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First-principles study of osmium under high pressure

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Abstract

Considering the effect of spin–orbit coupling, we have studied the equation of state, structural parameters and electronic structures of osmium under high pressure by first-principles plane-wave basis pseudopotential calculations. We find the following: (1) the calculated bulk modulus is less than that of diamond, and the value becomes smaller after taking into account the spin–orbit coupling; (2) the proposed isostructural phase transition (c/a ratio anomaly) around 25 GPa is not supported by the present calculations. By analysing the band structure, the density of states at the Fermi surface, and the equation of state for the cases with and without spin–orbit coupling, we find no electronic topological transition up to 150 GPa.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Osmium (Os) has attracted extensive interest, not only because it is the least compressible elemental metal, but also because of the possible isostructural phase transition suggested recently [1–12]. Experimentally, Cynn *et al* [1] reported that Os has a very high bulk modulus ($B_0 = 462$ GPa), which is even higher than that of diamond ($B_0 = 446$ GPa) [2]. However new values of the bulk modulus reported recently, 395 GPa by Kenichi, who carried out high-pressure powder x-ray diffraction measurements [3], and 411 GPa by Occelli *et al* from angle-dispersive x-ray diffraction [4], are still smaller than that of diamond. It is suggested that the discrepancy between the above experimental results possibly comes from the different quasi-hydrostatic conditions, which are better in the later experiments. In addition to the very large bulk modulus of Os, Occelli *et al* [4] have measured the equation of state (EOS) of Os up to 75 GPa, and claimed that a discontinuity in the first pressure derivative of the axial ratio c/a around 25 GPa can be identified, although the discontinuity of the EOS is not visible. They therefore suggested that a second order isostructural phase transition occurs at 25 GPa and that the maxima in the seventh band of hcp Os electronic structure likely drop below the Fermi

level with compression, resulting in the collapse of the small hole ellipsoid. In other words, they suggested the existence of Lifshitz or the electronic topological transition (ETT) [13]. However, this result is a bit surprising, since the Os is known to be one of the densest and stiffest metals with the high bulk modulus. At such low pressure as 25 GPa, one should not expect big enough electronic structure modifications to can accommodate the c/a anomaly. It is therefore in conflict with the idea that Os might be a poor candidate to look for the ETT.

Apart from those experimental results, many theoretical studies have been performed, but mostly for the calculations of bulk modulus. The calculated results are also quite scattered, ranging from 392 to 476 GPa for B_0, due to the inconsistency in different techniques. Nevertheless, most of the calculations suggested that the bulk modulus of Os is large but still smaller than that of diamond. The only existing theoretical report addressing the c/a ratio anomaly with pressure was made by Ma *et al* [10]. Their calculations tend to support the observed anomaly in the c/a ratio around 25 GPa; however, no obvious sign for an ETT is revealed.

To address those issues, systematic accurate first-principles calculations are highly demanded, and this is the main purpose of the present paper. In addition, it is well known that Os is one of the 5d transition metals with high valence electron density, and thus has strong spin–orbit coupling (SOC). However, none of the previous calculations has included the effect of SOC. In the present study, we perform systematic studies for the equation of state with full relaxation of the c/a axial ratio, and the electronic structure of Os from first-principles calculations, including the effect of SOC. Detailed description of our calculation method will be given in section 2, the results and discussion will be presented in section 3, and conclusions in section 4.

2. Calculation methods

Total energies and structural properties of Os under high pressure are studied by the first-principles plane-wave basis pseudopotential calculations using BSTATE (Beijing Simulation Tool for Atom Technology) code [14]. The norm-conserving pseudopotential of Hamann [15] type in the fully separable form of Kleinman and Bylander [16] is employed. The pseudopotential is generated with the $5d^6 6s^2$ atomic configurations of osmium. The generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof (PBE96) [17] is used for the exchange–correlation potential. To include the effect of SOC, we perform the calculations using the relativistic fully separable pseudopotential in the framework of non-collinear magnetism [18].

