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Melting curve of copper measured to 16 GPa using a multi-anvil press

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The melting temperature, T_m, of copper has been determined from ambient pressure to 16 GPa using multi-anvil techniques. The melting curve obtained ($T_m = 1355(5) + 44.5(31)P - 0.61(21)P^2$, with T_m in Kelvin and P in GPa) is in good agreement with both the previous experimental studies and with recent *ab initio* calculations.

Keywords: Copper; Melting temperature; High pressure; Multi-anvil press

1.   Introduction

Although the basic structure of the deep Earth has been known for many years, there are many aspects in which our current knowledge is deficient. Understanding the deep interior of our planet may be the key to understand the driving forces for large-scale processes, which govern the surfaces not only of the Earth but also of the other terrestrial planets. To this end, the determination of the composition and condition of the deep Earth is of extreme importance to Earth and planetary science and so has been the focus of many studies, both experimental and theoretical.

A parameter that is surprisingly ill determined is the temperature profile of the Earth's deep interior; although for example, geophysical measurements are able to determine that the pressure at the inner core – outer core boundary is close to 330 GPa [1] estimates of the temperature at this point vary by over 1500 K, from about 5800 to 6400 K [2]. One approach to determine the temperature is by the investigation of the melting curve of iron. Density measurements have revealed that the Earth's core is composed largely of iron alloyed with a small amount of light elements – on cosmochemical grounds most probably S, O or Si [3]. The boundary of the inner core marks the point where the solid inner core is crystallizing from the liquid outer core. As the pressure at this point is known, the temperature of the inner core boundary can, in principle, be determined from the melting curve of material

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with core composition. However, because of the very elevated pressure and temperature, such experiments are difficult to perform. Many workers have, therefore, chosen firstly to investigate the melting curve of pure iron, but even for this 'simple' material, there is a considerable disagreement between the results from different experiments and from computer simulations.

There have been several attempts to determine the melting curve of iron, including experiments using diamond anvil cells (DAC) [4] and shock techniques [5], as well as theoretical calculations [6, 7]. There are severe disagreements between different melting curves, in some cases by more than $1000\,K$. Above $100\,GPa$, there seems to be two trends to the proposed melting curves. The lower trend (lower dT_m/dP values) includes the melting curves of Laio *et al.* [6], obtained by computer simulation, and the experimental curve (DAC) of Boehler *et al.* [4], whereas the higher trend includes the *ab initio* calculations of Alfè *et al.* [7] and the shock-wave data of Brown and McQueen [5]. These melting curves are further summarized by Nguyen and Holmes [2]. The large differences between the theoretical melting curves have been attributed in part to the difficulties in simulating the effects of the electronic structure of iron, specifically the effects of its outer partially-filled d-orbitals [8].

Clearly, a direct comparison, under more tractable conditions, between experiment and simulation is highly desirable. In order to address the discrepancies between the melting curves of iron, Vočadlo *et al.* have produced the first principles of melting curves for aluminium (no d-electrons) [9] and copper (full d-orbitals) [10], both of which melt at much lower temperatures than iron. An agreement between the experimental and *ab initio* melting curves for these elements would serve to validate the *ab initio* methodology used to calculate the melting curve of iron.

Unfortunately, there have been, relatively, few experimental investigations into the melting behaviour of copper at high pressures. The first reported experimental work comes from Gonikberg *et al.* [11] who reported melting temperatures to $1.7\,GPa$ using differential thermal analysis (DTA). Subsequently, Cohen *et al.* [12] employed DTA to determine melting points in a piston cylinder apparatus to $4\,GPa$. Slight discrepancies between these two data sets at low pressures are explained as being due to the alloying of the copper with its steel capsule, but the agreement between the data sets at higher pressures is good. Mitra *et al.* [13] extended the pressure range to just over $6\,GPa$, locating the melting transition by measuring a discontinuity in the electrical resistance of a copper wire encased in parallel heating strips; high pressures were achieved using a tetrahedral anvil press, the data were later confirmed by Akella and Kennedy [14]. Most recently, Japel *et al.* [8] have reported laser heated diamond anvil cell measurements from 17 to $97\,GPa$ showing reasonable agreement with the simulated melting curve of Vočadlo *et al.* [10].

The results of Japel *et al.* [8] that were published shortly after the present experiments were completed, can be viewed as complementary to those presented here. The pressure range obtainable in the DAC is much greater than that of a multi-anvil press, but the precision to which the melting temperature can be determined in a DAC is, in general, much lower. Multi-anvil experiments provide an ideal method for extending solid–medium based melting curves to pressures up to $25\,GPa$. Here we report experimental melting data for copper from ambient pressure conditions to $16\,GPa$, thus spanning the gap between the previous data and the recent high-pressure diamond anvil call experiments.

