Structural and electronic properties of OsB_2: A hard metallic material

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We calculate the structural and electronic properties of OsB_2 using density functional theory with or without taking into account the spin-orbit (SO) interaction. Our results show that the bulk modulus with and without SO interactions are 364 and 365 GPa, respectively, both are in good agreement with experiment (365–395 GPa). The evidence of covalent bonding of Os-B, which plays an important role to form a hard material, is indicated both in charge density, atoms in molecules analysis, and density of states analysis. The good metallicity and hardness of OsB_2 might suggest its potential application as hard conductors.

Hard materials are of great interest due to their superior properties of higher compressional strength, thermal conductivity, refractive index, and chemical stability beside higher hardness.[1] Besides the two well-known superhard materials of diamond and cubic boron nitride (*c*-BN), experimental and theoretical efforts are devoted to searching for a new class of hard meterials. Covalent materials are much better candidates for high hardness than ionic compounds because electrostatic interactions are omnidirectional and yield low bond bending force constants, which result in low shear modulus.[2,3] Some potential hard materials such as C_3N_4 polymorphs,[4] Si_3N_4,[5] BC_2N,[6] and B_6O,[7] have been proposed and investigated intensively in recent years.

The pure osmium (Os) has an exceptionally high bulk modulus (395–462 GPa) while its hardness is of only 400 kg/mm^2.[8] The high bulk modulus of Os is mainly due to the high valence electron density, while the low hardness is related to the metallic bonds and the hexagonal close-packed crystal structure of Os. It has been found that many transition metals, such as W, Ru, and Zr, which are soft in their pure metals, can be converted into hard materials by combining with small covalent bond-forming atoms such as boron, carbon, oxygen, or nitrogen.[9–12] For Os related materials, OsO_2 has been predicted to be very stiff,[12] and some compounds like $OsB_{0.11}$, OsB_2, and Os_2B_3 have already been synthesized.[13,14] Recently, Cumberland *et al.* studied experimentally the mechanical properties of the OsB_2 compound, and showed that it is an ultraincompressible (365–395 GPa) and hard (≥ 2000 kg/mm^2) material.[3,15]

In this Brief Report, we carry out density functional calculations on the electronic properties and the bulk modulus of OsB_2, using the highly accurate full potential linearized augmented plane wave plus local orbital (APW+LO) method as implemented in the Wien2k code.[16] The nonoverlapping muffin-tin (MT) sphere radiis of 2.02 and 1.57 bohrs are used for the Os and B atoms, respectively. Expansion in spherical harmonics for the radial wave functions are taken up to l=10. The value of $R_{MT}K_{max}$ (the smallest muffin-tin radius multiplied by the maximum k value in the expansion of plane waves in the basis set) which determines the accuracy of the basis set used is set to 7.0. The total Brillouin

zones are sampled with 6000 k points, i.e., 672 k points in the irreducible wedge of the Brillouin zone. For the exchange-correlation energy functional, we use the local density approximation (LDA) in our calculations. Since Os is a heavy element, a fully relativistic calculation is performed for core states, whereas the valence states are treated in both scalar and fully relativistic fashions. The spin-orbit coupling (SOC) is self-consistently added via the second variational step scheme with relativistic $p_{1/2}$ local orbitals included.[17] We find there is no spontaneous spin polarization in OsB_2 in the framework of the local spin density approximation (LSDA) or LSDA+SO methods. Hereafter, for the sake of simplicity, we only discussed the results from the spin-restricted calculations.

OsB_2 has an orthorhombic lattice (space group *Pmmn*, No. 59) with the experimental lattice parameters $\mathbf{a}=4.6832\pm0.0001$, $\mathbf{b}=2.8717\pm0.0002$, and $\mathbf{c}=4.0761\pm0.0001$ Å. In the orthorhombic structure, two Os atoms occupy the 2*a* Wyckoff sites and four *B* atoms occupy the 4*f* sites, as shown in Fig. 1. We optimize both lattice and internal coordinates to get a relaxed structure for OsB_2. The total energy per unit cell as a function of volume is calculated and the results are fitted using the Murnaghan equation of state to get the bulk modulus.[18] The correspond-
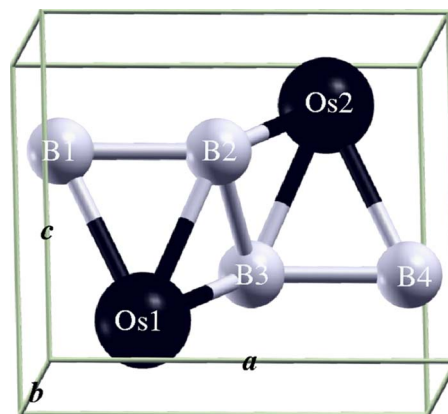

FIG. 1. (Color online) The crystal structure for OsB_2. The lattice vectors are denoted as **a**, **b**, and **c**.