It has been suggested by previous studies on hcp zinc [19, 20] that the calculations are very sensitive to the number of momentum space sampling points (k-points). Therefore, we perform a careful check for the convergence of calculated results with respect to the number of k-points and the cut-off energy for the plane-wave expansion of the wavefunction. Figure 1 shows the optimized c/a ratio as a function of the number of k-points and cut-off energy for Os under ambient pressure with experimental primitive-cell volume (188.56 Bohr^3). To get converged results, large number of k-points and high cut-off energy are required. In our final calculations, we have used the $18 \times 18 \times 14$ Monkhorst–Pack [21] mesh for the k-space integration (4536 total k-points), and the 42.25 Ryd for the cut-off energy for the wavefunction expansion, respectively. Accurate k-point integration has been done by the tetrahedron method [22].

We carry out total-energy calculations over a wide range of volumes. Structure optimizations are performed at each constant volume. We consider primitive-cell volumes ranging from 150 to 197 Bohr^3 with a very dense interval of 0.5 Bohr^3 attempting to find the possible kink of the c/a ratio versus pressure, which has been suggested by Occelli *et al* [4]. For

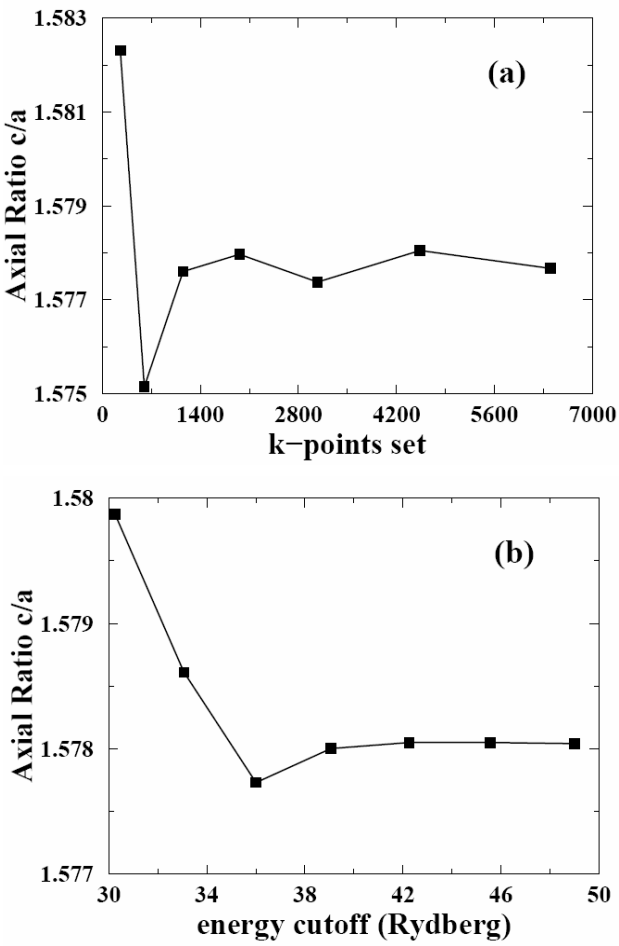

Figure 1. The convergence of calculated c/a ratio as a function of (a) number of k-points and (b) cut-off energies. The calculations are done for the Os under ambient pressure using experimental primitive-cell volume.

each volume point, we perform the self-consistent optimization for the cases with and without SOC.

3. Results and discussion

3.1. Equation of state

Total energy as a function of volume is obtained by the self-consistent total-energy calculations. The equilibrium volume (V_0), bulk modulus at ambient pressure (B_0) and its first pressure derivative (B_0') are estimated through a least-square fit of calculated points to the integrated form of the third-order Birch–Murnaghan (B–M) equation of states [23, 24]

$$E(V) = -\frac{9}{16}B_0\left[(4 - B_0')\frac{V_0^3}{V^2} - (14 - 3B_0')\frac{V_0^{7/3}}{V^{4/3}} + (16 - 3B_0')\frac{V_0^{5/3}}{V^{2/3}}\right] + E_0. \quad (1)$$

