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UCRL-JRNL-211837

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April 29, 2005

Physical Review Letters

Melting of copper and nickel at high pressure; the role of *d*-electrons

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PACS numbers: 61.25.Mv, 64.70.Dv

Abstract

Melting curves of Cu and Ni were measured to 97 GPa (3800 K) and 60 GPa (2970 K), respectively, in the laser-heated diamond cell. The measured melting temperatures of Cu are in good agreement with recent theoretical calculations. The melting slope (dT/dP) of Cu, which has a filled *d*-electron band, is about 2.5 times steeper than for Ni, which with one less electron, has a partially unfilled *d*-electron band. The relatively low melting slope obtained for Ni, measured using identical experimental methods as for Cu, is consistent with our previous measurements for other transition metals with partially filled *d*-bands, which are in serious disagreement with theoretical estimates. The present results confirm the key role *d*-shell electrons play in determining the high pressure melting curves.

Measurements of melting curves for transition metals made in the megabar pressure range, to temperatures of 3000 K to 4000 K, using a laser heated diamond-anvil cell (DAC) have lead to the discovery of unusually low melting slopes (dT/dP~0)[1-3]. These relatively flat curves have become controversial because they are in considerable disagreement with theoretical calculations which predict that melting temperatures of transition metals should rise with increasing pressure much more sharply than those determined experimentally[4]. The differences between the measured and predicted melting temperatures are much larger than the maximum experimental uncertainties associated with temperature measurement and the detection of melting in the laser-heated diamond cell.

In order to understand the physical basis for the low melting slopes, a theoretical model[5] was developed in which the *d*-electron density of states

liquid(DOS) and cohesive energy were described by the Friedel equation[6]. The model[5] predicts that for the case of partially filled *d*-electron bands the loss of structural periodicity associated with melting leads to a change in the liquid DOS and a lowering of the liquid energy relative to the solid. As a result, the melting temperature is lowered. According to this theory Cu, which has a filled band and a DOS which changes only slightly upon melting[7], should have a stiffer melting curve than its neighbor Ni which has an un-filled *d*-band. To test this prediction we have extended the Cu melting curve by over an order of magnitude in pressure, from 6.5 GPa[7] to near 100 GPa (3650K), and measured the Ni melting curve to 60 GPa (2410K). We show that the melting slope for Cu is about 2.5 times steeper than for Ni.

Previous experimental work on the melting curve of copper was conducted by Akella and Kennedy[9a] to 6.5 GPa and about 1300K in a piston cylinder apparatus using thermocouples and differential thermal analysis. The data collected by Akella and Kennedy lie below those collected by previous experimenters[9b-d], and slightly above the theoretical curve recently reported by Vocadlo et al.[10]. Our new data, extrapolated to lower pressures, is in agreement with Akella and Kennedy.

Measurements reported here were made in a diamond-anvil cell, described schematically in Fig. 1. Diamond culets measured 300 μm and were bevelled at an angle of 2° to 250 μm. The gasket used was a 350 μm thick tungsten disc, preindented to 50 μm. The gasket hole was laser cut to a diameter of 150 μm. Samples were solid metal, shaved from a larger piece of copper using a tungsten carbide knife. Copper used in this experiment was of 99.999+% purity (Aldrich Chemical Company.) Each time a sample was prepared, the top layer of the bar was removed, to ensure that the sample itself has not been significantly oxidized. Samples were on the order of 50 μm in diameter, and 10-15 μm thick. Due to the high reflectivity of copper, it was necessary to roughen the surface of the sample by pressing it between two unpolished plates of polycrystalline diamond (Syndie, De Beers) before loading. If too much of the laser power is reflected by the sample surface, it is impossible to reach the melting temperature.

