High-pressure melting curves of the transition metals Cu, Ni, Pd, and Pt

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Melting curves of Cu, Ni, Pd, and Pt were measured in a laser-heated diamond-anvil cell up to 43, 52, 28, and 28 GPa, respectively. The obtained results are compared with previous studies. In particular, the measurements made in Cu are in agreement with the literature. In Pt the experiments are consistent with Z method calculations indicating that earlier measurements probably underestimate the melting temperature of Pt at high pressure. Cu, Pd, and Pt show a qualitative similar melting behavior. In the case of Ni, experiments confirm that it has a low melting slope of 28 K/GPa. Ni is the only transition metal of groups 10 and 11 of the Periodic Table that shows such a slope since the other metals have a steeper melting slope of 41–47 K/GPa. The determined melting curves can be described with Simon equations which are reported. The present results increase the database on high-pressure melting and could contribute to improving the understanding of this phenomenon.

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I. INTRODUCTION

The melting behavior of metals under compression is an important field in condensed-matter physics and geophysics. However, the determination of melting curves under compression is challenging both for experimentalists and theorists. Extensive experimental and theoretical studies have been performed on the transition metals. Particularly, laser-heating diamond-anvil cell (DAC) experiments were carried out on Fe, Mo, Ni, Pt, and Ta, among other metals.[1–10] Theoretical studies have been also performed including different levels of theory.[11–16] They involve the use of various interaction potentials (*ab initio* or not) and statistical mechanic approaches. For some of the studied metals, like Ta, disagreements between experiments[5,6] and theory[11] have been observed, although better agreement is observed between recent experiments[10] and calculations.[11] In contrast, a very good agreement is obtained for metals like Cu[17,18] and no experimental studies have been performed for metals like Pd. In order to better understand the melting curve of transition metals, additional experimental efforts are needed. In this case we present melting-curve measurements of Cu, Ni, Pd, and Pt. Experiments in Cu were performed to validate the experimental method. Experiments in Ni and Pt will be compared with earlier experimental and theoretical results, which include recent Z method calculations.[16] Experiments in Pd will be compared with recent molecular-dynamics calculations.[19] The reported results increase the database on high-pressure (HP) melting and could contribute to improving the understanding of this phenomenon. A comparison of the melting curve of Cu, Ni, Pd, and Pt with those of Ag and Au shows that Ni has the lowest melting slope among studied transition metals belonging to groups 10 and 11 of the Periodic Table.

II. EXPERIMENTAL DETAILS

Measurements reported here were made using Boehler-Almax type DACs whose anvils have diamond culets smaller than 300 μm in diameter. The gaskets used were 200 μm thick tungsten foils pre-indented to 40 μm. The gasket hole was drilled with an electrical-discharge machine (EDM) to a diameter of one third of the culet size. Samples were metal foils of purity higher that 99.95% and thickness of 12.5 μm obtained from Goodfellow. The sample was loaded between thin layers of compressed MgO, which act as thermal insulation between diamond anvils and the sample and also as a pressure medium.

The melting curves of the studied metals were determined from temperature measurements and simultaneous visual observation at selected pressures. Measurements at ten different pressures were carried out for each metal. The onset of melting was detected by the laser-speckle method[20] observing the appearance of a rapid movement in the interference pattern of a red He-Ne laser ($\lambda = 632.8$ nm). The sample was heated from one side using a laser-heating setup equipped with a linearly polarized Nd:YLF laser (Quantronix, 25 W, TEM_{00} mode, $\lambda = 1.053$ mm). The laser energy applied on the samples was varied, keeping the beam profile unchanged by rotating the laser-beam polarization in combination with the use of a polarized beam splitter.[21] Series of at least five experiments were performed at each reported pressure on different portions of the samples. The melting temperature (T_m) was taken as the average value and the error assumed as the maximum absolute deviation from the average. Temperatures were measured from the heated surface of the sample by collecting its thermal emission (450–850 nm range) using an Ocean Optics USB4000 spectrometer. The temperature measurements setup was calibrated with the spectral irradiance of a calibrated tungsten incandescent lamp. The temperature was determined by fitting a Planck function to the thermal emission spectra assuming that the emissivity is independent of the wavelength.[20] Figure 1 shows a typical spectrum collected on temperature measurements and the fit to the Planck function. Pressure was determined at room temperature using the ruby scale.[22] After each heating cycle samples were optically inspected to check that there were no obvious signs of chemical reactions or oxidation in the metal surfaces.[23] Trying to avoid these problems, heating was constrained to a time period smaller than 10 s and laser power was gradually increased. In case of occurrence of thermal runaways, which may affect the chemical integrity of the sample,[24] results have not been included in this report. To minimize the

