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## Effect of the exchange-correlation energy and temperature on the generalized phase diagram of the 4d transition metals

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Very recently, we have used first-principles methods to calculate the zero-temperature phase diagram of all the 4d transition metals up to  $P \sim 500$  GPa. Even though we used a very accurate implementation of density functional theory and the accurate exchange-correlation functional of Wu and Cohen, we found that solid–solid transition pressures were underestimated by  $\sim 10$  GPa with respect to room-temperature measurements. Here, we report the dependence of the transition pressures on the choice of the exchange-correlation functional. We also perform first-principles calculations of the harmonic phonon frequencies of molybdenum and zirconium in different crystalline structures in order to extend the phase diagram to non-zero temperatures. We use the results to discuss the reasons for the earlier disagreements between calculated and experimental transition pressures.

**Keywords:** transition metals; high pressure; high temperature; molybdenum

### 1. Introduction

The transition metals are among the families of elements most intensively studied both in experiments and theory. Even though there have been many efforts to map and interpret systematic trends in their properties [1–3], our knowledge of transition-metal systematics is still far from being complete. Evidence for this includes the current major controversies over the high-pressure melting curves [4–6] and sizable gaps in the map of transition-metal phase diagrams at low and high temperatures, to cite some of the examples. In a recent work [7], we have reported a systematic investigation of the zero-temperature phase diagram of all the 4d transition metals over a wide range of pressures ( $0 < P < 500$  GPa). First-principles calculations were performed within the full-potential linearized augmented plane waves (FP-LAPW) [8] implementation of density functional theory (DFT) and the recent approximation for the exchange-correlation energy of Wu and Cohen (WC) [9]. We found that the sequences of solid–solid phase transitions observed across the 4d transition-metal series under pressure were reproduced correctly, whereas the transition pressures  $P_t$  calculated for Y and Zr were underestimated by  $\sim 10$  GPa, with respect to

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room-temperature measurements. Likely arguments aimed to explain the differences between theory and experiment might be based on: the effect of the exchange-correlation functional energy  $E_{xc}$  used; errors derived from the approximations made on the implementation of DFT used; and possible thermal effects. In this work, we assess the effect of  $E_{xc}$  on  $P_t$  by performing new calculations within two of the most commonly used approximations in the field of *ab initio* calculations, namely the generalized gradient approximation by Perdew, Burke and Ernzerhof (GGA-PBE) [10], and local density approximation by Ceperley and Alder (LDA-CA) [11]. Moreover, we have calculated the free energy of Mo in the bcc, fcc and hcp structures using first-principles techniques and within the harmonic approximation. The results obtained allow us to infer the shape of the high  $P$ - $T$  region of the phase diagram of Mo. We have carried out similar calculations for zirconium in the hcp and bcc structures and surprisingly found that hcp Zr is mechanically unstable at ambient pressures.

The remainder of this article is organized as follows. In Section 2, we summarize the essential ideas underlying the method of calculation used and technicalities. Next, we present our results; in Section 4 we give the discussion and conclusions.

## 2. Methods and technicalities

### 2.1. Total energy calculations

Total energies have been calculated with the FP-LAPW technique, since this is among the most accurate implementations of DFT for carrying out calculations on crystals. We use the well-known Monkhorst-Pack  $k$ -point scheme [12] for sampling over the first Brillouin zone. States having principal quantum number  $n < 3$  are treated as core states, while the rest of the states are treated as valence. All the FP-LAPW calculations have been performed using the WIEN2k code [13]. Extensive tests performed on Mo [7] indicate that the choices  $R_{MT}K_{max} = 9.5$ ,  $G_{max} = 18 \text{ bohr}^{-1}$ ,  $I_{orb}^{max} = 10$  and  $I_{pot}^{max} = 4$ , together with  $14 \times 14 \times 14$   $k$ -point sampling ( $14 \times 14 \times 7$  for *hcp*), give convergence to within  $\sim 1$  meV/atom, so we use this setup for all the calculations. As noted in Section 1, we have carried out new first-principles calculations within GGA-PBE and LDA-CA. The essential difference between GGA and LDA functionals is that, in LDA, the exchange-correlation energy is dependent on the electronic density  $n(\mathbf{r})$ , while in GGA, the dependence on the gradient  $\nabla n(\mathbf{r})$  is also present. In GGA-WC, the correlation part of  $E_{xc}$  is the same as in GGA-PBE but the exchange form is varied so as to reproduce more slowly varying electronic densities.

