***Ab initio* phase diagram of iridium**L. Burakovsky,¹ N. Burakovsky,² M. J. Cawkwell,¹ D. L. Preston,² D. Errandonea,³ and S. I. Simak⁴¹*Theoretical Physics Divisions, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA*²*Computational Physics Divisions, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA*³*Departamento de Física Aplicada-ICMUV, MALTA Consolider Team, Universidad de Valencia, Edificio de Investigación, C/Dr. Moliner 50, Burjassot, 46100 Valencia, Spain*⁴*Department of Physics, Chemistry and Biology, Linköping University, 58183 Linköping, Sweden*

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The phase diagram of iridium is investigated using the Z methodology. The Z methodology is a technique for phase diagram studies that combines the direct Z method for the computation of melting curves and the inverse Z method for the calculation of solid-solid phase boundaries. In the direct Z method, the solid phases along the melting curve are determined by comparing the solid-liquid equilibrium boundaries of candidate crystal structures. The inverse Z method involves quenching the liquid into the most stable solid phase at various temperatures and pressures to locate a solid-solid boundary. Although excellent agreement with the available experimental data (to $\lesssim 65$ GPa) is found for the equation of state (EOS) of Ir, it is the third-order Birch-Murnaghan EOS with $B'_0 = 5$ rather than the more widely accepted $B'_0 = 4$ that describes our *ab initio* data to higher pressure (P). Our results suggest the existence of a random-stacking hexagonal close-packed structure of iridium at high P . We offer an explanation for the 14-layer hexagonal structure observed in experiments by Cerenius and Dubrovinsky.

DOI: [10.1103/PhysRevB.94.094112](https://doi.org/10.1103/PhysRevB.94.094112)**I. INTRODUCTION**

Iridium (Ir) has a number of exceptional properties. With a melting point of 2719 K [1], it is the only refractory face-centered cubic (fcc) metal. Its shear modulus, $G = 210$ GPa [2], is the largest among the fcc metals, and of all the elemental metals only hexagonal close-packed (hcp) osmium (Os) has a higher shear modulus $G = 222$ GPa [2]. Ir is also one of the two most dense elemental metals having a $P = 0$ density of 22.65 g/cc at $T = 0$ and 22.56 g/cc at $T = 293.15$ K [1]; the corresponding values for Os are essentially the same: 22.66 and 22.59 g/cc [3]. Because it exhibits excellent mechanical properties and high resistance to oxidation and corrosion at elevated T , Ir is used in numerous applications as a static component at high T and/or in aggressive environments. Despite the technological applications, our current understanding of the mechanical properties of Ir is rather limited, and knowledge of its phase diagram is virtually nonexistent.

The similarity of the mechanical properties of Ir to those of the refractory hcp metals, especially Os, and the fact that in a number of binary systems Ir forms solid solutions with a hcp structure which are stable (that is, remain hcp) over a wide range of concentrations, suggested the possibility of a phase transformation into the hcp structure. Such a fcc-hcp phase transformation in Ir was reported in 1968 [4]. The transition P at room T was estimated to be 9 GPa, and the fcc-hcp phase boundary was predicted to be a straight line with a positive slope of 150 K/GPa.

Subsequent experimental studies could not confirm a fcc-hcp transition in Ir at room T (except perhaps for the study by Cerenius and Dubrovinsky [5] discussed below). It was, however, noted in [6] that the earlier data on the shock Hugoniot of Ir indicated the existence of a structural transformation above 1.14 Mbars. With the more recent shock Hugoniot data available in the online Shock Wave Database (SWD) [7], it is now possible to firmly establish the existence of a solid-solid transformation on the Ir Hugoniot. Figure 1

shows two parallel line segments shifted from each other by ~ 0.25 km/s that fit the U_s - U_p shock Hugoniot data on Ir. This situation is typical of a solid-solid phase transition on the Hugoniot; for instance, Fig. 3 of Ref. [8] shows that the α - ω and ω - β transitions in zirconium break the Hugoniot into three parallel segments shifted from each other by ~ 0.2 and ~ 0.3 km/s, respectively. The transition in Ir occurs at $1.10 < U_p < 1.36$ km/s or, if converted from U_s - U_p to P - U_p , at $140 < P < 180$ GPa [7], so we take the transition P to be 160 ± 20 GPa.

