

Melting of Copper and Nickel at High Pressure: The Role of d Electrons

Stefanie Japel,¹ Beate Schwager,¹ Reinhard Boehler,¹ and Marvin Ross^{1,2}

¹Max Planck Institut für Chemie, Postfach 3060, D-55020 Mainz, Germany

²Lawrence Livermore National Laboratory, University of California, Livermore, California 94551, USA

(Received 28 January 2005; published 12 October 2005)

Melting curves of Cu and Ni were measured in the laser-heated diamond cell to 97 GPa (3800 K) and 60 GPa (2970 K), respectively. The temperatures of Cu are in good agreement with recent theoretical calculations. The Cu melting slope (dT/dP) is about 2.5 times steeper than for Ni. The present results confirm the key role d -shell electrons play in determining the temperature dependence of high pressure melting curves in transition metals that have filled or partially filled d electron bands.

DOI: 10.1103/PhysRevLett.95.167801

PACS numbers: 61.25.Mv, 64.70.Dv

Measurements of melting curves for transition metals made in the megabar pressure range, to temperatures of 3000 to 4000 K, using a laser-heated diamond-anvil cell (DAC) have led to the discovery of unusually low melting slopes ($dT/dP \sim 0$) [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 (DOS) liquid 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 slope decreases. Pressure induces a net s - d electron transfer, which also contributes to lowering of the melting slope. According to this theory, Cu, which has a filled band and a DOS that changes only slightly upon melting [7], should have a steeper melting curve than its neighbor Ni, which has an unfilled d band. To test this prediction, we have extended the Cu melting curve by over an order of magnitude in pressure, from 6.5 [8] to near 100 GPa (3650 K), and measured the Ni melting curve to 60 GPa (2410 K). 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 [7(a)] to 6.5 GPa and about 1300 K in a piston cylinder apparatus using thermocouples and differential thermal analysis. Our new data, extrapolated to lower pressures, are in agreement with the Akella and Kennedy study.

Measurements reported here were made in a diamond-anvil cell, described schematically in Fig. 1. Diamond

culets measured 300 μm in diameter and were bevelled at an angle of 2° to 250 μm . The gasket used was a 350 μm thick tungsten disk, preindented to 50 μm . The gasket hole was laser cut to a diameter of 150 μm . Samples were solid metal, shaved from a copper bar 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 had not been significantly oxidized. Samples were on the order of 50 μm in diameter and 10–15 μm thick. Because of the 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.

The sample was sandwiched between an insulating layer of 1 μm grain size ruby powder (bottom) and a layer of powdered pressure media (Al_2O_3 , MgO, or CsCl) of 1–3 μm grain size (top), all of which were thoroughly dried in a vacuum furnace prior to loading. Runs were carried out in solid pressure media, rather than using a noble gas such as argon, xenon, or neon, because the grains of the powders were necessary for the retention of this roughened surface. In runs using Al_2O_3 as a pressure

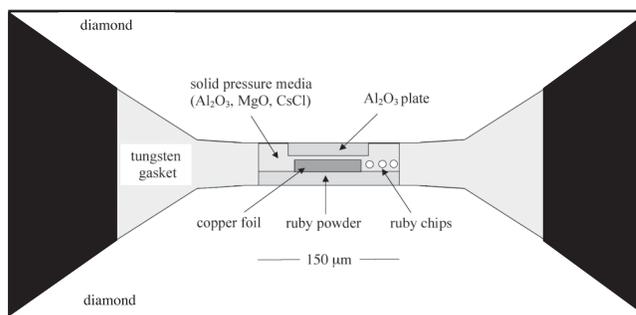


FIG. 1. Cross section of the DAC sample chamber. The sample is a 50–70 μm diameter copper foil, 10 μm in thickness. It is situated in a bed of 1 μm ruby powder, and overlain by a solid (1–3 μm powder) pressure medium (MgO, Al_2O_3 , CsCl). In the Al_2O_3 runs, a sapphire (corundum) disk 10 to 15 μm thick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

