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Melting of bcc Transition Metals and Icosahedral Clustering

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In contrast to polyvalent metals, transition metals have low melting slopes(dT/dP) that are due to partially filled *d*-bands that allow for a lowering of liquid phase energy through *s-d* electron transfer and the formation of local structures. In the case of bcc transition metals we show the apparent discrepancy of DAC melting measurements with shock melting of Mo can be understood by reexamining the shock data for V and Ta and introducing the presence of an icosahedral short range order (ISRO) melt phase.

I. Introduction

Measurements of the melting curves of transition metals to near megabar pressures using laser-heated diamond-anvil cells (DAC) [1-4] has led to new insights into the relationship of melting with crystal packing and electronic structure[5]. Fig. 1 shows the results of some of the measurements. In terms of the melting slope, (dT/dP), Ar, Al, and Cu, have the stiffest curves. The bcc metals Mo, Ta and W have nearly flat, unusually low melting slope curves, while the fcc metals Fe, Co and Ni are intermediate. Measurements for Ta, made at the Advanced Photon Source (APS)[3] using x-ray diffraction to detect melting, have confirmed the results reported by the Mainz group[1-5].

This paper is organized as follows. In Section II a brief description is provided of a semi-empirical model developed to probe the essential physics, and the role played by local liquid structures, which we identify, in Section III, as icosahedral short range order (ISRO). In Section IV the DAC and shock melting of bcc transition metals, Mo, V, and Ta, is examined and a new ISRO phase is proposed that reconciles the apparent discrepancy between the two static and dynamic methods. Section IV is the summary.

II. Free energy model

A more detailed description of the present model is given in reference [5]. The total binding energy of a transition metal can be written in the form, $U = U_{rep} + U_{d-band}$. U_{rep} is the repulsive contribution of the ions and *sp*-electrons, and $U_{d\text{-}band}$ is the cohesive energy of the *d*-band[6,7]. U_{rep} is modeled by the inverse power potential (r^{-6}) equation of state determined from computer simulations[8,9]. The Friedel equation[8], $U_{d-band} = -\frac{W}{20} n_d (10 - n_d)$ is used to approximate the *d*-band density of states and cohesive energy. W is the bandwidth and n_d is the effective number of *d*-electrons/ion. The model parameters, where available, are taken from the literature or approximated. While there is some amount of information available for the solid there is little in the way of experimental and theoretical available regarding the atomic ordering and electronic structure of the melt.

The Helmholtz free energy of the solid and liquid, is expressed in terms of the inverse power model[9,10],

$$F_e^s = U_{BM} + F_{th-inv6}^s + U_{d-band}^s \,, \qquad (1)$$

and

$$F_e^l = U_{BM} + F_{th-inv6}^l + U_{d-band}^l . \qquad (2)$$

U_{BM} is the lattice energy obtained here from Birch-Murgnahan (BM) fits to DAC room temperature isotherms adjusted to 0 K. The difference in free energy between the phases becomes,

$$\Delta F = (F_{th-inv6}^l - F_{th-inv6}^s) + \delta U_{d-band}^{l-s}, \qquad (3)$$

where $\delta U_{d-band}^{l-s} = (U_{d-band}^l - U_{d-band}^s)$. The term, in parenthesis, represents the change in the ion thermal free energy. The second term represents the change in *d*-band cohesive energy. This term has a negative value as a consequence of electronic band broadening and the formation of local structures in the liquid that lower the liquid energy. The melting temperature is determined at a given volume for $\Delta F=0$. At constant volume the solid and liquid U_{BM} terms cancel. Since the volume change of melting for transition metals at high pressure is ~1%, the error introduced by equating Helmholtz free energies is small. While the

present model is semi-empirical, it is thermodynamically rigorous, and capable of providing insight, such as the need for localized liquid structures and predictions that can be tested experimentally by new melting measurements.

III. Localized structures in *d*-electron metals.

In contrast to a crystalline solid, the liquid is not constrained by a fixed periodic structure and as a result it has the capacity to lower its energy by forming localized structures. This leads to the δU_{d-band}^{l-s} term in the free energy. The formation of lower energy structures in a melt may be thought of in terms of the Jahn-Teller[11] theorem in which a system can be stabilized by a structural distortion that removes the degeneracy of levels by forming localized bonds. The J-T effect exists in systems in which the highest occupied orbital is degenerate and not fully occupied as in the case of liquid transition metals with partially filled *d*-bands.

