

Supplementary Information

The equations of state of nine materials up to 0.43 TPa for extreme pressure science

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Fig. S1

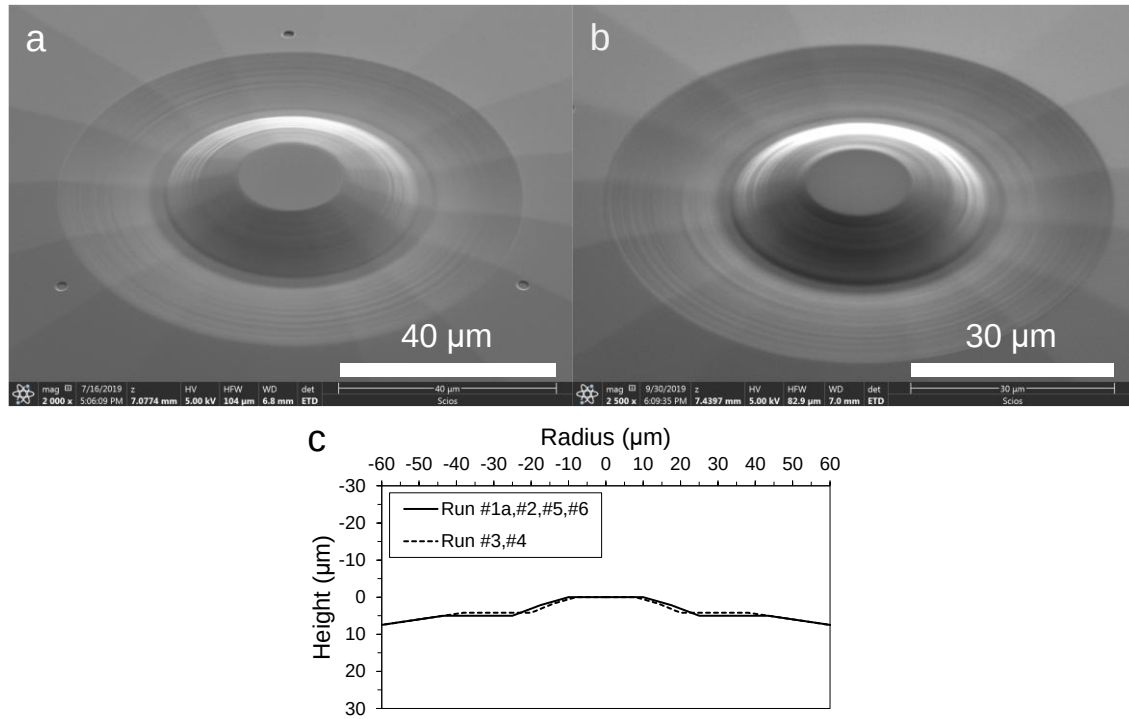


Fig. S1 | The toroidal anvil tip shape. **a,b** Scanning electron microscopic image (birds-eye image) of the toroidal diamond anvil tip with the culet size of 20 μm (**a**) and 16 μm (**b**) used in run #1a (**a**) and run #3 (**b**), respectively. **c** Profiles of toroidal diamond anvil tips used in each run. These anvil profiles are designed values, not measured ones. The height of the convex part was measured by interferometric measurement after FIB processing. The measured height agrees with the design value within ± 0.1 μm. Original anvil shapes were the culet-(bevel angle)-bevel size with 30-(8.5)-300 μm (Type Ia) for runs #1a, #3, #4, 60-(10)-350 μm for run #2 (Type Ia), and 20-(9.5)-300 μm (Type IIas) for runs #5, #6. In run #5, the conical support type of anvil seat was used. Typical ion beam current during FIB processing was 7 nA.