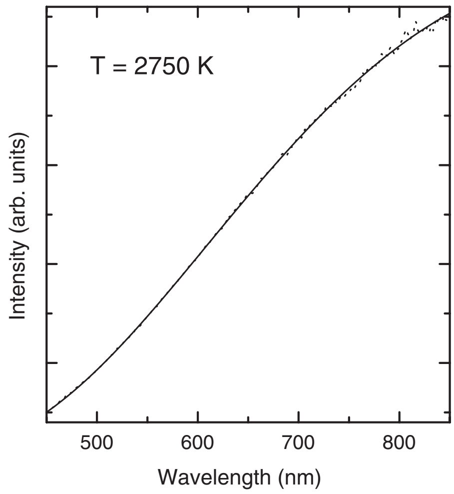

FIG. 1. Temperature measurement (dotted line) and the corresponding Planck fit (solid line).

TABLE I. Simon fits of the melting data of Ag, Au, Cu, Ni, Pd, and Pt. The melting temperature (T_m) is in K and the pressure (P) is in GPa. The melting slope ($\partial T_m/\partial P$) analytically obtained at ambient pressure from the Simon relation is given. The right column summarizes the range of values experimentally determined for melting slopes. The 27 K/GPa reported for Pt in Ref. 3 is not included since it is probably an underestimated value (see discussion).

Metal	Melting relation	$\partial T_m/\partial P$ (K/GPa)[a]	$\partial T_m/\partial P$ (K/GPa)[b]
Ag	$T_m = 1240(1 + \frac{P}{25.5})^{0.93}$	45	45–69
Au	$T_m = 1339(1 + \frac{P}{16.1})^{0.57}$	47	47–62
Cu	$T_m = 1356(1 + \frac{P}{16.8})^{0.51}$	41	36–43
Ni	$T_m = 1728(1 + \frac{P}{13.6})^{0.22}$	28	25–34
Pd	$T_m = 1828(1 + \frac{P}{19.2})^{0.48}$	46	–
Pt	$T_m = 2042(1 + \frac{P}{21.5})^{0.50}$	47	42–47

[a]This work.
[b]Summary of literature, Refs. 25,26, 29, 33, 37, and 41.

influence of undetected chemical reactions, each heating series was performed on a previously unheated zone of the sample.

III. RESULTS AND DISCUSSION

The melting curve of Cu is plotted in Fig. 2 together with previous experimental and theoretical results.[17,18,25–28] Previous results reported by Mirwald *et al.*[29] are not shown in the figure because they cannot be distinguished from those reported in Refs. 25 and 26. The agreement between different methods was very good and therefore Cu was used as a test case for our experiments. The results obtained here coincide with the literature, validating the experimental method in the pressure range covered by our experiments ($P < 52$ GPa) and giving credibility to the results obtained for Ni, Pd, and Pt.[30] The present results can be very well described by a Simon equation.[31] The fitted Simon relation is given in Table I and shown as a solid line in Fig. 2.

