Systematics of transition-metal melting

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We report high-pressure measurements for the melting curve of Ti, V, Cr, Mo, Ta, W, Fe, Co, and Ni. Measurements were made in a laser-heated diamond-anvil-cell to nearly 100 GPa and 4000 K. The bcc metals have surprisingly small melting slopes which approach zero at high pressure. The melting curves of Co, Ni, and Fe are nearly parallel. Several ab-initio calculations for the melting of Fe are incompatible with the present results.

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It is now understood that the crystal structures of metals exhibit sequences determined by changes in their electronic configuration. With increasing atomic number, at ambient conditions, the transition metals exhibit the structural sequence hcp-bcc-hcp-fcc as the *d*-electron bands become progressively filled.[1,2] This sequence can be explained by differences in the sum of one electron band-structure energies. While room temperature (RT) high pressure diamond-anvil-cell (DAC) studies using x-ray diffraction methods have extended our knowledge of the structural changes to about 500 GPa (Ref. 3) very little is known of the melting behavior of the transition metals. The only high pressure melting measurements for transition metals are for Co and Ni,[4] and Fe.[5,6] For the bcc transition metals in Groups VA and VIA there is virtually no melting data at high pressure.

In the present paper we present new melting data for the transition metals Ti, V, Cr, Mo, W, Ta, Fe, Co, and Ni using a laser-heated DAC up to pressures near 100 GPa where melting temperatures approach 4000 K. The experimental technique has been described elsewhere.[7,8] In the present study we made further improvements by using diamond-coated tungsten gaskets, which further increased the height of the pressure chamber, thus improving thermal insulation from the diamonds and reducing temperature gradients in the laser-heated samples. These gaskets allowed a significant expansion in the pressure range for routine use of Ar as a pressure medium. Most data were obtained in Ar and in some cases compared with those using other pressure media. We also directly compared data using different melting criteria: The *in situ* laser speckle method[7,8] gave the same results as the changes in the surface texture observed on recovered or quenched samples. Figure 1 shows a Mo sample before (top) and after melting (bottom) at 17 GPa. The temperature difference between top and bottom was 50 K. The formation of a bead in the bottom picture from a polished surface (top) can only be due to melting, thus eliminating arguments that the laser speckle method may indicate recrystallization of the sample. The highest pressures we attained are over an order of magnitude greater those in previous studies.[9]

For the purpose of discussion we have divided the transition metals into those which melt from bcc structures and those melting from close-packed structures. The bcc transition metals are known to have very stable structures. Total-energy calculations for Mo, W, Ta, and Cr predict the bcc structure to be stable to 420, 1250, 1000, and 700 GPa, respectively, followed by a transition to hcp.[10] DAC x-ray studies have confirmed the absence of RT phase transitions in Mo to 560 GPa and in W to 420 GPa.[3] The high structural stability of these materials provides an excellent opportunity to examine melting in the bcc phase over a wide pressure range.

Figure 2 shows the melting curves of the bcc transition metals Mo, Ta, W, V, Cr, and Ti. Ti is hcp at RT, but melts