There is now evidence that localization is present in transition metal melts in the form of clusters with icosahedral short range order (ISRO). Icosahedrons consist of 13 atoms, 12 atoms with five-fold symmetry surrounding a central atom, and have lower energies than equally sized close-packed clusters. ISRO clustering in stable and under-cooled melts of transition metals has been reported by Schenk et al.[12] and Lee et al.[13] using neutron scattering and *in situ* x-ray diffraction methods, respectively. Among these metals are Ni, Fe, Zr[12], Fe, Ti [13]. First principles molecular dynamics simulations made by Jaske et al. [14] found evidence for the existence of short range order in the stable and under-cooled melts of Ni, Zr, and Ta. Although it is impossible to create a crystalline structure in which each atom has five-fold symmetry, larger sized randomly packed ISRO clusters may evolve continuously and be interconnected throughout the liquid [15]. Since clusters have a lower energy and higher density than a normal liquid, they lower the melting temperature and Clapeyron slope. In terms of our model, ISRO clusters in bcc transition metals may be identified with a $\delta U_{d-band}^{l-s} < 0$.

Evidence for localized clusters persisting to high pressure comes from qualitative observations of the viscosity made of the melt motion using the laser

speckle method[1-4]. For all the metals studied, the vigor of motion decreased strongly with increasing pressure even far above the melting curve. This is consistent with pressure-induced *s-d* transfer leading to increased cluster formation. Often, the disappearance of motion limited the pressure range of these melting measurements. In case of iron for example, motion becomes undetectable above 100 GPa and is still not observed if the temperatures exceeds the melting temperatures (as measured by the change in optical reflectivity) by up to 1000 K, the highest temperature pursued.

IV. Diamond anvil and shock wave melting of bcc transition metals.

In this section we examine a troubling discrepancy between the DAC and shock melting measurements in the case of bcc transition metals. First we compare the results of measurements of the two techniques in the case of simpler and better understood metals, Al[16] and Cu[4,17]. In contrast to the conflicting data described below, it is seen in figure 2 that the DAC and shock melting results for both metals are in substantial agreement. The drawback in the case of the shock experiment is that the temperature is generally obtained from theoretical estimates and transitions are identified by discontinuities in the measured sound velocities. In a DAC the liquid phase is detected directly by observing a speckled pattern[1,2,4], or by x-ray crystallography[3].

Figure 3 shows the DAC[2,3] and shock melting points of three bcc transition metals Mo, V and Ta and their Hugoniot curves[18-21]. The experimental data (crosses) indicate the pressures at which discontinuities in the measured sound velocities were observed. Mo[18,19], V[20] and Ta [21] were reported to melt in the 8,000 to 10,000 K range. For Mo the discontinuity at 210 GPa and 4000 K has been interpreted as a transition from bcc to hcp, but which we refer to here as an uncertain phase(II)[18,19] since there is no theoretical basis for such an assignment. Mo is known to be stable in the bcc structure to a pressure of at least 416 GPa[19]. Since the bcc phase is energetically very favorable, and has a higher lattice entropy, temperatures near 4000 K are too low for the thermal electronic entropy to change the balance[22].

An extrapolation of the Mo DAC data points toward the first discontinuity near 210 GPa, suggesting that this should be melting. Extrapolations of the V and

Ta DAC melting data points predict to crossings of the Hugoniots and melting temperatures near 3000 to 4000 K. Unfortunately, no sound speed measurements, which might show a discontinuity, have been made for these two metals below about 150 GPa and 4000 K.

Of the three bcc metals, Molybdenum has been the most carefully studied by shock wave methods. Figure 4 shows the sound velocity measurements of Mo along the Hugoniot, as reported by Hixson et al[18,19]. Starting with a sound velocity of 5.1 km/s there is continuous linear rise with pressure (our dashed line) up to a discontinuous break at 210 GPa (~4000 K), to a state with a considerably smaller rise in the sound velocity. With further increases in pressure there is a second discontinuity, near 370-390GPa, interpreted as shock melting.