2.   Experimental method

Experiments were performed in a 1000 ton split-cylinder multi-anvil press at University College, London. Octahedral Cr-doped MgO assemblies (figure 1) were compressed by
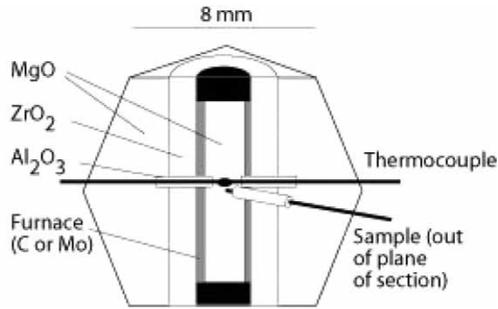
Figure 1. Section through a 14 mm edge-length octahedron used for experiments to 10 GPa. Higher pressure experiments used LaCrO3 furnaces and 10 mm cells.

Toshiba 'F'-grade WC cubic anvils. Experiments to 10 GPa (16 GPa) used 14 mm (10 mm) edge-length octahedra compressed by anvils with 8 mm (5 mm) corner truncations. The sample consisted of a 100 μm diameter 4N85 purity copper wire from Johnson Matthey. Melting was detected from a discontinuity in the resistance–temperature relationship of this wire (*e.g.* ref. [15]). An example of the observed discontinuity of resistance on melting is shown in figure 2. Experiments were not reversed, *i.e.* only the discontinuity on initial melting, and not on re-freezing, was used as a criterion for melting temperature. This risks a small metastable overstep in the melting temperature (considerably smaller than the precision of the current experiments), but reduces the risk of spurious results from contamination of the copper sample. Similarly, only one melting measurement was performed per experiment.

The thermocouple and sample wires were introduced into the hot spot of the furnace in a radial geometry within 500 μm diameter and alumina cylinders with 150 μm wall thickness for electrical insulation where the wires pierced the furnace. In the experiments below 10 GPa, graphite furnaces were used, and the Cu sample wire was used as a terminal lead for
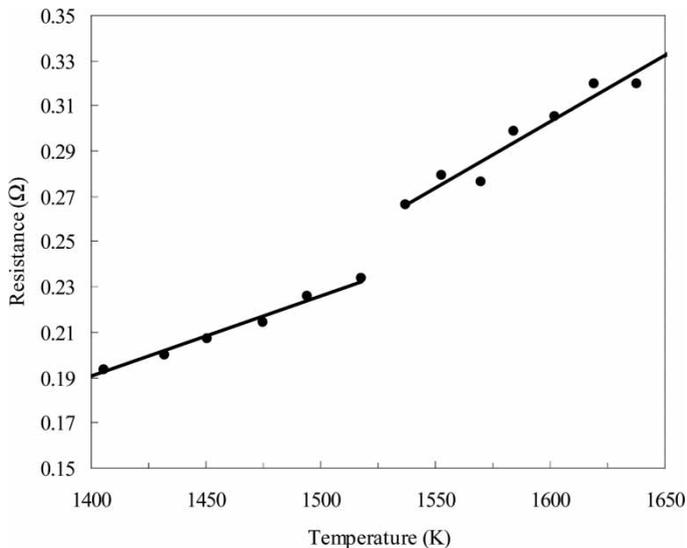

Figure 2. Example of temperature–resistance curve during copper melting experiment at 4 GPa. The solid lines are linear fits to the data above and below the melting temperature (1533 ± 13 K). There was always a positive discontinuity in resistance at melting, but the gradient of the curve could become steeper or shallower at high temperature. We believe that this is due to the deformation of the copper sample once molten.

electrodetection of melting; the thermocouple junction was within 150 μm of the Cu sample. At pressures above 10 GPa, the Cu sample wire was used to make the hot junction of the thermocouple, and the thermocouple wires were used as electrical terminals for resistance measurements. This arrangement reduced hot spots in the furnace because of holes for wire access and minimized the distance between sample and thermocouple junction. Indeed, the inspection of recovered cells confirmed that the position of melting in the sample and the thermocouple junction were always within 250 μm of each other and normally and considerably closer than this. We estimate the temperature difference between the sample and the thermocouple junction to be less than 20 K for both the cell designs. Tungsten–rhenium thermocouples (W97Re3–W75Re25) were used in all experiments. The thermocouple wire batch was calibrated from the room-pressure melting temperature of copper, which was consistently found to be within 5 K of the published value (1358 K, [16]). No correction was made for the effect of pressure on the thermocouple EMF. Furnaces were made from Mo or graphite for experiments below 12.8 GPa and from $LaCrO_3$ for higher pressures. There was no discernable effect of furnace type on the observed melting temperature.