The melting curve of Ni has been experimentally determined by Lazor[1] and Boehler's group.[5,17] The melting temperature of Ni increases with pressure as in Cu, but with a smaller slope. As a consequence of it, near 30 GPa, the melting temperature of Cu becomes higher than that of Ni. In contrast with experiments, molecular-dynamic calculations[32] predicted that the melting curve of Ni should increase with pressure as that of Cu, casting some doubts on the accuracy of the experiments. Our results, shown in Fig. 3, perfectly agree with the previous experimental results, confirming the low slope of the melting curve of Ni. Extrapolations of our results below 10 GPa also agree with the early data of Strong and Bundy.[33] Again, the present results can be well described by a Simon fit. The obtained Simon equation is

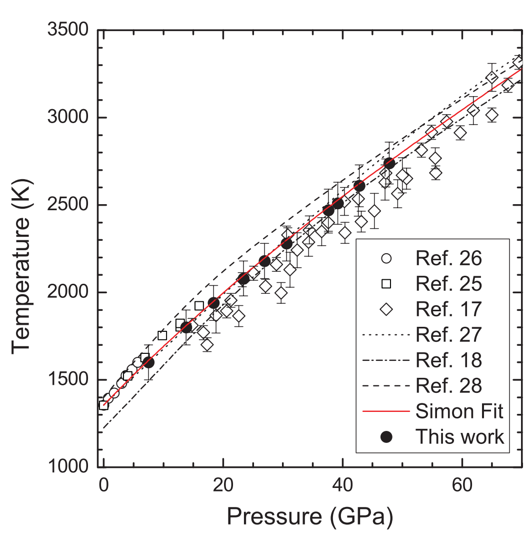

FIG. 2. (Color online) Melting curve of Cu. Solid circles represent the present data which are compared with previous results (references given in the inset). The Simon relation is plotted as a solid red line.

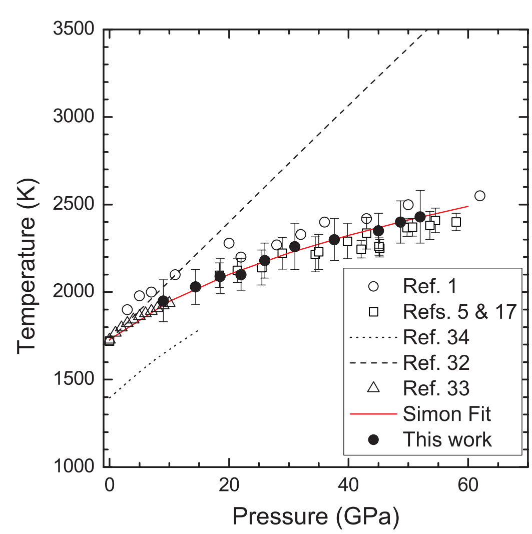

FIG. 3. (Color online) Melting curve of Ni. Solid circles represent the present data which are compared with previous results (references given in the bottom inset). The Simon relation is plotted as a solid red line.

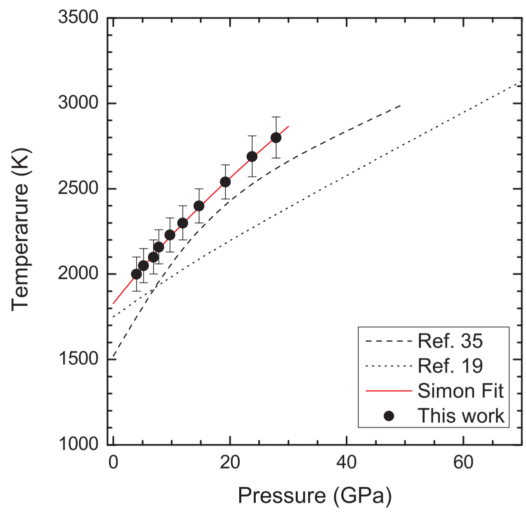

FIG. 4. (Color online) Melting curve of Pd. Solid circles represent the present data which are compared with previous results (references given in the inset). The Simon relation is plotted as a solid red line.