II. 14-LAYER HEXAGONAL SUPERSTRUCTURE OF Ir

In relatively recent experimental studies of Ir by Cerenius and Dubrovinsky [5], an unusual transition from fcc to a 14-layer hexagonal (hex) supercell was detected at ~ 60 GPa at room temperature. X-ray diffraction spectra showed a substantial increase in the intensity of the (111) peak of fcc-Ir accompanied by the appearance of a distinct sawtooth pattern characteristic of a hexagonal structure. Despite the low intensity of the peaks, sufficient signal-to-noise ratio made it possible to resolve them. Cerenius and Dubrovinsky noted that these peaks could not be explained by the formation of stacking faults or other types of defects (e.g., twinning) but might be due to a distortion of the fcc lattice of Ir and the formation of a superlattice structure. These peaks were properly indexed and associated with a 14-layer hex supercell with cell parameters $a = 2.60$ Å and $c = 29.7$ Å at 65 GPa. Hence, the supercell is ideal to within 0.1%: $c/a = 29.7/2.60 = 11.423$ vs $14\sqrt{2/3} = 11.431$. Subsequent theoretical studies based on *ab initio* approaches failed to confirm the existence of a transformation of fcc-Ir into another solid structure [9,10]. Those studies were carried out at $T = 0$ without taking phonon excitations into account. Specifically, in [9] all possible atomic-layer arrangements for a 14-layer hex cell were considered (only 60 14-layer structures exist, out of a total of $\sim 2^{14}$, because of a high level of degeneracy

FIG. 1. Shock velocity U_s vs particle velocity U_p along the principal Hugoniot in Ir; data from [7]. A solid-solid phase transition occurs at $1.10 < U_p < 1.36$ km/s.

[9]), and their $T = 0$ enthalpies were compared to that of fcc-Ir as functions of atomic volume. The enthalpies of these different 14-layer structures form a family of quasiparallel curves (Fig. 3 in [9]) with enthalpy differences that are virtually independent of volume. All of these curves remain above the fcc one, hence, no transition from fcc-Ir can be inferred based on thermodynamic considerations. However, according to [9], the enthalpy difference between fcc and the most stable of the 60 14-layer structures is only 12 meV/atom, or ~ 140 K; such a small difference can be easily overcome by the entropy term at finite T . Thus, at least some of the hex structures considered in [9] should be expected to become thermodynamically more stable than fcc with increasing T .

III. QMD STUDY OF THE PHASE DIAGRAM OF IRIDIUM

In the present work we determine the melting curve of Ir to ~ 600 GPa using the Z method, which we briefly describe in the following section. Our Z method calculations are carried out using the quantum molecular dynamics (QMD) code VASP (Vienna *ab initio* simulation package), which is based on density functional theory (DFT). We use the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional. We model Ir using the electron core-valence representation [$^{54}\text{Xe } 4f^{14}5d^7 6s^2$], i.e., we assign the nine outermost electrons of Ir to the valence. The valence electrons are represented with a plane-wave basis set with a cutoff energy of 370 eV, while the core electrons are represented by projector augmented-wave (PAW) pseudopotentials.

A. The $T = 0$ isotherm of fcc-Ir

We first calculated the $T = 0$ isotherm of fcc-Ir. This was done by performing a short QMD run and extracting the corresponding value of P . We used a $5 \times 5 \times 5$ (500-atom) supercell with a single Γ point. With such a large supercell, full energy convergence (to $\lesssim 1$ meV/atom) is already achieved, which was verified by performing short runs with $2 \times 2 \times 2$ and

FIG. 2. The $T = 0$ Ir EOS from VASP compared to the experimental and theoretical 300 K Birch-Murnaghan EOSs.

$3 \times 3 \times 3k$ -point meshes and comparing their output with that of the 500-atom run with a single Γ point.

Our results on the $T = 0$ isotherm are shown in Fig. 2. We note that each of the papers [5,11,12] that discuss Ir EOS data uses the third-order Birch-Murnaghan (BM) EOS

$$P(\rho) = \frac{3}{2} B_0 \left[\left(\frac{\rho}{\rho_0} \right)^{7/3} - \left(\frac{\rho}{\rho_0} \right)^{5/3} \right] \times \left\{ 1 + \frac{3}{4} (B'_0 - 4) \left[\left(\frac{\rho}{\rho_0} \right)^{2/3} - 1 \right] \right\}, \quad (1)$$

where B_0 and B'_0 are the values of the bulk modulus and its pressure derivative at the reference point $\rho = \rho_0$. Since the $P = 0$ values of the density of Ir at $T = 0$ and 300 K differ by $\sim 0.4\%$ (22.65 vs 22.56 g/cc [1]), and $T = 300$ K introduces a negligibly small thermal pressure correction, the $T = 0$ and $T = 300$ K isotherms can be described by the same values of B_0 and B'_0 . Consequently, we can compare room- T isotherm data to our $T = 0$ isotherm as determined from QMD. This comparison is shown in Fig. 2. The experimental results from two groups, each of which accessed $P \sim 65$ GPa, were presented as BM fits with different choices for B_0 and B'_0 : $B_0 = 306$ GPa and $B'_0 = 6.8$, and $B_0 = 354$ GPa and $B'_0 = 4.0$ from [5] (the former set results from fitting with both B_0 and B'_0 as free parameters, and the latter from fitting with $B'_0 = 4.0$ held fixed), and $B_0 = 383$ GPa and $B'_0 = 3.1$ from [11]. Another set of parameters, $B_0 = 340$ GPa and $B'_0 = 4.8$ comes from theoretical modeling [12]. Although excellent agreement of the QMD points with the available experimental data (up to $\rho \sim 26$ g/cc) is found for each of the (B_0, B'_0) sets, it is the third-order BM isotherm with $B'_0 = 5$ that best fits the QMD data at densities above the experimental range.