As in some experiments, the thermocouple wires were used as leads for resistance measurements, and in order to reduce the risk of thermal run-away in case of contamination of the thermocouple by molten copper, the temperature was increased in steps by setting the power to the furnace to fixed values. The precision quoted in the results is the minimum temperature-step size, which could be achieved by this method, and which was generally and significantly larger than the other errors. For the ambient pressure experiments, the error is the range of observed melting temperatures from three experiments. The pressure was calibrated at room temperature from the transitions of Bi (I–III, 2.25 GPa; III–V, 7.7 GPa) and ZnS (15.6 GPa). The following high-temperature calibrations were performed: Fe_2SiO_4 olivine-spinel (1273 K, 5.5 GPa); coesite-stishovite (1273 K, 9.4 GPa); $(Mg_{0.9}, Fe_{0.1})_2SiO_4$ olivine-wadsleyite (1473 K, 13.5 GPa; 1873 K, 15 GPa); $MgSiO_3$ enstatite-majorite (2073 K, 16.5 GPa).

3.   Results and discussion

The experimental results are shown in table 1 and compared with an earlier work in figure 3. Data were collected using a series of furnaces, which have a variety of different current and voltage characteristics. The results obtained were identical despite the changes in furnace composition, showing that there is no systematic offset because of leakage current. For the ambient pressure experiments the error shown in table 1 (± 5 K) is the range of observed

Table 1.   Melting points of copper from multi-anvil experiments.

Pressure (GPa)	Melting temperature (K)	Furnace
0	1354 (5)[†]	–
4	1533 (13)	Mo
6.9	1628 (18)	Mo
9.8	1753 (23)	graphite
12.8	1803 (15)	graphite
12.8	1823 (50)	$LaCrO_3$
16	1923 (15)	$LaCrO_3$

Note: Errors in parentheses.
[†]Experiment performed outside the press, but using the same batch of tungsten–rhenium thermocouple wire.
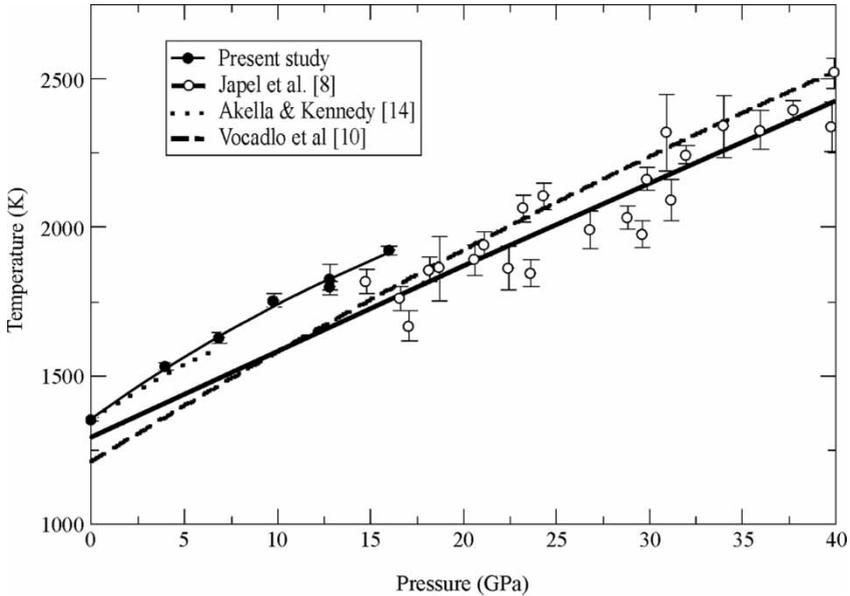
Figure 3. Melting temperature of copper. The experimental data from the present study are shown as filled circles with a bold line; the piston–cylinder experiments of Akella and Kennedy [14] are given by a dotted line; the diamond anvil cell experiments of Japel *et al.* [8] are shown as open circles with a solid line and the *ab initio* melting curve of Vočadlo *et al.* [10] is represented by a heavy dashed line. For clarity, only the first 40 GPa of the data of Vočadlo *et al.* [10] and Japel *et al.* [8] have been presented here, but the curves presented here have been fitted to the full pressure range.

melting temperatures from three experiments; for the high pressure experiments, the errors quoted represent the uncertainties arising from the thermal gradients and the minimum power increment possible.

