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Melting and liquid structure of aluminum oxide using a molecular-dynamics simulation

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The radial distribution function $G(r)$ for liquid aluminum oxide (corundum) is calculated by means of the two-phase molecular-dynamics method utilizing a previously developed pairwise interatomic potential. Our results agree very well with the recent experimental results of Ansell *et al.* [Phys. Rev. Lett. **78**, 464 (1997)], confirming a tetrahedral aluminum coordination in the liquid phase. The calculated melting curve is in good agreement with existing experimental data up to 25 GPa. The melting is calculated to involve a radical change from octahedral to tetrahedral coordination and an accompanying large volume expansion of about 20%, in good agreement with experiment. [S1063-651X(98)04102-6]

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Aluminum oxide (corundum) is a very important refractory ceramic material. It is known to exist in a number of different phases, such as α (hexagonal), β (hexagonal), γ (cubic spinel), η (cubic spinel), θ (monoclinic), κ (orthorhombic), δ (tetragonal), and χ (cubic). In technological applications, for instance, in wear-resistant cutting tool materials [1], the most commonly used phases are the stable α phase and the metastable κ phase. From a geophysical point of view, aluminum oxide is believed to be one of the major constituents of the Earth's composition [2]. Even though it is unlikely to exist in the Earth in any substantial quantity in the form of the pure oxide, the phase diagram of corundum is important since it is the end member in a number of Al_2O_3-containing systems. Corundum is often used as a pressurizing medium [3,4] and, when doped with Cr, as a pressure calibrant in diamond anvil cell high-pressure and temperature experiments [5–7], and also as a window material in shock-wave experiments [8,9]. Due to the most important refractory property of corundum, it is of particular interest to be able to describe the thermal stability of Al_2O_3 lattice against melting.

Corundum has been studied extensively both experimentally [5–7,9–12] and theoretically [13–20] with emphasis on properties at room temperature including phase transitions. However, few studies have been done at high temperatures especially in combination with high pressure. This is partially due to the difficulties of doing experimental studies at elevated temperatures, but also because of theoretical limitations. There is only one experimental study done as regards the pressure dependence of the melting temperature [21]. Recently, Ansell *et al.* [22] have measured the total structure factor $S(Q)$ and determined the corresponding radial distribution function $G(r)$ for supercooled and stable liquid Al_2O_3 using x-ray synchrotron radiation in the temperature range 2200–2700 K. These authors have shown that the internal structure does not change appreciably with temperature in the stable and supercooled liquid. These experiments give important microscopic data for a refractory material at temperatures that have not been accessible before. Tyrolerova and Lu [23] have also studied the melting of Al_2O_3. They found a 20% volume expansion on melting and speculated that this is due to large structural rearrangements. Theoretically, the melting transition can often be reasonably well calculated using the molecular dynamics (MD) approach [24–28]. The simplest way to study melting is to use MD to simulate a system of interacting atoms and increase the temperature until it becomes a liquid. This approach leads to an overestimation of melting temperatures due to superheating. One way of avoiding this overestimation is to calculate the free energies of the solid and liquid phases and at a given pressure (P) determine the temperature (T) where these energies are equal. However, such an approach has a number of difficulties and drawbacks [28]. Another approach, which is computationally less expensive, is to carry out a so-called two-phase simulation, where two phases (liquid and solid) are put together comprising a common interface and then simulated at a given P and T. Such a two-phase system usually develops into a homogeneous state and, depending on which phase remains in the computational box at the end of the simulation run, the corresponding conclusion on phase stability can readily be made.

In this paper we use the two-phase simulation method [24] and a previously developed interatomic potential [19,20,29] to calculate the melting curve of corundum and also the structure of liquid Al_2O_3. We will also compare the two-phase and one-phase simulation methods. The comparison between these two methods and experimental data shows that whereas the two-phase simulation approach produces a melting curve in reasonable agreement with the experiment, the one-phase method overestimates substantially the melting temperatures, and this inaccuracy increases with increasing pressure.