Figure 5 shows the sound velocities of V[20] and Ta[21] measured along the Hugoniot. The plots show discontinuities near 225 GPa and 295 GPa, for V and Ta, respectively, which are also interpreted as melting. A comparison of the Mo data in figure 4, with the V and Ta data in figure 5, makes obvious the absence of sound velocity data in V and Ta below 150 GPa, that would extrapolate to 1 bar following the same pattern set by Mo. In which case we expect an extrapolation up in pressure from 1 bar to intersect V and Ta sound velocity data near or below 150 GPa and 4000 K, in agreement with the extrapolations of DAC melting data.

Based on the analysis present ed here we favor a generalized phase diagram for bcc transition metals, as illustrated for V in figure 6, where the first discontinuity is from bcc to an ISRO melt near 144 GPa (3200 K). The experimentally observed second discontinuity in V crosses the ISRO-liquid melting boundary at 225 GPa (7800 K). A similar plot for Ta predicts the bcc-ISRO discontinuity at 172 GPa (3800 K). Hixson and Fritz[23], from an inspection of Mo and W Hugoniot data, suggested the possibility of a mixed phases in this intermediate pressure range.

V. Summary

Recently there have been some unusual melting phenomena reported that point to the importance of local structures in what have typically considered

relatively simple liquids. Falconi et al[24] have reported X-ray diffraction measurements in liquid Cs in which they observed a discontinuity in the density above 3.9 GPa, to a liquid with a coordination number of about 8, which they suggest results from dsp^3 electronic hybridization. The alkali metals are known to form stable spherical clusters according to magic sizes corresponding to N=2, 8,18, 20, 40, 58, ….. electrons, just like electrons in the inert gas atoms[25]. Therefore, the finding that Cs forms structures in the liquid with coordination of 8 is entirely consistent with the presence of clustering. Associated with this decrease in coordination number at 3.9 GPa there is a steep drop in the melting temperature, and negative melt slope ($dT/dP < 0$). A sudden steep drop in the melting point of Na near 31 GPa (1000 K) has been reported by Gregoryanz et al.[26] for which a physical mechanism was not attributed, but may be the result of closed shell clustering. The delocalized character of alkali metal electrons are believed to be responsible for the occurrence of the closed shell clusters. In contrast the properties of typical transition metal clusters are dominated by unfilled d-shells[25].

In the case of the rare gas Xe, melting measurements show a steep initial rise in temperature from 161 K to 2750 K near 17 GPa, followed by a sharp decrease in the rise, and a flattening of the melting curve from 30 to 80 GPa at about 3300K[27]. The sudden change in melting slope is attributed to the creation by *pd* hybridization of *5*-fold *d*-electron character, breaking the Xe s^2p^6 spherical rare gas symmetry. The absence of periodicity in the liquid permits formation of energetically favorable local clusters with *5*-fold icosahedral short range order (ISRO), thereby lowering the melting temperature.

The important conclusion of this work is that for the bcc transition metals, V, Ta and Mo, there are two shock discontinuities. We propose the lower pressure discontinuity is due to a bcc-ISRO transition, and the second at a higher pressure due to an ISRO- liquid transition. As a result there is no conflict between DAC and shock wave melting techniques. The validity of the proposed phase diagram can be tested by a series of sound velocity measurements below 150 GPa, along the V and Ta Hugoniots.

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References

1) R. Boehler, *Nature (London)* **363**, 534 (1993).

2) D. Errandonea, B. Schwager, R. Ditz, R. Boehler and M. Ross, *Phys. Rev. B* ***63***, 132104 (2001).

3) D. Errandonea, M. Somayazulu, D. Häusermann and D. Mao. *J. Phy.:Condens. Matter* **15**, 7635 (2003); D. Errandonea, *Physica* B **357**, 356 (2005).

4) S. Japel, R. Boehler, B. Schwager and M. Ross, *Phys. Rev. Lett.* **95**. 167801 (2005).

5) M. Ross, L.H. Yang, and R. Boehler, *Phys. Rev. B,* **70**, 184112 (2004).

6) F. Ducastelle, *J.Phyique,* ***31***, 1055 (1970).

7). D.G. Pettifor, *"Bonding and Structure of Molecules and Solids"*, (Clarendon Press, Oxford, 1995).

8) H.E. DeWitt, *"Strongly Coupled Plasmas (1978)"*, ed. G. Kalman and P. Carini (Plenum, New York, 1979) p.81.

