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Concerning the brittleness of iridium: An elastic and electronic view

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ABSTRACT

The brittleness of Ir has become a challenging and puzzling problem for decades and its fundamental mechanisms are controversial with each other in the literature. The present first principles calculation aims to get a deep understanding of the brittleness of Ir from an elastic and electronic view. It is found that Ir has normal pressure-dependent mechanical behavior, while the temperature-dependent behavior of Ir is unusual and contrary to that of other FCC metals, and that pressure decreases the brittleness of Ir, whereas temperature increases its brittleness, suggesting that the machining of Ir products should be performed at low temperature and high pressure. Moreover, electronic structure and crystal field theory reveal that Ir has the mainly octahedral bonding, which would be transformed to the mainly cubic bonding under high pressure, while become more octahedral and directional at high temperature. In addition, the implication and importance of the similarities between Ir and semiconductors are also discussed.

1. Introduction

During the past decades, iridium (Ir) has raised great research interests for ultra-high temperature applications due to its exceptional mechanical properties, catalytic activity, and high resistance to corrosion at elevated temperatures [1,2]. The brittleness of Ir, however, has become a challenging and puzzling problem to materials scientists since the discovery of this metal [2–9]. Unlike good ductility of common face-centered-cubic (FCC) metals, Ir single crystal undergoes brittle transgranular fracture after substantial plastic deformation, and polycrystalline Ir fails predominantly through intergranular fracture at temperatures up to 1000 °C [2].

Regarding the fundamental mechanism of the unusual brittleness of Ir, there are already a lot of experimental and theoretical investigations in the literature, while these results are not consistent with each other for many years [2–10]. For instance, segregation of impurities to the grain boundary was once believed to induce the brittle fracture of Ir [6], while later studies showed that brittleness is an intrinsic property of Ir, irrelevant to impurities [2]. Moreover, molecular dynamics (MD) simulation indicated that the ultrahigh dislocation densities and strain-hardening rates should be responsible for the brittleness of Ir [3], whereas experiments demonstrated that the dislocation and strain-hardening rates of Ir are similar to other FCC metals [4,5]. In addition, bond directionality of Ir is generally supposed to cause the brittleness [7–10], nevertheless these calculated findings are not compatible with each other, e.g. the electron localization functions of Al and Pt are similar to Ir [8,9], while these two FCC metals are ductile. Obviously, the brittleness of Ir is still a mystery to materials community, and it is of significance to further reveal its intrinsic mechanism.

Pressure- and temperature-dependent physical properties of materials are both scientifically important and technologically valuable. In this respect, there are only a few studies regarding Ir in the literature [11–13]. For instance, both experiments and first principles calculations were used to study the pressure-dependent lattice constant and phase transition of Ir [11,12], and MD simulation was failed to predict the correct elastic constants of Ir under pressure and temperature [13]. It should be pointed out that there is a lack of a systematic and thorough study of physical properties of Ir under pressure and temperature in the literature, and that the plastic theory is unfit to explain the unusual brittleness of Ir [3–5]. The present study is therefore dedicated, by means of first principles calculation, to investigate the pressure- and temperature-dependent mechanical properties of Ir, and to get a deep understanding of the brittleness of Ir from an elastic and electronic view.

2. Computational methods

The first-principles calculation is based on the well-established Vienna ab initio simulation package (VASP) within the density functional theory [14]. The calculation is conducted in a plane-wave basis, using the projector-augmented wave (PAW) method [14]. The exchange and correlation items are described by generalized gradient approximation (GGA) of Perdew et al. [15], and the cutoff energies are 400 and 500 eV for plane wave basis and

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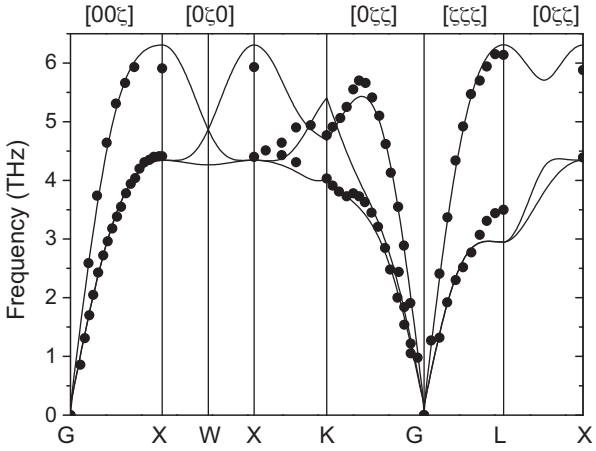

Fig. 1. Phonon dispersions of FCC Ir along various high-symmetry directions from the present calculation (solid lines) and experimental results (filled circles) [21].

augmentation charge, respectively. Temperature- and pressure-dependent elastic constants are calculated according to the method adopted by Wang et al. [16], and the main idea is presented as follows: first, volume-dependent elastic constants, $C_{ij}(V)$, are calculated at a volume range from $V/V_0 = 0.5$ to 1.5 with an interval of 0.025 using a universal-linear-independent coupling-strains method [17]; second, the Helmholtz free energy, $F(V,T)$, is obtained through combining electronic and vibrational free energy, and the volume as a function of temperature at various pressures, $V(T)_p$, is determined by fitting $F(V,T)$ into the Vinet's equation of states; third, the temperature dependent isothermal elastic constants, $Cs_{ij}(T)_p$, are calculated by substituting $V(T)_p$ into $C_{ij}(V)$, and the isentropic elastic constants, $Cs_{ij}(T)_p$ are finally obtained by taking the Davies' approximation. In the above procedure, the vibrational free energy is calculated in the framework of the supercell approach [18] with a cell size of $3 \times 3 \times 3$. After test calculations, the k-meshes of $15 \times 15 \times 15$, $21 \times 21 \times 21$, and $7 \times 7 \times 7$ are adopted for dynamic, elastic constants, and supercell calculations, respectively.