The sample was sandwiched between an insulating layer of 1 μm grainsize ruby powder (bottom) and a layer of powdered pressure media (Al_2O_3, MgO, or CsCl) of 1-3 μm grainsize (top), all of which were thoroughly dried in a vacuum furnace

prior to loading. Runs were carried out in solid pressure media because the grains of the powders aided in retention of this roughened surface by indenting the surface under pressure. It was impossible to perform runs using argon as a pressure medium because copper and argon have such similar melting curves that differentiation between copper melting temperatures and those of argon would have been impossible[14]. At least 3 ruby chips of about 5 μm in diameter were placed near the sample for pressure calibration. In runs using Al_2O_3 as pressure medium, an Al_2O_3 sapphire window of approximately 80 μm in diameter and 10 to 15 μm in thickness was additionally placed on top of the sample, to ensure that there was no contact between the copper and the front diamond. After the sample was loaded, the open cell was placed into a vacuum furnace and further dried. The cell was then closed under vacuum of 10^{-4} - 10^{-7} mbar.

The solid-liquid transition (melting point) was detected by the laser speckle method, in which direct visual observation of the solid-liquid transition was evidenced by the appearance of rapid, continuous motion in the interference pattern of a blue (488 nm λ) argon laser beam on the surface of the sample[1-3]. The sample was heated using Nd-doped yttrium-vanadate (YVO_4) and Nd-doped yttrium-lithium-fluoride (YLF) lasers (1.06-1.05 μm wavelength, respectively) in TEM_{00} mode with a combined CW power of 80 Watts. A series of five melting temperatures were measured for each data point reported. Temperatures were determined by fitting a Planck function to the thermal emission spectra of the hot spots, measured with a CCD detector from an area of 1-2 μm in diameter, to the spectral range from 550 to 800 nm using both temperature and emissivity as fitting parameters. Pressure measurements were made using the fluorescence spectra of the unheated ruby chips nearest the sample, according to the ruby pressure scale[8].After each experiment, the sample was recovered and visually inspected, and none showed signs of reaction or oxidation, which would have appeared as a darkening of the sample surface in the heated area.

The melting data for Cu and Ni are plotted in figs. 2 and 3 respectively. In fig. 2, the experimental data points from this study are shown for various pressure media: 1-3 μm MgO as open squares, 1–3 μm CsCl as open circles, 1-3 μm gamma Al_2O_3 powder + Al_2O_3 disc as filled circles, 1-3 μm gamma Al_2O_3 powder as filled triangles, and 1-20 nm gamma-alpha Al_2O_3 powder as open diamonds. Previous experimental

work by Akella et al.[9] covering the pressure range from 1 atm to 6 GPa is shown as a solid line, and the theoretical melting curve from Vocadlo et al.[10] as a dotted line.

In fig. 3, Ni data as reported by Errandonnea et al.[2] is shown as closed circles. Also shown are previously unreported Ni measurements (closed triangles) collected in Mainz, and those of Lazor et al.[11] (closed squares.) Except for the Ni data of Lazor[8a], which is in agreement with our measurements, all of the experimental data reported here were measured in this laboratory employing very similar experimental setups. The slope of the Ni melting temperatures is significantly shallower than that of copper (fig.[2]).

Melting curves of Cu (open circles) and Ni[2] (open squares) are compared to those of Pt[12] (open triangles) and Mo[2] (open diamonds) in figure 4. In order to better facilitate comparisons of the melting slopes, the temperature is plotted in reduced units (T_m/T_{mo}). T_{mo} is the melting temperature at 1 atm. The slope of the Ni melting tempeatures is significantly shallower than that of copper. In terms of the melting slope, Cu has the steepest slope, Mo has the lowest, and Ni and Pt are intermediate. This suggests that the transition melting slopes may obey a generalized rule in accordance with their place in the Periodic Table. While we have already shown that the low melting slope of Mo is a consequence of changes in the electronic density of states in going from solid to liquid[5], the relative increase in melting slopes from Mo to Ni and Pt to Cu can be explained, at least partially, in terms of the Clapeyron equation, $dT / dP = T\Delta V / \Delta H$. ΔV and ΔH, are respectively, the volume and enthalpy changes on melting. If we assume Mo, Ni, and Pt have close-packed-like liquids, Mo, which has an 8-fold coordinated bcc structure, will undergo a relatively smaller change in volume upon melting than will 12-fold coordinated fcc Ni. Since electron band calculations for transition metals have shown that the hcp-fcc total energy differences are smaller than the corresponding bcc-fcc differences[9], then the enthalpy change for Mo melting should be greater than for Ni. Based on these qualitative considerations alone, the *dT/dP* for a bcc transition metal is expected to be smaller than for the fcc or hcp metal. A more quantitative estimate of the slopes should include changes in the electron density of states.

