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COMMENT

Comment on 'Theoretical solid and liquid state shock Hugoniots of Al, Ta, Mo and W'

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Abstract

In this comment we discuss, in the light of previous experimental and theoretical results, the melting curve of Mo, Ta, and W. Its aim is to show that the melting estimates reported in Verma *et al* (2004 *J. Phys.: Condens. Matter* **16** 4799) are not reliable and largely overestimate the melting curves of these metals.

Our comment refers to a paper recently published by Verma *et al* [1]. These authors presented calculations of the Hugoniots, the room temperature equations of states, and the melting curves of aluminium (Al), molybdenum (Mo), tantalum (Ta), and tungsten (W) as a function of pressure up to above 10 Mbar (1 Mbar = 100 GPa). In order to obtain the melting curves, they used a previous published model based on dislocation-mediated melting developed by Burakovsky *et al* [2]. According to this model, melting temperatures should continuously rise with pressure. However, recent experimental studies have shown that this fact may be valid for Al [3], but not for the transition metals in groups VA and VIA of the periodic table (i.e. for Mo, Ta, and W) [4–6]. Here we consider the melting curves of Mo, Ta, and W in the context of the existent experimental and theoretical data in order to show that the melting curves reported by Verma *et al* [1] for these elements largely overestimate their melting temperatures at high pressure, being therefore not valid.

Before starting the discussion, we would like to mention that even though the authors of [1] affirmed in it that their results cannot be compared with experimental melting curves or those obtained by first principles simulations because neither data are currently available for these metals, the last few years have seen a major effort to measure and calculate melting curves of metals, including those of Al, Mo, Ta, and W. These melting curves have been measured up to 1 Mbar thanks to recent advances in the application of laser-heated diamond-anvil cells (DACs) [3–6]. Melting temperatures at high-pressure have also been determined with the use of shock-wave measurements [7–9], and a number of theoretical calculations have been performed to explain this phenomenon [10–16]. Figure 1 summarizes, for the case of Mo, the existent experimental melting data [4, 8] and part of the existent theoretical melting estimates [6, 13] and compares them with the results reported in [1]. These results disagree

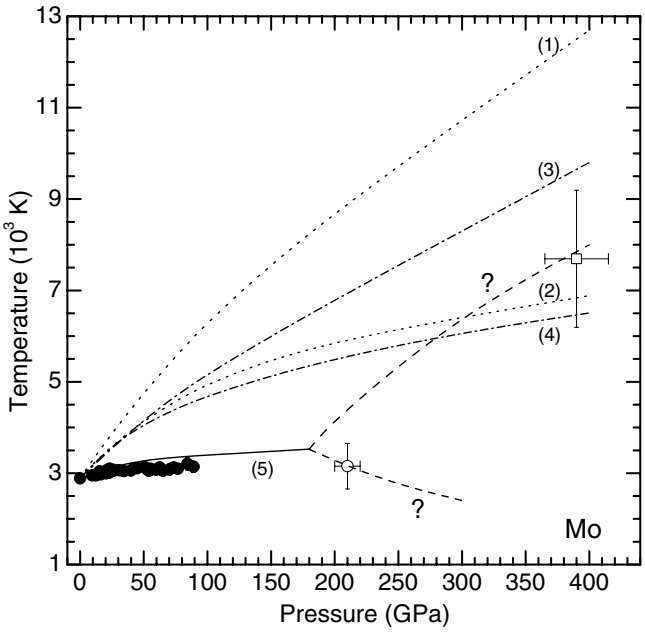

Figure 1. Melting curve of Mo. DAC melting (●) [4] and shock-wave data (□). The dot–dashed curves represent the dislocation-mediated melting model results: (3) [1] and (4) [13]. The dotted curves correspond to the Lindemann estimates obtained assuming: (1) $\gamma = \gamma_0$ and (2) $\gamma = \gamma_0(\frac{V}{V_0})$ as in [1], where γ is the Grüneisen parameter, V is the molar volume of the solid at melting and $\gamma_0 = 1.59$ and $V_0 = 9.4$ cm^3 mol^{-1} are their values at ambient conditions, respectively. The solid curve, (5), illustrates the results obtained assuming that vacancy formation plays a fundamental role in the melting process [5, 6]. The high-pressure high-temperature solid–solid transition observed in shock-wave experiments [8] is also shown (○) together with the solid–solid and solid–liquid phase boundaries proposed in [6] (dashed curves). Following [17] a 0.3 superheating correction has been applied to the shock-wave data.

both with DAC and shock-wave data and with the theoretical results obtained by Belonoshko *et al* [13], who calculated the melting curve of Mo using the same dislocation-mediated melting model used by Verma *et al* [1]. Similar discrepancies are also observed when comparing the existent experimental results for Ta and W [4–7, 9] with those reported in [1]. Therefore, we will focus the present comment on discussing the results summarized in figure 1.

The dislocation-mediated melting model is a Lindemann-like scaling model in which the solid to liquid transition is considered as a transition from a translationally symmetric system to a disordered system at the order–disorder transition temperature, the melting temperature. Basically, it is a one-phase melting model in which melting is based on the lattice instability of the solid, the liquid phase being neglected. Melting of a nearly free electron sp metal, like Al, can be treated quite naturally by this model. However, it has been proven not to be effective to estimate the melting of bcc transition metals [6, 14], in which d-electrons play a preponderant role. There is experimental and theoretical evidence that, upon melting, the valence electronic structure of bcc transition metals is significantly modified [14]. This change must be considered in order to properly calculate the melting behaviour of bcc transition metals, but this cannot be done with any one-phase approach to melting. This omission of the d-band physics results in an Al-like melting curve for Mo [14] as obtained in [1].

