

Ab-initio melting curve and principal Hugoniot of tantalum

S. Taioli¹, C. Cazorla^{2,3}, M. J. Gillan^{2,3}, and D. Alfè^{1,2,3}

¹ Department of Earth Sciences, University College London, Gower Street, London WC1E 6BT, UK

² Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, UK

³ London Centre for Nanotechnology, University College London, Gordon Street, London WC1H 0AH, UK

Abstract.

We report first principles calculations of the melting curve and principal Hugoniot ($P - V$ curve) of body centered cubic (bcc) tantalum in the pressure range 0-300 GPa. A description of lattice dynamics and thermal properties of bcc Ta using finite temperature density functional theory (DFT) is presented. The approach works within the projector augmented wave (PAW) implementation of DFT and explicitly treats in valence the 5p, 6s and 5d electrons. The principal Hugoniot ($P - V$ curve), obtained using the Rankine-Hugoniot equation, is investigated using the generalized gradient approximations (GGA). Very good agreement with the shock experiments is obtained with GGA in all the range of pressure. We also report the temperature-pressure relation on the shock Hugoniot and the full *ab-initio* melting curve of Ta.

1. Introduction

The past 10 years have seen remarkable developments in two branches of condensed matter physics. One is the improvement in the experimental set-up for studying phase transitions at high pressures by the use of shock-waves (Brown and Shaner 1984, Nellis et al. 2003) or laser-heated diamond-anvil cells (DAC) (Errandonea et al. 2001, Errandonea et al. 2003); the other is the improvement of the computational tools and computer power for calculating a number of materials properties from first principles, notably in transition metals and transition metals compounds. As well as contributing to our understanding of the high pressure phenomena and the control of the materials under extreme conditions, such advances also allow unprecedented access to the electronic and optical properties of matter.

Nevertheless, at high pressures and temperatures, when the behavior of materials is often anything but simple, the large discrepancies in the experimental results using different approaches cast a shadow on the reliability of the measurements, notably in the melting properties. The need of coherent experimental and theoretical results has been fuelled by both the fundamental desire to investigate the thermophysical properties of interacting many-fermion systems under extreme conditions and by the possibility to predict novel configurations that give materials entirely new properties.

Shock compression of materials is a well established (Zeldovich and Raizer 2002) technique, successfully applied to a broad range of materials such as aluminum, iron,

copper and tantalum, to reach hundreds of gigapascals of pressure and temperatures of thousands of degrees.

Transition metals, due to their stability under extreme conditions, have been widely used as both anvils and impactors in shock wave experiments. Tantalum is a transition metal with a body-centered cubic (bcc) phase, stable even at high pressure of hundreds of GPa in the bulk material (Moriarty et al. 2002). It presents a high chemical and thermodynamical stability, having a melting point at ambient pressure of about 3270 K and it is widely used in the microelectronics industry for producing integrated circuits.

As well as improving experimental lay-out, a large effort has been devoted to theoretical investigations, which, particularly in the case of transition metals, are still the subject of discussion. While the complexity of treating correctly the exchange correlation energy makes the high pressure phenomena very difficult to solve from first principles, theoretical investigations can shed some light to argue about the reliability of the experiments.

In a previous paper (Taioli et al. 2007) a general description of lattice dynamics, thermal properties and melting of tantalum using DFT was presented. The equation of state at zero temperature and the phonon dispersion curves were investigated using both local density approximation (LDA) or generalized gradient approximations (GGA). The main goal of this work is to calculate the principal Hugoniot (P-V curve) of tantalum by solving the Rankine-Hugoniot equation, though we also report the melting curve of Ta obtained from first principles calculations.

The paper is organized as follows. In the next section we report the technical details of the calculations. In section 3 the strategy to calculate the thermal equation of state and tests on the reliability of the techniques are investigated. In section 4 the pressure-volume and pressure-temperature relations on the shock Hugoniot are discussed, and the melting curve of tantalum is also presented. Finally, conclusions are given in section 5.