A detailed description of the molecular dynamics approach can be found elsewhere [30] and an introduction to the two-phase simulation technique is provided in an earlier paper [24]. A description of the ‘‘straightforward’’ one-phase simulation for calculating melting temperature can be found in a recent paper [31] on melting of MgO. Whatever the particular modification of the molecular dynamics approach is, one has to have a model describing the interaction between the particles constituting the studied system. Matsui [19] has developed a transferable pairwise potential describing interactions in the CaO-MgO-Al_2O_3-SiO_2 system. The potential was demonstrated to correctly reproduce a number

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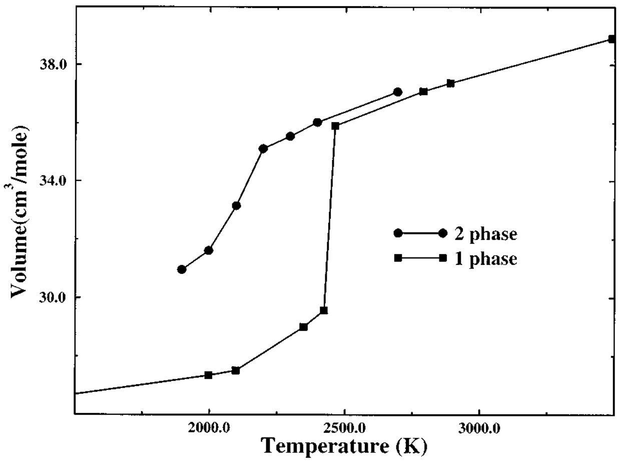

FIG. 1. Calculated zero-pressure temperature dependence of the volume of Al_2O_3 using simulations for one-phase and two-phase systems as described in the text.

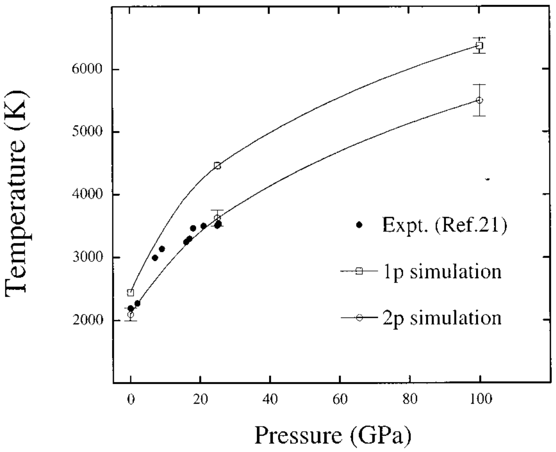

FIG. 2. Melting temperatures of corundum calculated using one-phase and two-phase MD simulations at zero pressure, 25 GPa, and 100 GPa. Open squares and open circles represent one-phase and two-phase simulations, respectively. Error bars show the achieved resolution of the melting temperature obtained in the simulations; compare Fig. 1. Experimental [21] data are shown by the filled circles.

of experimental properties [20,29]. In the present work it is this potential that we apply to describe the Al-Al, Al-O, and O-O interactions in corundum.

All simulations have been done using a constant pressure algorithm [32] with a Nosè [33] thermostat. The usual periodic boundary conditions were imposed and the equations of motion were solved numerically. The Coulomb interaction was calculated using the Ewald technique. Parameters for calculating the Ewald sum were obtained using Fincham [34] recommendations. The number of atoms in the case of the one-phase simulation was 1500. The calculations have been checked using systems of 3000 atoms and no relevant differences were noticed. In the case of the two-phase simulations, a solid and a liquid part, containing 1500 atoms each, were put together to comprise a system of 3000 atoms. In this case the results were checked using 12 000 atoms. The time step was, accordingly, 1 femtosecond (10^{-15} sec) and the results have been checked with a time step of 2 fsec. In critical cases, i.e., at temperatures close to melting, the simulations were checked using very long runs, up to 200 000 time steps. Generally 20 000 time steps were sufficient to get reliable results. The approach to equilibrium was controlled by a registration of the fluctuations of intermediate averages. The calculations were done using the program MOLDY, installed on the IBM SP2 massively parallel computer at the Parallel Computer Center in Stockholm (Sweden).

Melting is a first-order transition that is accompanied by a discontinuous behavior of thermodynamic parameters and abrupt changes of related properties, for example, structure. The molecular dynamic method provides a full track of all relevant parameters such as pressure, temperature, volume, and structure during the whole simulation run. The behavior of volume, for example, is very informative as regards the melting transition. For example, Vocadlo and Price [31] choose the change in volume as a major characteristic of the melting transition. The change in volume during the one-phase and two-phase simulations was calculated at zero pressure as a function of temperature. The results are displayed in Fig. 1, where the temperature dependence of the volume, as simulated using the one-phase initial configuration, shows a sudden increase between the temperatures 2425 K and 2475 K due to melting. At the same pressure, the two-phase simulation results in melting starting at 2200 K. Obviously, the volume change in the two-phase simulation is not so drastic because half of the computational box is liquid from the very beginning. Overheating at room pressure is about 200–300 K.