9) D.H.E. Dubin and H. DeWitt, *Phys. Rev.* B **49**, 3043 (1994).

10) J. Friedel, in *The Physics of Metals* I, J. Ziman, ed. (Cambridge Univ. Press, Cambridge, p.340, (1969)).

11) H.A. Jahn and E. Teller, Proc. Soc. London, Ser. A **161**, 220 (1937).

12**)** T. Schenk, D. Holland-Moritz, V. Simonet, R. Bellissent, and D.M. Herlach, *Phys. Rev. Lett*. **89**, 075507 (2002).

13**)** G.W. Lee, A.K. Gangopadhyay, K.F. Kelton, R.W. Hyers, T.J. Rathz, J.R. Rogers, and D.S. Robinson, *Phys. Rev. Lett*. **93**, 1982 (2004).

14**)** N. Jakse and A. Pasturel, *J.Chem.Phys.***120**, 6124(2004);N. Jakse and A. Pasturel, *Phys. Rev. Lett*. **91**, 195501(2003); N. Jakse, O. Le Bacq, and A. Pasturel, *Phys. Rev.B*. **70**, 174203 (2004).

15) H. Jónsson and H.C. Anderson, *Phys. Rev. Lett*. **60**, 2295 (1988).

16) R.Boehler and M. Ross, *Earth Planet. Sci. Lett.* **153**, 227 (1997).

17) D. Hayes, R.S. Hixson, and R.G. McQueen, Shock compression of condensed matter 1999, edited by M.D. Furnish, L.C. Chhabildis, and R.S. Hixson, (American Institute of Physics, Woodbury, NY,2000), p.483.
18) R.A. Hixson, D.A. Boness, J.W. Shaner and J.A. Moriarty, *Phys. Rev. Lett*. **62**, 637 (1989).
19) J.A. Moriarty, *Phys. Rev.,* B **45**,2004 (1992); J.A. Moriarty, *Phys. Rev.*,B **49**, 12431 (1994).
20) C. Dai, X. Jin, X. Zhou, J. Liu, and J. Hu, *J. Phys. D* **34**, 3064 (2002).
21) J.M. Brown and J.W. Shaner, Shock Waves in Condensed Matter, edited by J.R. Asay, R.A. Graham and G.K. Straub (Elsevier Science, New York, 1983).
22. M. Ross, unpublished calculations.
23) R.S. Hixson and J.N. Fritz, *J. Appl. Phys.* **71**, 1721 (1992).
24) S. Falconi, L.F. Lundegaard, C. Hejny, and M.I. McMahon, *Phys. Rev. Lett.* **94**, 125507 (2005).
25) J.A. Alonso, *Chem. Rev*. **100**, 639 (2000).
26) E. Gregoryanz, O. Degtyareva, M. Somayazulu, R.J. Hemley and H-k Mao, *Phys. Rev. Lett*.**94**, 185502 (2005).
27) M. Ross et al. *Phys. Rev. Lett.* **95** , xxx, 2005. To be published.

Figure captions.

Fig. 1. Melting curves of transition metals. References to individual elements are cited in [1-4].

Fig. 2. Melting curves of Al and Cu. DAC measurements: Al(solid curve) and Cu (dashed curve). Shock melting; Al (filled square) and Cu[empty square).

Fig. 3. DAC melting curves of three bcc transition metals[2,3], Mo[18,19], V[20] and Ta[21], and their Hugoniot curves. The experimental points (crosses) show the pressures at which discontinuities in the sound velocities were observed.

Fig. 4. Sound velocity of Mo[18] measured along the Hugoniot.

Fig. 5. Sound velocities of V[20] and Ta[21] measured along the Hugoniot.

Fig.6. Vanadium phase diagram. DAC melting points(empty circles)[2] extended linearly to 300 GPa (dashed curve). Hugoniot(solid curve) and shock melting point (large cross) [20].