2. Technical details

The present calculations have been performed with VASP (Kresse and Furthmuller 1996). In the finite-temperature formulation of DFT, in which the electronic excitations due to the temperature are taken into account, the relevant quantity is the electronic free energy, which has the following form

$$F_{static}(V, T_{el}) = E(V, T_{el}) - TS(V, T_{el}) \quad (1)$$

where E is the sum of kinetic, electron-nucleus, Hartree and exchange-correlation terms, and $S = -k_B T_{el} \sum_i [f_i \ln f_i + (1 - f_i) \ln(1 - f_i)]$ is the electronic entropy, with k_B being the Boltzmann constant, f_i the partial Fermi occupation of orbital i and T_{el} the electronic temperature. The ion-electron interaction has been treated using the projector augmented wave (PAW) technique (Blöchl 1994, Kresse and Joubert 1999), with single particle orbitals expanded in plane-waves with a cutoff of 224 eV, which ensures convergence of the structural parameters of Ta, like the equilibrium volume and the bulk modulus, to better than 0.05%. In a previous paper (Taioli et al. 2007) we tested different exchange-correlation functionals and various PAW potentials for bcc Ta. A very good agreement with the experimental zero temperature equation of state was found when using PBE and a PAW potential with inclusion of the 5p electrons in valence, and therefore here we used the same exchange-correlation and

PAW potentials. Brillouin zone (BZ) sampling was performed using $16 \times 16 \times 16$ Monkhorst-Pack (MP) grid of \mathbf{k} -points (Monkhorst and Pack 1976) on a primitive cell, which gives a converged value of the electronic free energy to within less than one meV. In agreement with previous studies (Boettger 2001, Bercegeay and Bernard 2005), we found that spin-orbit effects have a very small effect on the structural properties of Ta and have been neglected here altogether.

3. Components of the free energy

In a shock wave experiment the pressure P_H , internal energy E_H and volume V_H are related by the Rankine-Hugoniot relation (Poirer 1991) as follows:

$$\frac{1}{2}(P_H + P_0)(V_0 - V_H) = E_H - E_0 \quad (2)$$

where V_0 , E_0 and P_0 are the equilibrium volume, the internal energy and the pressure at the starting conditions. The measurement of temperature in shock experiments is usually difficult, however it can be indirectly obtained by integrating the following thermodynamic relation (Brown and McQueen 1986)

$$dT_H = -T_H(\gamma/V_H) dV + [(V_0 - V_H) dP_H + (P_H - P_0) dV]/(2 c_V) \quad (3)$$

where γ and c_V are the Grüneisen parameter and the constant-volume specific heat, respectively. Eqs. 2 and 3 can be solved if the Helmholtz free energy of the system is known as function of volume and temperature. We write this as a sum of two contributions:

$$F(V, T) = F_{static}(V, T) + F_{vib}(V, T) \quad (4)$$

where F_{static} has been defined in Eq. 1 and $F_{vib}(V, T) = F_{harm}(V, T) + F_{anharm}(V, T)$ is the contribution due to the vibrations of the ions, written as a sum of harmonic and anharmonic parts. Here we will neglect the anharmonic component of the free energy altogether. In the following two subsections we describe how we calculated these two contributions.

3.1. The perfect crystal

For any fixed T we calculated $F_{static}(V, T)$ at a number of different volumes, and fitted each isotherm to a third order Birch-Murnaghan equation of state (BMEOS). The parameters of the BMEOS $E_0(T)$, $V_0(T)$, $K_0(T)$ and $K'_0(T)$, have then been fitted to third order polynomials in T , and we report them in Table 1 for some values of T .

3.2. The harmonic crystal

In the high temperature limit, the vibrational free energy can be written as:

$$F_{harm}(V, T) = \frac{1}{N_{\mathbf{q}}} k_B T \sum_{\mathbf{q}, s} \ln \left[\frac{\hbar \omega_{\mathbf{q}s}(V)}{k_B T} \right] \quad (5)$$

where k_B is the Boltzmann constant, the $\omega_{\mathbf{q}s}$ are the vibrational frequencies, $N_{\mathbf{q}}$ is the number of \mathbf{q} points in the sum taken over phonon wave vectors \mathbf{q} in the BZ and branches s . In principle the phonon frequencies $\omega_{\mathbf{q}s}$ depend on temperature because of electronic excitations, however, here we neglected this dependence on T . The

Table 1. Birch-Murnaghan fitted parameters for bulk bcc Ta as a function of temperature.

T (K)	$E_0(T)$ (eV)	$V_0(T)$ (\AA^3)	$K_0(T)$ (GPa)	$K'_0(T)$
300	-11.73208	18.3419	190.88	3.8521
1408	-11.76216	18.3737	189.159	3.8672
3522	-11.91492	18.5003	184.749	3.8873
5400	-12.13376	18.6860	178.91	3.9003
7279	-12.42425	18.9318	171.857	3.9076
9157	-12.79214	19.2652	162.19	3.9255

phonon frequencies $\omega_{\mathbf{q}s}$ have been calculated using the PHON code (Alfè 1998), which implements the small displacement method (Kresse et al. 1995).

