

LETTER

A high-pressure phase transition of corundum predicted by the potential induced breathing model

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ABSTRACT

The possibility of high-pressure phase transitions in Al_2O_3 is investigated using the potential induced breathing (PIB) model, a nonempirical ionic model. A phase transition is predicted at moderate pressures from the corundum structure to the $\text{Rh}_2\text{O}_3(\text{II})$ structure. The calculated transition pressure ranges from 6–62 GPa and is sensitive to the choice of model charge density and density functional. Our results are consistent with a previous theoretical prediction of a pressure-induced phase transition in Al_2O_3 .

INTRODUCTION

Al_2O_3 is widely used as window material in shock-wave experiments and, when doped with Cr^{+3} , as a pressure calibrant in high-pressure diamond-anvil cell experiments. Thus, the possibility of pressure-induced phase transformations of corundum is of wide interest. The high-pressure properties of alumina are also important to geophysics because transitions in Al_2O_3 may indicate structures that must be considered as high-pressure mantle phases.

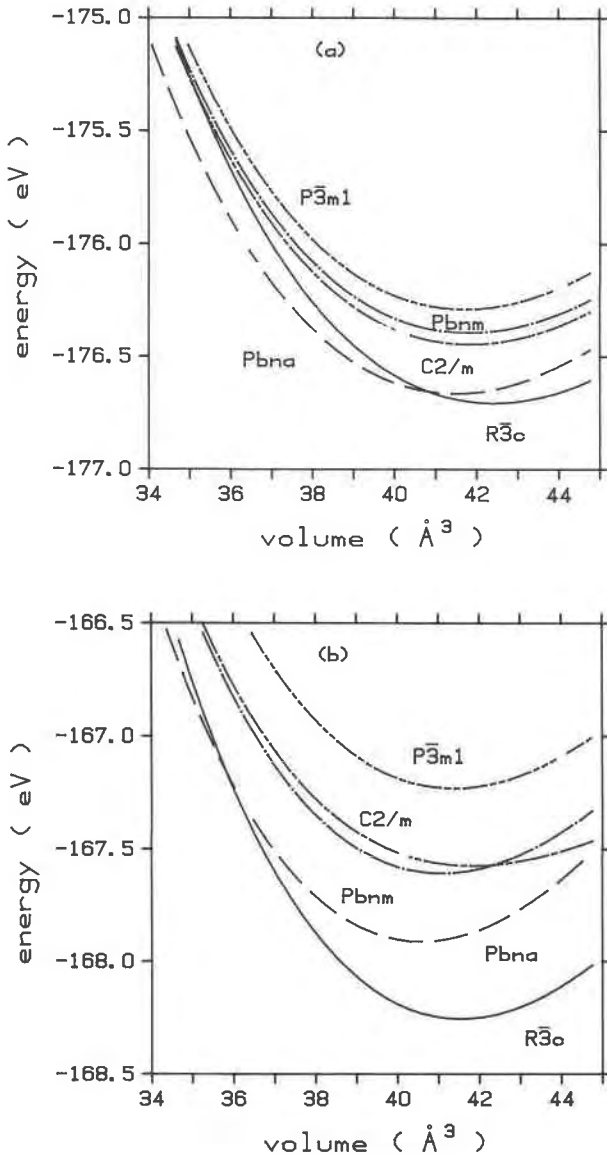
At present the experimental results regarding the phase stability of corundum do not seem to be consistent. Shock-induced changes of the optical properties of Al_2O_3 were suggested at 15 GPa (Barker and Hollenbach, 1970). Vereshchagin et al. (1974) reported a discontinuity around 100 GPa in the electrical resistance of alumina from uniaxial compression. Mao et al. (1985) reported that the R_1 ruby peak disappeared at pressures above approximately 190 GPa and related it to the onset of a structural change. Optical observations of Al_2O_3 quenched at 16.5 GPa from 1600 °C and lower temperatures by Gasparik (1988) also suggested a structural change. However, Xu et al. (1986) found that ruby was stable from 210 to 550 GPa at room temperature, and Jephcoat et al. (1988) reported no struc-

tural change in ruby up to 175 GPa at ambient temperature in energy-dispersive X-ray powder patterns using a synchrotron radiation source. Thus, the high pressure stability of corundum needs to be reconsidered.

