Correction of the pressure scales reliant to the thermal pressures shifts in iron (3d) vanadium (4d), iridium and platinum (5d) transition metals

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Abstract
In many published articles isobaric behavior in DAC chambers has been reported. On the other hand, a clear isochoric behavior in the chambers were reported. Thus, isochoric or isobaric condition remain an open question. In isochoric condition, upon increasing the temperature, at each pressure, the examined sample and the PTM both are subject to increases of their volumes which is suppressed by the chamber finite volume, provoking an increase in the thermal pressure over the whole system. For this reason, the pressure scale reported in DAC experiments do not represent the actual pressure experienced by the sample in the cell. The different response of the PTM’s to P,T changes is the reason for the variety of melting curves reported in the literature. It is concluded that the pressure scale in DAC experiments need a correction taking in to account the thermal pressure shift. Trusting the first principals DFT- Z methodology it is shown that the melting curve derived by this method should serve as an anchor for the pressure scale correction.
1. Introduction

In previous papers[1, see Appendix], it was argued that if isochoric conditions exist in diamond anvil cell (DAC) chambers the increasing of the applied temperature should provoke additional thermal pressure. However, in many published articles isobaric behavior was reported. Thus, isochoric or isobaric condition in the DAC’s chamber remains enigmatic. In the present contribution we argue that the pressure transmitting medium (PTM) and the packing procedure of the examined sample lead to these discrepancies.

In practice, a mechanical pressure gauge to measure thermal pressure does not exist. Therefore, the actual pressure must be estimated, either from the pressure shift of each measured point relative to the initial ambient pressure, or from first principles calculations of the lattice component in the P-V-T equation of state [2]. DFT ab initio simulations reveal good approximations to the actual pressure at the melt. Direct determination of the thermal pressure and temperature derived from experimental results were recently reported for iron [3], vanadium [4,5], iridium [6] and platinum [7]. This allows the extrapolation of the thermal pressure and the thermal temperature up to melt, thus correcting the pressure scale according to the actual pressure in the DAC’s chamber.

Many experiments have shown that the melting curves of the same element measured by laser-heated DAC (LH-DAC) in different experiments, reveal different melting curves using different packing related to different PTMs [1,8]. The pressure medium is expected to distribute the pressure homogeneously within the pressure chamber, preventing non-hydrostatic effects such as, pressure gradients, shear stress, or inhomogeneous pressure. Upon increasing the temperature at each pressure, however, the examined sample and the PTM both are subject to increases of their volumes. Nevertheless, the volume expansion is suppressed by the chamber finite volume, provoking an increase in the thermal pressure over the whole system. In some cases, the PTM melts and remains liquid during the whole experiment [1]. Therefore, the pressure reported in many publications do not necessarily represents the actual pressure experienced by the sample. Therefore, the different responses of the PTM’s to P,T changes must be taken into account and the pressure scale of reported melting curves should be corrected according to the actual pressure in the cell.
2. Analysis of the published data.

All the presented data in the present paper were downloaded and analyzed using B. Tummers, datathief [9]. The obtained melting curves were fitted by applying the constraint that the fitting volume parameter V of the experimental equation of state (EOS) at ambient temperature, must simultaneously fit the experimental melting and the EOS data where the Grüneisen parameter $\gamma$ is a fitting parameter assigned in the manuscript “combined approach” [see Appedix]. The corroboration of this fitting procedure is checked by the ab initio DFT-Z methodology [10].

2. $\varepsilon$- Iron

The isochoric behavior reported R. Sinmyo et al. (2019) [3] depicted in Fig.1(a) totally contradicts the isobaric behavior of $\varepsilon$ iron in laser heated DAC claimed by Anzellini et al. [11]. The reason of this discrepancy comes from the packing of the iron foil with $\text{Al}_2\text{O}_3$ PTM compared to the behavior of $\text{KCl}$ PTM in Anzellini’s experiment.

The melting curve reported by R. Sinmyo et al. (2019) [3] of iron metal $\varepsilon$-phase is depicted in Fig.1. The green squares in (a) are the melting data reported by Anzellini et al. [11], therein Fig.2. The black O are the experimental results obtained by Tateno et al. [12].The brown O’s are SW data of Nguyen and Holmes [13]. The red solid line is the melting curve extrapolated to high pressures and temperatures obtained by the combined approach. Note that the extrapolated melting curve in Fig.1(a) match the SW data of Nguyen and Starikov [13,14]. The corrected melting pressure and temperature scale, based on ab initio DFT-Z methodology [10], as deduced from Fig.1(a) and is displayed in Fig.1(b).
Fig. 1: Corrected pressure scale of iron metal. (a): Green squares and brown circles present the experimental DAC and shock waves reported by Anzellini et al. [11] and Nguyen et al. [13] fitted by adopting the combined approach constraint (red solid line). The pressure-temperature thermal increase colored asterisks were reported R. Sinmyo et al. (2019) [3]. The black O’s present Tateno et al. experimental results [12]. (b): Pressure – temperature corrected scale derived from (a) marked by the red asterisks.