B. Hexagonal polytypes of Ir

We calculated the $T = 0$ enthalpies $H = E + PV$ of various hex structures of Ir with the number of atoms per unit cell ranging from 2 (hcp) to 18 (18R). This was done by optimizing the value of c/a , i.e., determining the c/a that minimizes the energy at a fixed volume of a hex supercell,

FIG. 3. Phonon spectra of three hexagonal structures of Ir at three different temperatures at a pressure of 200 GPa.

and then performing a short QMD run and extracting the corresponding values of E and P .

We considered the following hex structures, or polytypes, which are listed below in the order “polytype” (or stacking symbol, as used in the rest of the paper), “number of atoms per unit cell,” “Pearson crystallographic symbol,” “common name” (if it exists):

2H 2 hP2 hcp	9R 9 hR3 α -Sm
3C 3 cF4 fcc	10H 10 hP10
4H 4 hP4 dhcp	12R 12 hR4
5H 5 hP5	14H 14 hP14
6H 6 hP6 thcp	15R 15 hR5
7H 7 hP7	16H 16 hP16
8H 8 hP8	18R 18 hR6

We used supercells with the number of atoms ranging from 540 (for $6 \times 6 \times 1$ 15R) to 686 (for both $7 \times 7 \times 2$ 7H and $7 \times 7 \times 1$ 14H) with a single Γ point. With such large supercells, just like for fcc-Ir, full energy convergence (to $\lesssim 1$ meV/atom) is already achieved, which allowed us to resolve the enthalpy differences to high accuracy. For P from 0 to ~ 900 GPa, we found that all of the hex structures of Ir have values of c/a equal to the ideal ones to within 1%, so that basically $c/a = N\sqrt{2/3}$, where N is the number of atoms per unit cell.

In Figs. 3 and 4 we show the phonon spectra of five hex structures of Ir calculated using the temperature-dependent effective potential (TDEP) method [13,14], which takes into account anharmonic lattice vibrations. It is seen that all the structures are dynamically stable (no imaginary phonon branches), and the T dependence of their phonon spectra is very weak.

Figure 5 shows differences between the $T = 0$ enthalpies of hexagonal structures of Ir and that of fcc-Ir (as a 3C hex structure) as a function of the number of atoms or, equivalently, the number of atomic layers per hex unit cell at a fixed pressure of 200 GPa. In this case, the unit cell volume is $\sim 11 \text{ \AA}^3$, and all the hex unit cell volumes are within 1% of their average value. Since the enthalpy curves are quasiparallel, their differences do not depend on volume, and since the hex unit cell volumes at a given P are virtually identical, we expect that the plot at any other fixed P will be similar to that in Fig. 5. In Fig. 5, only the structures having the lowest enthalpy among those with the same number of layers per unit cell are shown; there are multiple structures for $N \geq 6$. Specifically, for the hexagonal structures listed below, points in Fig. 5 indicate the following (periodic) stacking sequences: 2H (hcp) $\sim$ AB, 3C (fcc) $\sim$ ABC, 4H (double-hcp, or dhcp) $\sim$ ABAC, 5H $\sim$ ABCAC, 6H (triple-hcp, or thcp) $\sim$ ABCACB, 7H $\sim$ ABCABAC, 8H $\sim$ ABACBABC, 9R (α -Sm) $\sim$ ACABABCBC, 10H $\sim$ ABACBACABC, 12R $\sim$

FIG. 4. The same as in Fig. 3 for two more hexagonal structures of Ir.

ABABCACABCBC, 14H $\sim$ ABACBCBACABCBC, 15R $\sim$ ABABACACACBCBCB, 16H $\sim$ ABABACBCACACABCBC, 18R $\sim$ ABACACBCBACABABCBC.

The plot clearly exhibits distinct non-fcc minima for 7H/8H and for 14H, the enthalpy of which is the closest to that of fcc-Ir; the 14H-fcc enthalpy difference is 11 meV/atom, in agreement with [9]. Since none of the hex structures becomes more stable than fcc at $T = 0$ (or at $T = 300$ K, expect perhaps at very high P , according to the Ir phase diagram shown in Fig. 10), the appearance of the 14-layer superstructure in experiments by Cerenius and Dubrovinsky requires an explanation. Such an explanation is offered in the following section.