TABLE I. Structural parameters and bulk modulus of OsB_2.

	LDA	LDA+SO	Experiment
Lattice parameters (Å):			
a	4.6433	4.6581	4.6832±0.0001 (Ref. 14)
b	2.8467	2.8700	2.8717±0.0002 (Ref. 14)
c	4.0432	4.0560	4.0761±0.0001 (Ref. 14)
Bulk modulus (GPa)	365	364	365–395 (Ref. 15)

ing equilibrium lattice parameters, bulk modulus from both LDA and LDA+SO methods are compared with the experimental result, as shown in Table I. We can see that the equilibrium lattice parameters calculated both in the absence and in the presence of SO are very close with the experimental value. And the bulk modulus calculated in the absence and in the presence of SO are 365 and 364 GPa, respectively; both are in good agreement with the experimental result (365–395 GPa).[15]

As discussed above, the hardness of a material is largely determined by the bonding type in the system. Thus the electronic properties of OsB_2 such as the electron density, band structure, and the density of state (DOS) are calculated in the absence and in the presence of SO at the equilibrium geometries. We find that the electron density from the LDA calcu-
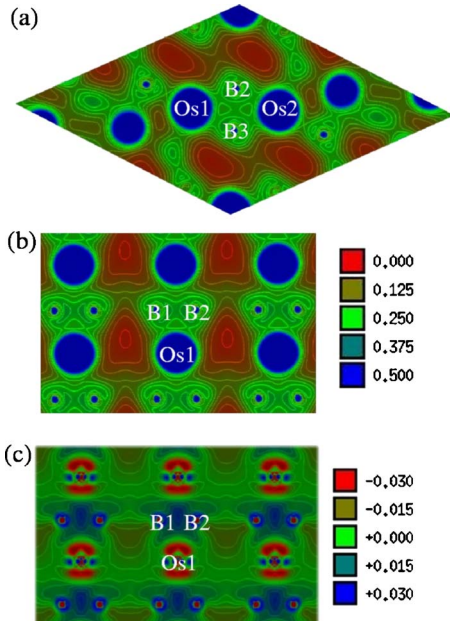

FIG. 2. (Color online) (a) The valence charge density contour (in e/a.u.^{3}) plot in the plane including Os1, Os2, B2, and B3. (b) and (c) show, respectively, the valence charge density and difference charge density contour (in e/a.u.^{3}) plot in the plane including Os1, B1, and B2. The charge density shown here is the result from the LDA+SO calculation. The LDA charge density has similar character. Os1, Os2, B1, B2, and B3 refer to the atoms labeled in Fig. 1(a).
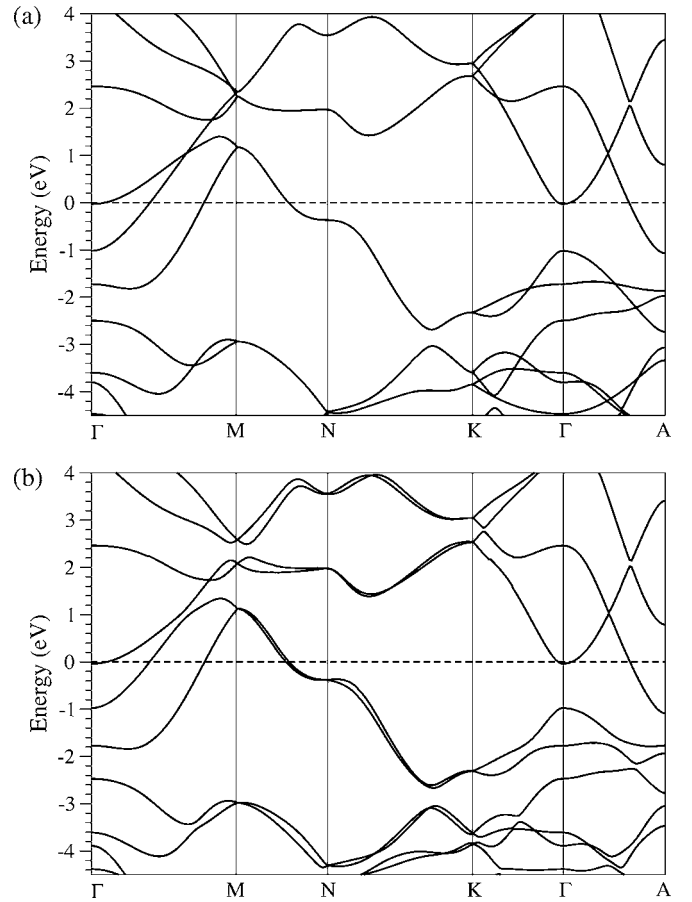