3. Results and discussion

We first derive the ground-state properties of FCC Ir. Accordingly, it could be seen that the lattice constant of 3.88 Å matches well with experimental value of 3.84 Å [19], and that the calculated pressure–volume data are in good agreement with experimental measurements [11], e.g., the calculated pressure values of Ir at the V/V_0 points of 0.947, 0.899, and 0.876 are 21, 47, and 63 GPa, respectively, which agree well with corresponding experimental values of 20, 46, and 62 GPa, respectively [11]. Moreover, the single-crystal elastic constants C_{11}, C_{12}, and C_{44} are calculated to be 573, 222, and 241 GPa, respectively, which are compatible with corresponding experimental values of 596, 252, and 270 GPa, respectively [20]. In addition, the phonon frequencies of FCC Ir are also calculated and shown in Fig. 1. One observes from this figure that the phonon dispersions derived from the present study agree well with experimental results by means of inelastic neutron scattering [21]. Especially, it should be noted that the present calculation well reproduces the pronounced dips in $[\zeta\,\zeta\,0]$ branches from experiments, which gives better performance than those calculated results from first principles and a bond-order potential in the literature [3,21].

The single-crystal elastic constants of FCC Ir are calculated as a function of pressure and temperature, respectively, and the derived results are summarized in Fig. 2. Several features could be observed from this figure. First, the three elastic constants of Ir increase almost linearly under pressure, and the pressure

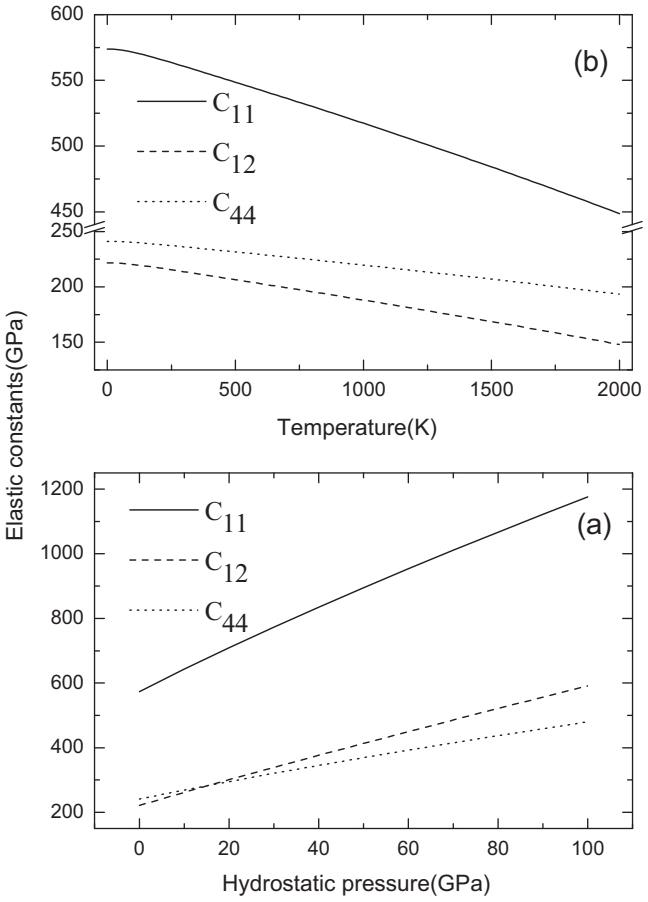

Fig. 2. Single-crystal elastic constants of FCC Ir as a function of (a) hydrostatic pressure and (b) temperature.

derivatives dC_{11}/dP, dC_{12}/dP and dC_{44}/dP are calculated to be 5.37, 3.48 and 2.10, respectively. It should be noted that the above pressure derivatives of Ir are similar to corresponding values of other FCC metals in terms of magnitude and the sequence of magnitude, e.g. 7.22, 3.83 and 2.39 for Al [22], and 5.54, 4.55 and 2.65 for Ni [23], respectively. Second, it can be seen from Fig. 2(b) that the three elastic constants of Ir decrease almost linearly under temperature, and the slopes of these lines, i.e. dC_{11}/dT, dC_{12}/dT and dC_{44}/dT, are calculated to be $-6.64\text{E}{-}02$, $-3.89\text{E}{-}02$ and $-2.54\text{E}{-}02$ GPa K^{-1}, respectively. Interestingly, the sequence of the above derivatives of Ir, i.e. $dC_{11}/dT < dC_{12}/dT < dC_{44}/dT$, is quite different from those of other cubic metals ($dC_{11}/dT < dC_{44}/dT < dC_{12}/dT$) [24,25], while similar to those of IV-semiconductors (Si and Ge) [26]. Third, the Cauchy pressure of C_{12}–C_{44} varies from negative to more positive with the increase of pressure, while becomes more negative with the increase of temperature, suggesting that the bonding of Ir should become more metallic under pressure, while more covalent at higher temperature.

The bulk moduli (B) and shear moduli (G) of polycrystalline Ir are derived from single-crystal elastic constants through the Voigt–Reuss–Hill's approximation [27], and as typical examples, Fig. 3(a) shows the B and G values of Ir at ambient pressure as a function of temperature. It could be seen that both B and G decrease almost linearly with the increase of the temperature. To investigate the brittle/ductile behavior of Ir, the pressure and temperature dependent G/B values of FCC Ir are calculated, respectively, and the results are shown in Fig. 3(b). It should be noted that the G/B value proposed by Pugh has been extensively used as an empirical parameter to express the brittleness/ductility of materials [28], i.e. the critical G/B value of 0.57 separates the