In reference [5] the melting curve for Mo was calculated for molybdenum by equating the difference in the solid and liquid Helmholtz free energies,

$$\Delta F = (F^{l}_{th\_inv6} - F^{s}_{th\_inv6}) + \Delta U^{l-s}_{d\_band}, \qquad (1)$$

and then determining the volume and temperature at which $\Delta F=0$. In this model the lattice and liquid energies at T=0 K are made to cancel. The first term in parenthesis, represents the change in the ion thermal free energy based on the inverse-6 power potential. The second term, ΔU^{l-s}_{d-band}, represents the change in *d*-band cohesive energy which is calculated by the Freidel approximation[6] using literature values for the Mo band width energy, the number of *d*-electrons and their volume dependence. It was determined that a small broadening of the liquid *d*-band width (~1%) leads to a lowering of the liquid energy relative to the solid. This is sufficient to depress the melting temperature and reduce the melting slope to a value in agreement with the diamond-anvil cell measurements[2,5]. In the case of an fcc transition metal we expect that melting to a close-packed liquid will result in a smaller change in ΔU^{l-s}_{d-band} than is the case for a bcc metal. If we approximate, $\Delta U^{l-s}_{d-band}(fcc) = \Delta U^{l-s}_{d-band}(bcc)/2$, then a steeper melting curve is obtained as shown in fig. 5. Total neglect of the effects due to a partially filled *d*-band ($\Delta U^{l-s}_{d-band} = 0$) results in a melting curve with a much steeper slope and an overall picture that is qualitatively similar to the measurements plotted in fig. 4.

The melting slope systematics, described in figs.4 and 5, are reproduced in Fig.6 by a larger set of solids. Fig.6 contains a plot of transition metal melting curves[1,2] and those of two well understood non-transition materials, Ar[14] and Al[15]. Except for the nickel data of Lazor[11] and the Pt data of Kavner and Jealnoz[12], all of the experimental data cited in this letter were collected using very similar experimental setups. The melting curves of Cu, Ar, and Al differ significantly from the bcc (W, Ta, Mo) and the fcc (Fe, Co, Ni) transition metals, which have much smaller melting slopes. Since Ar is a rare gas and Al is a nearly free electron polyvalent metal, their electronic structures remain essentially unchanged upon melting. Consequently, their melting curves are similar to that of Cu, which has a filled *d*-band below the Fermi energy that behaves as a repulsive core. This is not the case for the other transition metals.

The present study was undertaken to investigate the role played by *d*-electrons in transition metal melting by focusing on the neighboring metals Cu and Ni. While both metals melt from an fcc structure, it appears that their distinctly different melting curves are a consequence of a filled (Cu) and unfilled (Ni) *d*-electron band. In effect, the "withdrawal" of a single electron from the filled Cu *d*-shell, to "create" Ni, is

sufficient to cause a dramatic drop in the melting temperatures and slopes. The large difference demonstrates the important role played by partially filled *d*-bands, and argues that accurate theoretical calculations of the solid-liquid transition must include changes in the electronic properties, just as is now done in the case of solid-solid transitions[16]. Clearly, more theoretical work is needed.

Work by MR was partially supported by the University of California under the auspices of the US DOE with the LLNL under contract W-7405-Eng-48. MR also wishes to thank the Max-Planck-Institute für Chemie at Mainz for its continued hospitality.

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Figure captions

Fig. 1. Cross section of the DAC sample chamber. The sample is a 50 - 70 μm diameter copper foil, 10 μm in thickness. It is situated in a bed of 1 μm ruby powder, and overlain by a solid (1-3 μm powder) pressure medium (MgO, Al_2O_3, CsCl). In the Al_2O_3 runs, a sapphire (corundum) disc 10 to 15 μm thick was also used to prevent the melt from coming into contact with (and breaking) the front diamond.