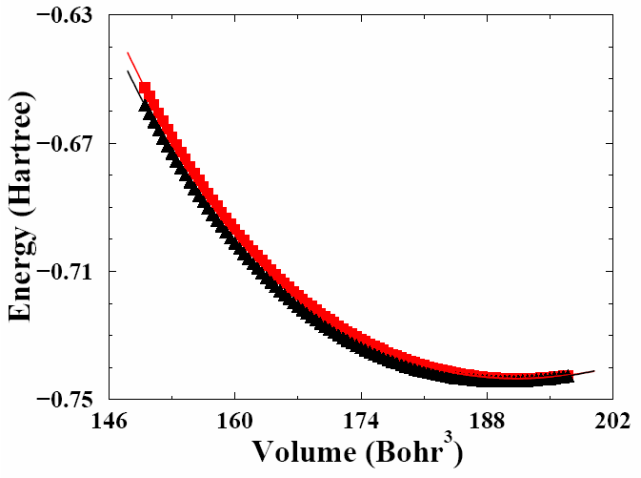

Figure 2. Calculated total energy versus volume for hcp Os. The black filled triangles (red filled squares) are for the case without SOC (with SOC). Solid lines are results from the three-order Birch–Murnaghan fitting to the EOS.

Table 1. The theoretical and experimental values of the equilibrium volume (V_0), bulk modulus (B_0) and its pressure derivative (B_0') for Os. The calculated values are presented for the cases with and without spin–orbit coupling (SOC), respectively. Values in parentheses are obtained by constraining the equilibrium volume to the experimental one. References are labelled in brackets.

	This study (GGA)		Others		
	SOC	No_SOC	GGA	LDA	Experiment
V_0 (Å^3)	28.365 (27.941)	28.140 (27.941)	28.484 [9] 28.672 [7]	27.498 [1] 27.502 [9] 28.50 [5] 27.638 [7]	27.941 [4] 27.956 [1]
B_0 (GPa)	382.8 (395.5)	394.9 (400.1)	382.3 [4] 442 [9] 443 [7]	437.3 [4] 444.8 [1] 489–366 [8] 471 [9] 476.1 [5] 457 [7]	411 [4] 462 [1] 395 [3]
B_0'	4.4 (4.6)	4.4 (4.5)	4.6 [4] 4.0 [9] 3.74 [7]	4.5 [4] 4.4 [1] 8.2–3.2 [8] 4.1 [9] 4.15 [7]	4.0 [4] 2.4 [1] 4.5 [3]

Using the obtained B_0, B_0' and V_0, the hydrostatic pressure P can be obtained from the volume derivative of equation (1)

$$P(V) = \frac{3}{2}B_0\left[\left(\frac{V_0}{V}\right)^{7/3} - \left(\frac{V_0}{V}\right)^{5/3}\right]\left\{1 + \frac{3}{4}(B_0' - 4)\left[\left(\frac{V_0}{V}\right)^{2/3} - 1\right]\right\}. \quad (2)$$

The calculated results are shown in figure 2 for the cases with and without SOC, respectively, and the fitted parameters are listed in table 1 in combination with other reported

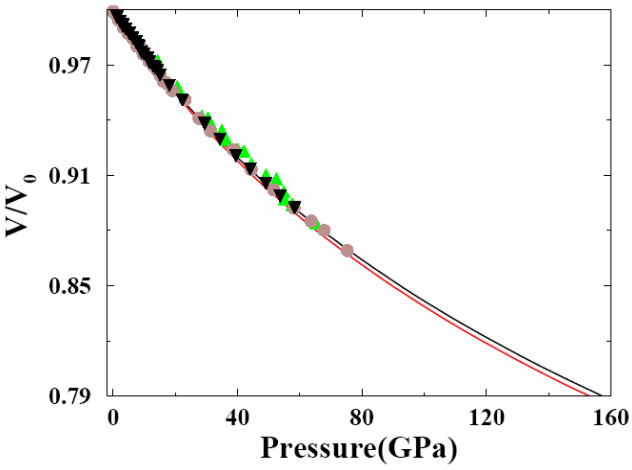

Figure 3. The calculated pressure–volume relations in comparison with experimental data (green filled triangles are from [1]; brown filled circles are from [4]; and black filled down triangles are from [3]). The black (red) line is for the case without (with) SOC.