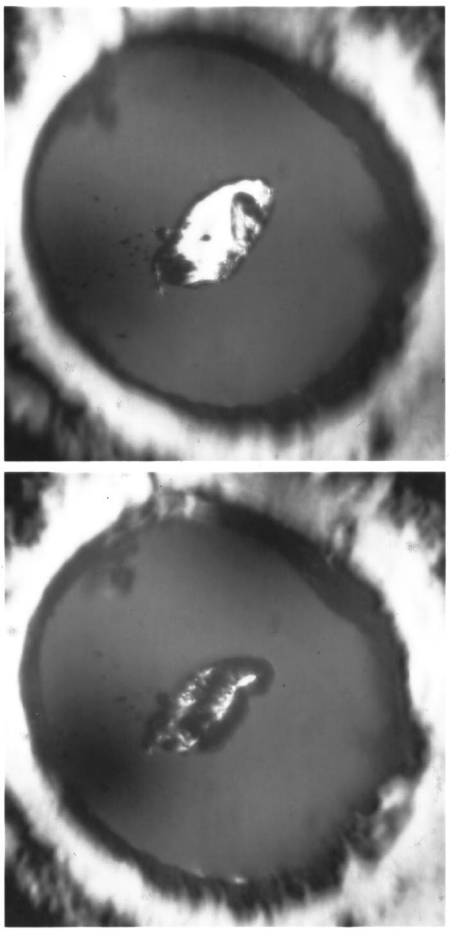

FIG. 1. A Mo sample shown before (top) and after melting (bottom) at 17 GPa.

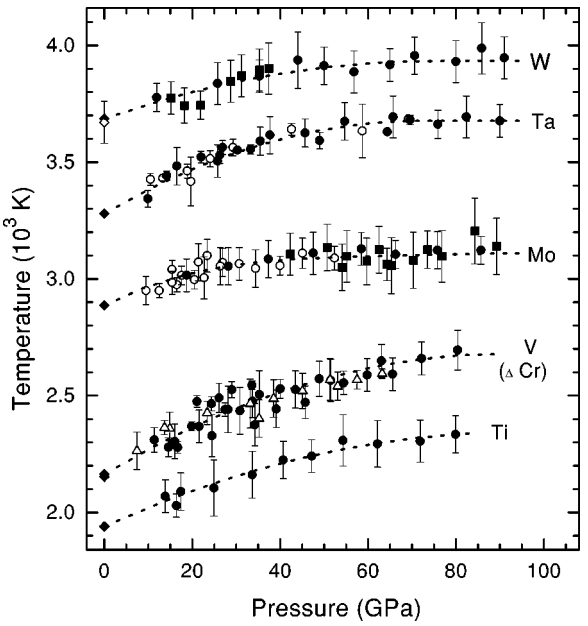

FIG. 2. Melting curves of Mo, Ta, W, V, Ti, and Cr. Solid circles and squares correspond to *in situ* measurements (laser speckle method) in an Ar or Al_2O_3 pressure medium, respectively. Empty circles correspond to the formation of beads as shown in Fig. 1. Open triangles represent the Cr data obtained in situ under Ar. Solid diamonds are 1 atm data. The open diamond represents melting measurements of W in vacuum using identical optics as in the high pressure experiments.

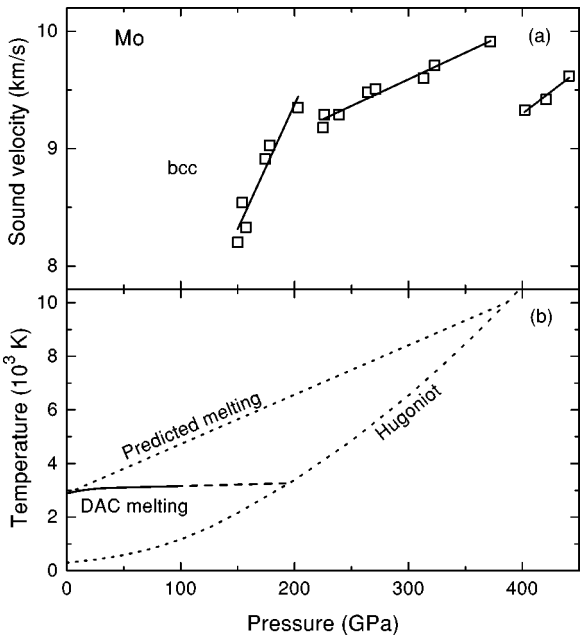

FIG. 3. (a) Experimental sound velocity data of Mo (Ref. 12); (b) DAC melting curve of Mo (solid line), predicted melting curve and Hugoniot temperatures (dotted lines) (Ref. 10). Extrapolation of DAC melting temperatures to higher pressures (dashed line) indicates that the break in sound velocities measured along the Hugoniot at 200 GPa is due to the onset of melting.

