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Theoretical studies of iridium under pressure

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Abstract

Recent experiments on Ir under pressure (Cerenius and Dubrovinsky 2000 *J. Alloys Compounds* **306** 26) show a transition to a superlattice structure comprising 14 atomic layers. This observation has implications for high-pressure applications since Ir, with its high bulk modulus and high thermal stability, is ideally suited for use as a gasket for high-temperature, high-pressure diamond anvil cell experiments. We perform first-principles total energy calculations to study the crystal phases and defect structures of Ir under pressure. We have extended the bond-orientation model (Chetty and Weinert 1997 *Phys. Rev. B* **56** 10844) to compute all of the $\sim 2^N$ defect structures as a function of atomic volume. We find Ir in the FCC structure to be extremely stable for pressures up to about 60 GPa. We also calculate the stacking fault energies of Ir.

1. Introduction

Iridium, being a central 3rd-row transition metal, has a relatively high bulk modulus and is therefore ideally suited for use as a high-pressure gasket. The stability of this FCC material under pressure is therefore of interest. The precise knowledge of the structure under pressure is needed if the gasket is to be used to calibrate a high-pressure device such as a diamond anvil cell.

A bulk modulus of 306 GPa has recently been measured for Ir [1], although a value as high as 355 GPa [3] has been reported. This value is more than 1.5 times the bulk moduli of the 1st-row transition metals and more than 50% that of diamond.

The sequence of ground-state structures across the transition metal rows, in general, is mainly due to the increase in the electron filling of the d-band. Also, the pressure-induced phase transition of transition metals is generally understood to be due to the transfer of electrons from the s- to the d-band. The relative incompressibility of Ir metal is as a result of the high promotional energies from the s- to d-band.

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Ir has an extremely high thermal stability, having the capacity to maintain structural and mechanical stability at temperatures in excess of 1600 °C, which makes it useful for high-temperature and high-pressure diamond cell experiments [4]. It is the metal of choice for use in high-temperature crucibles, thermocouples and encapsulators of nuclear-powered electrical generators in space technology. Ir is also not easily susceptible to corrosion, which makes it ideal for a host of ‘clean’ applications such as resistive heating experiments [1].

Ir has been the subject of study over recent years, with most investigations focussing on surfaces (see for example [5–8]). There are limited studies of the bulk metal and defects. For example, Ivanov *et al* [9] constructed an empirical potential based on the work by Greenberg *et al* [10], with which they studied elastic properties, phonon spectra, vacancies, interstitials, dislocations and stacking defects. However, despite the efforts at empirically modelling the system, the errors, for example in the intrinsic stacking fault [10], are still unacceptably high. Insofar as first-principles total energy calculations of the bulk are concerned, there appears to be a dearth of information available. Heid *et al* [11] have used a first-principles pseudopotential mixed-basis method to calculate the phonon dispersions and elastic constants for Ir with good agreement with experiment.

Recent experiments [1] on Ir at high pressure indicate a transition to a superlattice structure comprising 14 atomic layers. This has important implications for high-pressure applications. Both theoretical and further experimental investigations are needed to study Ir under pressure. In our work we investigate, using first-principles total energy methods, the possible high-pressure phases of Ir.

2. Bulk properties

We employ the plane wave pseudopotential method within the local density approximation. The Kohn–Sham equations [12] are solved selfconsistently using the pre-conditioned steepest descent method [13]. The electronic states are occupied using a Fermi distribution function with a thermal broadening of 0.001 hartree. The additional degree of freedom that arises in the determination of the occupation numbers results in an entropy-like term that is included to maintain the overall variational nature of the total energy functional [14]. The charge density is mixed using a Broyden [15] scheme.

We use the Kleinman–Bylander separable non-local pseudopotential based on the Troullier–Martins construction [16, 17]. The pseudopotential core radii (in Bohr) are chosen to be $r_s = 2.41$, $r_p = 3.14$ and $r_d = 1.15$. The $\ell = 0$ component of the pseudopotential is chosen as local component. Starting with unit vectors with small random components as the initial guess to the wavefunctions, we attain selfconsistency to better than 10^{-7} hartree.