Figure 3 shows that the results obtained here are identical, within error, to previous experiments at pressures below 7 GPa [12–14]. A further indication of the reliability of our high–pressure data can be obtained by extrapolating the melting temperatures obtained from the multi-anvil press to zero pressure, using a second-order polynomial fit (obtained by weighted non-linear least squares); this yields a value of 1400(38) K for the melting temperature at 1 atm, in good agreement with the published value (1358 K, [16]). The recent diamond anvil measurements [8] and *ab initio* simulations [10] of Cu-melting fall some 175–200 K below the present results.

Diamond anvil cell measurements and computer simulations are currently the main techniques for addressing the melting curve of iron under Earth's core conditions, which are significantly beyond low-pressure solid-media techniques used here and in previous studies. However, the present results do cover a sufficiently large pressure range to assess the first-order of the pressure dependence of the melting temperature in copper. Fitting the data in table 1 (including the value at P = 0) by weighted non-linear least squares to a second-order polynomial gave the relationship

$$T_{\mathrm{m}} = 1355(5) + 44.5(31)P - 0.61(21)P^2$$

with T_{m} in Kelvin and P in GPa; the figures in parenthesis are the estimated standard errors in the coefficients, referring to the least-significant figures (to aid reproducibility of calculations,

the coefficients for P and P^2 are quoted to one more significant figure than is justified by their precision). Thus at $P = 0$, we obtain a value of dT_m/dP of 45(3) K GPa^{-1}, whereas at 16 GPa, $dT_m/dP = 25(7)$ K GPa^{-1}. Our value of dT_m/dP at $P = 0$ is in excellent agreement with the experimental result of Mitra *et al.* (42 K GPa^{-1}, [13]), but somewhat higher than that of Akella and Kennedy (36.4 K GPa^{-1}, [14]) and Cohen *et al.* (36 K GPa^{-1}, [12]). In addition, the value from *ab initio* simulation of dT_m/dP (at 0 GPa) of Vočadlo *et al.* (38 K GPa^{-1}, [10]) falls within the range from 'low-pressure' experiments. The absolute value of T_m at $P = 0$ from ab initio calculations is expected to be ∼9% too low, because of the inherent limitations in the description of the exchange correlation energy in density functional theory (see ref. [10] for further discussion of this effect); neglecting this offset, these *ab initio* results follow a very similar trend to our experimental values, although they appear to show less curvature than our experiments, with dT_m/dP reducing by only 4 K GPa^{-1} (*i.e.* to 34 K GPa^{-1}) at 16 GPa.

The DAC measurements of Japel *et al.* [8], however, produce $T_m = 1311(69)$ K, when extrapolated to $P = 0$ (second-order polynomial, weighted least-squares fit) but give a value for dT_m/dP (at 17 GPa) of 28.1(35) K GPa^{-1}, close to our value at similar pressure. However, in these measurements, there is very little pressure dependence of the second derivative of the melting curve, d^2T_m/dP^2, (this is best seen when viewing the entire dataset that extends to ∼100 GPa), the coefficient of P^2 in the polynomial fit to all their data, −0.002(40) K GPa^{-2}, being effectively zero (values given are estimates based on the data extracted from the figures in ref. [8] as no numerical values for T_m *vs.* P are given). While there is a close agreement in dT_m/dP between our results at 16 GPa and those of Japel *et al.* [8] at 17 GPa, we believe that this is fortuitous, given the considerably different second derivatives in the two studies. There is a larger temperature error in the technically challenging diamond-cell experiments, which could add errors to higher order polynomial fits to such data, however, this should be largely mitigated by the wide pressure range available in the diamond cell (the data in ref. [8] spanned 80 GPa). We find it difficult, therefore, to understand the cause of the vanishingly small second derivative of the melting curve observed in the diamond cell study [8].

4. Summary

We have determined the melting curve of copper from ambient pressure to 16 GPa using multi-anvil techniques. The melting curve obtained is in good agreement with the previous experimental studies using multi-anvil cells, but agrees less well with recent results from diamond anvil cells. The ultimate aim of this study was to provide data that might be used to validate *ab initio* methodology for calculating melting curves. Apart from the expected offset in T (see [10] for discussion), the present results show good agreement with the simulated melting curve of Vočadlo *et al.* [10] and so, lend support for the usefulness of *ab initio* methodologies to study other melting curves, such as that of iron, for which a direct experimental measurement is difficult.

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