Ab-initio study of the structural and electronic properties of osmium under high pressure

A. Rubio-Ponce\textsuperscript{1}, D. Olguín\textsuperscript{2} and R. de Coss\textsuperscript{3}

\textsuperscript{1}Departamento de Ciencias Básicas, UAM-Azcapotzalco, Av. San Pablo 180, 02200 México, D. F. MEXICO
\textsuperscript{2}Departamento de Física, Centro de Investigación y de Estudios Avanzados, A.P. 14740, C.P. 07300 México, D. F. MEXICO
\textsuperscript{3}Departamento de Física Aplicada, Centro de Investigación y de Estudios Avanzados - Mérida, A.P. 73 Cordemex 97310, Mérida, Yucatán. MEXICO

E-mail: arp@correo.azc.uam.mx

Abstract. The structural and electronic properties of osmium (Os) have studied using the full potential linearized augmented plane wave method and the generalized gradient approximation for the exchange-correlation energy. The calculations were done including the spin-orbit (SO) coupling and for hydrostatic pressures up to 400 GPa. The total-energy as a function of the cell volume was computed assuming four different crystal structures, namely hcp, fcc, hcp − ω, and bcc. Contrary to previous non-relativistic LDA calculations our study shows that the equilibrium phase of Os correspond to the hcp structure and that remain stable in the studied range of pressures and no structural transition to the fcc, hcp − ω or bcc phases are obtained.

Keywords: Density functional theory, electronic band structure, hydrostatic pressure.

1. Introduction

The transition metal osmium (Os) has an hexagonal close packed (hcp) structure and the highest density among the elements under ambient conditions. Recently, there has been a lot of interest in the high pressure properties of Os after that the first measurement of the bulk modulus ($B_0$) and first derivative ($B'_0$) were made few years ago by Cynn et al., \cite{1}. These authors reported diamond anvil cell compression studies up to 60 GPa for Os. They found that Os is less compressible than diamond ($B_0 = 446(1)$ GPa and $B'_0 = 3.0(1)$)\cite{2}, and has a $B_0$ and $B'_0$ equal to $462(12)$ GPa and $2.40(5)$, respectively.

In the same direction, first principles calculations for Os under pressure, using the pseudopotential plane wave method and the local density approximation (LDA) for the exchange and correlation energy density functionals done by Hebbache and Zemzemi \cite{3}, predicted that in the limit of very low temperatures the face centered cubic (fcc) structure is more stable than the hcp structure. Also, they claimed that, for small compression pressures, i.e., $p < 115$ GPa, Os is harder than diamond, their calculated value for $B_0$ was larger than the corresponding value measured for diamond (see Table II and Fig. 3 on Ref.\cite{3}).

Recent high-pressure and low temperature measurements have shown that Os is more compressible than diamond. Values reported by Takemura ($B_0 = 395(15)$ GPa and $B'_0 = 4.5(5)$)\cite{4} and Occelli et al., ($B_0 = 411(6)$ GPa and $B'_0 = 4.0(2)$)\cite{5}, show these facts. On the other hand, using pulse–echo ultrasound and resonance ultrasound spectroscopy, Pantea, et
al., [6] have measured the low temperature $B_0$. They found that at any temperature $B_0$ does not exceed the diamond value, the reported values are 410 GPa and 405 GPa for zero-temperature and 300 K, respectively.

Sahu and Kleinman [7] using the fully relativistic linear augmented plane-wave method calculated the $B_0$ and its $B_0'$ for Os. In their calculations they used the LDA ($B_0$ = 453.59GPa and $B_0'$ = 5.26), as well as the generalized gradient approximation (GGA) ($B_0$ = 401.30GPa and $B_0'$ = 5.47) to compute the exchange and correlation energy density functional. From their results concluded that Os is softer than diamond.

2. Computational strategy
The structural and electronic properties of Os were obtained by using the full potential linearized augmented plane wave (FLAPW) method as it is implemented in the WIEN2k code [8], the exchange and correlation energy was evaluated within the GGA[9], and we have included the SO coupling as well. In the calculations, a step analysis was carefully performed to ensure the convergence of the total energy in terms of the variational parameters, here we chose the next values: muffin-tin radii (RMT) of 2.1 a.u., and the plane wave expansion parameter $R_{MT}K_{max} = 9.0$ (where $R_{MT}$ is the MT radius and $K_{max}$ is the plane wave cutoff), while the energy cutoff parameter was $G_{max} = 16$. At the same time an apropiate set of $k$–points in the irreducible part of the Brillouin zone was used. Convergence was assumed when the energy difference was less than $10^{-5}$ Ry in all cases.

In our study, we have considered the hcp ($P6_3/mmc = D_{6h}^5$, space group 194) as the stable crystal structure of Os. Then, three other hypothesis crystal structures were also considered in our calculations, namely: the hcp − ω ($p6/mmm=D_{6h}^5$, space group 191), the fcc (Fm3m = O$_h^5$, space group 225) and the bcc (Im3m = O$_h^5$, space group 229). The number of $k$–points used in the full irreducible part of the Brillouin zone (FBZ) was 240 for the hcp and hcp − ω phase, and 220 for the fcc and bcc structures. The Os atomic electronic configuration used in the calculations was: [Xe] 4$f^{14}$, 5$d^{6}$, 6$s^{2}$, where the 5$p$ orbitals were included by using the local orbital extension of the FLAPW method [8].