The Monkhorst–Pack special points technique [18] is used and the point group symmetry of the lattice is exploited to reduce the number of independent wavevector points in the Brillouin zone. For the one atom per cell FCC, we consider 110 special k -points in the irreducible part of the Brillouin zone which corresponds to a sampling of 4000 points in the entire zone.

The equilibrium lattice constant is found to be 3.85 Å, the bulk modulus 385 GPa and cohesive energy 10.23 eV, at an energy cut-off for the plane wave expansion of the wavefunctions of 100 Ryd. In table 1, our theoretical results are listed against known other results—both experimental and theoretical.

3. High-pressure studies

3.1. Experimental results

Recent experimental high pressure studies of Ir [1], using a diamond anvil cell, have indicated an unusual transition to a 14-layer supercell structure at pressures in excess of 60 GPa.

Table 1. Reference, lattice constant a_0 in Bohr, cohesive energy E_c in eV, bulk modulus B in GPa.

References	a_0	E_c	B
This work at 50 Ryd ^a	3.85	9.35	402
This work at 70 Ryd	3.85	9.58	399
This work at 100 Ryd	3.85	10.23	385
Plane wave pseudopotential method, [19]	3.86	—	420
Full-potential LMTO method, [20]	3.81	10.31	—
Experimental, [1]	3.84	—	306
Experimental, [21]	3.83	—	—
Experimental, [3]	—	6.94	355

^a Energy cut-off for the plane wave expansion of the wavefunction.

X-ray diffraction spectra show a substantial increase in the intensity of the (111) peak of Ir, accompanied by a distinct saw-tooth pattern at pressures above 60 GPa. Despite the fact that the intensities of the saw-tooth pattern are relatively low, these experimentalists claim a sufficient signal-to-noise ratio to discern these peaks. They could not explain the appearance of these new lines by the formation of stacking faults or other types of defects such as twinning, but they claim that it could correspond to a distortion of the FCC lattice. The saw-tooth pattern is consistent with a 14-layer superlattice structure. This transition was reversible as the pressure was reduced, and was observed on a second x-ray diffraction machine. It is not evident that these authors looked at more than one sample of Ir.

3.2. High-pressure phases

Transition metals usually exhibit crystal phase transitions between FCC, HCP and BCC (not necessarily in this order). We therefore chose to study Ir in these crystallographic phases under pressure using our first-principles total energy method. We use an energy cut-off for the plane wave expansion of the wavefunctions of 50 Ryd. We consider one atom per cell for FCC and BCC and two atoms per cell for HCP, and we choose a k -point sampling of the Brillouin zone that is comparable for all three systems. We present our results for the energy per atom versus volume per atom in figure 1. Clearly the BCC structure is inaccessible under pressure because it is substantially higher in energy compared with FCC. The equilibrium lattice parameters for HCP are calculated by varying both a and c independently: the equilibrium nearest neighbour distance, a , is found to be 2.74 Å, and c is found to be 4.42 Å, with a c/a ratio of 1.62. The HCP equilibrium volume per atom is 14.37 Å³, which is higher than the 14.27 Å³ obtained for FCC. The energy versus volume curves for FCC and HCP do not intersect at high pressure, and so our calculations predict no transition to the HCP structure.

3.3. Planar defects

We wish now to study the planar defects of Ir under pressure. For a supercell structure comprising N layers with periodic boundary conditions, there are $\sim 2^N$ distinct configurations. Among these configurations are the well known extrinsic (E), intrinsic (I) and twin (T) faults. Clearly it is impossible to study all $\sim 2^N$ defect structures using first-principles calculations. Hence, in this subsection, we only consider a finite number of defect systems. In table 2 we list the defect supercell structures that we considered, together with the energies of these systems as a function of lattice constant. The atoms maintain close-packed coordination in the faulted geometries and hence the relaxation energies are negligibly small [10].

