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LETTER TO THE EDITOR

Equation of state and metallization of ice under very high pressure

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Abstract. The equation of state and the electronic bandstructure of ice have been calculated in the recently proposed high-pressure phase XI (anti-fluorite structure) by using the local-density approximation with the augmented-plane-wave method. The calculated pressure of metallization 1.76 TPa is in agreement with the value of 1.0–1.5 TPa conjectured by Besson, but it is 2.5 times higher than that estimated by the classical Herzfeld theory and Thomas–Fermi–Dirac model. It has been also shown that the ionic model proposed for the ice XI phase is not adequate even for ultra-high pressure from the viewpoint of the bandstructure calculation.

The equation of state (EOS) and the electronic bandstructure of ice under very high pressure have attracted attention because of their relevance to the understanding of the interior structures of outer planets [1]. Several speculations on the phase diagram of ice under very high pressure have been reported [2, 3]. Recently a new high-pressure phase (cuprite structure) labelled as ice X has been discovered above 40 GPa [4, 5]. This phase has a symmetric hydrogen-bonded structure and oxygen atoms take the body-centred cubic (BCC) arrangement. In relation to this, Besson [3] proposed that at very high pressure the oxygen sublattice becomes the denser face-centred cubic (FCC) form and the phase X is transformed into the anti-fluorite structure labelled as ice XI and after this a pressure-induced insulator–metal transition occurs. The phase XI is assumed to have a strong ionic character [2, 3]—due to pressure ionization. According to the recent classical molecular dynamic calculation by Demontis *et al* [6], using a purely electrostatic and the Born-Mayer-type short-range interaction, the phase transition from ice X to ice XI should be observed at about 100–200 GPa. Besson also conjectured that highly dense ice has a similar electronic bandstructure to solid Ne (which has the highest metallization pressure of 150 TPa in solids [7]), because of its isoelectronic structure, so the metallization would take place at an ultra-high pressure of the order of 1.0–1.5 TPa; however, he did not give the reason why the metallization pressure of ice is about 1/100 of that of solid Ne. On the other hand the classical Herzfeld theory [8] using the mean molecular polarizability 1.44×10^{-24} cm^3 [9, 10] and the EOS from the Thomas–Fermi–Dirac (TFD) model [11] predicts the pressure of metallization to be 700 GPa with a volume of 3.64 cm^3 mol^{-1}.

In this letter we have calculated the EOS and the electronic bandstructure of ice in the anti-fluorite structure and have estimated the pressure of metallization by using the

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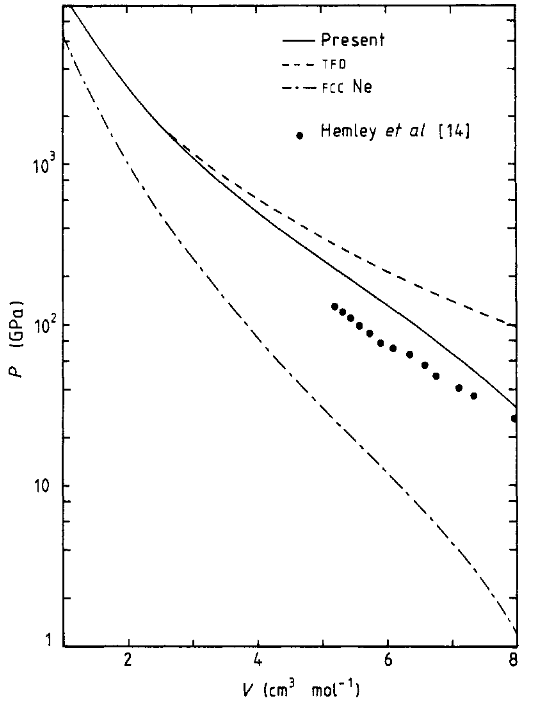

Figure 1. The P–V curves in the static lattice.

Table 1. Madelung energy E_M per molecule in units of e^2/r_s. For D^4_{6h} and T^6_h the u-parameters which give the lowest energies are listed and the structures of the oxygen sublattices are shown in the last row.

	Cuprite	D^4_{6h}	T^6_h	Anti-fluorite
E_M	−29.1286	−30.2196	−30.2962	−29.9697
u		0.401	0.428	
	BCC	HCP	FCC	FCC

local-density approximation with the augmented-plane-wave method. We have also shown that the ionic model proposed for ice XI is not adequate even for ultra-high pressure in view of the bandstructure calculation. In the present calculation the $(1s)^2$ electrons of oxygen atoms are treated as the core electrons localized inside the muffin-tin spheres centred at respective lattice sites of oxygens and the remaining eight electrons per unit cell are treated as the Bloch electrons having amplitudes in the whole crystal. In calculating the wave function of the Bloch electron the angular momenta are taken up to $l = 12$ and for each wave vector $\boldsymbol{k}$ the reciprocal lattice vectors $\boldsymbol{G}$ are included up to $|\boldsymbol{k} + \boldsymbol{G}|^2 \leqslant 19(2\pi/a)^2$ with a as the lattice constant. For the k-points in the Brillouin zone we take 10 points for an insulating phase with the use of the special-point technique and 256 points for a metallic phase. The pressure is calculated from

$$3PV = 2T_s[n] + U[n] - 3\int_V [\varepsilon_{xc}(n(r)) - \mu_{xc}(n(r))]n(r)\,dr \qquad (1)$$

where $n(r)$ is the electron density and $T_s[n]$ and $U[n]$ denote, respectively, the kinetic