The isochoric behavior of iron in the packing proposed by R. Sinmyo et al [3] is clearly observed in Fig.1(a). In addition, the linear behavior of the temperature increase as theoretically predicted by the P-V-T equation of state [2] is experimentally confirmed (Fig.1(a)).
Vanadium

The melting curve of vanadium reported by Y. Zhang et al. [18] was determined by in-situ x-ray diffraction in a LH-DAC and is depicted in Fig. 2 [therein Fig.4]. The magenta and blue solid lines present the melting curve of V fitted with the combined approach constraint, which is confirmed by the first principles simulations (DFT-Z method [10]). The colored asterisks represent the thermal pressure shifts as a function of the applied temperature at each pressure. The dashed black lines represent the 300K applied pressures. The angle (difference) between the dashed lines and the asterisk points, indicates that indeed thermal pressure (P_{th}) is provoked by increasing the temperature, thus confirming the assumption that isochoric conditions exist in the present DAC chamber with KCl PTM. The horizontal double arrow lines indicate the pressure thermal shifts (P_{th}) pinched to the melt. The temperature increase is marked by short green solid line.
**Fig. 2(a):** Thermal pressure at several applied pressures of vanadium metal. The red and blue solid lines represent the melting curve of V fitted with the combined approach approximation which further is confirmed by DFT-Z method simulation. The blue squares are the experimental melting points derived LH-DAC with V embedded in a liquid NaCl PTM [19]. The black diamonds represent V embedded in a solid KCl PTM. The 100 GPa melting point is V embedded in a MgO PTM. The colored asterisks are the thermal pressure shifts as a function of the applied temperature, reported by Y. Zhang [18]. The dashed black lines present the 300K initial applied pressures. The angle between the dashed lines and the asterisk points, indicates the thermal pressure ($P_{\text{th}}$) provoked by the increase of the temperature; while the horizontal double arrows indicate the thermal shifts ($P_{\text{th}}$). The bright green solid lines demonstrate the further increase of the temperature while crossing the melting curve. (b): The corrected pressure-temperature scales are derived from (a).

The contribution of Y. Zhang at al. [18] clearly demonstrates that all the experimental SW and the DAC data reported to-date, need corrections. As shown, there is no discrepancy between the static DAC and the dynamic SW measurements of V, if the calculated thermal correction of the cold experimental data and the radiation absorption by the LiF window, are taken correctly into account. The proposed approach is indeed confirmed by first principles, using the *ab-initio* DFT-Z method simulation [10].

**Iridium**

Iridium (Ir) have always attracted considerable interest in the scientific community due to its outstanding elastic and thermal properties. It is one of the most incompressible transition metal exhibiting face-centered cubic (fcc) structure up to 78 GPa with measured a bulk modulus $B_0 = 341(3)$ GPa [20]. Above $\sim$78GPa the r-hcp structure is dominant up to 600 GPa [21]. At room temperature (RT) Ir exhibits a density of 22.56 g/cc, and a shear modulus, $G_0 = 210$ GPa. Thus, thanks to its high shear modulus, chemical inertness, refractory nature, and phase stability, Ir is ideally suited for crucibles and thermocouples. The melting curve of fcc iridium up to 80 GPa is depicted in Fig.3(a) and the thermal corrected scale is shown in Fig.3(b). In addition, recent theoretical studies based on *ab initio* simulations [21] predict a second order phase transition to happen at $\sim 2000 \text{ K}$ and 150 GPa from fcc to a disordered hexagonal close-packed phase (r-hcp) as shown in Fig.3(c). The extrapolation of the combined approach up to 600 GPa (red solid line) with the fitting parameters 341/4.4/2.55 corroborate the assumption of L. Burakovsky [21,22] that the transition fcc to r-hcp relate to 5d electron rearrangement.
Fig. 3: (a) Experimental pressure – temperature dependence at 26 and 36 GPa of fcc Ir [18]. The melting curve is determined by theoretical DFT-Z method simulations [10]. The double arrows indicate the measured thermal shifts at the melt relative to the measured pressure marked by the dashed lines. (b) Ir melting curve, corrected pressure scale derived from Fig. 3(a). The blue solid line represents the constrained Lindemmann-Gilvarry melting formula with Vinet EOS (combined approach) assigned in the figure ($B_0, B'_0, \gamma_0$) 341/4.4/2.55 where $\gamma_0$ is a fitting parameter. The dashed lines represent the initial pressure as measured experimentally. The magenta solid line presents the DFT-Z simulation (L. Burakovsky [10]). (c): The blue asterisks presents the QMD-Z method calculations for the fcc and r-hcp phases. In the inset the of fcc Ir fitted by the third order Birch-Murnaghan (BM) and Vinet (V) EOS. The extrapolation of the combined approach up to 600 GPa (red solid line) with the fitting parameters 341/4.4/2.55 corroborate the assumption of L. Burakovsky that the transition fcc to r-hcp relate to 5d electron rearrangement revealing the loss of fcc-Ir stability which converts, by a second order phase transition, to the hexagonal structure.
Platinum

