volume of MgO at 4000 K and 35 GPa is about $10 \text{ cm}^3/\text{mol}$), ΔP is the value of pressure release (according to our estimates, it varies from 0 to 18 GPa), and C_p is heat capacity of the substance (about $100 \text{ J/mol}\cdot\text{K}$). One can see that the temperature effect can be large, a few hundred degrees, depending on the amount of the substance which was released from thermal pressure. The so called “yo-yo” oscillating pattern can also be explained, because as soon as thermal pressure is released, inhomogeneous laser heating generates thermal stress again and the process can go on forever. However, there is another physical process that acts in the opposite way, namely viscous heating. This process due to the dissipation of energy required to initiate the process of recrystallization can lead to a fast increase in temperature.

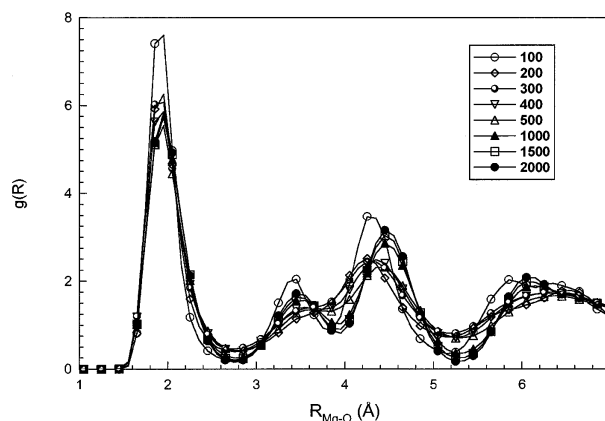


FIGURE 8. Radial distribution (RDF) of O atoms around Mg atoms as a function of distance from Mg atom shown after different number of timesteps (indicated on the figure) after beginning of recrystallization.

The observation of typical circular features of melting in annealed samples can be also due to recrystallization or be produced by subsequent run-away melting at higher temperatures. For example, Shen et al. (1993) wrote: “Note that if we turn off the laser power after the first change in texture, we do not observe typical circular feature of melting.” However, this is exactly the first change in texture that is accepted as an indication of melting. Interestingly, our simulation also produces (Fig. 6e) such features (atoms at the top and bottom of recrystallized MgO slab). We should, however, admit that this is a rather remote analogy.

The melting temperatures at 1 bar and moderate pressures measured in DAC with laser heating are in good agreement with the experimental data provided by alternative techniques. While we cannot neglect the possibility that this is simply because the method has no intrinsic deficiencies with regard to the suggested phenomenon of recrystallization, it could also be explained by the following reasons. First, textural changes (recrystallization?) are observed, and they indeed change the slope of power-temperature curve, but well before the melting temperature at a pressure of 1 bar (S.K. Saxena, personal communication). Second, high thermal stress might not appear because of other mechanisms of stress release at low pressures (e.g., brittle mechanism). This is a well known problem in mechanical tests, when study of plastic deformation in brittle materials requires creation of high confining hydrostatic pressure to prevent them from failing by fracture. This is the principle of the Griggs apparatus (Poirier 1985). In this regard DAC serves as a very efficient Griggs apparatus (when pressure is high) preventing microcracks from growing. Third, at low and moderate pressures melting temperature and the temperature at which recrystallization begins might be indistinguishable within rather large experimental temperature errors.

To conclude, we can say that the effects that serve as

indications of melting at high pressure might be as well due to the process of dynamic recrystallization which we simulated. The opposite conclusion (that it cannot be) could be reached only on the basis of thorough experimental studies with full control of all relevant parameters (temperature, pressure, deviatoric and thermal stress, and structure).

Melting of MgSiO₃ perovskite and iron

Belonoshko (1994) simulated the melting of MgSiO₃ perovskite in good agreement with experimental data (Zerr and Bohler 1993; Bohler and Zerr 1994). Why are experimental and simulated melting curves of MgSiO₃ perovskite in good agreement while those of MgO are totally different? Apart from other possible reasons and according to our suggested possibility of a high impact of thermal pressure on measured melting curves, it means either that MgSiO₃ perovskite is significantly harder than periclase (and it is) and is able to sustain thermal stress or that thermal stress was not as high in the perovskite experiment as in the experiment on periclase. Unlike the experiment on MgO, the initial material in the experiment on perovskite was different (enstatite). During heating the phase transition of initial enstatite material to perovskite with a negative volume effect could significantly release thermal pressure. It is also possible that the release of stress in perovskite was a result of the brittle mechanism. Indeed, Figure 2b of Zerr and Bohler (1993) shows that the perovskite part of the sample has a few clearly visible deep fractures. There are no such fractures in MgO sample [Fig. 1 in paper by Zerr and Bohler (1994)].