We find it useful to express the harmonic part of the Helmholtz free energy in terms of the geometric average $\bar{\omega}$:

$$\ln \bar{\omega} = \frac{1}{N_{\mathbf{q}}} \sum_{\mathbf{q},s} \ln(\omega_{\mathbf{q}s}) \quad (6)$$

which allows to write

$$F_{\text{harm}}(V, T) = k_B T \ln \left(\frac{\hbar \bar{\omega}}{k_B T} \right). \quad (7)$$

We calculated $\bar{\omega}$ at a number of different volumes, and then fitted $\ln \bar{\omega}$ to a third order polynomial in V . In Fig. 1 we report the calculated $\ln \bar{\omega}$ as a function of volume.

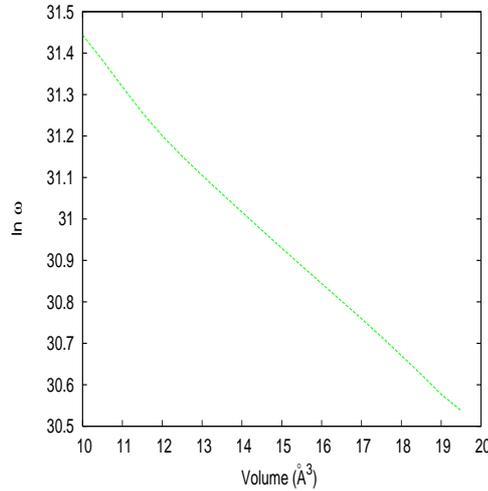


Figure 1. Geometric-mean phonon frequency $\ln \bar{\omega}$ of Ta as function of atomic volume V . $\bar{\omega}$ is in units of rad s^{-1} .

The technical parameters for the calculations of the phonon frequencies (size of the displacement, size of the supercell, number of electronic \mathbf{k} -points, number of \mathbf{q} -points for evaluating the sum in Eq. 6) were chosen in such a way to obtain free energies converged to within 1 meV/atom at $T = 300$ K.

4. Thermal equation of state on the Hugoniot and melting curve of Ta

Once the Helmholtz free energy of the system is known as function of V and T it is straightforward to solve the Rankine-Hugoniot equation 2, which provides $P_H(V)$ and $T_H(P)$ curves.

We compare our results with the available shock wave measurements of Nellis et al. (Mitchell and Nellis 1980, Nellis et al. 2003). As shown in the left panel of Fig. 2, the agreement is very good, with discrepancies of less than 5 GPa in the worse case. These discrepancies are similar to those found for the room temperature static $P(V)$ curve previously published (Taioli et al. 2007), and can be regarded as giving an indication of the accuracy of the GGA approximation. The temperature-pressure relation on the shock Hugoniot is compared with the experiments (Mitchell and Nellis 1980, Nellis et al. 2003) in the right panel of Fig. 2. The close agreement of our curve with experimental points supports the estimates of the temperature on the Hugoniot in these experiments. We also note that first principles calculations of the Hugoniot of Ta have been already reported by Cohen and Gülseren (Cohen and Gülseren 2001), and our results agree closely also with those calculation. As an independent test on

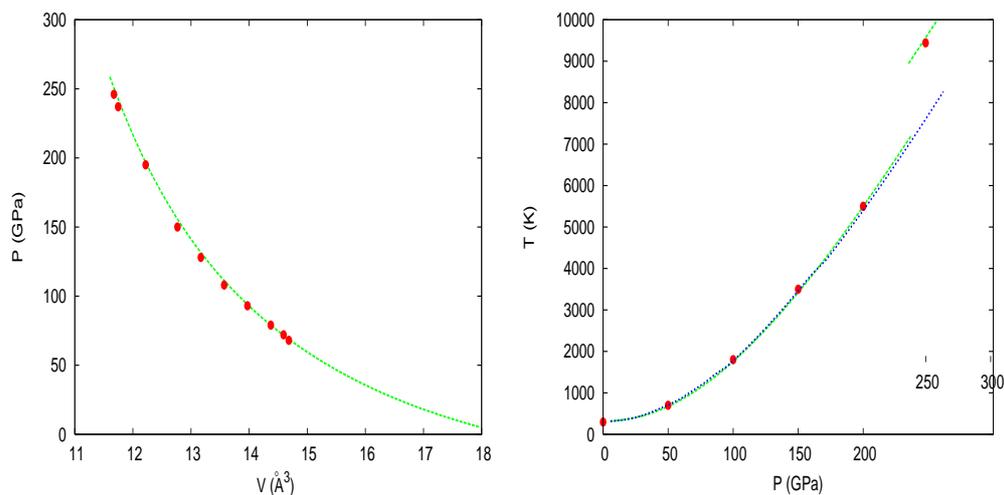


Figure 2. Principal Hugoniot (dashed line in the left panel) and temperature on the shock Hugoniot calculated using Eq. 2 (dashed line in the right panel) and Eq. 3 (point line in the left panel), respectively. Full circles show experimental data (Nellis et al. 2003).