FIG. 5. Differences between the $T = 0$ enthalpies of hexagonal structures of Ir and that of fcc-Ir as a function of the number of atomic layers per unit hex cell, at a fixed pressure of 200 GPa.

IV. POSSIBLE EXPLANATION FOR THE APPEARANCE OF THE 14-LAYER HEXAGONAL SUPERSTRUCTURE IN EXPERIMENTS BY CERENIUS AND DUBROVINSKY (CD)

It is possible that nonhydrostatic stresses were present in the CD DAC (diamond anvil cell) experiments. If so, fcc-Ir could lose its thermodynamic stability and the hex structure that is energetically the closest to fcc-Ir would become thermodynamically stabilized. Such a structure is 14H, with 14 atomic layers per unit cell, just like the one found in Ref. [5].

It is not clear from [5] how the DAC stress state was controlled—the use of a pressure-transmitting medium is not discussed. Even if a pressure-transmitting medium was used, the stress in the sample could still have been nonhydrostatic. Indeed, in the absence of high-temperature annealing, the hydrostatic limits of the most commonly used pressure-transmitting media are below 10 GPa [15]. Moreover, all known pressure-transmitting media freeze above 15 GPa [15], so that nonhydrostatic stresses will be certainly present at higher pressures, as the experimental study by Zhao *et al.* [16] on different crystalline materials in diamond anvil cells with different pressure-transmitting media clearly demonstrates. They confirmed that the stress state in a DAC is cylindrically symmetric with the stress parallel to the load axis being greater than the radial stresses. This relatively high uniaxial stress σ is responsible for nonhydrostatic conditions in the sample inside the DAC. The uniaxial stress is roughly proportional to the pressure, but for the vast majority of solids it is nevertheless at most a few GPa at megabar pressures. For instance, $\sigma \approx 0.01 P$ for He [17], $\sigma \approx 0.025 P$ for Au [18], $\sigma \approx 0.03 P$ for Ar [17], and $\sigma \approx 0.04 P$ for Fe [19]. However, for solids with significantly larger bulk and shear moduli, the values of σ can be an order of magnitude greater: $\sigma \approx 0.1 P$ for Re [18], $\sigma \approx 0.25 P$ for ruby [20], $\sigma \approx 0.3 P$ for Os [21], and $\sigma \approx 0.4 P$ for diamond [22]. Since the mechanical

properties of Ir are very close to those of Os (virtually identical densities, very similar values of both bulk and shear moduli, etc.), we expect that σ is also large for Ir, and may be responsible for the fcc-14H transition observed in experiment.

In the CD experiments the 14-layer superstructure first appears at P above ~ 60 GPa even though the difference between the enthalpies of this structure and fcc is independent of P . In the next section we consider the effect of nonhydrostatic stresses on the fcc-14H transition in Ir and estimate that it occurs at $P \sim 65 \pm 15$ GPa.

V. ESTIMATE OF THE fcc-14H TRANSITION PRESSURE UNDER NONHYDROSTATIC STRESS

The close energetic proximity of many hexagonal structures of Ir to fcc suggests that its energy surface in the multicoordinate space of structural variables is relatively flat. We therefore assume that if, under the proper PT conditions, a transition from fcc into another solid phase becomes thermodynamically possible, the energy barrier between the two structures is small and can be easily overcome; in other words, the corresponding Bain transition path is open. Thus, to find the transition pressure, we only need to establish the thermodynamic conditions for the transition, that is, the equality of the two free energies.

It was shown in [23] that a solid subject to uniaxial deformation is correctly described by including an additional “entropy” term $-TS = 2VG\sigma^2(1+\nu)/9B^2(1-\nu)$ in the free energy; here σ is the uniaxial stress, and B , G , and ν are the bulk modulus, shear modulus, and the Poisson ratio, respectively. Since $\nu = (1/2)(3B - 2G)/(3B + G)$, the above expression can be rewritten as

$$-TS = \frac{2VG\sigma^2}{B(3B + 4G)}.$$

This additional term increases the free energy, which thermodynamically destabilizes the nonhydrostatically stressed solid. We now estimate when this free energy increase is sufficient to bring the 14H-fcc free energy difference to zero, and therefore to initiate the fcc-14H transition observed in experiment [5].