Figure 1

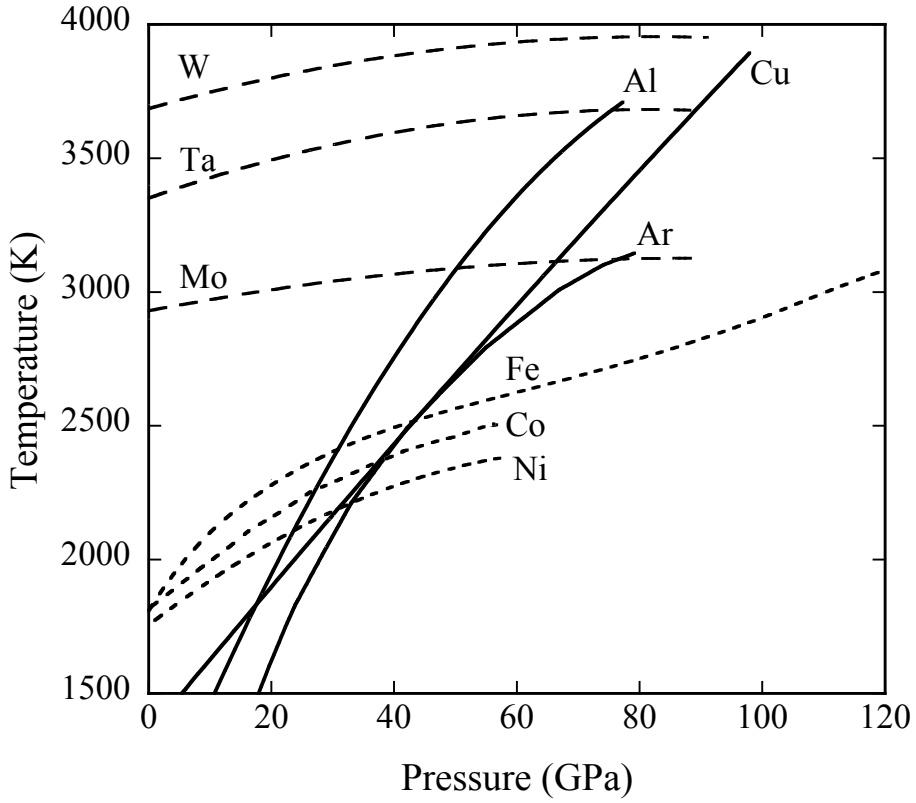

4000
3500
3000
2500
2000
1500
Temperature (K)
0
20
40
60
80
100
120
Pressure (GPa)
W
Ta
Mo
Al
Cu
Ar
Fe
Co
Ni