### 2.2. Free energy calculations

The free energy  $F(V, T)$  of Mo is calculated in the harmonic approximation, in which  $F(V, T) = F_{\text{perf}}(V, T) + F_{\text{harm}}(V, T)$ .  $F_{\text{perf}}$  is the free energy of the rigid perfect crystal, including thermal electronic excitations, and  $F_{\text{harm}}$  is calculated from the phonon frequencies  $\omega_{\mathbf{q}s}$  ( $\mathbf{q}$  the wavevector,  $s$  the branch). We calculate  $F_{\text{harm}}$  in the classical limit, in which  $F_{\text{harm}} = 3k_B T \ln(\beta \hbar \bar{\omega})$  per atom, with  $\beta = 1/k_B T$  and  $\bar{\omega}$  the geometric average of phonon frequencies over the Brillouin zone. We have checked that for the temperatures of interest this approximation is accurate enough. The methods used to calculate  $F_{\text{perf}}(V, T)$  and the frequencies  $\omega_{\mathbf{q}s}$  are similar to those used in earlier works [14]. For a set of temperatures in the interval  $0 < T < 10,000$  K, we calculated  $F_{\text{perf}}$  at a set of volumes, and fitted the volume dependence with a third-order Birch-Murnaghan equation. The temperature dependence of the coefficients in this equation was then fitted with a third-order polynomial. The phonon frequencies were calculated for the bcc, fcc and hcp structures at six volumes in the range of  $9.6$ – $8.2 \text{ \AA}^3/\text{atom}$ , as explained elsewhere [4,15]. We used supercells

containing 216(200) atoms for the fcc and bcc(hcp) structures and  $4 \times 4 \times 4$   $k$ -point sampling. The volume dependence of the average  $\bar{\omega}$  was then fitted with a third-order polynomial. Our results show that Mo in the fcc and hcp structures is mechanically unstable at pressures below  $\sim 350$  GPa. We note that similar results obtained with similar techniques have been reported very recently by Belonoshko et al. [16].

### 3. Results

#### 3.1. Effect of $E_{xc}$ on $P_t$

In Table 1, we present our estimations for the transition pressures of the  $4d$  transition metals obtained using different approximations for  $E_{xc}$ . As can be seen, results obtained for a same solid–solid transition may vary within  $\sim 10$  GPa or more if  $P_t$  is high. In general, transition pressures obtained with LDA-CA underestimate room-temperature measurements more than the other two approximations and GGA-PBE provides the closest results to the experiments. On the other hand, GGA-WC  $P_t$  lies between LDA-CA and GGA-PBE values in most of the cases. For yttrium, we find that the agreement between our calculated transition pressures and experiments is still not satisfactory for the transitions hcp  $\rightarrow$   $\alpha$ Sm and  $\alpha$ Sm  $\rightarrow$  dhcp. One reason may be that the energy curves corresponding to those structures follow each other so closely that the prediction of the transition pressures becomes quite challenging (see, for instance, Figure 2 in [7]). Also we note the possible existence of intermediate distorted crystalline structures as reported recently by Lei et al. [21], and not considered in this work.

#### 3.2. Mo at high pressures and temperatures

In thermodynamic equilibrium and for a given  $P$  and  $T$ , condensed matter systems adopt the structure of minimum Gibbs free energy,  $G$ . In order to deduce the phase boundary between two competing structures, said  $A$  and  $B$ , one has to impose the condition that the two Gibbs free energies are equal, that is  $G_A = G_B$ . One way to find  $G$  is to calculate first the Helmholtz free energy  $F$ , since they are related by the formula  $G = F + PV$  (where  $P = -\partial F/\partial V$ ). We have calculated the free energy of Mo in the bcc, fcc and hcp structures by means of first-principles methods and within the harmonic approximation, and we have used the results to obtain the

Table 1. Estimated transition pressures,  $P_t$ , of Mo, Zr and Y under pressure obtained with different exchange-correlation energy functionals.

Element	Transition	$P_t$			Experiment
		LDA	PBE	WC	
Mo	bcc $\rightarrow$ fcc	639	667	662	
Zr	hcp $\rightarrow$ $\omega$	-7	2	-4	3 <sup>a</sup>
	$\omega$ $\rightarrow$ bcc	14	26	22	30 <sup>b</sup>
Y	hcp $\rightarrow$ $\alpha$ Sm	-3	4	-1	15 <sup>c</sup>
	$\alpha$ Sm $\rightarrow$ dhcp	1	20	4	30 <sup>c</sup>
	dhcp $\rightarrow$ fcc	60	67	33	44 <sup>d</sup>
	fcc $\rightarrow$ bcc	470	518	513	

Note: Pressures are in units of GPa.

<sup>a</sup>See [17].

<sup>b</sup>See [18].

<sup>c</sup>See [19].

<sup>d</sup>See [20].