The melting temperatures as obtained by the one-phase and two-phase MD simulations are compared with existing experimental [21] data at pressures up to 25.4 GPa (Fig. 2 and Table I). The melting temperature at room pressure is somewhat (100 K) underestimated in the two-phase simulations, while it is overestimated in the one-phase simulations (200 K). Note that the agreement (or disagreement) between experiment and simulation has no bearing on the fact of overheating. The overheating is an intrinsic feature of a model combined with a particular method of simulation. The

TABLE I. Calculated and experimental melting temperatures (K) as a function of pressure (GPa).

	Calculation		
Pressure	One-phase simulation	Two-phase simulation	Experiment [a]
0.0	2425–2475	2000–2200	2200
2.0			2275
7.0			3000
9.0			3140
16.0			3250
17.0			3300
18.0			3470
21.0			3500
25.0	4425–4500	3500–3750	3510
25.4			3540
100.0	6250–6500	5250–5750	

[a] Reference [21].

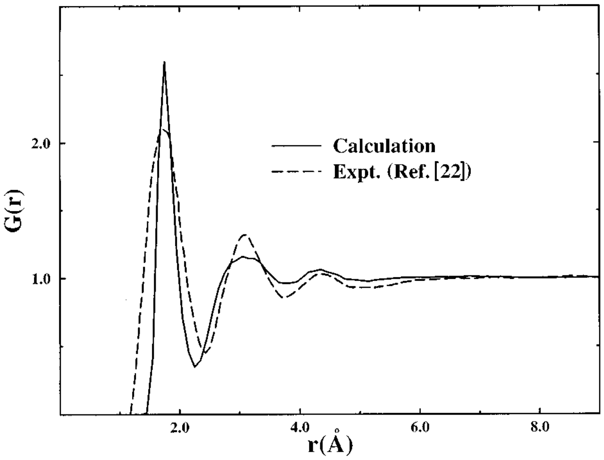

FIG. 3. Radial distribution function $G(r)$ for Al_2O_3 calculated at 2663 K using the two-phase MD simulation at zero pressure together with the experimental data of Ansell *et al.* [22].

true value of overheating can be calculated only when compared with the correctly calculated melting temperature (e.g., by a two-phase simulation) for a given model of a solid. The overheating increases with increasing pressure (Fig. 2) and amounts to at least 700 K at 25 GPa and approximately the same value at 100 GPa. The pressure dependence of the overheating follows the dependence of the enthalpy of melting [27].

The overall agreement between the experimental and the calculated MD simulation (two-phase) melting curve seems to be most reasonable. It suggests that the model of interaction developed by Matsui [19] is able to correctly reproduce the interactions in the liquid, where the structure is substantially different from that of solid. Therefore, one can expect the model to be successful also when applied to simulate solid-solid transitions.

TABLE II. Calculated radial distribution function $G(r)$ at 2663 K using the two-phase MD simulation at zero pressure together with experimental data.

r (Å)	Calculation	Experiment [a]
1.2	0.0	0.0710
1.6	0.4161	1.9200
1.8	2.6001	2.079
2.0	1.2013	1.440
2.4	0.3977	0.460
2.8	1.0340	1.022
3.0	1.1325	1.2867
3.2	1.1449	1.2555
3.6	1.0106	1.0683
3.8	0.9619	0.8638
4.0	0.9726	0.9266
4.4	1.0623	1.0270
4.8	0.9920	0.9371
5.0	0.9855	0.9312
5.2	0.9761	0.9298
5.6	0.9955	0.9546
6.0	1.0060	0.9839

[a] Reference [22].

