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High pressure study and electronic structure of the super-alloy HfIr₃

I. Halevy¹,²*, S. Salhov¹, M. L. Winterrose², A. Broide¹, A. F. Yue², A. Robin¹, O. Yeheskel¹, J. Hu³ and I. Yaar¹

¹. Nuclear Research Center - Negev, P.O. Box 9001, Beer-Sheva 84190, Israel
². Department of Materials Science California Institute of Technology, Pasadena, CA 91125, USA
³. Geophysical Laboratory of Carnegie Institution of Washington, Washington, DC 20015, USA

Abstract
The crystallographic structure of HfIr₃ was studied as a function of pressure using X-ray diffraction technique. No phase transition was observed up to a pressure of 27.6 GPa, with a total volume contraction of \( V/V_0 = 0.92 \). The bulk modulus value, calculated from the X-ray experimental data and from the sound-velocity technique, are \( B = 279 \pm 4 \) and 297.9\( \pm 2.5 \) GPa, respectively. The relatively high value of the bulk modulus, combined with a high density value of \( \rho = 20564 \) kg/m³, and a high hardness value of 6.05\( \pm 0.26 \) GPa, positions this compound as a possible application for extreme environments. The electronic structure of HfIr₃, studied with the full potential linearized augmented plane calculations technique, indicates that the main cause for the unusual properties of this compound are the Iridium unfilled 5d-shell of this atom.

Keywords: Hafnium, Iridium, Super– alloys, High pressure, Electronic structure, LAPW.

1. Introduction
In a recent theoretical investigation based on density functional theory (DFT) calculations [1], the most stable four component face-centered cubic (fcc) and body-centered cubic (bcc) alloys that can be constructed out of 32 different metals were identified. In the above study, it was found that a significant part of these compounds are iridium based. Iridium is a high melting, high density element; second only the osmium in the periodic table. The high bulk modulus value of iridium, 366 GPa [2], is due to the high cohesive energies arising from the unfilled 5d-shell of this atom. The high bulk modulus value and extremely good corrosion resistant suggest that iridium and iridium based alloys are interesting materials from the scientific point of view, with possible application for extreme environments.

Two of the inter-metallic compounds that exist in the hafnium-iridium system, shown in figure 1 [3], HfIr₃ and HfIr have high melting points, 2430°C and 2470°C, respectively. In the present study, the crystal structure of one of these compounds, HfIr₃, is investigated as a function of applied pressure. HfIr₃ has a cubic fcc, AuCu₃-type, Pm3m (space group number 221) structure, shown in figure 2. The present study has three goals, (a) preparing of a well characterized and homogeneous HfIr₃ sample; (b) studying some mechanical and physical properties of this compound, at ambient and high pressures; (c) determining the electronic structure and explaining the special mechanical and physical properties of this

* email: ihaley@bgu.ac.il
Visitor Associate at Caltech

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compound, using theoretical DFT full potential linearized augmented plane wave (LAPW) calculations. HfIr₃ is a good candidate for understanding super hard materials involving high-pressure and high temperature extreme parameters.

![Figure 1](image1.png)

**Figure 1**: The hafnium-iridium phase diagram as shown by Okamoto [3].

![Figure 2](image2.png)

**Figure 2**: The HfIr₃ crystal structure. The large (black) and small (green) spheres stand for Hf and Ir atoms, respectively [4].

### 2. Experimental Details

#### 2.1 Sample preparation

Stoichiometric sample of HfIr₃ was prepared by arc-melting of high purity hafnium (99.5%) and iridium (99.95%) lumps. The foil sample dimensions for the high pressure measurements were about 50μm in height and 180μm in diameter. The sample was heat treated, 850°C, under Ar atmosphere to relax the sample and avoid preferred orientations, after that the sample was cut to a 120μm diameter for loading. A diamond-anvil cell with 500μm culets was used, with silicon under argon atmosphere. The sample was then annealed in an evacuated quartz tube at 850°C for 4 days.

#### 2.2 Sample characterization

##### 2.2.1 High pressure application

The pressure (up to 27.6 GPa) was applied via a Merrill-Bassett type diamond anvil cell (DAC) and a “Tel-Aviv”-type DAC [4]. The experiments were conducted using a polychromatic X-ray beam, and the pressure was measured utilizing the fluorescence of Ruby technique [5]. Oil as a pressure medium in the sample cavity. The pressure distribution inside the sampling space was checked at different regions, and was determined to vary by less than 5%.