the results we also calculated the $T_H(P)$ curve by integrating Eq. 3, which can easily be performed after γ and c_V have been calculated as function of V and T . The values of these thermodynamical quantities on the Hugoniot are reported on the left (γ) and right (c_V) panels of Fig. 3, and the $T_H(P)$ curve is shown in the right panel of Fig. 2. The $T_H(P)$ curves obtained with the two different numerical methods are very close to each other. The calculated heat capacity along the principal Hugoniot for Ta agrees well with first-principles results obtained by Wang who used the full-potential linearized augmented plane wave method (Wang et al. 2002).

To calculate the melting curve of Ta we applied the method of the coexistence of phases, applied with the help of an auxiliary reference system. The full *ab-initio* melting curve has then been obtained by calculating free energy differences between the reference system and the *ab-initio* system.

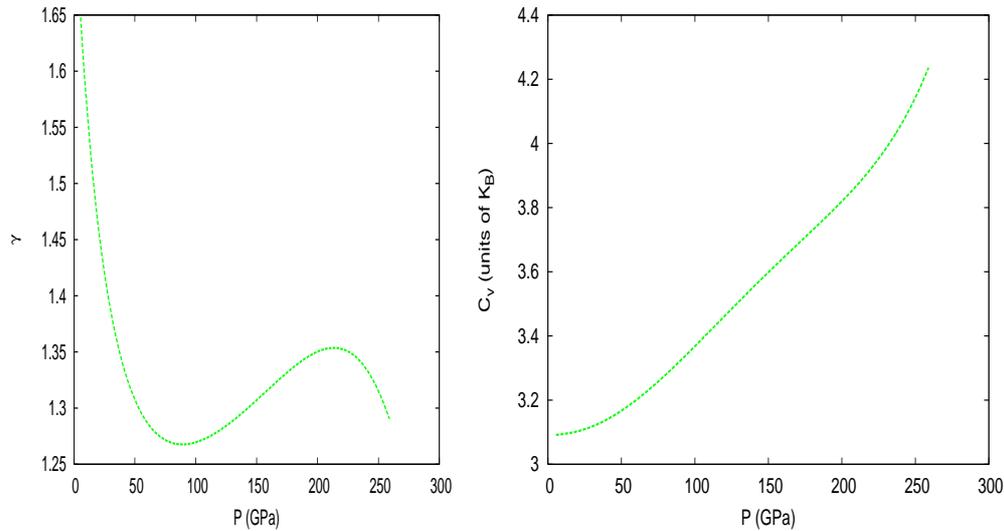


Figure 3. Variation with pressure of the Grüneisen parameter (left) and of the total constant-volume specific heat per atom (right, units of k_B) on the Hugoniot.

The technical details of the method and the melting curve of Ta have been reported in a previous paper (Taioli et al. 2007), here we only show the melting curve in Fig. 4, where we compare our results with the available DAC and shock wave experiments and previous theoretical results by Moriarty et al. (Moriarty et al. 2002) and Strachan et al. (Strachan et al. 2004). The interpolated value of the melting temperature at zero pressure ($T_m = 3270$ K) is in very good agreement with DAC experiments (Errandonea et al. 2001) ($T_m = 3270$ K), but as pressure is increased the agreement with DAC experiments quickly deteriorates, and at ~ 100 GPa the difference between our DFT calculations and these DAC experiments is already about 2000 K. At 307 GPa our calculated value $T_m = 9783 \pm 85$ K, is in good agreement within the statistical error bars with shock waves experiments (Brown and Shaner 1984), which estimate $T_m = 8500 \pm 1500$ K.