Figure 2

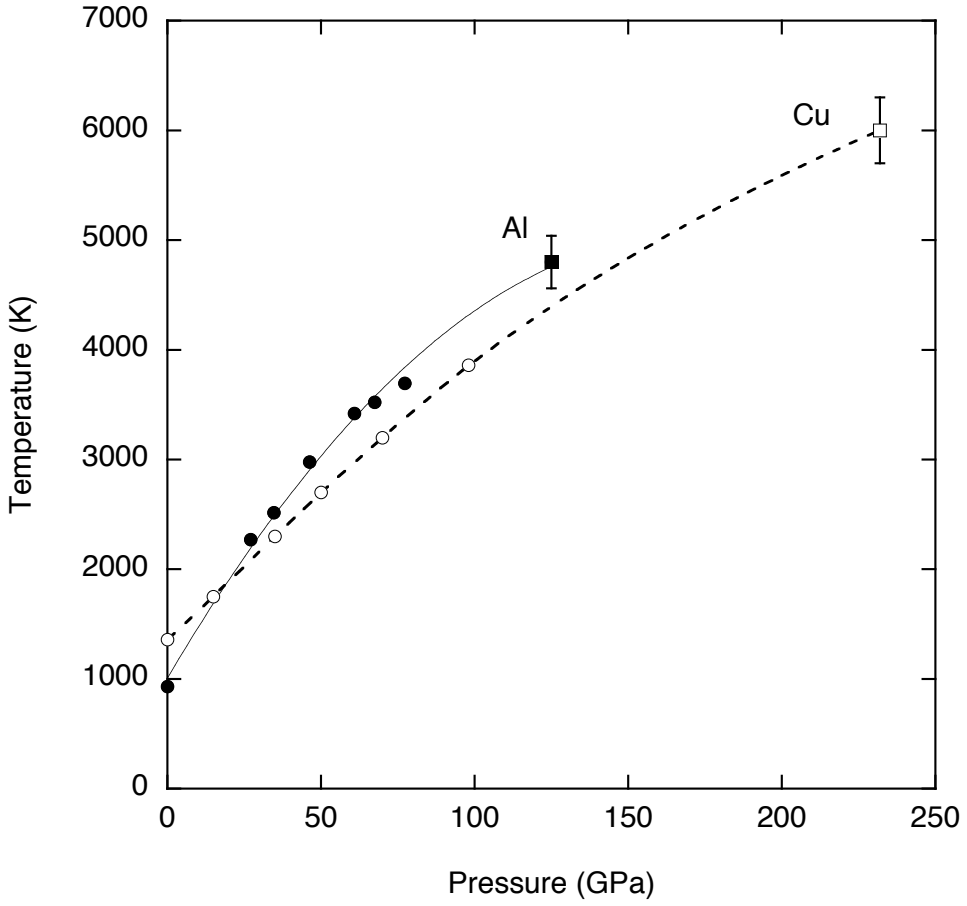

7000
6000
5000
4000
3000
2000
1000
0
Temperature (K)
0
50
100
150
200
250
Pressure (GPa)
Cu
Al

Figure 3

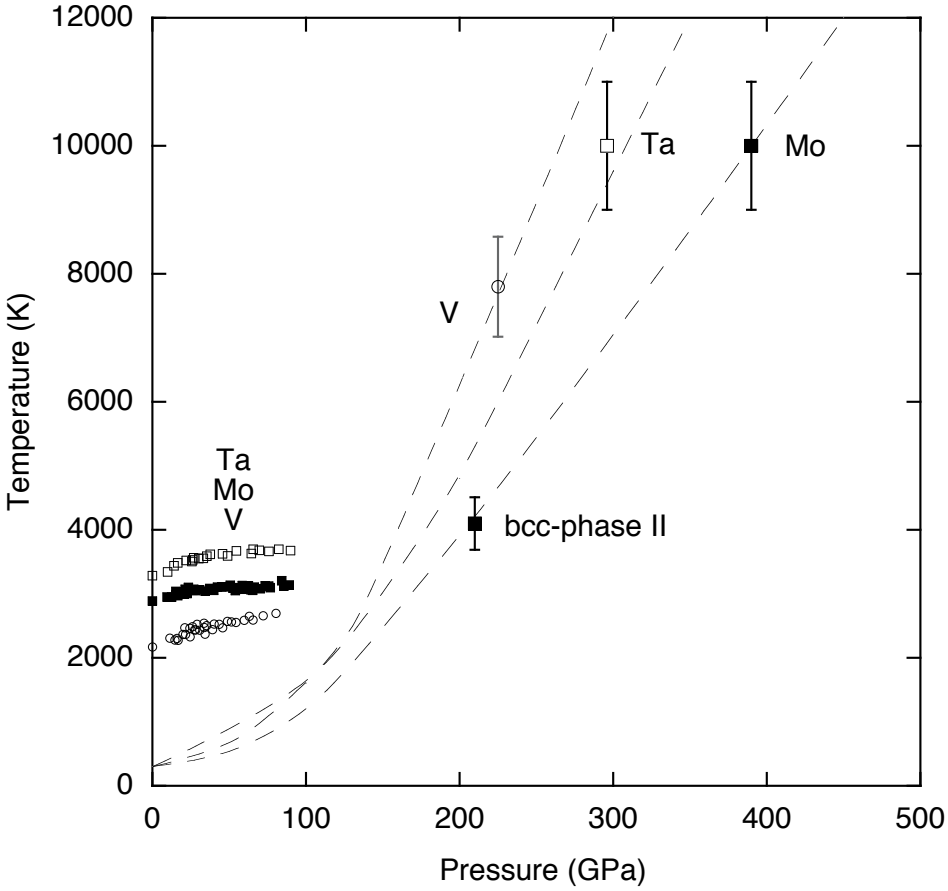

12000
10000
8000
6000
4000
2000
0
Temperature (K)
0
100
200
300
400
500
Pressure (GPa)
Ta
Mo
V
V
Ta
Mo
bcc-phase II