results from the literature. The comparison of the pressure–volume relation between our results and experimental values [1, 3, 4] is presented in figure 3. Our calculated equilibrium volume is only 0.68% larger than the experimental one. From figure 3, it is evident that our calculated EOS curves are in excellent agreement with the measurements of Occelli *et al* [4] and Kenichi [3], but systematically deviate from that of Cynn *et al* [1]. The calculated bulk modulus (394.9 GPa) also agrees well with the experimental results reported by Occelli *et al* [4] and by Kenichi [3], but not with that by Cynn *et al* [1]. Our results suggest that the bulk modulus of Os is smaller than that of diamond. Cynn *et al* [1] have suggested that the SOC may affect the results. However, our calculations including SOC again agree with Occelli *et al*'s experiments [4]. Furthermore, after including SOC, the calculated bulk modulus (382.8 GPa) becomes even smaller, further suggesting the smaller bulk modulus of Os compared with diamond.

Considering the fact that the calculated equilibrium volume is slightly different from the experimental one, we have tried to constrain the equilibrium volume to the experimental one and get the new values of $B_0 = 395.5$ GPa, which is also less than the bulk modulus of 446 GPa for diamond. The claim that the difference between the experimental and the theoretical results reported by Cynn *et al* [1] can be attributed to the neglect of spin–orbit interactions in the case of the 5d transition metals is therefore invalidated. Thus the bulk modulus for Os is actually high, but does not exceed the value for diamond from the calculational perspective.

3.2. Axial ratio c/a and lattice parameters

Figure 4(a) shows the calculated pressure dependence of c/a ratio for Os over the whole range of 0–160 GPa together with experimental results [3, 4]. It is seen clearly that the calculated c/a ratios are also in good agreement with experimental data except that the suggested kink at 25 GPa is not visible from our calculated curves. Compared with experimental data, the calculations slightly underestimate the c/a ratio, but the maximum deviation for the whole pressure range is less than 0.2%. It is also seen that the effect of SOC is very small. The difference between the cases with and without SOC is less than 0.05%. The calculated c/a

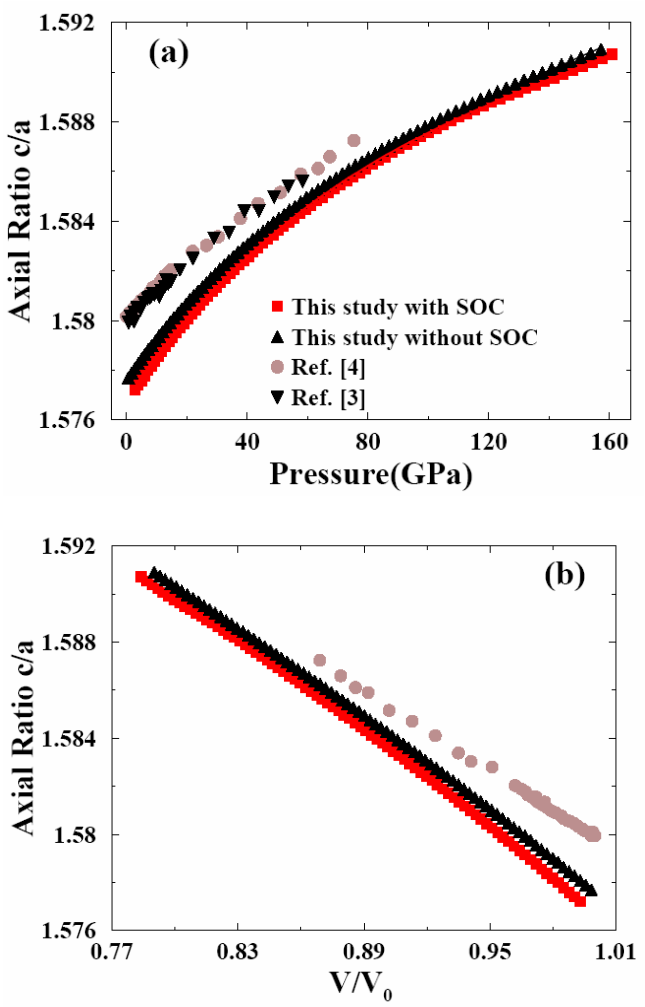

Figure 4. The calculated c/a ratio of Os as a function of (a) pressure and (b) relative volume.

