

High-density structures and phase transition in an ionic model of H₂O ice

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A self-consistent ionic model of water (protons and O²⁻ ions) has been used to explore the low-temperature, high-pressure properties of ice. Interionic interactions were calculated with the electron-gas model, and the self-consistent changes in the electronic structure of the oxide ions were modeled with Watson spheres. A phase transition is predicted at about 330 GPa from the observed, low-pressure, symmetric hydrogen-bonded cuprite structure to a fully ordered antiferroite structure. The transition pressure is higher than the 100-GPa estimate obtained from a molecular-dynamics study [Phys. Rev. Lett. **60**, 2284 (1988)] that employed more approximate potentials.

The properties of solid H₂O have attracted considerable attention not only because of their importance in planetary science but also due to the large variety of solid phases that arise as a consequence of the anisotropic intermolecular interactions. Recently, Hemley *et al.*¹ used synchrotron radiation to study the crystal structure of solid H₂O to about 128 GPa in a diamond-anvil cell. For pressures greater than about 25 GPa, the structure contained a body-centered cubic (bcc) oxygen sublattice. The measured equation of state indicates a more compressible solid than calculations based on molecular pair potentials. Recent molecular-dynamics calculations,² based on a primitive ionic model consisting of protons and O²⁻ ions, found the stable structures in the relevant pressure range to be first cuprite (with a bcc oxygen sublattice) and then antiferroite [with a face-centered (fcc) sublattice] at higher pressures. In light of the synchrotron results, which show no phase transition, we have refined the previous ionic model of ice to include a more accurate description of the short-range interionic interactions. As a result, we now predict the bcc oxygen sublattice structure to be stable up to 330 GPa.

In a recent constant-pressure molecular-dynamics² (MD) study of water ice at high densities, we used an entirely electrostatic model of the interionic forces to investigate possible new phases. The interaction between the O²⁻ ions was taken as the bare Coulomb interaction ($4/r$) and the interaction between H⁺ and an O²⁻ ion was the bare Coulomb interaction ($-2/r$) plus the short-range nonpoint Coulomb interaction, i.e., the electrostatic interaction between charge distributions with the bare Coulomb interaction subtracted off. To generate the nonpoint Coulomb term, we used a wave function for the O²⁻ ion from a Watson-sphere³ calculation (described below) with a radius 1.65 bohr. The low-pressure structure of this crude model is cuprite, with a bcc arrangement of the O atoms, which is in agreement with experiment.¹ When subjected to pressures of about 100 GPa, the MD cell exhibited a transition to an antiferroite structure, in which

the O²⁻ ions have fcc arrangement. Upon heating this latter phase, the protons became "free" and, at least in the model, ice became a fast-proton conductor.² Unfortunately, recent synchrotron experiments find the bcc structure to be stable up to 128 GPa, which seems to rule out the presence of an antiferroite phase.

The purpose of the present paper is to report on the results of a more accurate version of the ionic potential model of ice than used in the previous MD calculation. To that end, we now include the short-range repulsions between the O²⁻ ions, as calculated with the Gordon-Kim electron gas scheme.⁴ More importantly, we have obtained self-consistent results for both the cuprite and antiferroite structures, by which we mean that for each volume we have calculated the electrostatic potential of the crystal and have determined the electronic structure of the ions appropriate for that crystal potential. As we shall see, use of self-consistent interaction potentials is essential to obtain a reasonable description of the energetics of these phases. The model does not allow for any effects of polarization of the electronic distributions.³

In an ionic solid, the electronic structure of a constituent ion is changed from that in the gas phase due to the electrostatic potential in which the ion sits. The O²⁻ ion, for example, is not even stable in the gas phase and owes its stability in a crystal to the electrostatic potential of its surroundings. Watson⁴ introduced an approximate way to include the effects of the electrostatic site potential on the electronic structure of an ion. For a given crystal structure and volume, the total electrostatic potential (calculated from the bare Coulomb interactions only) from all other ions in the crystal is calculated at the site of one of the ions. This potential is then approximated by placing a charged sphere (with charge q and radius r_s) around the ion in question, such that the potential inside that sphere q/r_s matches the electrostatic site potential. In the present study, the charge on the sphere was chosen to be 2 to ensure charge neutrality. This simple site potential is included in a Hartree-Fock calculation, which

determines the crystal-stabilized wave function for the ion. The atomic self-energy E_a , i.e., the energy of the stabilized wave function in the absence of the crystal field, changes as the electronic structure of the ion is perturbed,^{4,5} which, in turn, makes a contribution to the pressure of the system as is described hereafter.