The peculiar feature of MgO melting curve is that thermal pressure along the curve is almost constant and equal to 18 GPa [the thermal pressure was calculated using the equation of state by Belonoshko and Dubrovinsky (1996a, 1996b), which is very precise in experimental data range]. Interestingly, the thermal pressure along the iron melting curve (Boehler, 1993) from 100 to 200 GPa is also practically constant and equals to 22 GPa (the thermal pressure was calculated using the latest assessment of the equation of state for (γ iron)). Deformation maps (Frost and Ashby 1982) of MgO and Fe are very similar. Therefore, the simulated effect might be relevant in the case of iron as well. According to the deformation maps of Fe and MgO, dynamic recrystallization begins at high stresses (more than 0.01–0.1 of shear modulus) and high temperatures ($T/T_m > 0.7$ –0.8). Hence, if the suggested phenomenon is indeed what has been observed instead of melting, the corrected iron melting temperatures would be higher than that measured by Bohler (1993) by 25 to 40% at 200 GPa, i.e., 5000 to 5600 K. This is in good agreement with the data of Williams et al. (1987), the recent revision of shock-wave data on iron melting (Anderson and Ahrens 1996), and the Brown and McQueen (1986) melting point (5625 K at 240 GPa, according to Boness and Brown (1990)). A similar correction of MgO melting temperatures would lead to very

good agreement with the existing theoretical predictions (Fig. 1).

CONCLUSIONS

This study demonstrates that accounting for thermal stress in DAC experiments with laser heating might be important. Thermal stress, when achieving some critical value can activate phenomena that have not been taken into account previously. The dependence on visual observation of melting can be misleading. In our opinion, there are two major reasons for the existing controversies between melting curves obtained by different (including theoretical) methods. First, the physical processes that take place in DAC are poorly understood, or, better said, we are not aware of what kind of physical effects are essential for this or that particular behavior. Second, all the experimental determinations of melting curves used techniques that did not allow in situ control of pressure, temperature, stress, and phase composition in the sample. Even the latest experiments (Mao et al. 1996) do not provide data on stress in the sample. If stress is high enough, once activated, recrystallization can become a stationary process. As it was demonstrated, the structure of a material during a stationary recrystallization process becomes liquidlike. Therefore, even the absence of sharp peaks in measured X-ray pattern, characteristic of liquid structure, cannot guarantee measurement of a truly hydrostatic melting temperature.

Measurements of pressure before and after heating (not during the experiment) in the pressurizing medium (not in the sample) might be misleading. Depending on the size of the spot, the type of laser radiation used, particular geometry of a cell, the size and shape of a sample, conditions might be very different. To no surprise, when pressurizing media are different (Williams et al. 1987; Bohler 1993) and different criteria are used for the identification of onset of melting, the obtained temperatures of melting are quite different. Despite the significant progress achieved in the assessment of high-pressure melting transitions, one has to admit that a definite answer has yet to be provided by careful experiments with full in situ control of all relevant parameters.

It was also suggested (H. Keppler, personal communication) that the discrepancy between theoretical and experimental MgO melting temperatures can be explained by other reasons. For example, it was pointed out that MgO is a very hygroscopic material. Because a few percent of H₂O dramatically decrease the melting point of silicates and oxide systems, this could easily account for the low melting points observed in the experiments. This explanation is possible. However, the room-pressure MgO melting point was measured rather close to the previously determined. Because the room-pressure T_m was measured without a gasket, it is unlikely that the sample in that case contained less H₂O than when it was subjected to confining pressure of argon at high pressure.

Another reason for the discrepancy could be that neglect of defects leads to overheating in computer exper-

iments. We should note, however, that we calculated MgO melting curve using two-phase modeling, which resolves the problem of overheating.

In conclusion, we want to emphasize that all the above is presented not to provide definite answers but rather to suggest consideration of the impact of thermal stress on the behavior of a sample in the DAC when undertaking an experimental study.

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