The structural parameters are obtained by fitting the calculated total energy of each primitive cell to the third–order Birch–Murnaghan equation of state (EOS)[10]

3. Results
Our calculated lattice parameters for Os–hcp, considering SO coupling, are $a = 2.7693\text{Å}$ and $c = 4.3676\text{Å}$, where the $c/a$ ratio was optimized for each unit cell volume ($c/a = 1.5771$). This value is in excellent agreement with the experimental data (namely, $c/a = 1.5794$ [4]), which means that there is not change in the total energy.

Then, our calculated value for $B_0$ and $B_0'$ was 390.74 GPa and 4.57, respectively, in agreement with previous experimental reports [4, 5, 6, 11] and other calculations [7, 12, 13, 14, 15, 16, 17].

For the hcp − ω structure we optimized the lattice parameters $a$ and $c$, as was done in the hcp case, the found values were $a = 4.3420\text{Å}$, $c = 2.7281\text{Å}$, and $c/a = 0.6283$, while $B_0$ = 370.97GPa and $B_0'$ = 4.55. For the other hypothetical two cases, the found structural parameters were $a = 3.8716\text{Å}$, $B_0$ = 385.64GPa, and $B_0'$ = 4.72 for fcc; and $a = 3.1139\text{Å}$, $B_0$ = 316.09GPa, and $B_0'$ = 4.80 for bcc. In our calculations, all the found values for $B_0$ are lower than the corresponding value for diamond, in agreement with previous theoretical results [15, 16, 17, 18].

For the different studied crystal structures, the hcp phase has the lowest total energy (see the inset in Fig. 1). With respect to the hcp curve, the minimum of the energy for the hypothetical crystal structures fcc, hcp − ω, and bcc is located at 137, 338, and 778 meV, respectively. Our calculations confirm the interpretation that the hcp is the most stable crystal structure for Os, in disagreement with the pseudopotential calculations carried out by Hebbache and Zemzemi [3].
Figure 1. (Color online) Gibbs free energy difference at 0K vs. pressure for the different Os structures. Note that there is not predicted phase transition for the calculated hydrostatic pressures up to 400 GPa.

Looking for a possible phase transition between the different crystal structures considered in this work, we have calculated the Gibbs free energy $G = E + PV - TS$ per atom at 0K, where $G$ is equivalent to the enthalpy. The intersecting point of the different functions $G_{hcp}(P)$, $G_{fcc}(P)$, $G_{hcp-\omega}(P)$ or $G_{bcc}(P)$ defines the pressure of the rigid lattice transition between the different structures. According to our calculations, no phase transition is obtained for the $hcp$, $fcc$, $hcp-\omega$ or $bcc$ crystal structures for these pressures, as it is clearly shown in Fig. 1, where no crossing for the different curves is obtained.

As it is well known, to describe properly the electronic properties of the heavy metals it is very important to take into account, in the calculations, the SO coupling effects [19, 20]. Thus, we compare in Fig. 2 the calculated density of states (DOS), solid lines show the calculation including SO coupling, while dashed show the calculation without SO. As we have found, energies just below $E_F$, the 6s (Fig. 2a) electrons contribute in an important way to the electronic properties of Os. Fig. 2b depicts the contribution of the 5p orbitals, the states are located around $-45eV$. With the SO interaction these states split in two new bands with a gap of 10.7eV, and are the more affected states. Fig. 2c shows the 5d states, as in the case of the 6s orbitals, the introduction of SO coupling produces not changes on these orbitals. Then, the states around $-47eV$ are derived mainly from the 4f orbitals, as it is shown in Fig. 2d. The SO coupling splits these states in two new bands with a gap of 2.8 eV. Our results show that the electronic properties of Os at $E_F$ are mainly governed by the 5d electrons, while the contribution of the 5p and 4f electrons is almost negligible. These facts mean that at $E_F$ the electronic hybridization is mainly obtained from the 6s and 5d states, while hybridization of the 5p and 4f states is almost negligible.

4. Conclusions
Our calculated P-V equation of state for Os is in good agreement with recent experimental data. We found that Os has a $B_0$ and $B'_0$ equal to 390.74 GPa and 4.57 respectively and is more compressible than diamond. In contradiction with the previous non-relativistic LDA-calculation[3], we found that Os in the $hcp$ phase has lower energy than the $fcc$, $hcp-\omega$ and $bcc$ structures. The $hcp$ structure remains stable for pressures up to 400 GPa and structural transition to the $fcc$, $hcp-\omega$ or $bcc$ was not found. On the other hand, the SO coupling should
Figure 2. (Color online) Partial contributions to the calculated DOS. The splitting of the lower bands occurs only for the p and f states.

be included to properly describe the Os electronic band structure. At this moment, diamond is the hardest known material and also has the highest known bulk modulus $B_0 = 443$ GPa.

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