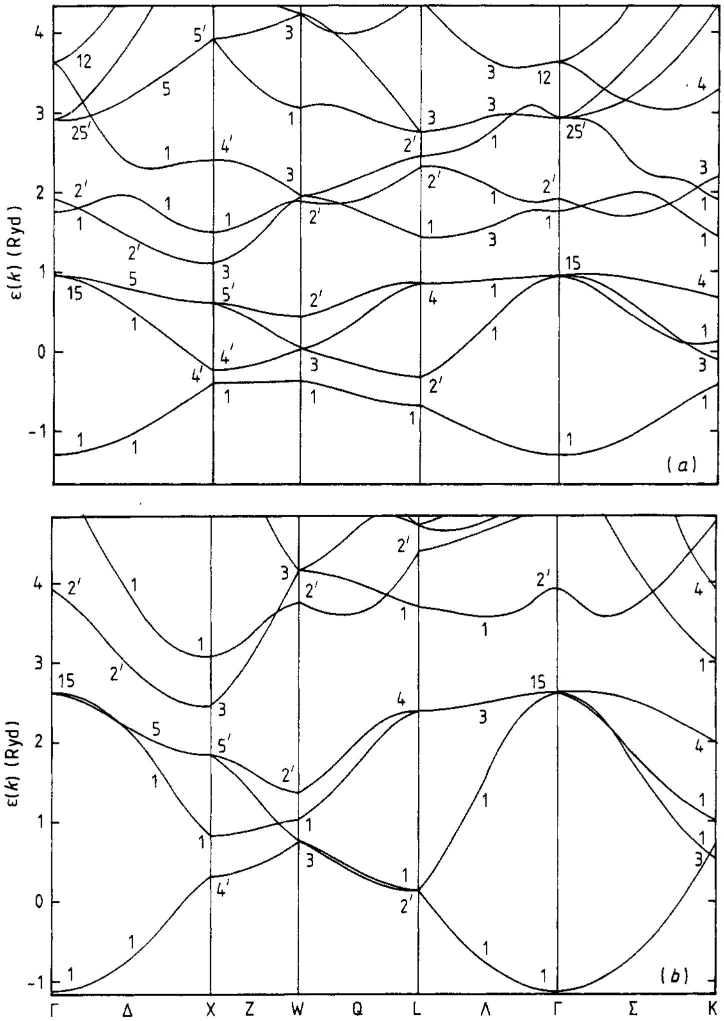

Figure 2. The electronic bandstructures in the ice XI phase at (*a*) $V = 4.0\,\mathrm{cm^3\,mol^{-1}}$ and (*b*) $V = 2.0\,\mathrm{cm^3\,mol^{-1}}$.

energy of the non-interacting electron system having the same density $n(r)$ and the classical electrostatic energy, both of which are taken per unit cell with volume V. For the exchange–correlation energy density, $\varepsilon_{\mathrm{xc}}(n)$, Ceperley and Alder's result parametrized by Perdew and Zunger is used and $\mu_{\mathrm{xc}}(n) = (\mathrm{d}/\mathrm{d}n)(n\varepsilon_{\mathrm{xc}}(n))$. The details of the method of calculation are given in [12].

Figure 1 shows the P–V curve in the static lattice where the present result is compared with those of the TFD model and FCC Ne. Besson suggested that ice has a similar EOS to solid Ne at very high pressure because the EOS of the isoelectronic substances such as (Kr, RbBr) and (Xe, CsI) are indistinguishable within experimental errors at very high pressure as demonstrated by Aleksandrov *et al* [13]. However, ice XI is less compressible than solid Ne due to the presence of protons in contrast to Besson's assumption. The present results give higher pressures than experiment [14] which showed that the BCC oxygen sublattice persists up to 128 GPa. Here we remark that from the viewpoint of