curves do not show any kink and are perfectly smooth and continuous: (1) The calculated c/a variation with pressure can be well fitted by a cubic curve over the whole range of 0–160 GPa. This result is at odds with that of Occelli *et al* [4]. They have identified two distinct compression regions below and above 25 GPa, and it is because of this anomaly that they concluded the high-pressure isostructural phase transition in Os, but we do not reproduce this from theoretical calculations. (2) The volume dependence of c/a can be well fitted by a quadratic curve, in contrast with Occelli's results, which suggested a linear function for the low pressure range [4].

In contrast with our results, Ma *et al* [10] have performed structure optimization at constant pressure and suggested that the experimentally observed anomaly in the c/a ratio around 25 GPa can be reproduced. At the present stage, it is still very hard to judge what causes the discrepancy between their and our calculations. Nevertheless, it is worth noting that the experimentally suggested kink is very weak and strongly depends on the fitting process to the data points. In the reported experiments, it is clear that the densities of the data points for the regions below and above 25 GPa are quite different. On the other hand, we also want to point

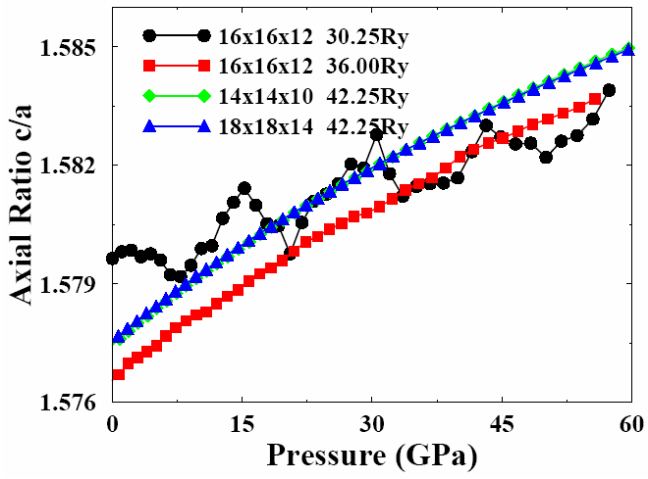

Figure 5. The calculated axial ratio c/a versus pressure at four different sets of parameters (number of k-points and the cut-off energy for the plane wave expansion) for hcp Os.

out that the calculations for the c/a ratios are very sensitive to the number of k-points and the cut-off energy. We have calculated axial ratios c/a at four different sets of parameters (figure 5) and found that the smoothness of the c/a ratio as a function of pressure is very sensitive to the parameters.

The changes of the lattice parameters a and c versus pressure are plotted in figures 6(a) and (b). It is seen that the curves are also excellently smooth and no anomaly is found, although we slightly overestimate them (less than 0.5%). Figures 6(c) and (d) show the lattice parameters a and c as a function of the volume together with experimental results. It indicates that the a and c axes change smoothly and agree well with experimental observations within the relative volume range of 0.87–1.

In order to evaluate the anisotropic lattice properties of hcp Os, the a- or c-axis compressibility has been calculated. Generally, the compressibility along a specific axis of x is defined as $k_x = -(1/x)(\partial x/\partial P)$ [18, 25]. Its dependence on relative volume is calculated from a fit to the curves of a and c versus pressure in the whole pressure region considered. The calculated results with SOC, shown in figure 7, suggest that the a-direction of the lattice is slightly more compressible than the c-direction.