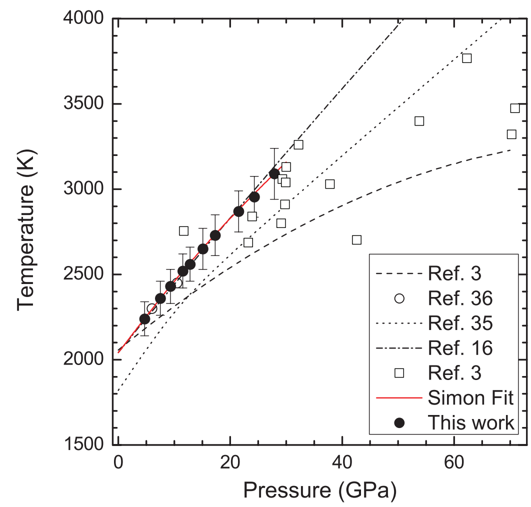

FIG. 5. (Color online) Melting curve of Pt. Solid circles represent the present data which are compared with previous results (references given in the bottom inset). The Simon relation is plotted as a solid red line. The dashed curve represents the melting relation given in Ref. 3: $T_m = 2057 + 27.1P - 0.1497P^2$, where T is in K and P is in GPa. Open squares represent melted Pt experimentally detected in Ref. 3.

given in Table I and plotted in Fig. 3. Noticeably there are previous molecular-dynamics calculations up to 15 GPa,[34] which underestimate the melting temperature by 300 degrees, but give a pressure evolution similar to experiments. Clearly additional theoretical efforts are needed to better understand and describe the melting behavior of Ni. Note that previous studies were not *ab initio* having the interatomic potentials used problems to reproduce not only the melting curve but also the room-temperature equation of state.[32,34] It would be interesting to have state-of-the-art melting calculations performed for Ni to compare with the available experimental database.

In Fig. 4 we show the melting curve of Pd. In this case there are no experimental data to compare with. The results can be also described by the Simon relation, which is given in Table I and represented in Fig. 4. *Ab initio* and molecular-dynamics studies have been done for the melting curve of Pd.[19,35] The recent calculations reported by Liu *et al.*[19] give a lower melting temperature than experiments. The underestimation increases with pressure, reaching 500 degrees at 30 GPa. On the other hand, the earlier calculations of Jeong and Chang[35] agree well with the experimental results up to 20 GPa. According to that study, beyond 20 GPa there is a decrease of the melting slope ($\partial T_m/\partial P$) that it is not reproduced by the smooth evolution of our experimental results.

Figure 5 shows the results obtained for Pt. For this metal there were previous experiments performed by Kavner and Jeanloz[3] and Boehler[36] as well as calculations.[16,35] There are large differences between the most exhaustive experiments[3] and the calculations. Therefore, more efforts were needed to solve the discrepancies. As can be seen in Fig. 5, we systematically obtained higher melting temperatures than Kavner and Jeanloz.[3] This discrepancy could be explained by the fact that in their work at a given pressure there is a melting temperature scattering of several hundred degrees (see Fig. 5). The melting curve expression reported by them (plotted as dashed curve in Fig. 5) corresponds to the lowest melting temperature observed at each pressure and therefore should be interpreted as a lower bound to the melting curve. The highest melting temperatures reported in Ref. 3 (e.g., ∼3100 K at ∼30 GPa) agrees well with the present results. On the other hand, our results also agree with the low-pressure data reported by Boehler[36] and with earlier piston-cylinder experiments.[33,37] For the sake of simplicity, the piston-cylinder data are not included explicitly in the plot because they are well reproduced by the melting relation reported in Ref. 16 (dot-dashed line in Fig 5).

Regarding calculations, Jeong and Chang[35] gave melting estimates that are around 200 degrees smaller than our experimental results. However, the pressure evolutions are comparable. On the other hand, our melting temperatures follow very well the predictions made by Belonoshko[16] using the Z method. This method has been demonstrated to provide an upper bound to the melting curve of metals.[38] However, in the case of Pt, it appears to work successfully as previously shown in Al.[39] As in the other studied metals, the experimental results can be described by a Simon equation. The fitted relation is presented in Table I and the fit shown in Fig. 5. The obtained Simon equation has different parameters than that reported by Belonoshko *et al.*[16,40] However, both relations give a similar melting curve within the pressure range covered by our experiments (see Fig. 6 for a comparison). Differences between both reported relations will appear beyond 40 GPa, giving the extrapolation of the equation shown in Table I a lower melting slope.