Fig. 2. Melting curve of copper. Experimental data points from this study are shown for various pressure media as: open squares (MgO), open circles (CsCl), filled circles (Al_2O_3 disc), filled triangles (1-3 μm Al_2O_3 powder), and open diamonds (nanocrystalline Al_2O_3 powder). Previous experimental work by Akella et al. [9] covering the pressure range from 1 atm to 6 GPa is shown as a solid line. The theoretical melting curve from Vocadlo et al. [10] is a dotted line.

Fig. 3. Ni melting data as reported by Errandonnea et al.[2] is shown as closed circles. Also shown are previously unreported Ni measurements (closed triangles) collected in Mainz, and those of Lazor et al.[8a] (closed squares.) The data are in agreement.

Fig. 4. Reduced meelting temperatures of Cu (open circles), Pt[8b] (open triangles), Ni[2] (open squares), and Mo[2] (open diamonds), versus pressure.

Fig. 5. Melting curve systematics. Mo melting curve including $\Delta U^{l\to s}_{d\,band}$(solid curve); approximating $\Delta U^{l\to s}_{d\,band}(fcc) = \Delta U^{l\to s}_{d\,band}(Mo)/2$ (long dashed curve); and $\Delta U^{l\to s}_{d\,band} = 0$,(short dashed curve).

Fig. 6. Melting curves of Cu, Al[15], Ar[14], W[2], Ta[2], Mo[2], Fe[2], Co[2], Ni[2] as indicated. All data were collected in this laboratory, using very similar methods.