from bcc. W, Ta, and Mo show a gradually increasing melting temperature with increasing pressure up to 40 GPa. At higher pressures, the melting slopes approach $dT/dP \sim 0$. The $3d$ metals V, Cr, and Ti have noticeably higher melting slopes at all pressures. V and Cr have virtually identical melting curves. Ti, at RT, is known to undergo a first order transition from bcc to the ω phase at 8 GPa.[11] The ω phase has a hexagonal lattice and remains stable to 87 GPa.[11] The melting curve shows no indication of a phase transition.

High pressure melting data for Mo and Ta have been previously obtained from shock experiments. In this technique, the discontinuous change in the sound velocity in the sample during melting provides a sensitive probe for melting. For Mo Hixson *et al.*[12] reported two transitions along the Hugoniot. Figure 3(a) shows the experimental sound velocity-pressure data.[12] On the same pressure axis, Fig. 3(b) shows the DAC melting curve, the predicted melting curve, and Hugoniot temperatures.[10]

Hixson *et al.*[12] identified the first transition at 200 GPa as that of bcc to a new solid phase and the 390 GPa transition to be melting, at a calculated temperature of 10 000 K. This interpretation is most likely in error, because subsequent x-ray diffraction measurements made up to 560 GPa (Ref. 3) at RT show no evidence for phase transitions from bcc. Moreover, an extrapolation of our Mo melting measurements to higher pressure (dashed line) leads to an intersection with the Hugoniot at 190 GPa at a temperature of roughly 3300 K. This is nearly the same as the temperature of 3500 K calculated at the 200 GPa shock transition by Moriarty.[10] We are unable to draw any conclusions regarding the significance of the 390 GPa transition also reported by Hixson *et al.* other than it does not appear to be melting. For Ta a marked discontinuity in the measured sound velocities occurs near 295 GPa.[13] Assuming there are no solid-solid phase transitions along the Hugoniot, an extrapolation of the present melting curve to higher pressure leads to an estimated melting temperature near 4000 K.

Figure 4 shows our DAC melting results for Fe, Co, and Ni. Ni melts from fcc and Co which is hcp at ambient conditions melts also from fcc. Fe melts from fcc above 5 GPa and from hcp above 100 GPa. Our results for Fe have been reported previously[5] and new data have been added since using improved techniques.[8] We also recently measured a melting temperature of 2590 K at 59.5 GPa using Ar as a pressure medium. Our measurements agree well with the Ni and Fe data of the Uppsala group,[4,6] but their Co melting curve is significantly higher than ours.[4] The three metals are known to have RT compression curves that are nearly identical up to 200 GPa.[14] We now find that their melting curves, measured in an inert pressure medium, are nearly parallel.

The melting curve of Fe is one of the more intensely studied subjects in high pressure research. The melting temperature of Fe constrains the temperature in the Earth's center and is a key element in predicting the heat flow in the core and mantle. The pressure at the boundary between solid-inner and liquid-outer core (ICB) is about 330 GPa and the estimated melting temperatures of Fe at that pressure from different studies range from 5000 to 7000 K. Very high temperatures at the ICB are in conflict with models for heat flow and cooling rate of the Earth and the fact that the lower mantle is solid, as evident from seismic data.