Given the wave function for the ions, the interaction between them can be determined with the modified (Gordon-Kim) electron-gas model⁶ (MEG), in which the interaction between two atoms (ij) is written as

$$V_{ij} = \int d^3r (E[\rho_i + \rho_j] - E[\rho_i] - E[\rho_j]), \quad (1)$$

where

$$E[\rho] = C_k \rho^{5/3} - C_x \rho^{4/3} + E_c[\rho] + \rho \Phi[\rho]. \quad (2)$$

The terms in $E[\rho]$ represent the kinetic, exchange, correlation, and Coulomb potentials, respectively. The constants C_k and C_x are the usual constants for the noninteracting electron-gas kinetic and exchange density functionals.⁶ To correct for problems such as the exchange self-energy, these constants are then multiplied by numerical correction factors that depend only on the number of electrons.⁶ Φ is the electrostatic potential and $\rho_{i(j)}$ is the electronic density of atom $i(j)$. For the present study, the interaction between two O^{2-} ions consisted of the short-range part calculated with the MEG model, plus the point Coulomb interaction ($4/r$). The short-range interaction between the protons and the oxide ions consist only of the nonpoint Coulomb interaction, i.e., the interaction is totally electrostatic. Since for each structure and volume there is a different O^{2-} wave function, the interaction potentials are volume and structure dependent.

We have determined the (classical) 0 K lattice energy E_l as a function of volume for the ionic model of water in the structures found in the molecular dynamics study; the cuprite and antiferite structures. For the present calculations, we have chosen to use a variation of the MEG model applicable to solids, where the lattice energy is determined directly, with no prior calculation of the individual interaction potentials.⁵ The contribution to the pressure from the lattice energy is calculated for each structure by fitting the lattice energy as a function of volume and evaluating $P_l = -\partial E_l / \partial V$.

As noted above, the self-energy of the atoms is dependent on volume due to the change in the atomic wave function. The increase in atomic self-energy (E_a) with decreasing volume yields a contribution to the pressure (P_a), which can again be determined by numerically evaluating $P_a = -\partial E_a / \partial V$. P_a is quite large (100–200 GPa) over the range of volumes (4–7 cm^3/mol) studied here. At larger volumes (6–7 cm^3/mol), the lattice pressure P_l is negative, but the atomic self-energy pressure P_a is large and positive, yielding a net positive total pressure.

The classical Gibbs free energy is given at 0 K by

$$G = E_l + E_a + (P_l + P_a)V. \quad (3)$$

We plot G for the cuprite and antiferite structures in Fig. 1. At about 330 GPa the two curves cross, indicating a phase transition at this pressure from the cuprite to the antiferite structure. Since the curves are almost tangen-

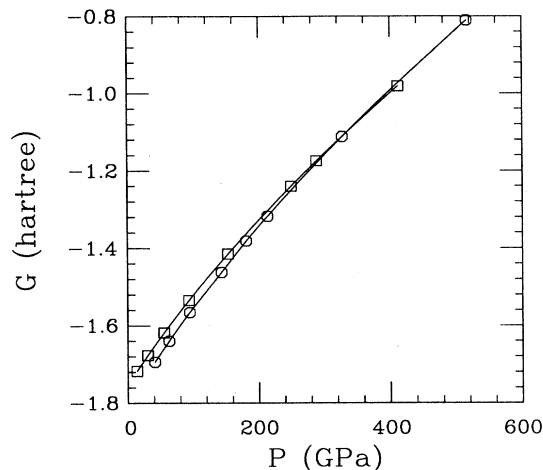


FIG. 1. Free energy vs pressure for the cuprite (circles) and antiferite (squares) structures. Note that the curves cross at about 330 GPa, indicating where a transition would occur from cuprite to antiferite. A constant (74 hartree) was added to each curve.

tial, small errors in either curve could shift the estimated transition pressure by a considerable amount.

In Fig. 2 we compare the pressures at 0 K versus volume for the cuprite and antiferite structures with the experimental room-temperature results of Hemley *et al.*¹ Classically, we expect very little thermal pressure at these densities, so the comparison should not be greatly affected by the difference in temperatures. At the estimated transition pressure (330 GPa), we have connected the curves to indicate the volume change on the transition (about 6%). At low pressures, there is close agreement with ex-

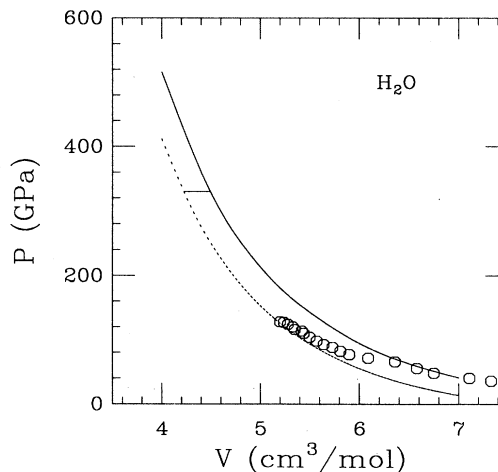


FIG. 2. Pressure vs volume for H_2O . The circles are the room-temperature experimental results of Ref. 1. The solid curve is from the present calculation with the cuprite structure while the dashed curve is for the antiferite structure. The solid line connecting the two curves at 330 GPa indicates where a phase transition takes place from the cuprite to the antiferite structure.