##### 2.2.2 Microstructure

The microstructures of the sample were examined by scanning electron microscopy (SEM) and the phases analyzed by energy dispersive spectroscopy (EDS) to determine their chemical compositions.
2.2.3 X-ray

The X-ray diffraction pattern of the sample taken at ambient pressure is depicted in figure 5. The measurement was carried out using Cu-K\(_{\alpha 1}\) radiation with nickel filter and SiO\(_2\) monochromator, in the angle range of 2\(\Phi\)=20-150\(^\circ\), with step size of 0.02\(^\circ\) and measurement duration of 6 sec per step.

The high-pressure energy dispersive X-ray diffraction studies were taken at the X17-C beamline of the National Synchrotron Light Source (NSLS) [6]. The energy dispersive data was collected with a high pure germanium detector at a fixed Bragg angle (2\(\Phi\)=12\(^\circ\)). The high-pressure powder X-ray diffraction measurements were taken at discrete pressure steps in the range of 0-27.6 GPa. The data was collected by the EDS technique, using the white beam of the superconducting wiggler at the X17-C beamline. Typical data collection time was about 10 minutes. In the lower range of the High-Pressure range, angle dispersive measurements were carried out in transmission configuration using the image plate technique. The data was analyzed using a commercial Rietveld analysis software packages [7,8].

2.2.4 Mechanical properties

Micro hardness measurements were made using a diamond-pyramid based microscope, loaded at 1N (≈100 grf) for 15s. Vickers micro hardness tests of the HfIr\(_3\) sample were carried out on both as cast and annealed samples. The calibration sample was as-cast Cu with the hardness of 0.93(0.3) GPa. The elastic moduli measurements where carried out utilizing the sound-velocity technique [9]. The density, \(\rho\), combined with the longitudinal and transverse sound wave velocity, \(V_L\) and \(V_T\) respectively, were measured. In an isotropic and homogeneous sample, the elastic moduli are [10,11]:

\[
C_L = \rho V_L^2
\]

(1)

\[
G = \rho V_T^2
\]

(2)

\[
E = \frac{G(3C_L - 4G)}{C_L - G}
\]

(3)

\[
B = \frac{EG}{3(3G - E)}
\]

(4)

\[
\nu = \frac{(C_L - 2G)}{2(C_L - G)} = \frac{E}{2G} - 1
\]

(5)

The density was measured by liquid displacement method (Archimedes technique).
3. Results

The optical micrograph and SEM pictures of HfIr₃, figure 3, indicates that no extra phase exists in the bulk sample. EDS analysis (EDS - Energy Dispersive System) revealed no impurities, as can be seen in the graph depicted in figure 4. The EDS calculations were done using the energy of: IrL, IrM, HfL and HfM, lines. The energy spectrum was taken in the range of 0-20keV, the ZAF [12] calculation yield the expected atomic ratio of 74.76% iridium and 25.24% hafnium, the expected ratio for HfIr₃ sample.

![Figure 3: The morphology of the HfIr₃ annealed sample, no evidence of a second phase exists.](image)

![Figure 4: EDS analysis indicates the stoichiometric ratio and the purity of the sample.](image)
The X-ray diffraction spectrum of HfIr₃ at ambient pressure is shown in figure 5. Rietveld analysis of the data confirms the existence of an isotropic single Pm₃m (221) cubic structure, with a unit cell parameter of a=3.9315(5) Å [13]. This pattern confirms that neither HfIr nor iridium traces exist in the annealed sample within the detection limit of the XRD technique.

![X-ray diffraction pattern of HfIr₃](image)

**Figure 5:** Powder X-ray diffraction pattern of the HfIr₃ sample, taken with a Cu-Kα₁ radiation at ambient pressure. (Cu-Kα₁, λ=1.5406Å). The open symbols are the collected data, the red line is the Ritveld fitted to the AuCu₃ symmetry and the blue line is the difference between the data and the fitted line.

Three measurements were taken in the range of 0-5 GPa with the Angle-dispersive system in transmission configuration with the image plate (2D) technique. Since iridium has high absorption for the X-ray radiation, only poor statistics could be achieved in these measurements. The only results obtained from these measurements confirms the value of the unit cell parameter in the ambient and low pressure range and checks that there is no significant preferred orientation in the sample.