A theoretical study by Cohen (1987) suggested a lattice instability in alumina at elevated pressures. He used the PIB model and related the lattice instability to a pressure-induced phase transition in Al_2O_3 . In the present study we further examine the possibility of a pressure-induced phase transformation of corundum. The sensitivity of the PIB calculation to assumptions about the short-range kinetic energy and charge density is examined. Although two approximations tend to model some properties of corundum better than others when compared with experiments, both suggest a phase transition to the same structure at elevated pressures.

PIB MODEL AND ENERGY CALCULATION

The PIB model (Boyer et al., 1985; Mehl et al., 1986) is an ab-initio model in the sense that no experimental values are used. It is a model of the Gordon-Kim type, where the crystal charge density is approximated by overlapping Watson-sphere-stabilized ions. The total energy of the crystal is expressed as the sum of three terms: (1) the long-range electrostatic energy; (2) the self-energies of



each ion in a Watson sphere potential; and (3) the short-range interactions between ions, which include the short-range electrostatic overlap energy, the overlap kinetic energy, and the overlap exchange and correlation energies. In an ab-initio model such as PIB, a physical model is used for the charge density, and the total energy is then calculated using the local density approximation (LDA) (Schluter and Sham, 1982), rather than calculating the crystal charge density self-consistently (Kohn and Sham, 1965). The PIB model differs from most other lattice dynamical models by coupling the long- and short-range forces (Cohen et al., 1987). There are effective many-body forces that, for example, cause the Cauchy condition to be violated in cubic crystals.

We calculated the dependence of the static-lattice Helmholtz free energy on volume over a wide range of volumes for the corundum and other trial structures. Two versions of the PIB model were used. In the first model, designated TF, we used self-interaction-corrected charge densities (Perdew and Zunger, 1981) and the Thomas-Fermi kinetic energy functional for the self-energies. This is the procedure followed by Cohen (1987). In the second version, designated KS, we used LDA charge densities, and the Kohn-Sham self-energy, as was used in Isaak et al. (1990). In the Thomas-Fermi kinetic energy functional, the kinetic energy is proportional to $\rho^{5/3}$, where ρ is the charge density. In the KS model, $\rho^{5/3}$ is used for the overlap kinetic energy, but the self-consistent kinetic energy of the noninteracting system (Kohn and Sham, 1965) is used for the kinetic energy of the ions in the self-energy. In general we find structural parameters and lattice dynamics to be superior for the second model, and equations of state and elasticity to be better for the first model

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Fig. 1. Calculated total energy versus volume for one Al_2O_3 in different structural types using the PIB model with the TF (a) and KS (b) approximations (see text). Each structural type is labeled by a space-group symbol shown in Table 1.

TABLE 1. Structural parameters and equations of state at zero pressure of Al_2O_3

	Corundum $R\bar{3}c$		Experi- mental*	$\text{Rh}_2\text{O}_3(\text{II})$ $Pbna$		Orthorhombic perovskite $Pbnm$		B-RES $C2/m$		A-RES $P\bar{3}m1$		Cubic perovskite $Pm\bar{3}n$	
	TF	KS		TF	KS	TF	KS	TF	KS	TF	KS	TF	KS
V_0 (\AA^3)	42.40	41.56	42.47	41.35	40.56	41.81	41.11	41.80	41.80	41.71	41.35	45.65	44.81
c/a	2.59	2.68	2.73	1.45	1.47	1.49	1.54	0.61	0.57	1.67	1.74		
b/a				1.01	1.02	1.02	1.02	0.25	0.24				
β ($^\circ$)								101.7	101.5				
$z(\text{Al})$	0.361	0.357	0.352										
$x(\text{O})$	0.296	0.301	0.306										
K_0 (GPa)	264	356	254	283	359	251	319	260	247	260	317	235	316
K_0'	3.93	3.93	4.3	3.90	4.01	4.12	4.21	3.91	5.16	3.91	3.90	3.98	4.11
$\partial \ln a/\partial P^\dagger$	8.9	11.0	12.2										
$\partial \ln c/\partial P^\dagger$	10.9	14.6	13.6										

Note: Prime represents pressure derivative. V_0 is the volume for one Al_2O_3 formula unit.

* Finger and Hazen (1979).

† Units are 10^{-4} (GPa $^{-1}$).