In Fig. 3 and Table II we show the calculated and experimental radial distribution function of liquid Al_2O_3. $G(r)$ shows a strong peak at 1.76 Å and progressively weaker peaks at 3.08 and 4.25 Å. Experimentally, peaks have been observed at 1.76 Å (strong peak) and at 3.08 and 4.25 Å (also with progressively weaker peaks). The calculated intensity of the first peak is somewhat higher than the experimental value, whereas for the second peak it is a little bit less than observed experimentally. For the third peak, the calculated and experimental peak intensities are close. The first peak in $G(r)$ at 1.76 Å is found to arise from Al-O pairs. This is comparable to the distance of closest approach, 1.72 Å, based on the 0.36 and 1.36 Å ionic radii of Al^{3+} and O^{2-} ions, respectively [35]. In Fig. 4 we have plotted our calculated coordination number as a function of distance for the Al-O, O-O, and Al-Al pairs. It is common to derive the coordination number from the content of particles lying within a sphere with a radius corresponding to the position of the first minimum in the pair distribution function [36]. It is clear from Fig. 4 that this gives a coordination of 4. Thus, in the liquid phase the aluminum atoms are surrounded by four oxygen atoms, while the coordination is 6 in the solid phase. This agrees very well with the value of 4.4±1 derived by Ansell *et al.* [22] from their experimental data. The tetrahedral coordination of Al can be also supported by the following fact, as also suggested by Ansell *et al.* [22]. In the α phase of solid Al_2O_3, the Al-O nearest-neighbor distance is 1.91 Å. Meade *et al.* [37] have measured the x-ray structure factor for SiO_2 glass and have shown that the difference in the bonding distance between tetrahedral and octahedral Si is around 1.15 Å. In our simulation the corresponding difference in Al_2O_3 is around 1.15 Å, again suggesting that Al^{3+} is tetrahedrally coordinated in the liquid phase. If the Al-O bond length is 1.76 Å, corresponding to the first peak position in our calculated $G(r)$, then the O-O distance in the tetrahedron becomes 3.05 Å. This value compares very well with the calculated second peak of 3.05 Å, giving additional support to the picture of a tetrahedral coordination in melted corundum.

Our results show that the experimental data for the pressure dependence of the melting temperature of corundum can

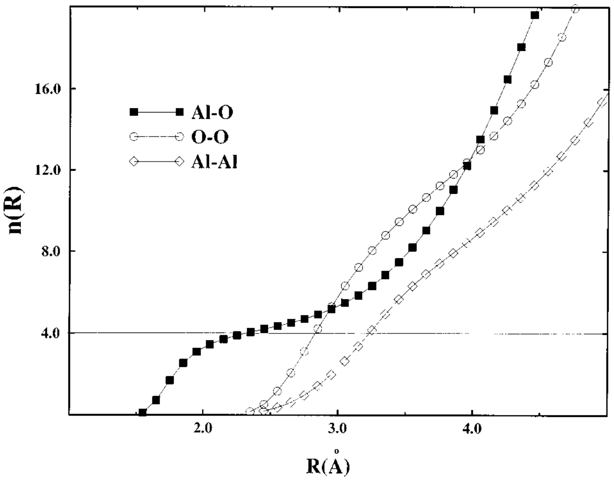

FIG. 4. Calculated number of particles $n(R)$ within a sphere of radius R for the Al-O, O-O, and Al-O pair distributions at 2663 K.

be well reproduced using the pair interaction developed by Matsui [19] and the two-phase molecular dynamics simulation method [24]. This suggests that this model can be used for predicting, for example, high-pressure solid-solid transitions in Al_2O_3. Two melting curves, calculated by the one-phase and two-phase simulation methods, show large differences with increasing pressure. Accordingly, the overheating in the one-phase simulation can be substantial and therefore this method is not a suitable tool for predicting melting temperatures at high pressure. At the very least, such simulations have to be reversed in order to assess the possible magnitude of overheating. Such reversal, however, leads to large hysteresis, especially at high pressure [38], and a direct comparison of the melting temperatures becomes difficult.

We conclude that our calculations nicely reproduce the structure of liquid aluminum oxide and, in agreement with experiment, show that a major structural rearrangement takes place upon melting. The main driving force for the solid-liquid phase transition is the change in the Al coordination from octahedral to tetrahedral.