Free energy calculations at 200 GPa (Fig. 11) show that the T dependence of the free energy difference between fcc and 14H is very weak, thus this difference is approximately constant between $T = 0$ and 300 K, the temperature at which the experiment of Ref. [5] was carried out. Since the $T = 0$ fcc-14H free energy difference is also P independent, we make the reasonable assumption that the fcc-14H free energy difference at $T = 300$ K is ~ 10 meV/atom (essentially its $T = 0$ value) and does not depend on P . Hence, the following relation holds for the 300 K free energies of the two phases at all P : $F_{14H} = F_{fcc} + \Delta F$, where $\Delta F = 10$ meV/atom is P independent. The nonhydrostatic stress σ increases F_{fcc} to $F'_{fcc} = F_{fcc} + 2VG\sigma^2/B(3B + 4G)$. The fcc-14H transition occurs when $F'_{fcc} = F_{14H}$, hence

$$\begin{aligned} F_{14H} - F_{fcc} &= \frac{2VG\sigma^2}{B(3B + 4G)} = 10 \text{ meV/atom} \\ &= 1.60 \text{ GPa } \text{\AA}^3/\text{atom}. \end{aligned} \quad (2)$$

Note that V , B , G , and σ are P dependent. We model their P dependence with the corresponding power-series expansions up to terms of order P^2 , which hold at small to moderate compressions [24]:

$$\begin{aligned} V &= V_0 \left[1 - \frac{P}{B_0} + \frac{B'_0 + 1}{2} \left(\frac{P}{B_0} \right)^2 \right], \\ B &= B_0 + B'_0 P + \frac{B''_0}{2} P^2, \quad G = G_0 + G'_0 P - \frac{G'_0}{3B_0} P^2. \end{aligned}$$

The formula for V follows from $B \equiv -V dP/dV$. Here we use $V_0 = 14.15 \text{ \AA}^3/\text{atom}$ (which corresponds to $\rho_0 = 22.56 \text{ g/cc}$), $B_0 = 366 \text{ GPa}$, $B'_0 = 5.0$, $B''_0 = -0.0161 \text{ GPa}^{-1}$ [which follows from Eq. (1) with the above B_0 and B'_0 values], $G_0 = 210 \text{ GPa}$, and $G'_0 = 3.4$ [25]. Since the P dependence of σ for Ir has not been measured, and the mechanical properties of Ir are comparable to those of Os, we use the Os σ - P relation for Ir, i.e., we use $\sigma = 0.3 P$ [21]. Since this choice of σ is somewhat uncertain, we allow the coefficient 0.3 to vary by 20%, i.e., 0.3 ± 0.06 .

With $\sigma = 0.3 P$, the solution to Eq. (2) is $P = 62.2 \text{ GPa}$. With $\sigma = 0.24 P$ and $\sigma = 0.36 P$, the solutions are, respectively, $P = 81.1 \text{ GPa}$ and $P = 49.9 \text{ GPa}$. Hence, we estimate that nonhydrostatic stresses in a DAC would induce a fcc-14H solid-solid phase transition in an Ir sample at a pressure of $65 \pm 15 \text{ GPa}$.

VI. DIRECT Z METHOD APPLIED TO THE MELTING CURVE OF IRIDIUM

We now turn our attention to the calculation of the melting curves of the solid structures of Ir using the direct Z method. The direct Z method (usually referred to as the “Z method” in the literature) was developed to calculate melting curves using first-principles based software, specifically VASP. The direct Z method was introduced in our paper on the *ab initio* melting curve of Mo [26]. The method has since been applied to the study of a large number of melting curves of different materials, and comparisons with experimental data on the melting curves of Pb, Ta, Fe, and Pt at the European Synchrotron Radiation Facility (ESRF) show good agreement [27] (e.g., direct Z method [28] vs experiment [29] for Fe).

In the case of Ir, it is important to note that, if a material has more than one thermodynamically stable crystal structure, the direct Z method yields the solid-liquid equilibrium boundaries of those structures. The phase having the highest solid-liquid equilibrium T over some pressure range is the most stable, thus the physical melting curve, including triple points, is the envelope of the solid-liquid equilibrium boundaries.

Here we applied the direct Z method to the study of the melting curve of Ir. We calculated the melting curves of the following eight solid structures: fcc, hcp, dhcp, 7H, 8H, 9R, 14H, and 15R. We used the same supercells as for the $T = 0$ enthalpy calculation described above. We simulated four melting points for each of the four structures fcc, hcp, 9R, and 14H, and then, after these four melting curves were obtained, we simulated two melting points for each of the remaining four structures, dhcp, 7H, 8H, and 15R, to check if they lie close to any of the fcc, hcp, 9R, or 14H melting curves. At a given density we performed a sequence of very long runs,

each up to 25 000 time steps or 25 ps, with initial temperatures separated by relatively small increments of 375 K.