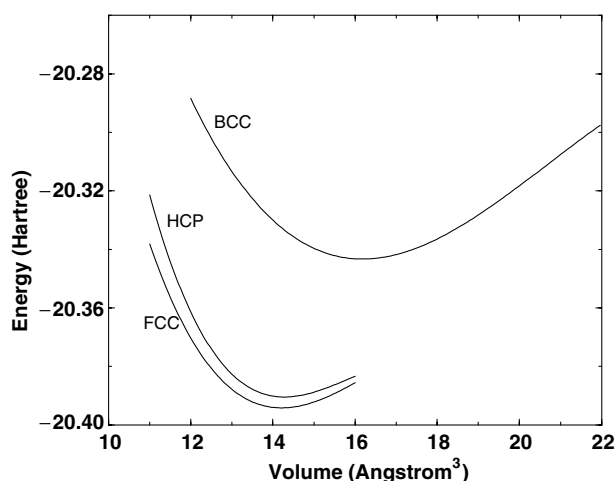


Figure 1. Energy versus volume for BCC, HCP and FCC phases of Iridium.

Table 2. Cubic fit to energy versus nearest neighbour distance, and bond-orientation parameters, for various defect structures.

a_0	a_1	a_2	a_3	Bond-orientation parameters	Supercell structures
87.608 1822	-115.598 58	21.137 3154	-1.283 052 87	$6\epsilon_8(a)$	abcabc
99.039 8503	-122.348 853	22.472 3882	-1.371 334 44	$6\epsilon_3(a)$	ababab
87.929 5048	-115.701 217	21.144 2002	-1.282 791 03	$\epsilon_3(a) + 2\epsilon_4(a) + \epsilon_5(a) + 2\epsilon_6(a)$	ababac
87.676 9923	-115.603 458	21.132 4679	-1.282 403 07	$2\epsilon_5(a) + 4\epsilon_7(a)$	abcabc
102.412 925	-134.898 875	24.653 8463	-1.495 788 76	$2\epsilon_5(a) + \epsilon_6(a) + 2\epsilon_7(a) + 2\epsilon_8(a)$	abcabab

In the following subsection we use this data and apply a novel technique to calculate the energies of all possible defects using a bond-orientation scheme.

3.4. Extracting the parameters for the bond-orientation model

The details of the bond-orientation model are found in [2]. In figure 2 we display the six distinct local configurations in which any atom in this system may be found. From the cubic fits to the energies of the bulk and defect structures, the $\epsilon_i(a)$ parameters are extracted by solving the equations listed in table 2 simultaneously. All energies are referred to the FCC structure, which effectively sets $\epsilon_8(a) = 0$. A hidden symmetry which exists in the system results in a maximum of five linearly independent equations for the parameters. This is due to the fact that only certain sequences of the $\epsilon_i(a)$ are possible, e.g. immediately following an $\epsilon_8(a)$ local geometry, there can only be an $\epsilon_7(a)$. The energy of *any* defect structure may be calculated from an appropriate combination of the $\epsilon_i(a)$. This is NOT a second-nearest neighbour model but includes all interactions up to two planes above and below the plane in question ... this means that the model includes interactions beyond the second-nearest neighbour distance.

3.5. The bond-orientation model applied to the 14-atom supercell

In this subsection we study the planar defects of the 14-atom supercell to investigate the claims of Cerenius *et al* [1] that a 14-layer superlattice structure exists for Ir for pressures in excess of 60 GPa. The cut-off of 50 Ryd obviously precludes us from studying all $\sim 2^{14}$ defect structures.

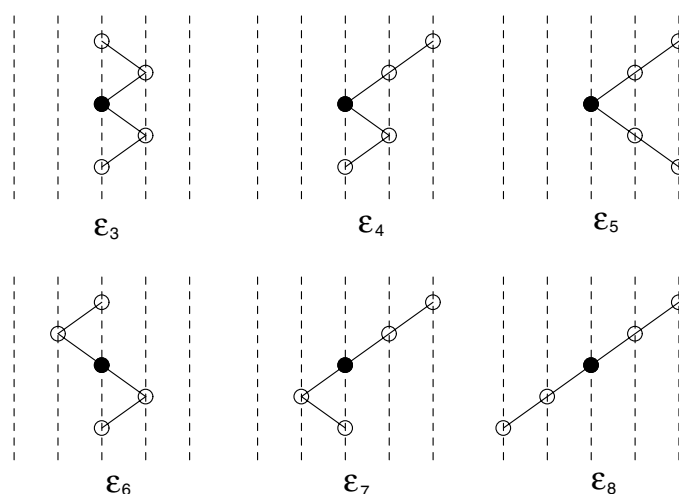


Figure 2. Energy parameters for different stacking sequences of (111) planes.