Perhaps the most interesting of the 5d series is platinum as it exhibits fcc to r-hcp phase transition upon increasing the pressure as shown in Fig.4.

Recent reported thermal shifts by Anzellini et al. [7] (therein Fig.6), a difference in the pressure shifts between the fcc and r-hcp phases is clearly recognized as demonstrated in Fig.4(a). The corrected pressure scale as derived from (a) (colored double arrows) is proposed in Fig.4(b).

![Fig.4](image)

Fig.4: (a) Melting curve platinum based on the DFT-Z method (green pentagrams) compared to the combined approach utilizing the EOS parameters proposed by Zha et al. [26] (red solid line). $\gamma_0$ is a fitting parameter marked in the figure 273/4.2/2.63. (b) Corrected melting scale of platinum (r-hcp structure) pinched to the melt.
Discussion

In many published articles isobaric behavior in DAC chambers has been reported [7,11]. On the other hand, in the present contribution we have demonstrated clear isochoric behavior of the chambers. Thus, isochoric or isobaric condition in the remain an open question. In the present contribution we argue that the pressure transmitting medium (PTM) and packing procedure of the of the examined sample could explain this discrepancy.

Iron: In iron metal the volume expansion while raising the temperature and pressure, as reported by Anzellini et al., relates to the fact that approaching the melt from the solid with KCl PTM, a mixture of the $\varepsilon, \beta, \gamma$ phases exist [14]. The existence of the $\gamma$ phase at high pressures and temperatures have been reported by Mikaeylushkin et al. [15] showing that the $\gamma$ phase can exist even at 165 GPa when quenched to room temperature (RT). In addition, S.K. Saxena al al. [16] reported observation of the $\beta$ phase above 110GPa and 3000K. Deep look in to Fig.1a of Anzellini et al. reveal that at 133GPa and 4292K (green dots) at the angle 11.58(2$\Theta$) there exist a possible reflection which is ignored by the authors. This reflection could be analyzed as (111) gamma ($\gamma$) phase or dhcp (100) ($\beta$) phase. Thus, while approaching the melt from the solid iron a possible mixture of $\varepsilon, \beta, \gamma$ phases exist. This explains the discrepancy between Anzellini et al. [11] and Sinmyo et al. [3].

Vanadium: In the vanadium case, the actual pressure in the LH-DAC chamber can be estimated from first principles calculations utilizing the P-V-T equation of state [2]. However, the use of experimental data to directly determine the actual pressure at the melt in a LH-DAC experiment, has not, up to now, been possible. In the present contribution, a method to directly derive the thermal pressure and the thermal temperature pinched to the melt is proposed. The corrected scale (actual pressure) of V melting curve is depicted in Fig.2(b). Note that the experiment proposed by Zhang et al. was performed with KCl PTM [18], while the experiment reports by D. Errandonea et al. was performed with NaCl PTM [19].

Iridium: In the case of iridium, the extrapolation of the combined approach up to 600 GPa (Fig.3(c) red solid line) with the fitting parameters 341/4.4/2.55 corroborate the assumption of L. Burakovsky that the transition fcc to r-hcp relate to 5d electron
rearrangement revealing the loss of fcc-Ir stability which converts, by a second order phase transition, to hex structure, with a layer stacking BACBCBACABCBC [21].

**Platinum:** The elastic properties of platinum show high density, low strength, usually used as crucibles at low temperatures. In addition, platinum is used as pressure standard in DAC high pressure X-ray experiments as well as high-pressure shock experiments. There have been earlier reports of experimental melting curve for Pt. However, the melting curves established by the various experimental studies [23] do not agree even within the experimental errors.