As in our previous work on Os [30], we could directly observe melting in the computational cell, and then determine the corresponding melting temperature (T_m) and pressure (P_m) (at a given density). Our strategy for detecting the melting point was as follows. The conversion of the initially ordered solid state into a disordered liquid during a QMD run was detected in one of three ways: (i) visual observation of atomic motion in the computational cell (vibrations around equilibrium sites in a solid vs diffusion between the sites in a liquid); (ii) a drop in the value of the equilibrium T and the corresponding jump in the value of the equilibrium P ; or (iii) change in the radial distribution function (a long sequence of well-pronounced peaks in a solid vs a few peaks in a liquid). If the system did not melt during the 25 ps of running time, we started the next run with an initial T slightly higher (by 375 K) than the previous one, etc. The first run in which the system melts during the 25 ps of running time was assumed to correspond to the true melting point; during this run the complete melting process (transition from ordered solid to disordered liquid) is usually observed. We refer to such a run as the melting run. With an even higher initial T , the system melts at an earlier time than in the melting run, and the duration of the melting process decreases; both the time when melting begins and the duration of the process decrease with increasing T , and for a sufficiently high initial T the system melts immediately.

We performed 13 QMD runs for each of the 24 melting points on the eight melting curves; our simulations covered a range of initial T of 4500 K in each case. We carried out a total of 312 runs which, with an average of $\sim 17\,500$ time steps per run, amounted to a total of ~ 5.5 million time steps for our melting simulations.

Figures 6 and 7 illustrate the T and P evolution of fcc-Ir runs with initial temperatures of 36 625, 37 000, and 37 375 K; these runs correspond to the *ab initio* fcc-Ir melting point at ~ 500 GPa shown in Fig. 10 as an open green box. In the 36 625 K run, the system remains a superheated solid. In the

FIG. 6. Time evolution of temperature in three fcc-Ir QMD runs with initial temperatures (T_0) separated by 375 K. The middle run is the melting run, during which T decreases from $\sim 17\,500$ K for the superheated state to $\sim 14\,000$ K for the liquid at the corresponding melting point.

FIG. 7. The same as in Fig. 6 for the time evolution of pressure. During melting P increases from ~ 485 GPa for the superheated state to ~ 500 GPa for the liquid at the corresponding melting point.

37 000 K run (which is the melting run in this case), the system starts melting at about 18 ps, and the melting process takes approximately 2 ps. With an additional 375 K increase in the initial T , melting begins at ~ 9 ps and the process takes about 1 ps. The corresponding values of both T_m and P_m are then determined by averaging over the last 5 ps of the 37 000 K run: during this time the system represents a fully equilibrated liquid.

Similarly, Figs. 8 and 9 illustrate the T and P evolution of the 9R-Ir runs that correspond to its ~ 515 GPa *ab initio* melting point shown in Fig. 10 as an open blue box.

The melting curve of fcc-Ir, as the best fit to the corresponding four QMD melting points, is described by (T_m in K, P in GPa)

$$T_m^{\text{fcc}}(P) = 2719 \left(1 + \frac{P}{31.2} \right)^{0.59}, \quad (3)$$

which implies the initial slope $dT_m(P)/dP = 51.4$ K/GPa. Other theoretical values for the $P = 0$ slope are 62 [31], 51.9 [32], and 48 K/GPa [33]. Very recently, Kulyamina *et al.* [34] analyzed all of the isobaric-heating data on Ir available in the literature and determined the value of the

FIG. 8. The same as in Fig. 6 for three 9R-Ir QMD runs.

FIG. 9. The same as in Fig. 7 for three 9R-Ir QMD runs.

initial slope of the Ir melting curve to be 46.25 K/GPa, thus our QMD results are in good agreement with the available isobaric-heating data. It is interesting to note that the analytic melting curve of fcc-Ir suggested by Kulyamina *et al.*, $T_m(P) = 2707(1 + P/35.0)^{0.598}$, which they expected to hold to only ~ 5 GPa, is almost identical to ours, which is valid over a much wider range of P .

The melting curves of hcp, 14H, and 15R are close or slightly below the fcc melting curve. However, the melting curves of dhcp, 7H, 8H, and 9R are all close to each other and cross that of fcc; in other words, another solid phase becomes thermodynamically more stable than fcc-Ir under high PT conditions. We chose 9R to be the prototype solid structure at high PT ; its melting curve, as the best fit to the corresponding

FIG. 10. Phase diagram of Ir obtained from the Z methodology: fcc-Ir melting curve (green line), liquid Ir solidified into solid fcc (green bullets), 9R-Ir melting curve (blue line), liquid Ir solidified into solid rhcp (blue bullets), and the (tentative) fcc-rhcp solid-solid phase boundary (violet). Open green and blue boxes are, respectively, the *ab initio* melting points of the fcc-Ir and 9R-Ir for which the time evolution of T and P is shown in Figs. 6, 7 and 8, 9. Also shown are the principal Hugoniot (dashed line) and the solid-solid transition point from Fig. 1 (red box with error bars).

four QMD melting points, is given by (T_m in K, P in GPa)

$$T_m^{9R}(P) = 2553 \left(1 + \frac{P}{27.5} \right)^{0.60}. \quad (4)$$

The fcc and 9R melting curves cross each other at $(P, T) = (64, 5250)$, the fcc-9R-liquid triple point. Both melting curves are shown in Fig. 10.