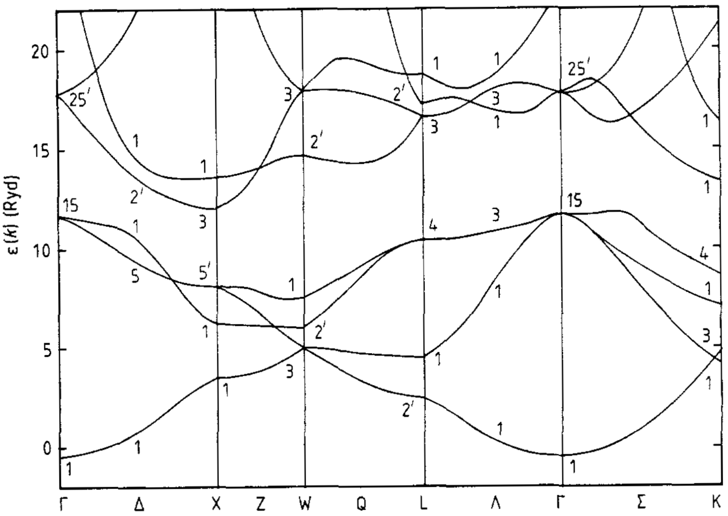

Figure 3. The electronic bandstructure of FCC Ne at $V = 0.33$ cm^3 mol^{-1}.

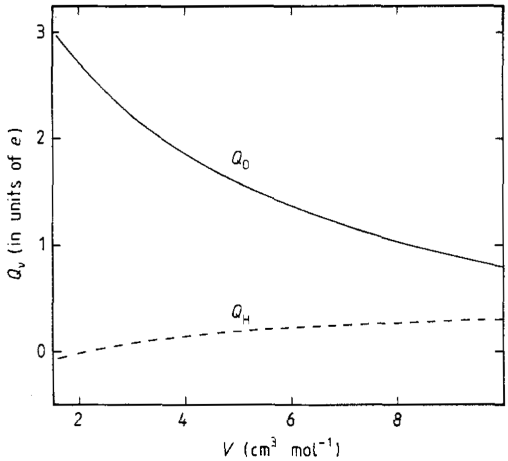

Figure 4. The volume variation of the total charge Q_ν inside the νth muffin-tin sphere.

the Madelung energy E_M per molecule ice XI is more stable than ice X at ultra-high pressure where the atoms are highly ionized. However, there are other structures with the close-packed oxygen sublattice. Among them $D_{6h}^4(P6_3/mmc)$ and $T_h^6(Pa3)$ give lower E_M than the anti-fluorite structure. Therefore it seems more probable that a highly dense ice has the sequence of phase transitions given by cuprite$\rightarrow D_{6h}^4 \rightarrow T_h^6$ and accompanying this the oxygen sublattice becomes BCC → HCP → FCC, which will be discussed elsewhere. In table 1 we tabulated the values of E_M in units of e^2/r_s with r_s as the radius of the sphere occupied by one electron and $-e$ as its charge.

Figures 2(*a*) and (*b*) show the electronic bandstructures at $V = 4.0$ and 2.0 cm^3 mol^{-1}, respectively. In figure 2(*a*) the two lower bands are the valence bands which consist of the 2s and 2p bands of oxygens and the highest occupied state is at the Γ point (Γ_{15}). The lower unoccupied bands result from the bonding and anti-bonding combinations of the 1s states of two hydrogens in the unit cell and the lowest unoccupied state is at the X point (X_3). The indirect gap Γ_{15}–X_3 disappears at $V = 2.50$ cm^3 mol^{-1} with the pressure of 1.76 TPa. This value of pressure, which gives the lower boundary for the metallization in the XI phase, is in agreement with that conjectured by Besson, but it is 2.5 times higher than that proposed by the Herzfeld theory. The electronic bandstructure of ice XI near the bandgap closing is very similar, except for the bandwidths, to that of FCC Ne which is shown in figure 3 for $V = 0.33\,\mathrm{cm}^3\,\mathrm{mol}^{-1}$. However, the bandgap closing mechanisms are different for these cases: in the case of Ne the X_3 state results from the unoccupied 3d states of Ne atoms which are very high in energy as they have a larger principal quantum number than the valence 2p states. This produces a very high metallization pressure of 150 TPa. On the other hand in the XI phase of ice the X_3 state comes from the anti-bonding combination of hydrogen 1s states. Though this state is not so high in energy as is seen in figure 2(*a*), it moves downwards very slowly relatively to the top of the valence band, under compression, due to the spherical nature of the 1s orbitals.

In order to look into the ionic nature of ice XI, we have calculated the following quantity

$$Q_\nu = Z_\nu - \int_{V_\nu} n_\nu(\xi)\,\mathrm{d}\xi \qquad (2)$$

where Z_ν and $n_\nu(\xi)$ denote, respectively, the atomic number of the νth nucleus and the electron density inside the νth muffin-tin sphere with the volume V_ν. Here we take the radius of the sphere to be $\sqrt{3}/8a$. Figure 4 shows the volume variation of Q_ν. The bandstructure calculation shows that as the crystal is compressed, the electron density at the oxygen site becomes more diffusive moving rapidly in between the spheres and a part of it also moves gradually into the hydrogen sites to neutralize proton charges. Thus the XI phase cannot be described by the ionic model even for ultra-high pressure.

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