Figure 1

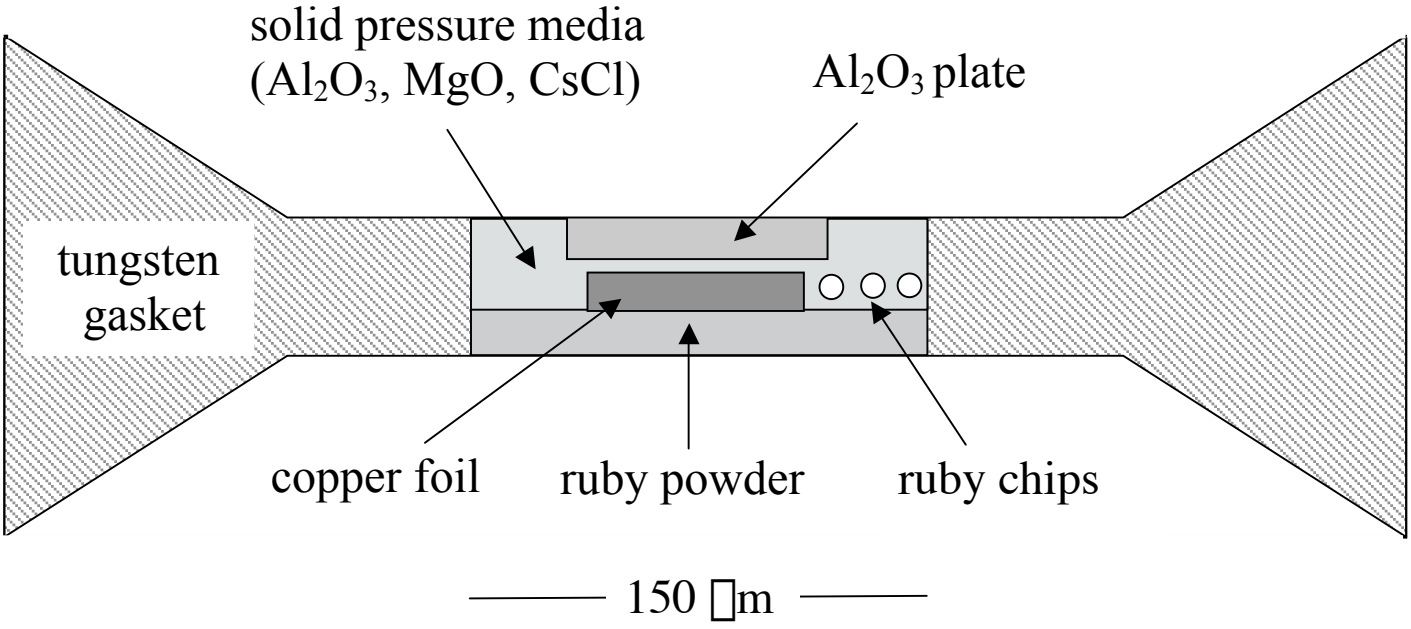

solid pressure media
(Al_2O_3, MgO, CsCl)
Al_2O_3 plate
tungsten gasket
copper foil
ruby powder
ruby chips
150 μm

Figure 2

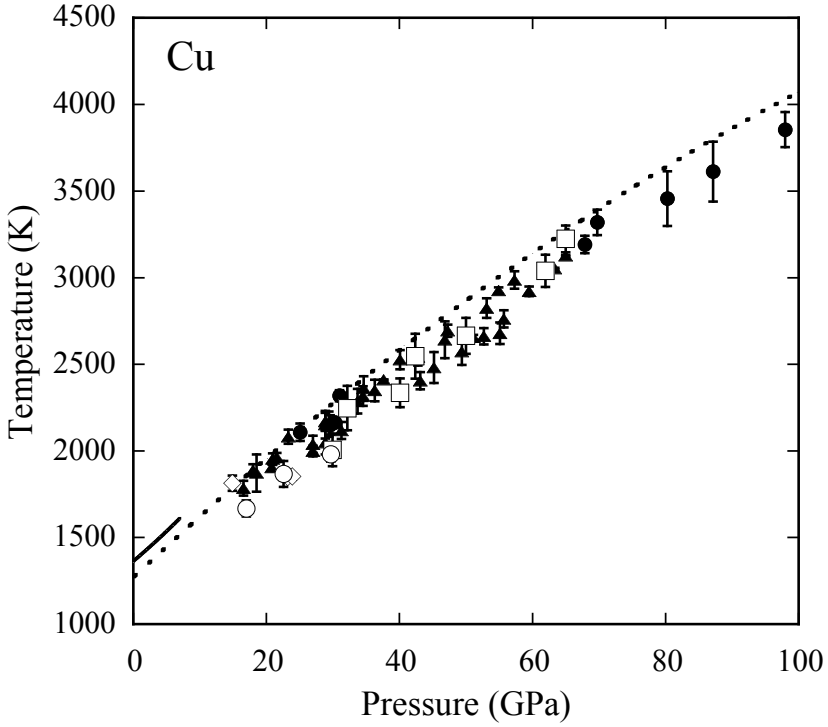

Cu
Temperature (K)
Pressure (GPa)
4500
4000
3500
3000
2500
2000
1500
1000
0
20
40
60
80
100