Since the solid-liquid equilibrium boundaries (melting curves) for a number of solid structures of Ir are indistinguishable within mutual error bars, these structures have very close free energies. Consequently, the most stable structure cannot be determined using the Z direct method, and an alternative approach is needed.

VII. INVERSE Z METHOD APPLIED TO THE PHASE DIAGRAM OF IRIDIUM

To cope with this difficulty, and to locate solid-solid phase boundaries in Ir, we use the inverse Z method introduced in our earlier work [27] where it was applied to the study of the phase diagrams of Pt and Ta; see [27] for more detail. The method is based on solidifying the initially liquid state into a final solid structure at a given fixed T . Since the solidification kinetics is approximately governed by the factor $\exp\{\Delta F/k_B T^*\}$, where $\Delta F \equiv F_l - F_s$ is the liquid-solid free energy difference at the solidification temperature T^* , in the case of several energetically competitive solid phases the most stable solid phase has the largest ΔF and is therefore the fastest to solidify. Hence, the inverse Z method yields the most stable solid phase at a given (P, T) .

The subsequent identification of the crystal structure of the final state can be done by means of a number of techniques: (i) comparison of radial distribution functions (RDFs); (ii) comparison of x-ray diffraction patterns in reciprocal momentum space; and (iii) geometric structure analysis (coordination number, angles between interatomic bonds, etc.). Two different final-state crystal structures at (P_1, T_1) and (P_2, T_2) then bracket the corresponding solid-solid phase boundary.

We applied the inverse Z method to locate a solid-solid phase boundary in Ir. We used a computational cell of 686 atoms prepared by melting a $7 \times 7 \times 7$ solid bcc supercell which should avoid any bias towards solidification into either fcc or any of the hex structures. We carried out NVT simulations using the Nosé-Hoover thermostat with a time step of 1 fs. Complete solidification typically required from 15 to 25 ps, or 15 000–25 000 time steps, which is comparable with the duration of a typical direct-Z NVE run; the 25 inverse-Z runs (Fig. 10) contributed to a total of ~ 0.5 million time steps, in addition to ~ 5.5 million from direct-Z melting simulations.

We found that Ir solidifies into fcc below the violet curve in Fig. 10, while above this curve it solidifies into a hex structure. This coexistence curve is described by the equation (T in K, P in GPa)

$$T(P) = \frac{10500}{1 + (P/64)^{1.5}}. \quad (5)$$

The Ir principal Hugoniot [35] $T(P) = 293 + 0.087653 P^{1.9332}$ crosses this curve at $(P, T) = (166.5, 2020)$; the transition pressure of 166.5 GPa is consistent with 160 ± 20 GPa from SWD.

The RDFs did not allow us to discriminate between different hex structures: hcp, dhcp, thcp, 9R, etc. Upon fast quenching of the hex structures to low T , where RDFs are more discriminating, we observed all of the above four hex structures, and perhaps some other hex structures as well. Hence, the inverse Z method indicates that there may be a number of energetically competitive hex structures of Ir at high PT . Our results indicate that structures with different stacking sequences are energetically very close. Hence, the energy cost of forming an interface between two such structures is virtually zero. Consequently, the actual layer stacking could be nonperiodic and, in principle, random. A random-stacking hex close-packed (rhcp) structure was first introduced for hard-sphere colloids [36], and has since been the subject of literature discussions [37,38]. In general, when different stacking sequences become energetically degenerate, that is, the energy difference between any two such structures is ~ 1 – 10 meV per atom, or ~ 10 – 100 K, then any two adjacent layers can occur with equal probability in the resulting structure.

We are not aware of any direct reference to elements with a rhcp structure, except for our own suggestion that Pt may be such an element (having rhcp as its high PT phase [27]). In view of the fact that a rhcp phase may have been discovered experimentally in Au above 250 GPa by Dubrovinsky *et al.* [39] (see [27] for more detail), all three third-row fcc noble metals, namely Ir, Pt, and Au, are good candidates to be rhcp elements. We also note that a structure similar to rhcp was conjectured to be the most stable solid phase of Fe at earth core PT conditions [40].