Figure 4

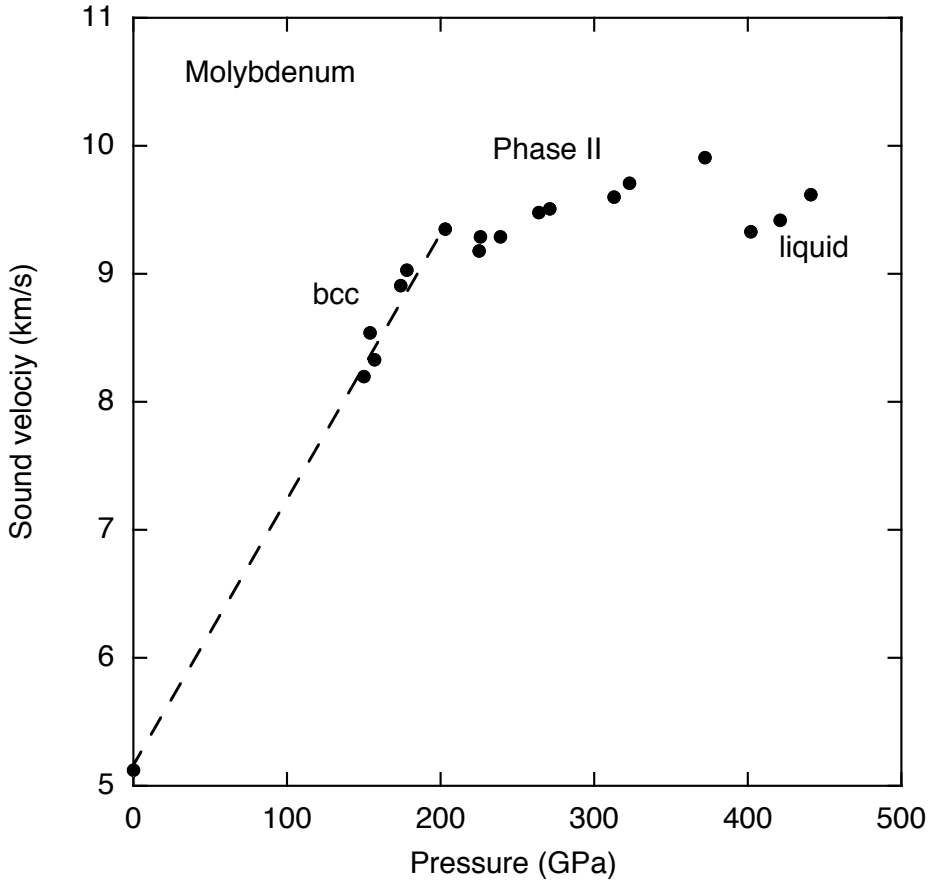

Molybdenum
Phase II
bcc
liquid
Sound velociy (km/s)
Pressure (GPa)
11
10
9
8
7
6
5
0
100
200
300
400
500