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[1] P. Hansson, M. Halvarsson, and S. Vuorinen, Surf. Coat. Technol. **76-77**, 256 (1995), and references cited therein.
[2] D.L. Anderson, *Theory of the Earth* (Blackwell, Boston, 1989).
[3] Q. Williams and R. Jeanloz, J. Geophys. Res. **96**, 2171 (1991).
[4] R. Boehler, Nature (London) **363**, 534 (1993).
[5] P.M. Bell, H.K. Mao, and K. Goettel, Science **226**, 542 (1984).
[6] H.K. Mao, J. Xu, and P.M. Bell, J. Geophys. Res. **91**, 4673 (1986).
[7] J.A. Xu, H.K. Mao, and P.M. Bell, Science **232**, 1404 (1986).
[8] W.J. Nellis and C.S. Yoo, J. Geophys. Res. **95**, 21 749 (1990).
[9] C.S. Yoo, N.C. Holmes, and E. See, in *Shock Compression of Condensed Matter—1991*, edited by S. Schmidt, R.D. Dick, J.W. Forbes, and D.G. Pasker (North-Holland, Amsterdam, 1992), p. 733.
[10] A. P. Jephcoat, R.J. Hemley, and H.K. Mao, Physica B **150**, 115 (1988).
[11] P. Richet, J.A. Xu, and H.K. Mao, Phys. Chem. Miner. **16**, 207 (1988).
[12] P.A. Urtiew, J. Appl. Phys. **45**, 3490 (1974).
[13] R.H. French, J. Am. Chem. Soc. **73**, 477 (1990).
[14] W.C. Mackrodt, Philos. Trans. R. Soc. London, Ser. A **341**, 301 (1992).
[15] W.Y. Ching and Y.N. Xu, J. Am. Chem. Soc. **77**, 404 (1994).
[16] M.S.T. Bukowinski, A. Chizmeshya, G.H. Wolf, and H. Zhang, Mol. Eng. **6**, 81 (1996).
[17] H. Cynn, D.G. Isaak, R.E. Cohen, M.F. Nicol, and O.L. Anderson, Am. Mineral. **75**, 439 (1990).
[18] F.C. Marton and R.E. Cohen, Am. Mineral. **79**, 789 (1994).
[19] M. Matsui, Miner. Mag. **58A**, 571 (1994).
[20] M. Matsui, Phys. Chem. Miner. **23**, 345 (1996).
[21] G.Y. Shen and P. Lazor, J. Geophys. Res. **100**, 17 699 (1995).
[22] S. Ansell, S. Krishnan, J.K. Richard Weber, J.J. Felten, P.C. Nordine, M.A. Beno, D.L. Price, and M.L. Saboungi, Phys. Rev. Lett. **78**, 464 (1997).
[23] P. Tyrolerova and W.K. Lu, J. Am. Chem. Soc. **52**, 7779 (1969).
[24] A.B. Belonoshko, Geochim. Cosmochim. Acta **58**, 4039 (1994).
[25] A.B. Belonoshko and L.S. Dubrovinsky, Geochim. Cosmochim. Acta **59**, 1883 (1995).
[26] A.B. Belonoshko and L.S. Dubrovinsky, Am. Mineral. **81**, 303 (1996).
[27] A.B. Belonoshko and L.S. Dubrovinsky, Geochim. Cosmochim. Acta **60**, 1645 (1996).
[28] J.R. Morris, C.Z. Wang, K.M. Ho, and C.T. Chan, Phys. Rev. B **49**, 3109 (1994).
[29] M. Matsui, Geophys. Res. Lett. **23**, 395 (1996).
[30] M.P. Allen and D.J. Tildesley, *Computer Simulation of Liquids* (Clarendon, Oxford, 1987).
[31] L. Vocadlo and G.D. Price, Phys. Chem. Miner. **23**, 42 (1996).
[32] M. Parrinello and A. Rahman, J. Appl. Phys. **52**, 7182 (1981).
[33] S. Nosé, Mol. Phys. **52**, 255 (1984).
[34] D. Fincham, Mol. Simul. **13**, 1 (1994).
[35] A. Navrotsky, *Physics and Chemistry of Earth Materials* (Cambridge University Press, New York, 1994).
[36] R.L. McGreevy, in *Solid State Physics*, edited by H. Ehrenreich and D. Turnbull (Academic, New York, 1987), Vol. 40, p. 268.
[37] C. Meade, R.J. Hemley, and H.K. Mao, Phys. Rev. Lett. **69**, 1387 (1992).
[38] A.B. Belonoshko, High Press. Res. **10**, 583 (1992).