VIII. DISCUSSION OF THE RESULTS

We have applied the Z methodology, a technique for the computation of both melting curves and solid-solid phase boundaries, to the study of the phase diagram of Ir, and our results compare favorably with the existing experimental data. Although excellent agreement with the available experimental data (to $\lesssim 65$ GPa) is found for the Ir EOS, it is the third-order Birch-Murnaghan EOS with $B'_0 = 5$ rather than the more widely accepted $B'_0 = 4$ that describes our VASP data to higher P . Our inverse Z results suggest the existence of a random-stacking hexagonal close-packed structure of iridium at high P . The fcc-rhcp phase boundary is described by Eq. (5), which crosses the Ir Hugoniot at PT conditions in agreement with those from shock-wave experiments. As another consistency check for Eq. (5), we calculated the full (ions+electrons+phonons) free energies of fcc-Ir and the five hex structures of Ir for which phonon spectra are shown in Figs. 3 and 4, using the TDEP method [13,14]. Differences between the full free energies of the five hex structures and that of fcc-Ir as a function of T at $P = 200$ GPa are shown in Fig. 11. It is seen that dhcp-Ir becomes more stable than fcc-Ir at $T \approx 1600$ K, and at higher T , dhcp, fcc, and 9R are all within 10 meV/atom of each other. At least two more hex structures, 7H and 8H, are expected to be in this 10 meV/atom energy band as well, since the free energy differences are very weak functions of T , and so the $T = 0$ proximity of both 7H and 8H to fcc, dhcp, and 9R (Fig. 5) should not change much

FIG. 11. Differences between the full free energies of five hexagonal structures of Ir and that of fcc-Ir as a function of temperature, at a fixed pressure of 200 GPa.

as T goes up. (This is consistent with the near degeneracy of the melting curves of dhcp, 7H, 8H, and 9R, as noted above.) The rhcp phase is formed by those five or more energetically close structures. The full free energy calculations predict the fcc-rhcp transition temperature at 200 GPa to be $T_{tr} \approx 1600$ K. As it follows from Eq. (5) that $T_{tr}(P = 200 \text{ GPa}) \approx 1610$ K, the fcc-rhcp phase boundary described by Eq. (5) is consistent with independent full free energy calculations, as well as the experimental shock-wave datapoint at 160 ± 20 GPa.

The present study demonstrates that the Z methodology is a powerful technique for the calculation of phase diagrams. With knowledge of the $T = 0$ solid-solid transition points from the cold free-energy calculations, and of the solid-solid-liquid triple points from the direct Z method, complete solid-solid phase boundaries can be constructed, as the previous examples of Pt and Ta [27] and the present example of Ir clearly demonstrate. We emphasize, however, that the inverse Z method has its limitations; its application to the study of phase diagrams of other substances should be carried out with caution. Specifically, in order to implement the inverse Z procedure correctly, one must ensure that (i) the solidification process is initiated, which requires an adequate degree of supercooling, and (ii) it is not hindered by geometric constraints imposed by the computational cell. As regards (i) we typically choose T^* , a fixed solidification temperature, to be below $0.85T_m$ (at least 15% supercooling) and to be above $T_g \sim 0.5T_m$, where T_g is the vitrification temperature. (If $T^* \leq T_g$, the final state may either be a glass or remain a supercooled liquid.) At T^* much closer to T_m solidification may never run to completion. Therefore, phase boundaries lying close to the melting curve cannot be determined using the inverse Z method. For instance, on the phase diagram of Li [41] the inverse Z method can be used to locate the lower- T portions of the solid-solid phase boundaries but cannot be applied to the hR1 phase, all of which is situated near the melting curve. Regarding (ii), the computational cell must be sufficiently large, of order 500 atoms; the most stable solid

phase may not fit into a smaller cell because of geometric constraints, and may in principle be replaced by a less stable structure during solidification. Based on numerous tests we conclude that 450–500 atoms is always adequate for inverse Z calculations, hence the 686-atom bcc supercell for Ir is a very safe choice in this respect. Last but not least, the inverse Z method cannot be applied to phase boundaries separating isostructural phases with different electronic structures, such as the γ and α phases of Ce. Indeed, those phases correspond to localized and delocalized $4f$ electron, respectively. Since the electronic structure cannot be changed during a QMD run, the initially disordered state (liquid) with localized $4f$ electron could only solidify into a solid with localized $4f$ electron, i.e., into γ -Ce, but not into α -Ce, and vice versa. Consequently, the α - ϵ phase boundary in Ce cannot be determined using the inverse Z method.

We have offered the following explanation for the 14-layer hex structure observed by Cerenius and Dubrovinsky: the enhanced uniaxial stress along the loading direction in the DAC, which is present whether or not a pressure-transmitting medium is used, results in fcc-Ir thermodynamic instability and its transformation into the energetically closest hex structure, 14H. This fcc-14H transition is estimated to occur at a pressure of 65 ± 15 GPa and was experimentally observed at ~ 60 GPa.

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