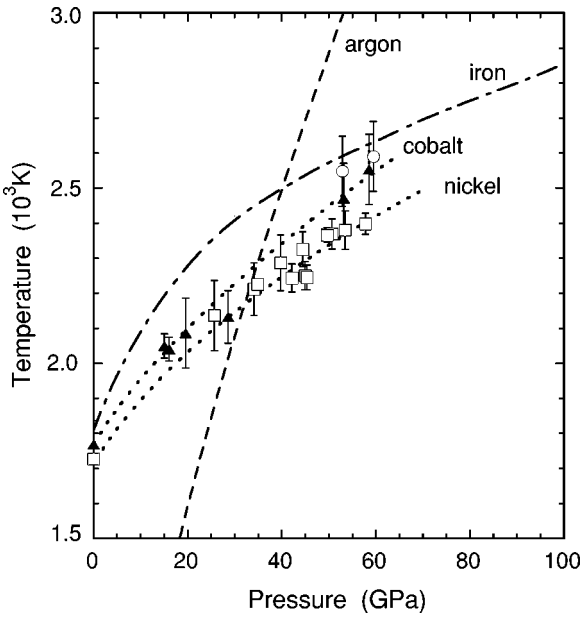

FIG. 4. Melting curves of Fe from Boehler (Ref. 5) (dashed-dotted curve), and new data (open circles), Co (solid triangles), and Ni (open squares). All new measurements were made using Ar as pressure medium below and above the Ar melting curve (also shown).

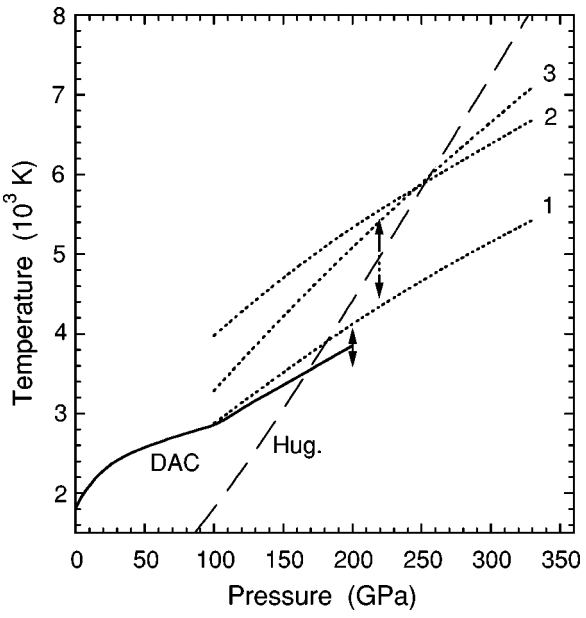

FIG. 5. Comparison of DAC melting data for Fe to 200 GPa (Ref. 5) (solid curve), calculated Hugoniot temperatures (Ref. 24), and melting curves from *ab initio* calculations 1 (Ref. 22), 2 (Ref. 20), and 3 (Ref. 21). Arrows indicate uncertainties in the DAC measurements and the Hugoniot temperatures, respectively.

Up until recently all discussions of the Fe phase diagram were complicated by the need to account for a solid-solid transition at a pressure of 200 GPa reported by Brown and McQueen.[15] However, Nguyen and Holmes[16] have reported new measurements of the sound velocity in shock compressed Fe which show that melting occurs at 220 GPa and that that there is not such solid-solid transition at 200 GPa. DAC x-ray studies to identify a possible new high P-T phase of Fe are also contradictory.[17–19]

Figure 5 shows the melting curve of Fe (Ref. 5) measured to 200 GPa in the DAC, along with recent theoretical predictions employing *ab-initio* methods.[20–22] Except for the results of Laio *et al.*[22] the disagreement with the DAC measurements is significant, even below 100 GPa, where the melting temperatures of Fe are now well constrained by a variety of measurements from different laboratories (see Ref. 8 for review).

Unfortunately, measuring shock melting temperatures in metals accurately is quite difficult. The shock temperature measurements made for Fe by Yoo *et al.*,[23] which lie between 6500 and 7000 K, are now considered as too high and should be omitted from further discussions. Since shock melting temperature cannot be determined from Hugoniot measurements we plotted the Hugoniot temperatures calculated in Refs. 15 and 24. The calculated Hugoniot temperature at 220 GPa is 4977 K. Since the calculated temperatures have been estimated to have an uncertainty of about 10%, the shock melting point lies almost equidistant from all the *ab-initio* studies allowing each to make the same righteous claim.