3.3. Electronic structure and search for ETT

The variation of the electronic band structure with compression is examined for the cases with and without SOC. Our calculated band structures are consistent with previous results [26–29]. A comparison of band structures under zero pressure for the cases with and without SOC is given in figures 8(a) and (b). The main effect of SOC is the splitting at some degenerate symmetry points or lines. Figures 8(c) and (d) present the calculated band structures under different pressures. Special attention is paid to the seventh band, dot-dashed line (red), along the M–L symmetry line in the BZ since it has been thought to be responsible for the anomaly observed in hcp Os in [4]. However, as seen from figures 8(b)–(d), the maxima in the band hole ellipsoid never fall below the Fermi energy even for the highest pressures considered, which contrasts with the speculation of Occelli *et al* [4]. In particular, no noticeable changes in band structures are detected when the pressure is enhanced up to 150 GPa. The three-dimensional Fermi surfaces calculated by Ma *et al* also find the absence of a clear sign in the

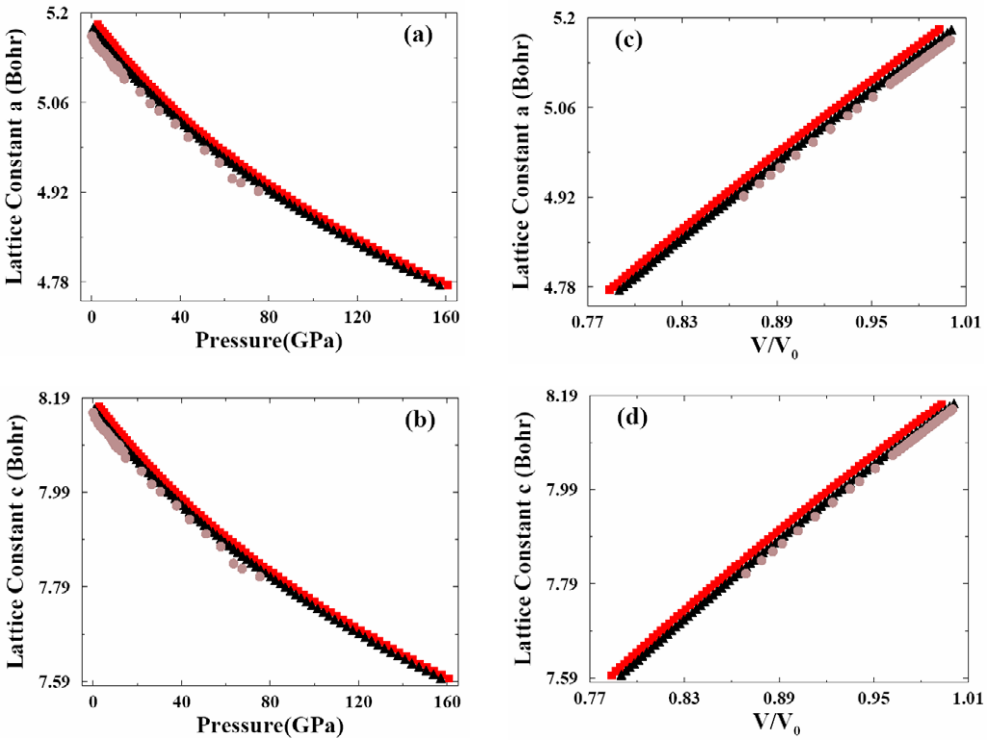

Figure 6. The calculated lattice constants a and c as functions of pressure and relative volume. The black filled triangles (red filled squares) are for the case without SOC (with SOC). Brown filled circles denote experimental data in [4].