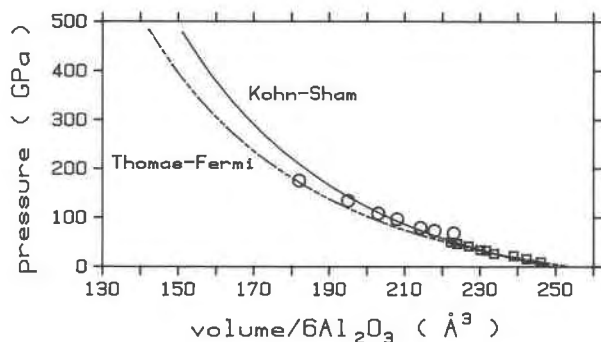


Fig. 2. Calculated and experimental equations of state for corundum. The experimental data are from Jephcoat et al. (1988) (circles) and Richet et al. (1988) (squares).

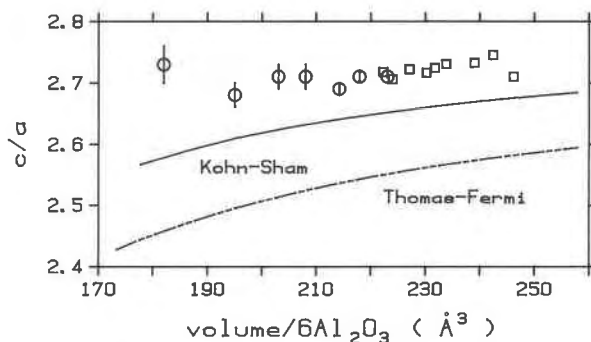


Fig. 3. Calculated and experimental c/a ratio of corundum. The experimental data are from Jephcoat et al. (1988) (circles) and Richet et al. (1988) (squares).

(Cohen, 1987; Isaak et al., 1990). We present results for both models here to show that the general predictions about the phase relations are insensitive to the details of the models. These calculations do not include thermal effects, but we do not expect these to be large, at least up to room temperature. Isaak et al. (1990) found that free-energy calculation only changed the phase transition by 11 GPa in MgO, compared with the static-lattice result.

We minimized the total static energy with respect to the structure parameters at a series of volumes, and fitted the calculated energies to a third-order Birch equation (Birch, 1978). By comparing the free energies of the various structures over a wide pressure range, we determined the stable phase at each pressure.

RESULTS AND DISCUSSION

The calculated total energies are shown in Figure 1 as functions of volume. Cubic perovskite has the highest energy among the examined structures and is off the scale of Figure 1. In order of increasing density the structural types are corundum, Rh_2O_3 (II), B-type rare-earth sesquioxide (RES), *Pbnm* perovskite, and A-type RES. This pattern is identical to the systematics found by Pistorius (1976), with the exception of the perovskite-like structure.

In Table 1 we give the resulting structural and equation-of-state parameters at zero pressure for each structure type. For corundum, the TF approximation gives a better equation of state and zero-pressure volume, but the rest of the structural parameters are improved with the KS approximation. Both the TF and KS equations of state agree well with the low-pressure data of Richet et al. (1988; Fig. 2). The highest-pressure, and best-constrained, datum of Jephcoat et al. (1988) is in good agreement with the TF equation of state.

Linear compressibilities of the a and c axes are shown in Table 1. Similar results were obtained experimentally by Jephcoat et al. (1988) and Richet et al. (1988). We also find that the axial ratio, c/a , for corundum (Al_2O_3) decreases slightly with increasing pressure for both approximations (Fig. 3). The decreasing trend in the c/a ratio

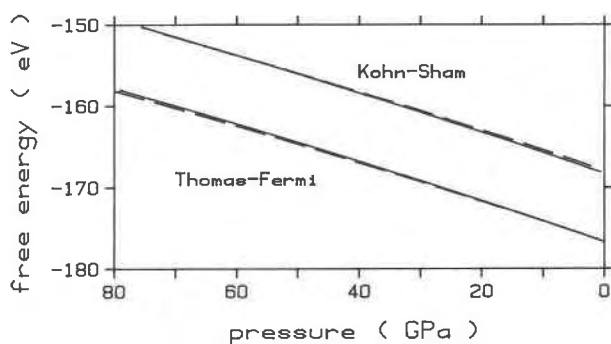


Fig. 4. Calculated free energy dependence on pressure for Al_2O_3 in the corundum (solid lines) and the Rh_2O_3 (II) (dashed lines) structures. Upper curves are for the KS and lower curves are for the TF approximations.

upon compression is in good agreement with Finger and Hazen (1979). Jephcoat et al. (1988) reported that, within the errors of their experiment, the c/a ratio was constant with pressure. Richet et al. (1988) noted that the c/a ratio decreased upon compression, and attributed this to non-hydrostaticity.