Figure 6 shows a comparison of the melting curves for Ti, V, Cr, Mo, Ta, W, Ar,[25] and Al,[26] and a band representing melting temperatures of Fe, Co, and Ni. The bcc metals have lower melting slopes compared to Fe, Co, and Ni, particularly in the lower pressure range. But the data suggest that the difference in melting slopes will diminish at very high pressure. Clearly, Al which is an fcc polyvalent metal characterized by sp^3 bonding electrons is very different from the transition metals in which d-electrons play a dominant role.

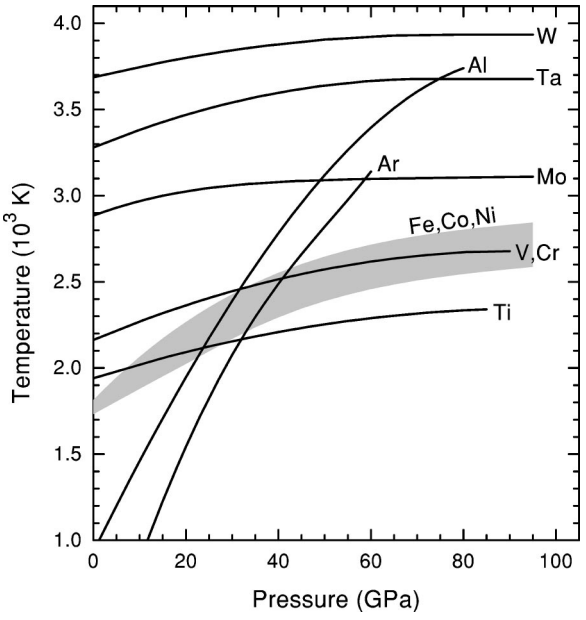

FIG. 6. Melting curves for Ti, V, Cr, Mo, Ta, W, Ar (Ref. 25), and Al (Ref. 26). The gray band represents melting temperatures for Fe, Co, and Ni as shown in Fig. 4.

This suggests that testing the validity of the *ab-initio* studies for Fe using calculations made for Al at 1 bar pressure[20–22] is not especially meaningful. The benchmark for Fe should be another transition metal. We may also conclude from Fig. 6 that many of the melting laws and much of the intuition drawn from experience with rare gases and simple metals may lack universality.

An explanation of the trend that bcc metals generally have melting slopes smaller than close-packed metals and rare gases[9] was proposed by Wittenberg and DeWitt[27] who suggested that this was a consequence of the close-packed-like structure of the liquid. Since the packing ratio for bcc ($\sim$0.68) is lower than for fcc or hcp ($\sim$0.74) it can be expected that the volume change for the melting of a bcc solid will be smaller than for a close-packed solid. Hence, dT/dP will be lower for bcc melting. The close-packed nature of liquid Mo and W has been confirmed by recent measurements of the electronic structure of liquid transition metals using time resolved ultraviolet photoelectron spectroscopy (UPS).[28,29] Electron band theory calculations of the electronic structure of metals has shown that the stability of the bcc structure is favored by a Fermi energy which falls in the minimum between two peaks of the electron density of states (DOS). The UPS measurements for liquid Mo and W show a marked increase in the DOS of states at the Fermi surface and an elimination of the minimum.

A question unanswered is whether there may be another factor at play in the Fe melting, not considered by theory. It is well known, from theoretical calculations, that the energy range of the close-packed structures is about 7 mRy/atom near 200 GPa.[30] Since this energy is much less than the thermal energy near melting at 4000 K, then stacking faults or slip planes, which represent a mixture of close-packed planes, may be present. Some evidence for such a possibility comes from several reported findings of additional structures in Fe.[17,18] These defects would lead to a lowering of the perfect lattice melting temperature. Clearly, a definitive understanding of the Fe phase diagram requires accurate x-ray diffraction measurements near the melting temperature at megabar pressures.

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