periment for the results with the cuprite structure. As the volume decreases, the theoretical curve for cuprite becomes too high in pressure. The antiferite structure has a considerably smaller volume and, in fact, agrees fairly well with experiment at pressures around 100 GPa, which perhaps suggests that the ionic model is not entirely inappropriate to ice at such high pressures. The overall agreement between the present results and experiment is considerably better than that obtained when a molecular interaction potential is used.¹

The nearest-neighbor distance between O^{2-} and the H^+ ions is given in both the cuprite and antiferite structures by $r_{OH} = \sqrt{3}a/4$, where a is the lattice parameter. For a given volume, the lattice constant in the antiferite structure a_a is $2^{1/3}$ times that in the cuprite structure a_c , so the nearest-neighbor r_{OH} distance is larger in the antiferite structure and the electrostatic site potentials, which are dominated by the nearest-neighbor interactions, are smaller. For example, at the calculated transition pressure r_s (the radius of the Watson sphere) in the cuprite structure is approximately 1.43, while that in the antiferite structure is about 1.51. Thus, the electronic structure of the O^{2-} ions will not be the same in the two crystal structures at the same pressure, and the intermolecular interactions will be different. This disparity in interaction potentials will likely cause some inconvenience in applying traditional computer-simulation techniques to the modeling of the cuprite-antiferite phase transition.² These calculations may require the use of methods such as those proposed by Car and Parrinello,⁷ in which the electronic structure and total energy are calculated at each ionic configuration.

In summary, we have found that a classical, nonpolariz-

able, ionic model for water consisting of O^{2-} and H^+ ions yields an equation of state that is in reasonable agreement with recent synchrotron data. We find that the low-pressure cuprite structure, which, like the experiment, show a bcc arrangement of the O^{2-} ions, transforms at high pressures to an antiferite structure, with an fcc arrangement of the O^{2-} ions. Our previous computer simulations, using a simpler potential model, found evidence for a fast-ion phase at high temperatures in the antiferite structure.² It seems very likely that this will also hold true for the present model as well. The existence of such a fast-ion phase could be relevant to the modeling of the Jovian planets, where temperature and pressures are quite high.⁸ The present calculations are static and classical, but because of its light mass, the proton dynamics are likely to be quantum in nature, even under these extreme conditions. However, to go beyond the present calculations and include quantum effects on the proton motion in a fast-ion phase would involve calculational sophistication beyond the accuracy of the present nonpolarizable ionic model.⁹ More extensive calculations, including quantum effects, would be justified if new high-pressure experiments find a transition to a structure with close-packed oxygen atoms, since this would likely also imply the existence of a fast-ion phase.

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¹R. J. Hemley, A. P. Jephcoat, H. K. Mao, C. S. Zha, L. W. Finger, and D. E. Cox, *Nature (London)* **330**, 737 (1987).

²P. Demontis, R. LeSar, and M. L. Klein, *Phys. Rev. Lett.* **60**, 2284 (1988).

³For an example of a model that incorporates deformable oxygen ions, see M. J. Mehl, R. J. Hemley, and L. L. Boyer, *Phys. Rev. B* **33**, 8685 (1986).

⁴R. E. Watson, *Phys. Rev.* **111**, 1108 (1958).

⁵C. Muhlhausen and R. G. Gordon, *Phys. Rev. B* **24**, 2147

(1981); R. LeSar and R. G. Gordon, *ibid.* **25**, 7221 (1982).

⁶M. Waldman and R. G. Gordon, *J. Chem. Phys.* **71**, 1325 (1979).

⁷R. Car and M. Parrinello, *Phys. Rev. Lett.* **55**, 2471 (1985).

⁸For a discussion of modeling of the Jovian planets, see W. B. Hubbard, in *Simple Molecular Systems at Very High Density*, edited by A. Polian, P. Loubeyre, and N. Boccara (Plenum, New York, 1989), p. 203; see also W. J. Nellis, D. C. Hamilton, N. C. Holmes, H. B. Radousky, F. H. Rhee, A. C. Mitchell, and M. Nicol, *Science* **240**, 779 (1988).

⁹A technique that could be used to treat the quantum dynamics is discussed in M. Sprik and M. L. Klein, *J. Chem. Phys.* **89**, 1592 (1988).