As pressure is increased, the free energy of the Rh_2O_3 (II) structure becomes lower than that of corundum (Fig. 4). The pressure at which the transition occurs is sensitive to the details of our charge-density and kinetic-energy calculation. For the TF and KS approximations, the phase transition is predicted at 6 and 62 GPa, respectively. A similar phase transition in Rh_2O_3 was also recognized for a quenched sample at 6.5 GPa and 1200–1500 °C (Shannon and Prewitt, 1970). The volume decreases at the phase transition by 2.3% in both the TF and KS calculations. Thus, the point of intersection of the free-energy curves is sensitive to small changes in the model because the free-energy curves are nearly parallel, as is usually the case with structural phase transitions. However, under both the TF and KS approximations, qualitative agreement is obtained: both predict pressure-induced phase transitions of Al_2O_3 from the corundum to the Rh_2O_3 (II) structure at a pressure below 100 GPa. Metastable co-

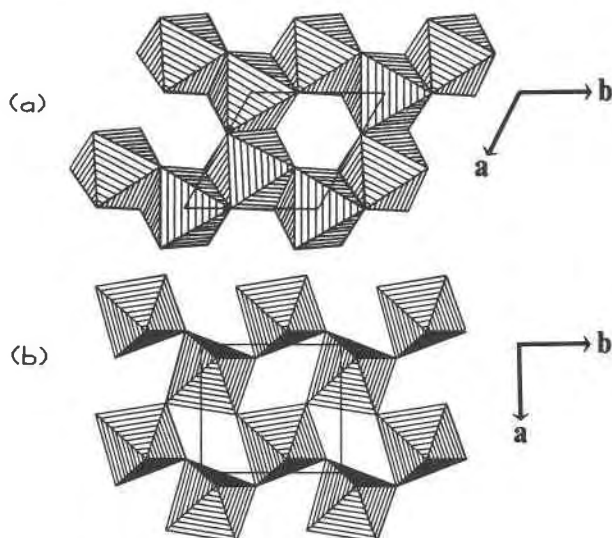


Fig. 5. Arrangement of cation octahedra for the corundum (a) and the $\text{Rh}_2\text{O}_3(\text{II})$ (b) structures. For corundum we used ambient X-ray data by Finger and Hazen (1979). For the $\text{Rh}_2\text{O}_3(\text{II})$ structure, we used the calculated data at around 20 GPa using the TF approximation. The lattice parameters are; $a = 4.73 \text{ \AA}$, $b = 5.15 \text{ \AA}$, and $c = 6.84 \text{ \AA}$. Volumes are for the six Al_2O_3 formula units in a hexagonal cell.

corundum can also transform at higher pressures to other structures. Orthorhombic perovskite, in particular, is a possible phase at more elevated pressures. The transition pressure from corundum to orthorhombic perovskite is calculated as 70 or 140 GPa using TF or KS, respectively.

The corundum and $\text{Rh}_2\text{O}_3(\text{II})$ structures are compared in Figure 5. The corundum and $\text{Rh}_2\text{O}_3(\text{II})$ structures are related by a combination of a shear in the (001) plane and tilting of the octahedra. The latter may be related to the C_{44} instability found at much higher pressure by Cohen (1987). Nevertheless, nearest-neighbor bonds are broken, and thus the transition is predicted to be reconstructive. There is probably a significant kinetic barrier for the transition, so that corundum can persist high above its equilibrium stability field at room temperature. High temperature is probably necessary to drive the transition.

CONCLUSIONS

Our static lattice calculations for Al_2O_3 with the corundum structure show good agreement in the equation of state and pressure dependence of the axial ratio, c/a , when compared with room-temperature experimental results. We find that, by using the PIB *ab-initio* model and comparing the calculated free energies, Al_2O_3 is stable at ambient conditions in the corundum structure but is predicted to adapt the $\text{Rh}_2\text{O}_3(\text{II})$ structure at high pressure. The absolute pressure at which the predicted phase change occurs is sensitive to the details of the calculation. Using the TF and KS approximations to the kinetic energy, we

obtained a range of calculated transition pressures from about 6 to 62 GPa.

ACKNOWLEDGMENTS

We thank R. J. Hemley, A. P. Jephcoat, T. Gasparik, B. J. Baer, A. Gratz, and W. A. Dollase for useful discussions. We also express gratitude to L. Finger for kindly sending us a copy of STRUPL084. HC and MFN were supported by NSF DMR 87-14897 and IGPP-LANL Grant 194. Calculations were performed on the Cray X-MP at the San Diego Supercomputer Center. The IGPP contribution number is IGPP-3324.

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