The unit cell parameter of the HfIr₃ at ambient pressure is a=3.93150Å with Rwp of 3.1%.

The rest of the high-pressure powder X-ray diffraction data was converted to angle dispersive data, and analyzed using Rietveld analyses technique. All of the refined results indicate a single cubic HfIr₃ phase with the AuCu₃ type, Pm₃m structure. Each spectrum displayed in figure 6 (representing a distinct pressure) was elevated compared to the previous one in order to show the tendency of the lines. The Miller indexes of the various peaks are indicated at the top of the figure. The location of the spectra structure crystal lines are pressure dependent as the crystal shrink, while the X-ray fluoresce lines are fixed in energy and used for energy calibration check at any spectrum (noted as Hf(Kα₁+Kα₂) and Ir(Kα₁+Kα₂)).
An example for a Rietveld analysis of X-Ray data for a pressure of 6.2 GPa, indicating a small preferred orientation in the (2 2 0) plain is depicted in figure 7. Swinging the sample on the $\psi$ axis within $\pm 5^\circ$ reduced the preferred orientation effect remarkably. The change of the unit cell parameter as a function of applied pressure is listed in Table 1. As pressure increases, the unit cell parameter shrinks monotonically with no phase change.

Figure 6: X-ray EDS powder diffraction of HfIr$_3$ as a function of pressure. Typical data collection time was around 10 minutes. Some of the diffraction are suffering a bit preferred orientation.

Figure 7: Powder X-ray diffraction pattern of the HfIr$_3$ sample, measured at a pressure of 6.2 GPa. The line is the best fit for the data in circles obtained using Rietveld analysis. The difference between, is depicted in bottom of the graph. From the data, we can conclude that a small preferred orientation in the (2 2 0) plain exists.
Table 1. The HfIr₃ phase, volume and unit cell parameters as a function of pressure. The results are taken from Rietveld refinement [8] of the measured diffraction X-ray patterns depicted in Figures 5 and 6.

<table>
<thead>
<tr>
<th>Pressure [GPa] (±5%)</th>
<th>HfIr₃</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>V[Å³]</td>
</tr>
<tr>
<td>0</td>
<td>60.76800</td>
</tr>
<tr>
<td>0.1</td>
<td>60.71120</td>
</tr>
<tr>
<td>0.2</td>
<td>60.69628</td>
</tr>
<tr>
<td>1.9</td>
<td>60.46538</td>
</tr>
<tr>
<td>4.5</td>
<td>60.25012</td>
</tr>
<tr>
<td>6.2</td>
<td>59.56540</td>
</tr>
<tr>
<td>7.2</td>
<td>59.48328</td>
</tr>
<tr>
<td>9.4</td>
<td>59.13910</td>
</tr>
<tr>
<td>11.4</td>
<td>58.63521</td>
</tr>
<tr>
<td>13.7</td>
<td>58.13009</td>
</tr>
<tr>
<td>17.2</td>
<td>57.50989</td>
</tr>
<tr>
<td>19.7</td>
<td>57.10779</td>
</tr>
<tr>
<td>20.2</td>
<td>56.90713</td>
</tr>
<tr>
<td>23.2</td>
<td>56.48062</td>
</tr>
<tr>
<td>24.6</td>
<td>56.38069</td>
</tr>
<tr>
<td>26.8</td>
<td>55.96999</td>
</tr>
<tr>
<td>27.6</td>
<td>55.79582</td>
</tr>
</tbody>
</table>

The volume-pressure curve, calculated from the data listed in Table 1, are depicted in figure 8. For comparison, we added the equation-of-state of iridium, measured by the same system, which consider having a very high bulk modulus value of 366 GPa [2]. The relationship between pressure and volume change for both materials was determined by the Vinet equation of state (EOS) [14]:

\[
P(V) = 3B \left( \frac{V}{V_0} \right)^{2/3} \left( 1 - \left( \frac{V}{V_0} \right)^{1/3} \right) \exp \left( \frac{3}{2} \left( B' - 1 \right) \left( 1 - \left( \frac{V}{V_0} \right)^{1/3} \right) \right)
\]

Where, B is the isothermal bulk modulus at room temperature and ambient pressure, and B' is the partial derivative of the isothermal bulk modulus against pressure under the same conditions. This constitutive relation was shown to be universally valid for all solids under a wide range of pressure values [14]. Any attempts to fit the data to other EOS formalism, like Holzapfel [15] or Birch [16] gave similar results. No hysteresis was observed for the volume data while increasing or decreasing pressure. From the results of the fit, a volume contraction of V/V₀=0.92 at 27.6 GPa, and a bulk modulus value of B=279±4 GPa was derived for a fixed B'=4, closer to the value of 285.31 GPa calculated in the past [17]. For iridium, we got a value of B=309±6 with B' fixed as 4, closer to the value of 366 GPa obtained in the past [2]. It is clear from the comparison between the equation-of-state of
iridium metal and to the equation-of-state of HfIr₃ that the composite is softer then the Iridium metal.