To conclude, we would like to compare the melting curves of different metals of groups 10 and 11 of the Periodic Table. The melting curves of Ag, Au, Cu, Ni, Pd, and Pt are shown together in Fig. 7. The reported melting data of Ag[26] and Au[41] have been also fit to a Simon equation. The equations are given in Table I. In Fig. 7 it can be seen that the melting curve of all the metals, with exception of Ni, have a high melting slope. At ambient pressure the melting slopes obtained analytically from the Simon equations go from 41

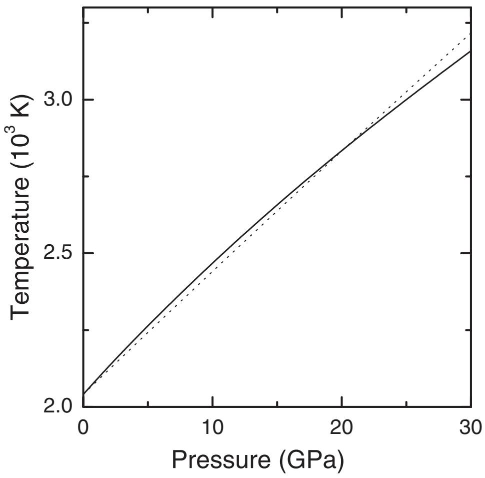

FIG. 6. Simon relations reported here (solid line) and in Ref. 16 (dotted line) for Pt.

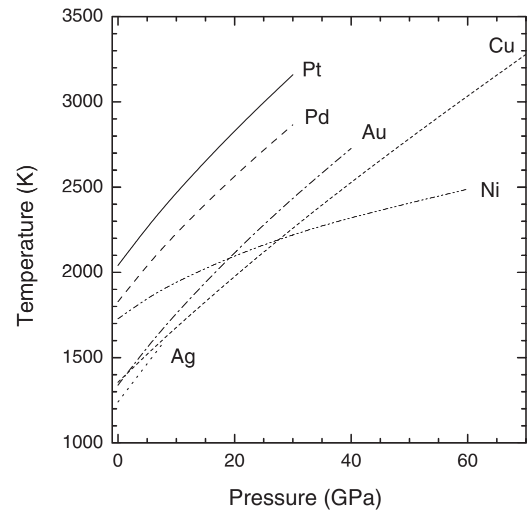

FIG. 7. Comparison of the melting curves of Ag, Au, Cu, Ni, Pd, and Pt.

to 47 K/GPa (see Table I). These values are within the range of experimentally determined melting slopes (see Table I). The only discrepancy is with the 27 K/GPa melting slope reported for Pt,[3] which has been discussed above. In contrast, Ni has a low melting slope; which at ambient pressure is at least 30% smaller than that of the other metals. According to the Clapeyron equation $\partial T_m/\partial P = \Delta V/\Delta S$, the volume and entropy changes on melting (ΔV and ΔS) should be, respectively, smaller and/or larger in Ni than in the other metals studied here. Since the six metals melt from the fcc structure, as a first approximation, ΔS should be similar in all of them. Therefore, Ni should have a relatively smaller ΔV upon melting. Previously it was proposed that the flattening of the melting slope in transition metals like Ni may be caused by the formation of locally preferred liquid structures which may be favored by a pressure-driven s-d electron transfer.[14] Another hypothesis that should not be neglected is the transformation of Ni from the fcc structure to another solid phase before melting at high pressure and high temperature.[42] From the present results no conclusion can be extracted on these hypotheses. As mentioned above, the better understanding of the melting behavior of Ni requests accurate calculations performed using state-of-the-art methods. Such an effort is beyond the scope of this work. However, we hope the present results will trigger these kind of studies.

IV. CONCLUDING REMARKS

Summing up, we report a careful and exhaustive high-pressure study of the melting curve of Cu, Ni, Pd, and Pt. In the case of Cu, the obtained results agree with previous studies validating our experimental method. We also found that Pd and Pt have a similar behavior than Cu. For Pt, our results agree with recent theoretical calculations.[16] Finally, the behavior found for Ni cannot be fully described by existent calculations.[32,34] We expect this fact will lead to future studies on Ni. The reported results increase the database on high-pressure melting extending the knowledge on the physical properties of the solid state under extreme conditions. They may have implications for other fields including Earth and planetary sciences.

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