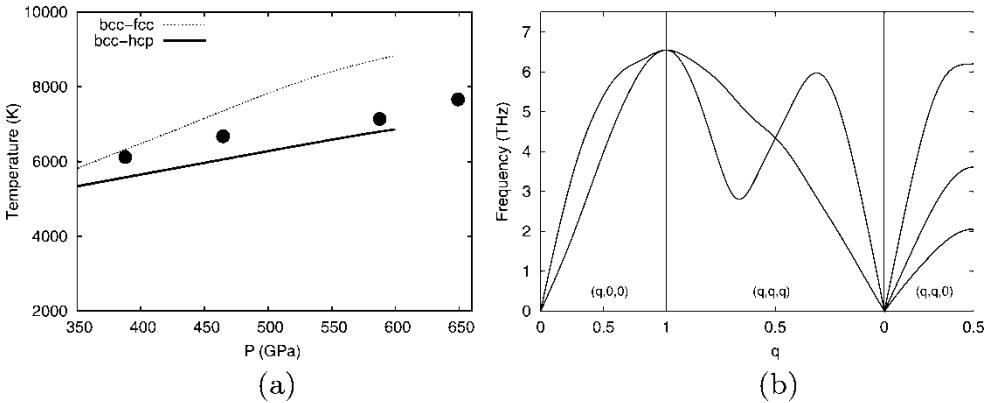


Figure 1. (a) High- $P$  and high- $T$  solid–solid phase boundaries of Mo calculated using first-principles techniques and within the harmonic approximation. Dots show results obtained by Belonoshko et al. [16] for the bcc–fcc boundary. (b) Calculated GGA-WC phonon frequencies of Zr in the bcc structure at volume  $V = 18.43 \text{ \AA}^3/\text{atom}$ .

corresponding bcc–fcc and bcc–hcp phase boundaries at elevated  $P$  and  $T$ . In Figure 1(a), we show our results together with the bcc–fcc boundary calculated by Belonoshko et al. [16] using similar methods to the ones used here; the agreement between ours and Belonoshko’s estimations appears to worsen as  $P$  increases. Belonoshko et al. are the first authors to report evidence for the existence of a high- $T$  solid phase of Mo different than bcc, however they restrict their analysis to the fcc structure only. Based on our calculations, we prove that at extreme conditions Mo is more stable in the hcp structure than in the fcc structure, since the two phase boundaries in Figure 1(a) lie well below the melting line of Mo calculated for the bcc structure [4] and the bcc–hcp boundary is below the bcc–fcc one. The results presented here are of relevance to the map of the complete high- $P$  and  $T$  phase diagrams of Mo and also for the interpretation of data obtained for transition metals in static-compression diamond-anvil cell experiments.

### 3.3. Phonon frequencies of Zr

We have calculated the phonon frequencies of Zr in the hcp and bcc structures using the GGA-WC the approximation for  $E_{xc}$  and the same first-principles methods used for Mo. In Figure 1(b), we plot the results obtained for the bcc structure at volume  $V = 18.43 \text{ \AA}^3/\text{atom}$ , which corresponds to the transition pressure  $P_t = 22 \text{ GPa}$ . We find that Zr in the hcp structure is mechanically unstable (phonon frequencies in the region around the  $\Gamma$  point are negative) up to pressures of  $\sim 6 \text{ GPa}$ ; it is noted that the  $c/a$  ratio of the hcp structure has been optimized at each studied volume. This outcome is at odds with experimental data, as hcp appears to be the stable phase of Zr at room temperature and zero pressure [17]. Work addressed to understand such disagreements between theory and experiments is in progress at present.

## 4. Discussion and conclusions

In this work, we have analyzed the effect of the approximation used for  $E_{xc}$  on the prediction of the zero-temperature phase transitions observed in the  $4d$  transition metal series under compression. Although the sequences of solid–solid transitions are reproduced correctly with DFT, we find that the estimated  $P_t$ s may vary within 10 GPa or more depending on the  $E_{xc}$  functional used. GGA-PBE appears to provide the most accurate  $P_t$  results with respect to room-temperature

measurements. We have also explored the high- $P$  high- $T$  regions of the phase diagram of Mo by carrying out first-principles calculations within the harmonic approximation. We have shown that at extreme conditions, that is  $T > 5000$  K and  $P > 350$  GPa, solid Mo is more stable in the hcp structure than in either the bcc or fcc phases. Regarding Zr, we provide the phonon frequencies obtained in the bcc structure at volume  $V = 18.43 \text{ \AA}^{-3}$ /atom and found that hcp Zr is incorrectly predicted to be mechanically unstable up to pressures of  $\sim 6$  GPa.

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