Here we extend the bond-orientation model [2] to include the energy dependence on volume in order to be able to study the systems under pressure.

The expressions for the ideal structures in terms of the bond-orientation model parameters $\epsilon_i(a)$ are:

$$E(\text{FCC}) = 14 \times \epsilon_8(a) \quad \text{and} \quad E(\text{HCP}) = 14 \times \epsilon_3(a). \quad (1)$$

Since the $\epsilon_i(a)$ are functions of the nearest neighbour distance a , the energy of these systems may be calculated as a function of the atomic volume.

For example, the twin stacking fault (T) whose structure in the 14-atom supercell is given by CABCABCABCACB may be expanded in the following way:

$$E(\text{T}) = 2 \times \epsilon_5(a) + 4 \times \epsilon_7(a) + 8 \times \epsilon_8(a). \quad (2)$$

In figure 3 we present energy versus nearest neighbour distance for all $\sim 2^{14}$ defect structures in the 14-atom supercell (with periodic boundary conditions). There are only 60 distinct curves due to the high level of degeneracy. The energy of all the defect structures are bounded below by the FCC curve, and above by the HCP curve. There is a relatively large energy jump between the FCC curve and that for the lowest energy defect structure whose equilibrium volume is slightly larger than that for FCC. There is no common tangent with a negative gradient that links the FCC with any of the defect structures. Our model calculations show that these defect structures are not more energetically favourable under pressure compared with FCC. Our investigations hence show that FCC is very stable for pressures in the region of 60 GPa.

4. Stacking faults

Using our plane wave pseudopotential method, we calculate the stacking fault energies of Ir. Firstly, we consider Ir in the FCC structure using a 12-atom supercell oriented along the (111) direction with a choice of Monkhorst–Pack parameters for the k -point sampling of (442). We also consider the HCP structure with the same supercell size and sampling of the Brillouin zone.