**Figure 8.** The volume-pressure curve derived from the X-ray high-pressure diffraction Rietveld refinement for the HfIr₃ sample (lower curve) compared to the results obtained by us in the past for Iridium metal (upper curve), in agreement with the data published by Cerenius et al [18]. The solid line is the result of a modified Holzapfel Equation fit to the experimental data [15].

The dynamic elastic moduli of the sample were calculated from the measured sound wave velocity and from the sample density. The density was measured by liquid displacement method (Archimedes’ technique) and found to be 20564±50 kg/m³. The actual density is found to be 0.997 of the theoretical value. The measured velocities were \(V_L=5006±10\) Km/sec and \(V_T=2816±3\) m/sec for the longitudinal and transverse wave velocities, respectively. The calculated shear, Young’s, and bulk moduli are: 163.1±0.9 GPa, 413.7±2.8 GPa, and 297.9±2.5 GPa, respectively, and the Poisson’s ratio is 0.269±0.008 (the dynamic bulk modulus is adiabatic [19]). The compressibility \(\chi=\beta^{-1}\). The relationship between the isothermal compressibility, \(\chi_T\) and the adiabatic compressibility, \(\chi_S\) is [19]:

\[
\chi_T = \chi_S + T\beta^2/\rho C_P
\]  

(7)

where \(T\) is the temperature in K, \(\beta\) is the volume thermal expansion coefficient, \(\rho\) is the density, and \(C_P\) is the heat capacity at constant pressure. This relationship implies that the isothermal compressibility will generally be higher than the adiabatic one. Therefore the adiabatic bulk modulus, \(B_S\), should be slightly higher than the isothermal one, \(B_T\).

The hardness of the annealed HfIr₃ was derived as 6.05±0.26 GPa with similar value for the as cast sample. The Hardness – Vickers values are 1760 [MN m⁻²] for both materials [20] but the bulk modulus values are 320 GPa and 110 GPa for the Iridium and Hafnium, respectively.
4. Calculation

The calculations were done at ambient pressure using the full potential linearized plane wave (LAPW) method, as embodied in the WIEN97 code [21]. The unit cell in these calculations is divided into two parts, the atomic spheres and the interstitial region. The wave functions inside the atomic spheres are described by atomic like functions, while in the interstitial region plane waves are used [22]. Exchange and correlation effects are treated within the density functional theory, using the generalized gradient approximation (GGA) [23], where not only the local density, but also its gradient determines the magnitude of the effect. The value of $V_{zz}$ (the electric field in the z direction) in these calculations is given by an integral of the charge density $\rho(r)$ over the unit cell,

$$V_{zz} = \int \rho(r) \frac{2P_2(\cos \theta)}{r^3} dr,$$

(8)

where $P_2$ is the second-order Legendre polynomial. In most cases, the charge asymmetry inside the atomic sphere, where the $V_{zz}$ value is being calculated, determines more than 90% of the $V_{zz}$ value. Inside this sphere, the contribution to $V_{zz}$ can be further divided into s-d, p-p and d-d components, so that the physical origin of the efg (electric field gradient) can be analyzed [22].

The Hafnium and Iridium atoms in HfIr$_3$ are located at the (1a) 0 0 0 and (3c) 0 ½ ½ sites, respectively. The Hafnium 1a site is symmetric, resulting with zero $V_{zz}$ value at the Hafnium site. The (3c) site is symmetric only in the xy plane, resulting with a calculated $V_{zz}$ value of -1.56 V/m$^2$ at the Iridium site and an asymmetry parameter value, defined as $\eta = (V_{xx} - V_{yy})/V_{zz}$, of zero.