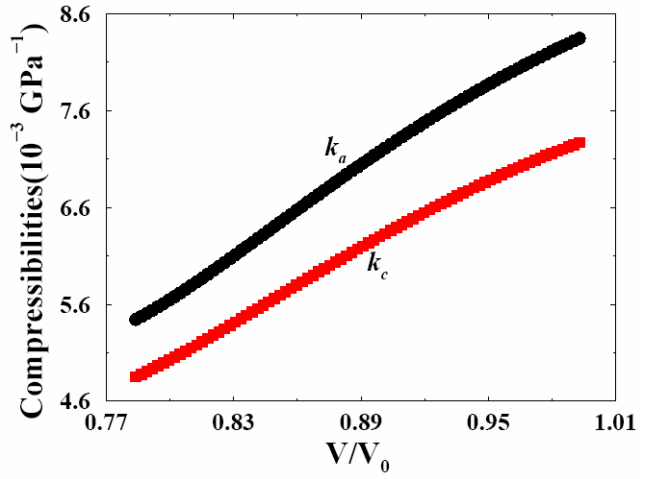

Figure 7. The calculated axis compressibility (k_a and k_c) of hcp Os versus the relative volume for the case with SOC.

change of the electron topology up to 80 GPa [10]. This further substantiates the validity of our band structures, thus the proposed ETT around 25 GPa is not supported by the calculated band structures.

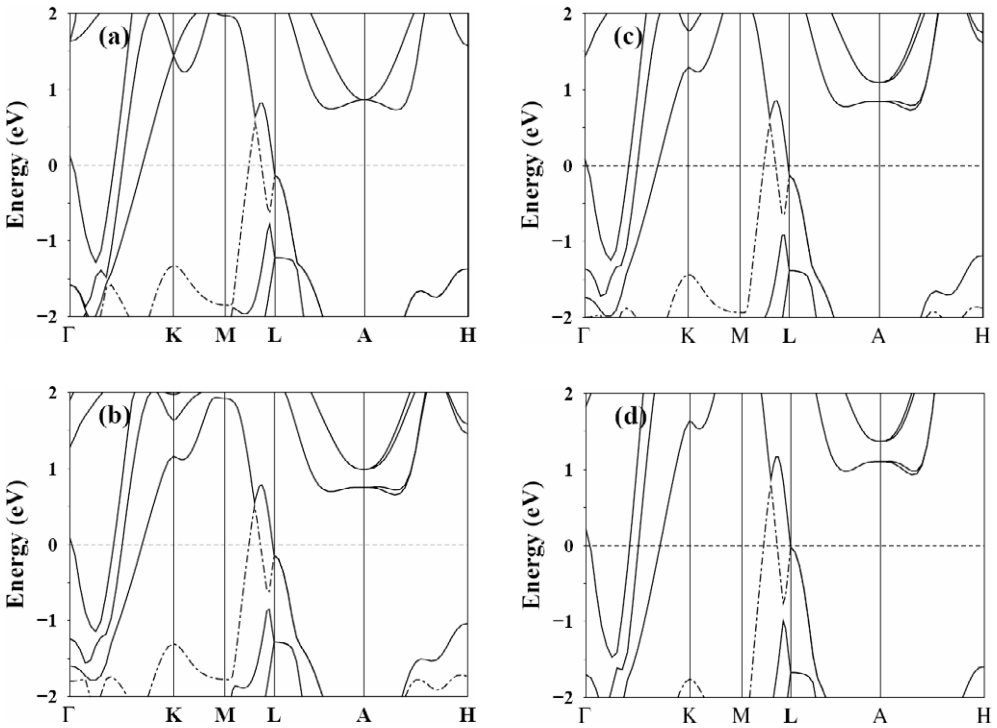

Figure 8. Calculated band structures of hcp Os. Panel (a) is for the case without SOC at the pressure of 0 GPa. Panels (b), (c) and (d) correspond to the pressure of 0, 27 and 129 GPa for the case with SOC, respectively.

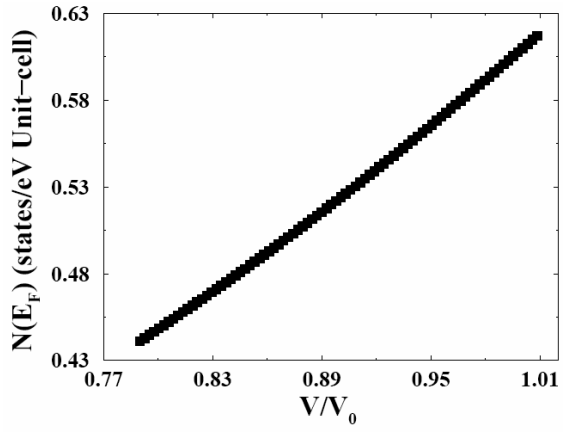

Figure 9. Total density of states of hcp Os at Fermi level versus relative volume for the case without SOC.