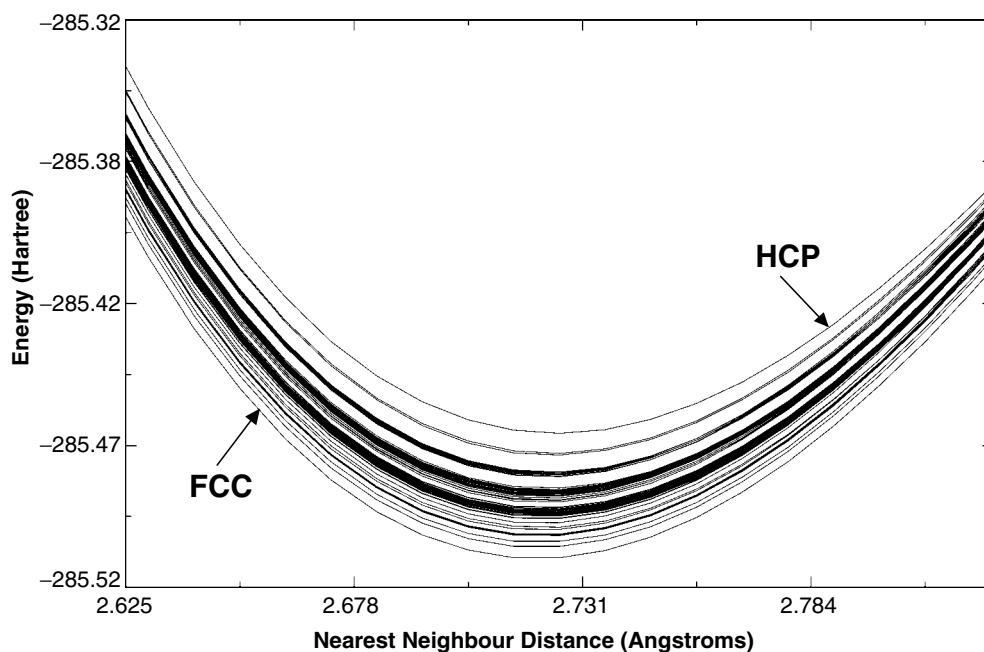


Figure 3. Energy versus nearest neighbour distance for all $\sim 2^{14}$ defect structures in the 14-atom supercell (with periodic boundary conditions). There are only 60 distinct curves due to the high level of degeneracy.

Table 3. Supercell structure, best estimate of formation energy (E_F) in meV, and lower bound for E_F in meV.

Supercell	E_F	Lower bound for E_F
HCP	80	—
T	54	—
E	128	122
I	139	137

We consider the twin (T), the extrinsic (E) and intrinsic (I) stacking faults. The supercells for each of these systems are listed below:

- (T) ...ABCAB \dot{C} BACBA \dot{C} ...
 (E) ...ABCAB \dot{C} B \dot{A} BCABC...
 (I) ...ABCAB \dot{C} \dot{B} CABC....

The dot in the above structures symbolizes those atomic planes that are locally HCP-like. The T supercell has 12 atoms per cell and, as such, its energy may be compared directly with that of the FCC supercell since they have an identical k -point sampling. Because of periodic boundary conditions, the T supercell has two twin faults. In table 3 we list the energies of these systems.

The E (13 atoms/supercell) and the I (11 atoms/supercell) supercells with enforced periodic boundary conditions have a dissimilar number of atoms compared with the FCC supercell. Therefore, the samplings of the Brillouin zone along the z direction are not identical. Because the E supercell has a larger number of atomic planes than the FCC supercell in

the z direction, we require a greater sampling of the Brillouin zone in this direction for the FCC structure than for the E supercell if we wish the samplings of the Brillouin zone to be comparable. We choose a k -point mesh of (442) for the E supercell, and initially compare this energy with that of the FCC structure using a (443) mesh to give us a best estimate of the formation energy of this stacking fault. We subsequently compare the energy for the E supercell with that of FCC using a (442) mesh, in order to obtain a lower bound for the formation energy. For similar reasons, we choose a k -point mesh of (443) for the I supercell, and compare this energy with that of the FCC supercell using a (442) mesh. The lower bound for the formation energy is found by comparing the energy of the I supercell with that of FCC using a (442) mesh in both cases. These formation energies, together with the lower bound in each case, are shown in table 3.

The energies for the faults are in qualitative agreement with simple bond-orientation arguments. The T fault, which has only one HCP-like faulted plane, has an energy of 54 meV which is comparable with the HCP energy of 80 meV. The E fault has an energy of 129 meV which is roughly in proportion to the number of HCP-like planes. Finally, we calculate the I fault to have an energy of 139 meV which is comparable to that of the E fault, as they have the same number of faulted HCP-like planes. With the smaller system size, the I fault is slightly more susceptible to finite size effects.

5. Conclusions

According to our theoretical computations, no exotic phase or superlattice structure exists for Ir under pressure. A question remains as to whether relativistic effects will alter our conclusions: our pseudopotential construction is based on a scalar-relativistic formulation and in this sense the computations effectively take into account relativistic core–valence interactions. Explicit inclusions of spin–orbit splittings in our work will have a negligible effect because of the anticipated small corrections involved . . . of order millielectronvolts.

It is clear that further experimental investigations are needed in order to explore the apparent high-pressure 14-layer superlattice structure of Ir observed by Cerenius *et al* [1]. However, it should be noted that our work assumes hydrostatic pressure, whereas in the actual experiment huge uniaxial stresses could well develop. Under these circumstances, it is difficult to predict what metastable structures could exist.

The bond-orientation model extended to describe systems under pressure is a convenient and accurate means of computing the energies of planar defect structures.

Using first-principles methods, we have also calculated the stacking fault energies of Ir.

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