The difference in the thermal pressure shifts between the fcc and r-hcp is clearly observed as demonstrated in Fig.4(a) permitting to correct the melting scale of Pt (r-hcp structure) pinched to the melt.

**Conclusions**

The pressure scale reported in DAC experiment do not represent the actual pressure experienced by the sample in the cell. The different response of the PTM’s to P,T changes is the reason for the variety of melting curves reported in the literature.

Trusting the first principals DFT- Z methodology it is shown that the melting curve derived by this method should serve as an anchor for the pressure scale correction.

While deriving the actual pressure sensed by the explored sample the thermal pressure shifts must be taken into account when constructing the melting curve.

The corrected pressure scales for metallic Fe (3d), V (4d), Ir and Pt (4d) transition metals are presented for the first time.
References

[1] Joseph Gal, Physica B condensed matter, Vol. 619,413082 (2021)

[2] L.V. Altschuler, S.B. Kormer, A.A. Bakanova and R.F. Trunin
Soviet Physics JETP, Vol. 11(3) (1960) 573.

[3] R. Sinmyo, K. Hirose, Y. Ohishi,
Earth and Planetary Science Letters, Volume 510, 15 March 2019, Pages 45-52

“Melting curve of iron to 290 GPa determined in a resistance-heated diamond-anvil cell: implications for the Earth and planetary core”

[4] D. Errandonea, S. G. MacLeod, L. Burakovsky, D. Santamaria-Perez, J. E. Proctor, H. Cynn, and M. Mezouar,
PHYSICAL REVIEW B 100, 094111 (2019)

“Melting curve and phase diagram of vanadium under high-pressure and high-temperature conditions”

[5] Joseph Gal, Physica B: condensed matter, Volume 619, 15 October 2021, 413082

“LLPT in molten Ar (see Vanadium)”

[6] Simone Anzellini, Leonid Burakovsky, Robin Turnbull, Enrico Bandiello and Daniel Errandonea,
Crystals 2021, 11 452

“P–V–T Equation of State of Iridium Up to 80 GPa and 3100 K”

[7] S. Anzellini, V. Monteseguro, E. Bandiello, A. Dewaele, L. Burakovsky and D. Errandonea,
Nature Scientific Reports (2019) 9:13034

“In situ characterization of the high pressure – high temperature melting curve of platinum”
[8] A.Dewaele, M. Mezouar, Nicolas Guignot and Paul Loubeyre, PRL 104, 255701 (2010).
“High Melting Points of Tantalum in a Laser-Heated Diamond Anvil Cell”

[9] B. Tummers, DataThief III. 2006 <https://datathief.org>

[10] L. Burakovsky, S.P. Chen, D.L. Preston and D.G. Sheppard, Journal of Physics: Conference Series (2014 ) 500 162001Z
“Z-methodology for phase diagram studies: platinum and tantalum as examples”

[11] S.Anzellini, A.Dewaele, M.Mezouar, P.Loubeyre, G.Morard VOL 340, 326 SCIENCE 2013.
“Melting of iron at Earth's inner core boundary based on fast X-ray diffraction”

[12] S. Tateno, K. Hirose, Y. Ohishi, Y. Tatsumi, SCIENCE VOL 330 (2010)
“The Structure of Iron in Earth’s Inner Core”

[13] J.H. Nguyen and N.C. Holms, Nature 427339(2004).
“Melting of iron at the physical conditions of the Earth's core”

[14] Sergey V. Starikov and Vladimir V. Stegailov PHYSICAL REVIEW B 80, 220104R (2009)
“Atomistic simulation of the premelting of iron and aluminum: Implications for high-pressure melting-curve measurement”
[15] Joseph Gal, arXiv:1912.06182 (2019)

“Melting curves of Al,Cu,U and Fe metals utilizing the Lindemann-Gilvarry criterion and parameterization of the equations of state”

[16] A.S. Mikhaylushkin, S.I. Simak, L. Dubrovinsky, N. Dubrovinskaia, B. Johansson, and I.A. Abrikosov
PRL 99, 165505 (2007)

“The existence of the γ phase at high pressures and temperatures”

[17] S. K. Saxena, L. S. Dubrovinsky Yoo, C. S. J. A. Akella, J. Campbell, H. K. Mao, R. J. Hemley,
Technical note-Science 275 (1997) 46,

“Observation of the β phase above 110GPa”

[18] Y. Zhang, Y. Tan, H.Y Geng, N.P Geng, N.P Salke, Z.Gao, J. Li, T. Sekine,
Q. Wang, E.Greenberg, V.B Prakapenka, J.F. Lin,
PR B 102, 214104 (2020) (KCl PTM)

“Melting curve of vanadium up to 256 GPa: Consistency between experiments and theory”

[19] D. Errandonea, S. G. MacLeod, L. Burakovsky, D. Santamaria-Perez, J. E. Proctor, H. Cynn, and M. Mezouar,
Phys. Rev. B 100, 094111 (2019)

“Melting curve and phase diagram of vanadium under high-pressure and high-temperature conditions” (NaCl PTM).