FIG. 3. (a) Band structure of OsB_2 from the LDA calculation. (b) Band structure of OsB_2 from the LDA+SO calculation. $\Gamma=(0,0,0)$, $M=(0,0.5,0)$, $N=(0.5,0.5,0)$, $K=(0.5,0,0)$, and $A=(0,0,0.5)$.

lation is almost the same as that from the LDA+SO calculation. Here we show the electron density for OsB_2 from the LDA+SO calculation in Fig. 2. Two charge density contour plots (one in the plane including Os1, Os2, B2, and B3, and the other in the plane including Os1, B1, and B2) are shown in Figs. 2(a) and 2(b), respectively. There are some electrons between Os atoms and their neighbor B atoms, indicating covalent bonding in OsB_2. To gain a more detailed insight into the bonding characters of OsB_2, we plot the difference density (the difference between total density and superposition of atomic densities) in Fig. 2(c). We can see that some electrons are transferred from both B and Os atoms to B-B bonds and Os-B bonds. Clearly, two neighbor B atoms form a very strong covalent bond. And the bonding between the Os atom and its neighbor B atoms is also covalent. The fact that the Os-B bond is covalent rather than ionic is also evident from Bader's atoms in molecules (AIM) theory,[19] which indicates there is only about 0.05 electron transferred from an Os atom to B atoms. Moreover, there is some region where the charge density is rather low, implying that the bonding in this system is directional but not metallic, as can be seen from Figs. 2(a) and 2(b). Since there are eight B atoms around an Os atom, forming a three-dimensional network instead of a plane, the anisotropy in OsB_2 is not expected to be very large. As discussed above, the strong co-
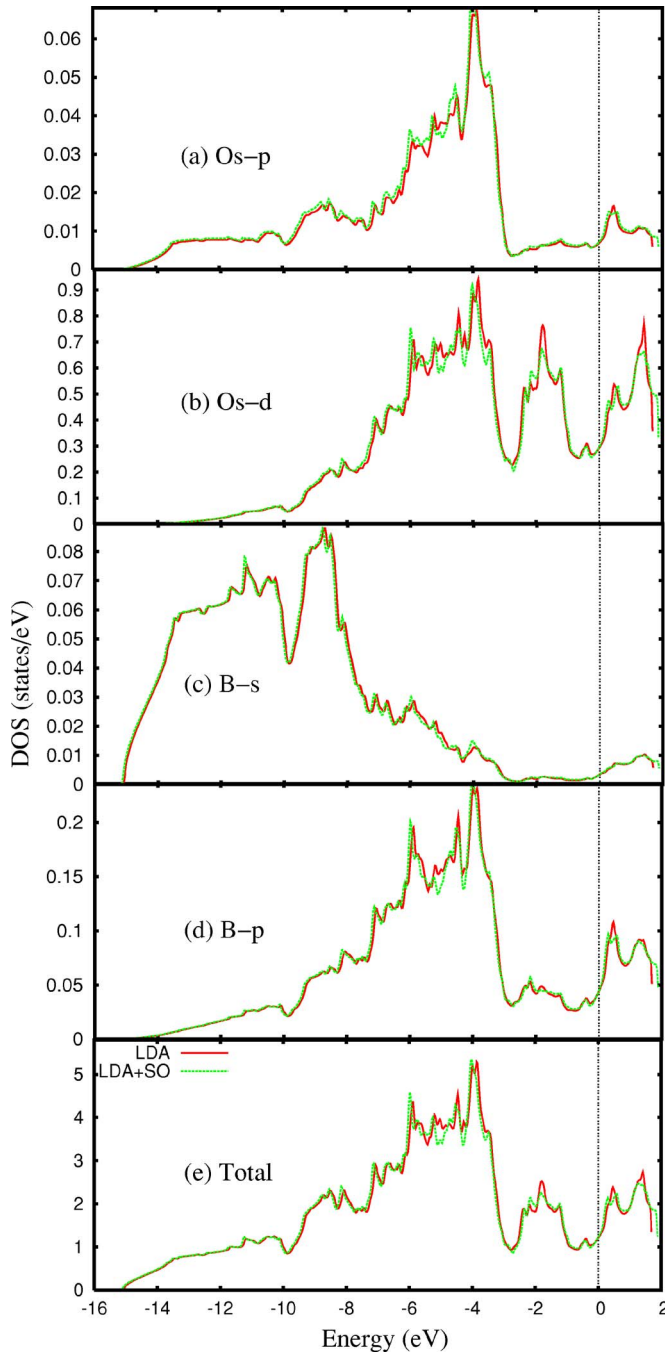
FIG. 4. (Color online) Partial and total DOS of OsB_2 from the LDA and LDA+SO calculations.