medium, an Al_2O_3 sapphire window of approximately $80\ \mu\text{m}$ in diameter and 10 to $15\ \mu\text{m}$ in thickness was additionally placed on top of the sample, to ensure that there was no contact between the copper and the front diamond. At least 3 ruby chips of about $5\ \mu\text{m}$ in diameter were placed near the sample for pressure calibration. 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 ($488\ \text{nm}$) 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 lasers (1.06 – $1.05\ \mu\text{m}$ wavelength, respectively) in TEM_{00} mode with a combined power of $80\ \text{W}$. 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 – $2\ \mu\text{m}$ in diameter, to the spectral range from 550 to $800\ \text{nm}$ using both temperature and emissivity as fitting parameters. Pressure measurements were made before and after heating using the fluorescence spectra of the ruby chips nearest the sample, according to the ruby pressure scale [9]. During the experiment, the heated sample is subjected to both a pressure relaxation due to annealing of the pressure medium, and to a thermal pressure increase. Uncertainty in the sample pressure, as argued in the review paper by Boehler [10] is on the order of $1\ \text{GPa}$. Pressure uncertainties of that order have no significant effect on the slope of the melting curve. 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 – $3\ \mu\text{m}$ MgO as open squares, 1 – $3\ \mu\text{m}$ CsCl as open circles, 1 – $3\ \mu\text{m}$ gamma Al_2O_3 powder + Al_2O_3 disk as filled circles, 1 – $3\ \mu\text{m}$ gamma Al_2O_3 powder as filled triangles, and 1 – $20\ \text{nm}$ gamma-alpha Al_2O_3 powder as open diamonds. Previous experimental work by Akella *et al.* [7] covering the pressure range from $1\ \text{atm}$ to $6\ \text{GPa}$ is shown as a solid line, and the theoretical melting curve from Vocadlo *et al.* [11] as a dotted line.

In Fig. 3, Ni data as reported by Errandonea *et al.* [2] are shown as closed circles. Also shown are our new Ni measurements (closed triangles) and those of Lazor *et al.* [12] (open squares.) The solid line is a fit to the new data. Except for the Ni data of Lazor [12], all of the experimental data reported here were measured in this laboratory em-

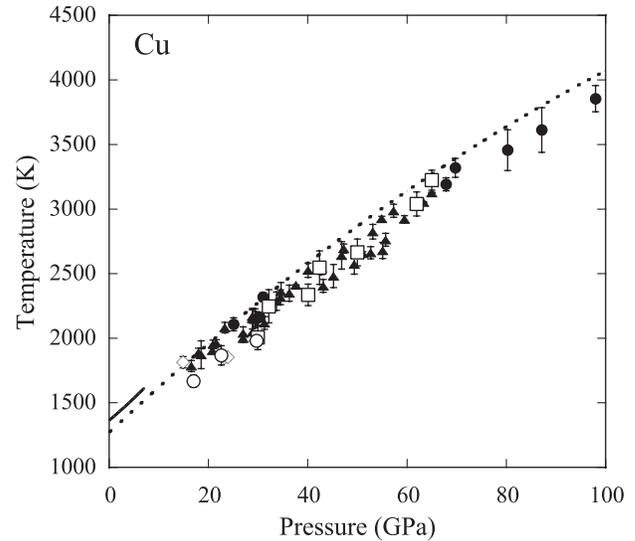


FIG. 2. Melting curve of copper. Experimental data points from this study are shown for various pressure media as open squares (MgO), open circles (CsCl), filled circles (Al_2O_3 disk), filled triangles (1 – $3\ \mu\text{m}$ Al_2O_3 powder), and open diamonds (nanocrystalline Al_2O_3 powder). Previous experimental work by Akella *et al.* [7(a)] covering the pressure range from $1\ \text{atm}$ to $6\ \text{GPa}$ is shown as a solid line. The theoretical melting curve from Vocadlo *et al.* [11] is a dotted line.

ploying very similar experimental setups. Nickel measurements were made in a diamond-anvil cell with diamond culets measuring $380\ \mu\text{m}$ in diameter (bevelled at an angle of 2° to $170\ \mu\text{m}$ in some cases). The gaskets were made from a $350\ \mu\text{m}$ thick tungsten disk, preindented to $50\ \mu\text{m}$ and coated with diamond powder. The gasket hole was

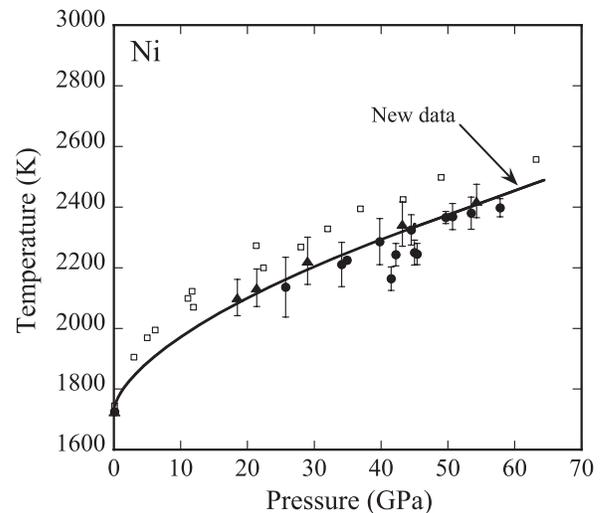


FIG. 3. Ni melting data as reported by Errandonea *et al.* [2] is shown as closed circles. Also shown are previously unreported Ni measurements (closed triangles, fit with a solid line) collected in our laboratory, and those of Lazor *et al.* [12] (open squares). The data are in agreement.