5. Discussion and conclusions

Our work reports a detailed *ab-initio* study of the principal Hugoniot ($P - V$ curve) and of the temperatures on the shock Hugoniot ($P - T$ curve). The principal Hugoniot has been obtained by solving the Rankine-Hugoniot equation using free energies obtained by first principles calculations; the temperature on the shock Hugoniot has been calculated by both solving the Rankine-Hugoniot equation and integrating the differential equation 3, the latter being the standard tool employed in shock experiments to deduce temperatures on the Hugoniot. A very good agreement has been found with the most recent shock data on tantalum (Nellis et al. 2003) in the range of pressures (0-300 GPa) and temperature (300-10000 K) investigated. We have also reported the values of the specific heat c_V and the Grüneisen parameter γ on the Hugoniot.

The agreement between the calculated Hugoniot and the experimental results also supports the reliability of the *ab-initio* melting curve of Ta, reported already in a previous paper (Taioli et al. 2007). Our results support other theoretical data

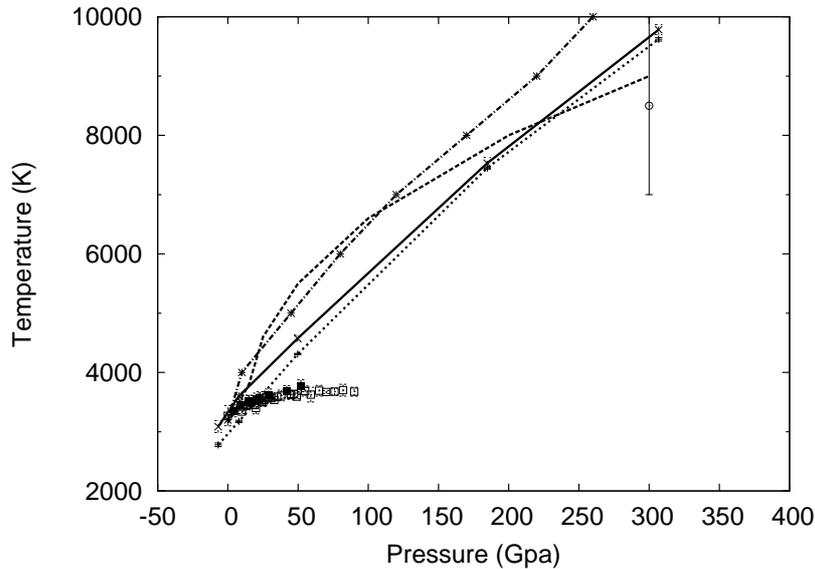


Figure 4. Phase diagram of Ta obtained using an auxiliary reference system with the coexistence MD approach (point line), and the resulting *ab-initio* curve obtained after adding free energy corrections (solid line). Also reported are DAC melting (Errandonea et al. 2001) (filled and open squares), shock melting (Brown and Shaner 1984) (open circle) and calculations from Ref. (Moriarty et al. 2002) (point-dashed line) and Ref. (Strachan et al. 2004) (dashed-line).

previously obtained on melting properties of tantalum, though our melting curve is somewhat lower. Furthermore, our melting curve is in good agreement with DAC experiments in the very low pressure regime, but starts to differ with increasing pressure. At high pressure our calculated melting curve disagrees substantially from DAC experiments, but is in good agreement with the shock datum at 300 GPa. This disagreement with DAC measurements has been already found previously (Moriarty et al. 2002) and it is a common feature in transition metals which melt from a bcc crystal structure, such as Ta and Mo for example. These experiments would call into question the reliability of DFT-based calculations at high pressure and temperature. However, although one can argue about the correctness of the different approximations for the exchange-correlation functional (LDA, GGA), which in some cases such as MgO (Alfè 2005), Al (Vočadlo and Alfè 2002, Alfè 2003) and silicon (Sugino and Car 1995, D. Alfè and M. J. Gillan 2003) can make noticeable differences in the calculated melting temperatures, we believe that it is very unlikely for DFT to be so much in error in the present case, given the large quantity of experimental data accurately predicted by this level of theory. We suggest that at least some of the DAC experiments may suffer from a imperfect diagnostic tool to detect melting, like the use of the intensity of X-ray diffraction peaks (Errandonea et al. 2003) which might lead to underestimate the melting temperature. Another possible problem in DAC experiments is the temperature measurement. Recently, an analysis of the spectroradiometrics effects of the dispersion and adsorbance properties of diamond has found that chromatic effects induced by the diamond windows can be substantial, and may lead to an underestimate of melting temperatures of several hundred degrees (Benedetti et al. 2007). Applying this analysis to the melting curve of Fe Benedetti et al. (Benedetti et al. 2007) concluded that, for example, the melting

curve of Boehler (Boehler 1993) and that of Saxena and Dubrovinski (Saxena and Dubrovinski 2000) are at least a few hundred degrees too low at megabar pressures.

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