The calculated Hafnium and Iridium partial s, p, d and f contribution to the total density of states (DOS) in HfIr$_3$ is plotted in figure 9 as a function of energy. The main feature of the DOS is determined by the d-electrons distribution, shown in figure 9 (c). This feature include two groups of peaks, the first group lies in the energy interval from -6 to 1.75 eV contains mainly Iridium 5d-states, and the second energy interval, from 2 to 7 eV above $E_{Fermi}$, contains a mixing of Hafnium and Iridium 5d-states. The Iridium 6s, p and 4f-electrons, depicted in figure 9 (a), (b) and (d) respectively, are partly hybridized with the Iridium 5d-states. The same 6s-5d, p-5d and 4f-5d hybridization can be seen in the Hafnium DOS, were a smaller degree of hybridization can be seen. This DOS feature can be interpreted using the electronic configuration scheme of Hafnium and Iridium depicted in figure 10. The unfilled 5d-states of Hafnium and Iridium having 2 and 7 electrons respectively, lies in the upper part of the energy scheme and though responsible for the main contribution to the DOS of HfIr$_3$. The greater number of Iridium 5d-electrons in the unfilled state is the reason for the wider and more dominate contribution of these electrons, compared to the contribution from Hf 5d-electrons.
Figure 9: Calculated, (a) s, (b) p, (c) d and (c) f electrons density of states (DOS) for Hafnium (---) and Iridium (---) atoms.

Figure 10: Electronic configuration scheme of (a) Hafnium and (b) Iridium atoms [taken from ref. 24].

The partial valence s–d, p–p and d–d and the lattice contribution to the efg at the Iridium 3c-site are listed in table 2. In contrast to most compounds, were the main contribution to the Vzz value comes from the p–p interaction next to the probe nucleus, in HfIr3 the negative p–p contribution to Vzz is reduced from a value of -9.277 V/m² to a value of -1.428 V/m², due to positive s–d and d–d contributions. This unusual situation can be also attributed to the
wide and dominate distribution of Iridium 5d-electrons in this compound, as seen in figure 9 (c).

Table 2. The valence s–d, p–p, d–d and the lattice partial contribution to the $V_{zz}$ value at the Iridium 3c-site.

<table>
<thead>
<tr>
<th>Contribution to the $V_{zz}$ value at the Iridium 3c-site ($10^{21}$ V/m²)</th>
<th>s-d</th>
<th>p-p</th>
<th>d-d</th>
<th>Lattice</th>
<th>$V_{zz}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.381</td>
<td>-9.277</td>
<td>6.468</td>
<td>-0.132</td>
<td>-1.428</td>
<td></td>
</tr>
</tbody>
</table>

Based on the total electronic DOS at the Fermi level calculated for 0 K ($N(E_{Fermi}^0)$), the band contribution ($\gamma_{band}$) to the value of the electronic specific heat coefficient ($\gamma$) can be evaluated using the above equations,

$$\gamma_{band} = \frac{\pi^2 k_B^2}{3} N(E_{Fermi}^0)$$

where $k_B$ is the Boltzmann constant. This equation serves as a link between band structure calculations and electronic specific heat measurements [22]. From the calculated results, depicted in figure 9, a value of 51.35 (states/Ry/f.u.) is calculated for $N(E_{Fermi}^0)$. This gives, according to equation 9, a $\gamma_{band}$ coefficient value of 8.9 (mJ/mol/k²), a typical value for an intermetallic system like HfIr₃ having a considerable amount of 303 electrons per formula unit.

5. Summary

The crystallographic structure of HfIr₃ was studied as a function of pressure using X-ray diffraction technique. No phase transition was observed up to a pressure of 27.6 GPa, with a total volume contraction of $V/V_0 \approx 0.92$. The bulk modulus (B) value, calculated from the X-ray experimental data and from the sound-velocity technique, are $B=279\pm4$ and $297.9\pm2.5$ GPa, respectively, in good agreement with the value of 285.31 GPa calculated in the past [17]. The relatively high value of the bulk modulus, combined with remarkably high density value of $\rho=20564$ kg/m³, and a high hardness value of 6.05±0.26 GPa, positions this compound as a suitable candidate for a superalloy, as predicted by DFT calculations made in the past [1]. The electronic structure of HfIr₃, studied with the full potential linearized augmented plane wave (LAPW) calculations technique, indicates that the main cause for the unusual properties of this compound are the Iridium and Hafnium unfilled 5d-shell of this atom.

References