[20] S. Anzellini, L. Burakovsky, R. Turnbull, E. Bandiello and D. Errandonea,
Crystals, 11, 452. (2021)

“P–V–T Equation of State of Iridium Up to 80 GPa and 3100 K”
[21] L. Burakovsky, N. Burakovsky, M. J. Cawkwell, D. L. Preston, D. Errandonea, and S. I. Simak,
PHYSICAL REVIEW B 94, 094112 (2016),
“Ab initio phase diagram of iridium”

[22] L. Burakovsky, M. J. Cawkwell, D. L. Preston, D. Errandonea and S. I. Simak,
Journal of Physics: Conf. Series; Volume 950 042021(2017)
“Recent ab initio phase diagram studies: Iridium:

[23] Nishant N Patel and Meenakshi Sunder
AIP Conference Proceedings 1942, 030007 (2018)
“High Pressure Melting Curve of Platinum up to 35 GPa”

[24] D. Errandonea,
PRB B 87, 054108 (2013)
“High-pressure melting curves of the transition metals Cu, Ni, Pd, and Pt”

[25] A. Kavner and R. Jeanloz,
J. Appl. Phys. 83, 7553 (1998).
“High-pressure melting curve of platinum”

[26] Chang-Sheng Zha, Kenji Mibe,William A. Bassett, Oliver Tschauner, Ho-Kwang Mao, and Russell J. Hemley,
JOURNAL OF APPLIED PHYSICS 103, 054908 (2008)
“P-V-T equation of state of platinum to 80 GPa and 1900 K from internal resistive heating/x-ray diffraction measurements”
Appendix

1. **Gilvarry-Lindemann approximation**: The Combined Approach.

According to Lindenmann’s criterion the melting temperature $T_m$ is related to the Debye temperature $\Theta_D$ as follows: Assuming a Debye solid, $T_m = C V^{2/3} \Theta_D^2$, where $V$ is the volume and $C$ is a constant to be derived for each specific metal. Assuming that $\gamma = \gamma_0 \left( \rho / \rho_0 \right)^q$ and $q=1$ one gets the approximation:
The third-order Birch–Murnaghan (BM) equation of state
\[ P(V) = \frac{3}{2} B_0 \left[ \left( \frac{V_o}{V} \right)^{7/3} - \left( \frac{V_o}{V} \right)^{5/3} \right] \left[ 1 + \frac{3}{4} (B_o' - 4) \left( \frac{V_o}{V} \right)^{2/3} - 1 \right] \]

We imply the constrain that the fitting parameter \( V \) of the experimental equation of state (EOS) at ambient temperature must simultaneously fit the experimental melting data for deriving \( \gamma_0 \).

For the reader who wants to use the combined approach the Matlab program for the vanadium case:

```matlab
dB=B'
B=B0
V=13.9:-0.086:4
Vo=13.9;
VVo=V/Vo;
A=1.5*B*(VVo.^-2.333)-(VVo.^-1.666);
C=1-(0.75*(4-dB));
D=C*((VVo.^-0.6666)-1);
E=D.*C;;
P=E.*A;
x=VVo;
Gama=1.63
EX=exp(2*Gama*(1-x));
Tm=2300*x.^0.6666;
TM=EX.*Tm;
plot(P,TM,'r')
plot(P,V,'b')
```

Here \( B=B_0, dB=B_0', \) Gama= \( \gamma_0 \) is a fitting parameter, TM is the melting curve according to the Gilvarry-Lindemann criterion.

### 2. Lindemann-Gilvarry vs. Simon-Glatzel fitting curve

The Simon-Glatzel equation is in fact combination of Murnghan EOS and Lindemann’s criterion: \( T_m = T_{ref} (B_0' (P-P_{ref}/B_0+1)^{2(\gamma-1/3)+f}, \) here \( f \) is the coefficient in Mores potential.

The advantage of the constraint Gilvarry-Lindemann procedure, as proposed in the present contribution, is that the volume, the bulk moduli and \( \gamma_0 \) are simultaneously derived.