TABLE II. Calculated elastic constants and Voigt shear modulus G of orthorhombic OsB_2. Unless otherwise stated, all results are computed with atomic internal coordinates unrelaxed. All values are in units of GPa.

	WIEN2K LDA	WIEN2K LDA+SO	VASP LDA	VASP LDA (relaxed)
C_{11}	628.9	608.5	622.4	597.2
C_{12}	194.7	198.3	185.8	188.7
C_{13}	235.0	220.9	225.3	217.5
C_{22}	627.8	590.3	624.9	584.5
C_{23}	126.8	129.9	124.1	164.0
C_{33}	923.2	855.7	910.4	833.8
C_{44}	185.5	175.1	182.0	80.2
C_{55}	313.5	292.6	311.4	214.5
C_{66}	218.6	205.9	233.9	209.2
G	251.8	235.1	253.6	197.1

sults. Figures 3(a) and 3(b) show the band structures near the Fermi energy in the absence or presence of SO, respectively. Due to the spin-orbit interaction, some bands are split: some bands crossing each other in Fig. 3(a) no longer cross in Fig. 3(b), and more noticeably almost all bands in the direction of M-N-K are split in the LDA+SO result. Except for the band splitting in the presence of SO, the both band structures have main features in common. Both Figs. 3(a) and 3(b) show that the bands are dispersive but not flat indicating not too large anisotropy in OsB_2. We note that there are several bands crossing the Fermi level which are rather dispersive in the whole Brillouin zone, indicating good electronic mobility in OsB_2. The metallicity is uncommon in superhard materials. Most of the superhard materials are insulators or semiconductors.[11] This special character of OsB_2 should bring it special application on electron conductivity. Figure 4 shows the total and partial DOS with or without SOC which are obtained using a modified tetrahedron method of Blöchl et al.[21] We can see some minor differences between the results with or without SOC. Figure 4(e) also implies the good metallicity due to the substaintially large total DOS at the Fermi level. From the calculated partial DOS in Fig. 4, one can see that the electronic structure of OsB_2 is governed by a strong hybridization between the Os-d and B-p states, while with a rather small contribution from the Os-p and B-s states. This strong hybridization of Os-d and B-p also indicates the strong covalent bonding of Os-B.

Besides the bulk modulus, we want to mention that the shear modulus is also relevant for the noncubic OsB_2 materials. The shear modulus can be computed from the elastic constants. Unfortunately, the force calculation when including the spin-orbit coupling has not been implemented in the WIEN2K package yet. As an approximation, in the calculation of elastic constants, we keep the relative positions of the atoms fixed at small elastic strains of the lattice. Both calculations with and without SOC are carried out. The procedure for computing elastic constants is similar to that used by Zhou et al.[22] For comparison, we also compute the elastic

valent bonding of Os-B plays an important role to form a hard material, since the highly directional bonding is needed to withstand both elastic and plastic deformations. OsB_2 might be a potential superhard material for effectively cutting ferrous metals, including steel, since diamond reacts with steel producing iron carbide.[3] A recent report showed that the hardness of the Fe-based alloys is less than 1300 kg/mm²,[20] which is far less than that of the OsB_2($\geq$2000 kg/mm²).[15]

Although the LDA electron density is almost indiscernible from the LDA+SO calculation, we note that there are some differences in the band structures and DOS between two re-

constants with VASP (Ref. 23) using LDA without SOC. In these calculations, we perform two series of calculations with atomic internal coordinates fixed or relaxed, respectively. Our results are reported in Table II. We can see that the Voigt shear modulus G calculated using the WIEN2K package (235.1 GPa with SOC and 251.8 GPa without SOC, respectively) are consistent with that (253.6 GPa) calculated using VASP with fixed atomic internal coordinates, but are much larger than that (197.1 GPa) calculated using VASP with a relaxation of the atomic internal coordinates. The results produced by VASP are in good agreement with those reported by Zhou *et al.*[22] Thus we find that it is not a very good approximation that computing the shear modulus with atomic internal coordinates fixed.

In conclusion, the mechanical and electronic properties of OsB_2 are studied using the highly accurate full potential linearized APW+LO method. The OsB_2 is found to be metallic, which is uncommon in hard materials. The calculated bulk modulus with and without SOC are 364 and 365 GPa, respectively, which are in good agreement with the experiment $(365-395$ GPa).[15] The evidence of covalent bonding of Os-B, which plays an important role to form a hard material, is manifested both in the difference charge density, AIM analysis, and DOS analysis. Our results indicate that OsB_2 might serve as hard conductors.

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