Figure 3

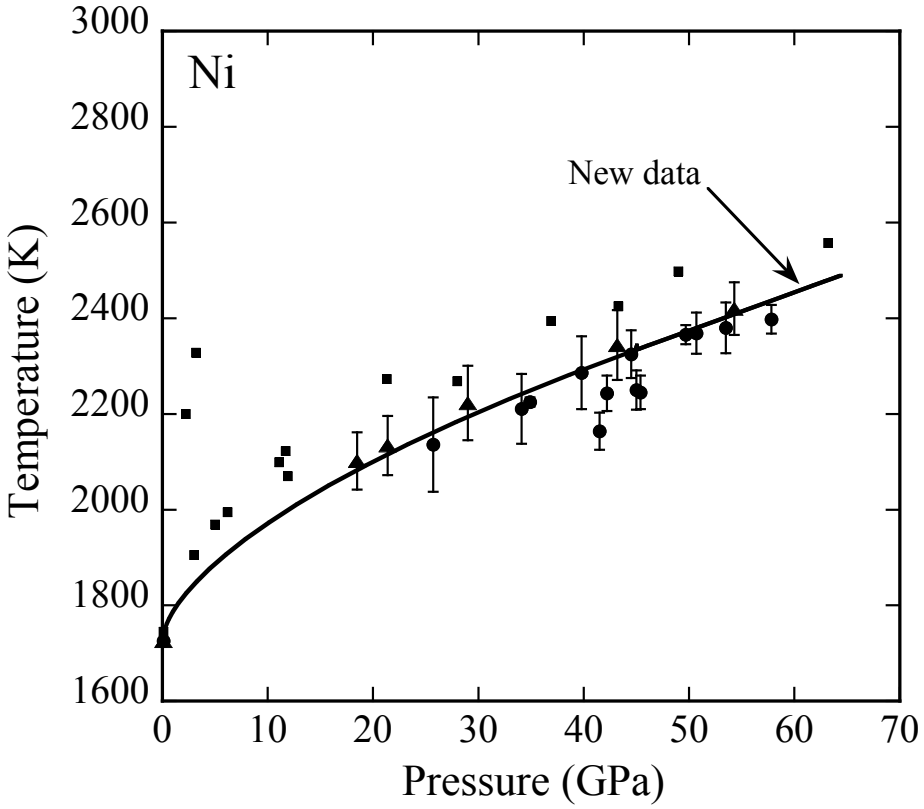

Ni
New data
Temperature (K)
Pressure (GPa)
3000
2800
2600
2400
2200
2000
1800
1600
0
10
20
30
40
50
60
70