either drilled or laser cut to a diameter of 150 μm . Samples were made either from Ni powder pressed to give a foil or from pieces of solid metal pressed to give disks. They were about 50 μm in diameter with a thickness of about 15 μm . The pressure medium used was argon, and ruby chips were used for the pressure calibration. Melting temperatures were determined using the same method as described for copper above. 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 [13] (open triangles) and Mo [2] (open diamonds) in Fig. 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 temperatures 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 eightfold 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

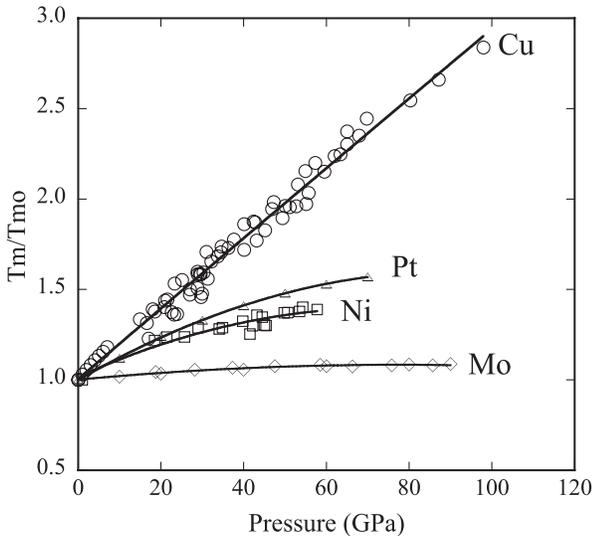


FIG. 4. Reduced melting temperatures of Cu (open circles), Pt [13] (open triangles), Ni [2] (open squares), and Mo [2] (open diamonds) versus pressure.

than the corresponding bcc-fcc differences [7], 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 Ref. [5] the melting curve for Mo was calculated for molybdenum by equating the difference in the solid and liquid Helmholtz free energies,

$$\Delta F = (F_{\text{th-inv6}}^l - F_{\text{th-inv6}}^s) + \delta U_{d\text{-band}}^{l-s}, \quad (1)$$

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 parentheses represents the change in the ion thermal free energy based on the inverse-6 power potential. The second term, $\delta U_{d\text{-band}}^{l-s}$, 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 ($\sim 1\%$) 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 $\delta U_{d\text{-band}}^{l-s}$ than is the case for a bcc metal. If we arbitrarily set, for example, $\delta U_{d\text{-band}}^{l-s}(\text{fcc}) = \delta U_{d\text{-band}}^{l-s}(\text{bcc})/2$, then a steeper melting curve is obtained as shown in Fig. 5. Total

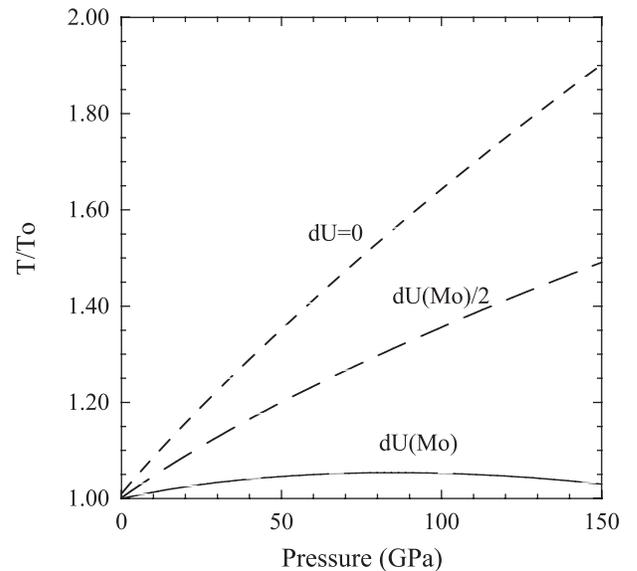


FIG. 5. Melting curve systematics. Mo melting curve including $\delta U_{d\text{-band}}^{l-s}$ (solid curve), approximating $\delta U_{d\text{-band}}^{l-s}(\text{fcc}) = \delta U_{d\text{-band}}^{l-s}(\text{Mo})/2$ (long-dashed curve), and $\delta U_{d\text{-band}}^{l-s} = 0$ (short dashed curve).