On top of that, the dislocation-mediated melting model makes several assumptions that are not necessarily valid at extreme pressure and temperature conditions; for example, the bulk

modulus (B_0) is linearly extrapolated to high pressure using only its first pressure derivative at ambient conditions (B_0'), and the shear modulus (G_0) is also similarly extrapolated to high pressure [2]. Furthermore, comparison with experimental data on over half of the elements in the periodic table shows that the melting relation proposed by Burakovsky *et al* is accurate to 17% at ambient pressure. Hence, it is not surprising that the dislocation-mediated melting model could lead to an overestimation of the melting temperature of Mo, Ta, and W at high pressures. In addition, by making a comparison between [1] and [13], it can be seen that the choice of different sets of ambient pressure parameters (B_0, B_0', G_0, and G_0') leads to quite different results, as shown in figure 1 (see curves (3) and (4)). At 1 Mbar, Belonoshko *et al* obtained for Mo a melting temperature close to 4200 K, while Verma *et al* obtained a melting temperature above 5000 K. At 4 Mbar, they estimated melting temperatures around 6500 and 10 000 K, respectively. Disagreements between both theoretical calculations also include the slope of the melting curve ($\partial T/\partial P$). According to Belonoshko *et al*, above 50 GPa the melting curve of Mo bends towards the pressure axis, the melting slope being quite low above 3 Mbar ($\partial T/\partial P \simeq 4$ K GPa^{-1}), but in [1] a large melting slope is observed even at such extreme pressures ($\partial T/\partial P \simeq 15$ K GPa^{-1}). The observation of such a large $\partial T/\partial P$ at 4 Mbar is also in contradiction with the systematic experimentally observed on bcc transition metals [4–6] and with the current theoretical understanding of melting [18], which predicts that at certain compression all the melting curves begin to flatten. The fact that differences between the two melting curves calculated using the same theoretical model [1, 13] are as large as their respective differences from the existent experimental results, which suggests that the dislocation-mediated melting model is not a reliable approach for estimating the melting curves of Mo and the rest of the bcc transition metals, should be emphasized.

After commenting on the drawbacks of the dislocation-melting model used in [1] to calculate the melting curves of Mo, Ta, and W, we will compare these melting curves with the existing experimental results and with the Lindemann law estimates [19]. The Lindemann expression is an empirical law based on low-pressure data obtained from noble gases, which neglects anharmonicity, cooperative effects, and disregards liquid phase. It is known that it cannot be extrapolated to estimate the melting behaviour of metals at extreme pressures [6, 20], since even on including a volume dependence on the Grüneisen parameter (γ)—as was done in equation (9) of [1]—this approximation overestimates the melting curves of metals [20]. This fact is illustrated by curves (1) and (2) of figure 1, which represents the Lindemann estimates when considering γ as a pressure independent and dependent parameter. In the best of the cases, curve (2) can be considered as an upper bound for the melting curve of Mo. The fact that in the results reported in [1] the Lindemann rule gives a much slower rise of the melting temperature with pressure as compared to that of dislocation-mediated melting suggests that the results obtained using the second approach largely overestimate the melting curve of Mo, Ta, and W. This is confirmed when comparing with the existent experimental results. Melting of Mo, Ta, and W up to 1 Mbar have been determined using laser-heated DACs by means of three different techniques [4–6]: the laser speckle method, the visual observation of surface texture changes on quenched samples, and using x-ray diffraction to detect melting. The three techniques give similar results, which also agree with earlier piston-cylinder apparatus and wire explosion experiments [21–23]. The flat melting curve systematically observed, in all these experiments, has been confirmed by a phenomenological model that interprets melting in terms of generation of vacancies [5, 6] (see curve (5) in figure 1). These facts clearly raise serious questions about the reliability of the melting curves theoretically calculated for Mo, Ta, and W in [1].

Finally, our last comment is related to the presence of a solid–solid transition in Mo under compression. As the authors of [1] pointed out, it is well known that anomalies in the

melting curve exist due to structural transitions in the solid phase under compression [24, 25]. Usually, the interception of a solid–solid boundary line with a melting curve would produce a discontinuous change of the melting slope. According to shock-wave experiments, a solid–solid transition has been detected in Mo at 200 GPa and 3100 K (see figure 1). Thus, a large increase in the melting slope is expected to occur below 2 Mbar, which would make the existent melting data below 1 Mbar converge with the shock-wave data (see the dashed curve in figure 1) [6]. A similar phase diagram is expected for Ta and W [6]. Therefore, any estimation of the melting curve above 2 Mbar that does not take into account the existence of a high pressure and high temperature phase observed in Mo is meaningless.

In summary, in this comment we have shown that in spite of the fact that the authors of [1] performed scientifically sound calculations of the Hugoniots and the room temperature equations of states of Mo, Ta, and W, the melting curve estimates they presented are not reliable. Former experimental and theoretical results have been used to support our comments.

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