Figure 4

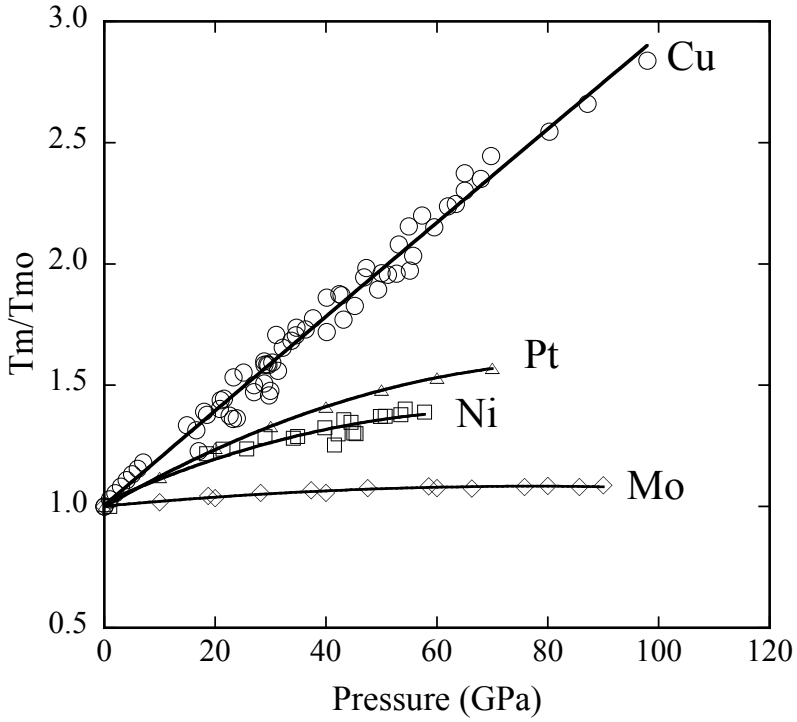

3.0
2.5
2.0
1.5
1.0
0.5
Tm/Tmo
0
20
40
60
80
100
120
Pressure (GPa)
Cu
Pt
Ni
Mo

Figure 5

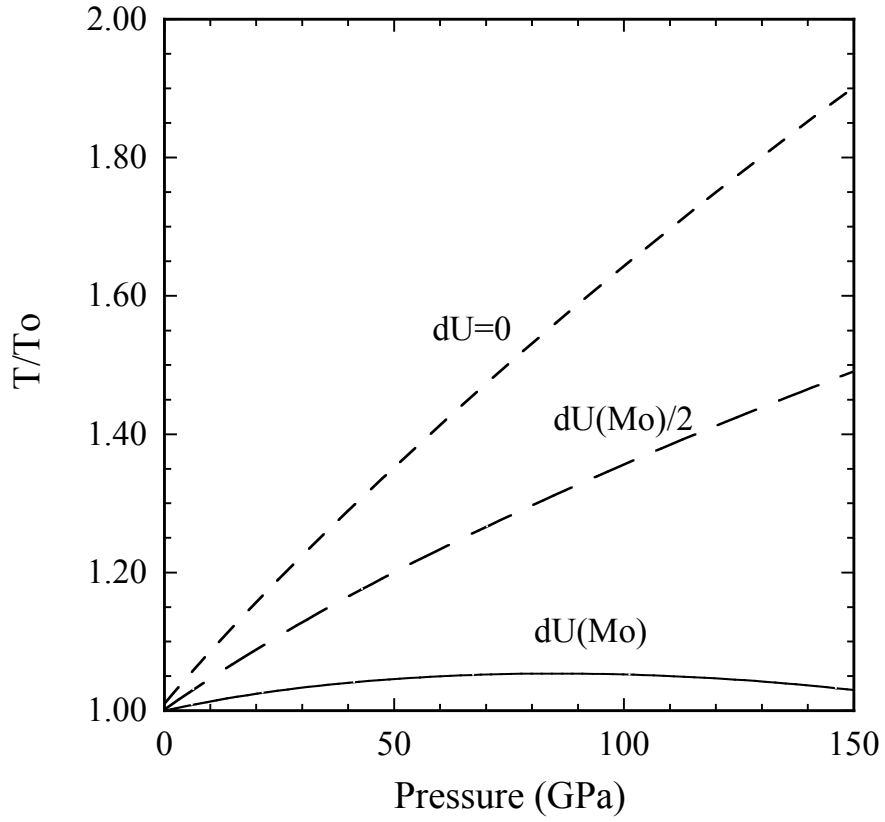
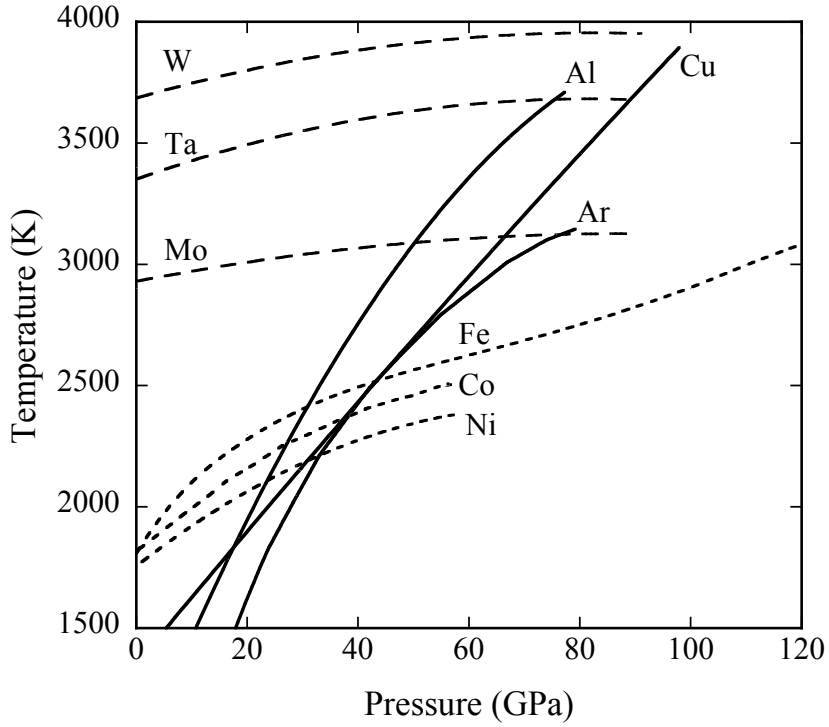

2.00
1.80
1.60
1.40
1.20
1.00
T/To
dU=0
dU(Mo)/2
dU(Mo)
0
50
100
150
Pressure (GPa)

Figure 6


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