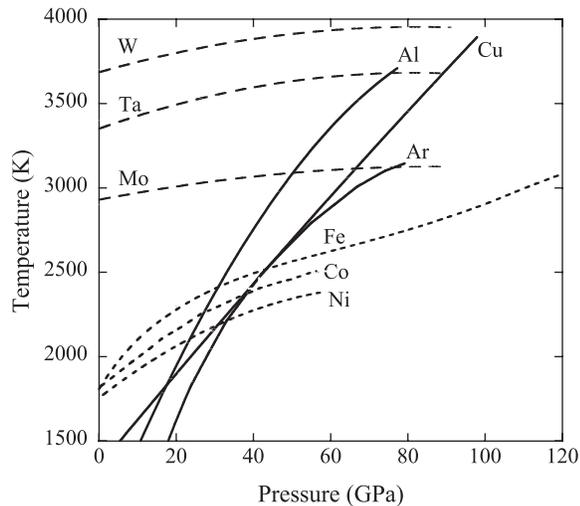


FIG. 6. Melting curves of Cu, Al [15], Ar [14], W [2], Ta [2], Mo [2], Fe [2], Co [2], and Ni [2] as indicated. All data were collected in this laboratory, using very similar methods.

neglect of the effects due to a partially filled d band ($\delta U_{d\text{-band}}^{l-s} = 0$) 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. Figure 6 contains a plot of transition metal melting curves [1,2] and those of two well understood nontransition materials, Ar [14] and Al [15]. Except for the nickel data of Lazor [12] and the Pt data of Kavner and Jeanloz [13], 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 partially filled d bands, hence 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 lowering of the melting slope. 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 careful theoretical work is needed.

The work of M.R. was partially supported by the University of California under the auspices of the U.S. DOE by the Lawrence Livermore National Laboratory. M.R. thanks the Max-Planck-Institute für Chemie at Mainz for its continued hospitality.

- [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. Phys. Condens. Matter* **15**, 7635 (2003).
- [4] D. Alfe, L. Vocadlo, G. D. Price, and M. J. Gillan, *J. Phys. Condens. Matter* **16**, S973 (2004).
- [5] M. Ross, L. H. Yang, and R. Boehler, *Phys. Rev. B* **70**, 184112 (2004).
- [6] J. Friedel, in *The Physics of Metals I*, edited by J. Ziman (Cambridge University Press, Cambridge, 1969), p. 340.
- [7] (a) J. Akella and G. C. Kennedy, *J. Geophys. Res.* **76**, 4969 (1971); (b) L. H. Cohen, W. Klement, Jr., and G. C. Kennedy, *Phys. Rev.* **145**, 519 (1966); (c) N. R. Mitra, D. L. Decker, and H. B. Vanfleet, *ibid.* **161**, 613 (1967); (d) M. G. Gonikberg, G. P. Shakhovskoi, and V. P. Butuzov, *Zh. Fi. Khim.* **31**, 1831 (1957).
- [8] A. Pasquarello, K. Laasonen, R. Car, C. Lee, and D. Vanderbilt, *Phys. Rev. Lett.* **69**, 1982 (1992); G. Kresse and J. Hafner, *Phys. Rev. B* **48**, 13 115 (1993).
- [9] H. K. Mao, J. Xu, and P. M. Bell, *J. Geophys. Res.* **91**, 4673 (1986).
- [10] R. Boehler, *Rev. Geophys.* **38**, 221 (2000).
- [11] L. Vocadlo, D. Alfé, G. D. Price, and M. J. Gillan, *J. Chem. Phys.* **120**, 2872 (2004).
- [12] P. Lazor, G. Shen, and S. K. Saxena, *Phys. Chem. Miner.* **20**, 86 (1993).
- [13] A. Kavner and R. Jeanloz, *J. Appl. Phys.* **83**, 7553 (1998).
- [14] C. S. Zha, R. Boehler, D. A. Young, and M. Ross, *J. Chem. Phys.* **85**, 1034 (1986).
- [15] R. Boehler and M. Ross, *Earth Planet. Sci. Lett.* **153**, 223 (1997).
- [16] D. G. Pettifor, *J. Phys. C* **3**, 367 (1970); H. L. Skriver, *Phys. Rev. B* **31**, 1909 (1985).