Analysing the behaviour of the total density of states at the Fermi level, $N(E_F)$, as a function of pressure may provide a more average view on electronic structure transformations with pressure [25]. Calculated values of $N(E_F)$ for the case without SOC as a function of the relative volume for Os are plotted in figure 9. The case with SOC is similar (not shown).

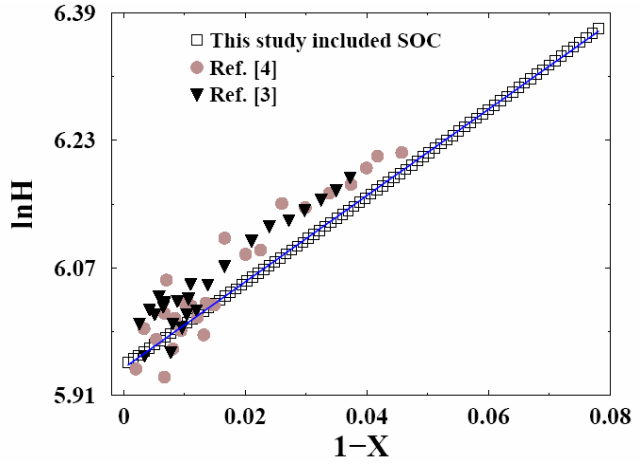

Figure 10. Universal equation of state (i.e. ln H versus $(1-X)$) for Os, where $H = [PX^2/3(1-X)]$ and $X = (V/V_0)^{1/3}$. The linear fit to ln H versus $(1-X)$ yields ln $H = 5.944\,15+5.416\,31(1-X)$.

The curve displays a monotonic and smooth decrease with reduced volumes because increasing pressure enhances band dispersion. We do not note any local anomaly of the $N(E_F)$ curve.

We come back to the dependence of the calculated total energy on the primitive volume. If an ETT occurs under pressure, the dependence of the calculated total energy on the primitive volume should show anomaly near the transition pressure. However, our calculated total energies for the whole pressure range can be perfectly fitted to a single B–M EOS (figure 2). To further check this, we focus on the region around the volume of 180 Bohr^3, which corresponds to a theoretical pressure of ∼25 GPa. Three independent fittings of B–M EOS are performed, for the data below 25 GPa, above 25 GPa and for the entire pressure range, respectively. The three curves almost completely overlap and are not resolvable. As we learn from the studies on metal zinc [30] and the intermetallic compound AuIn [31, 32], the universal equation of state (UEOS) can help identifying the existence of an ETT, because an ETT involves relative changes in the electron energy band population, and leads to change in the pressure derivative of the bulk modulus, resulting in the deviation of the UEOS from a linear variation [33, 34]. The calculated UEOS curve for the case with SOC is plotted in figure 10. The curve is completely linear and no change in slope can be seen, but experimental data scatter widely.

Therefore, from the electronic band, the total density of states at the Fermi level and the fit of the EOS, we have not found any theoretical signature of the proposed ETT.

4. Conclusions

In the present study, the equation of state, structural parameters and electronic structures of Os under high pressure are studied by systematic and accurate first-principles plane-wave basis pseudopotential calculations, for the cases with and without SOC. The calculated bulk modulus of Os is less than that of diamond, and the value becomes smaller after taking into account the effect of SOC. At the same time, the calculated pressure dependence of c/a does not show any kink and is perfectly smooth and continuous. The proposed isostructural phase transition around 25 GPa is not supported by the present calculations. By carefully analysing the band structure, the density of states at the Fermi surface and the EOS for the cases with and without SOC, we find no ETT up to 150 GPa.

Acknowledgments

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