Figure 5

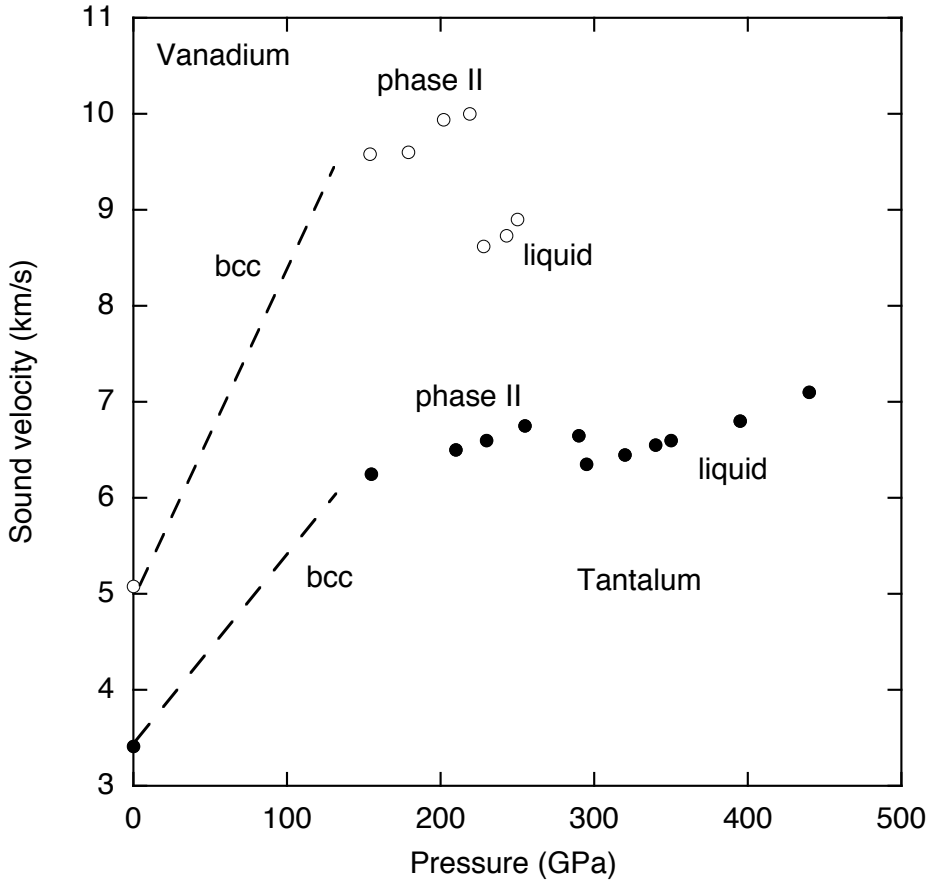
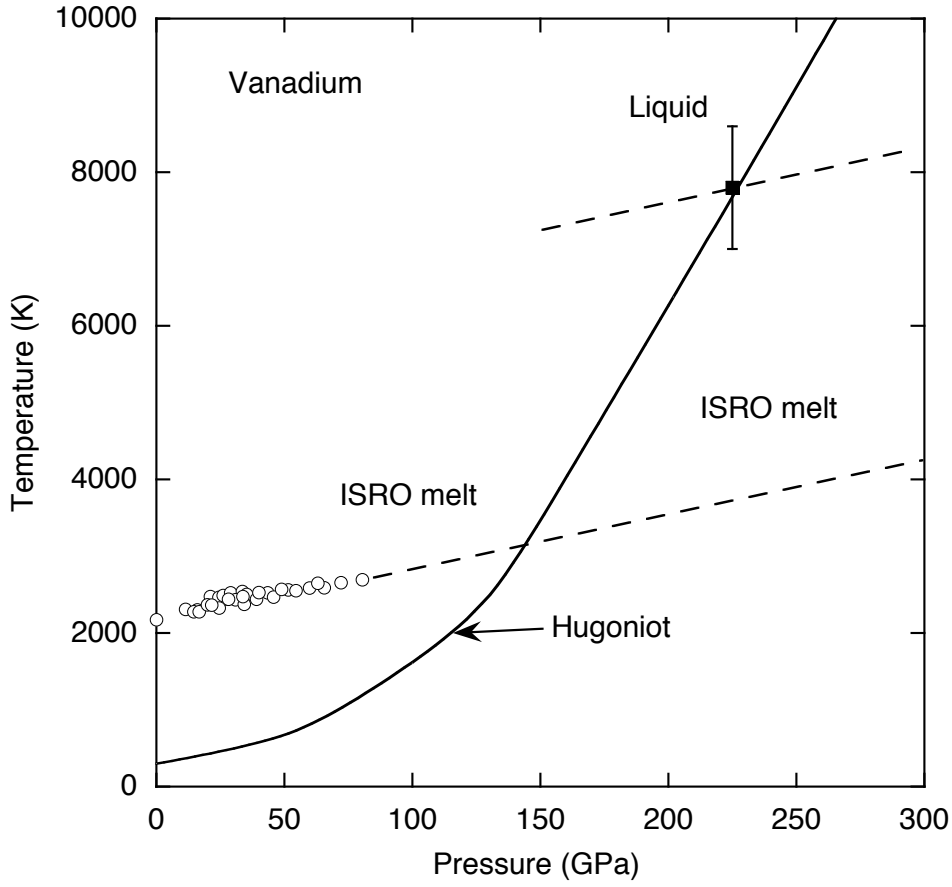

Vanadium
phase II
bcc
liquid
phase II
liquid
bcc
Tantalum
Sound velocity (km/s)
Pressure (GPa)
11
10
9
8
7
6
5
4
3
0
100
200
300
400
500

Figure 6


10000
8000
6000
4000
2000
0
Temperature (K)
0
50
100
150
200
250
300
Pressure (GPa)
Vanadium
Liquid
ISRO melt
ISRO melt
Hugoniot