Fig. S2

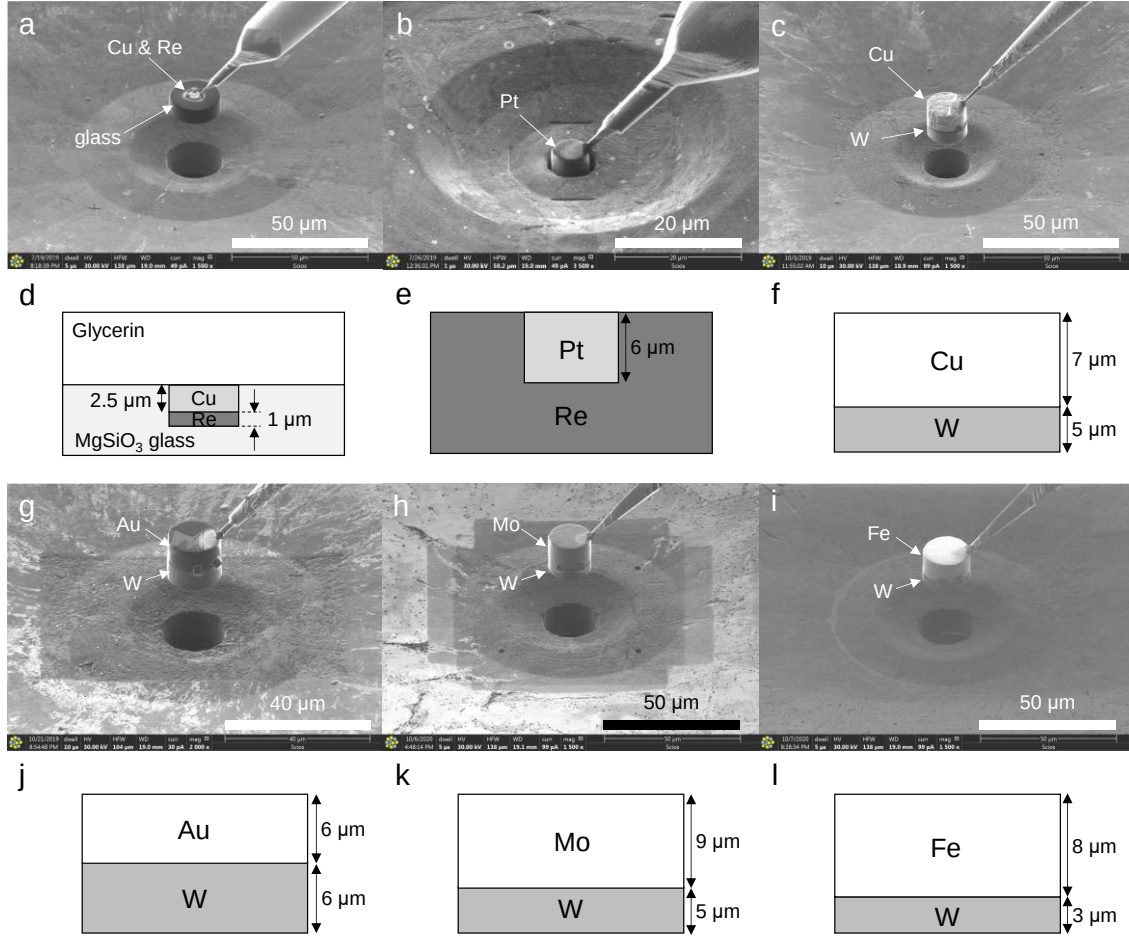


Fig. S2 | Sample configurations. **a-c** Scanning ion microscopic (SIM) images of samples used in runs #1a, #2, #3, just before filling to sample chamber, respectively. Tungsten needle was cut off from the sample after loading. Carbon deposition was used for the connection of two samples, and we did not use platinum deposition to avoid a contamination of platinum. **d-f** Schematic image of sample configurations (cross-section) for run #1a, #2, #3, respectively. **g-i** Scanning ion microscopic (SIM) image of samples used in run #4, #5, #6, just before filling to sample chamber, respectively. **j-l** Schematic image of sample configurations (cross-section) for run #4, #5, #6, respectively (not in scale). These sample configurations were just for the t-DAC runs.

Fig. S3

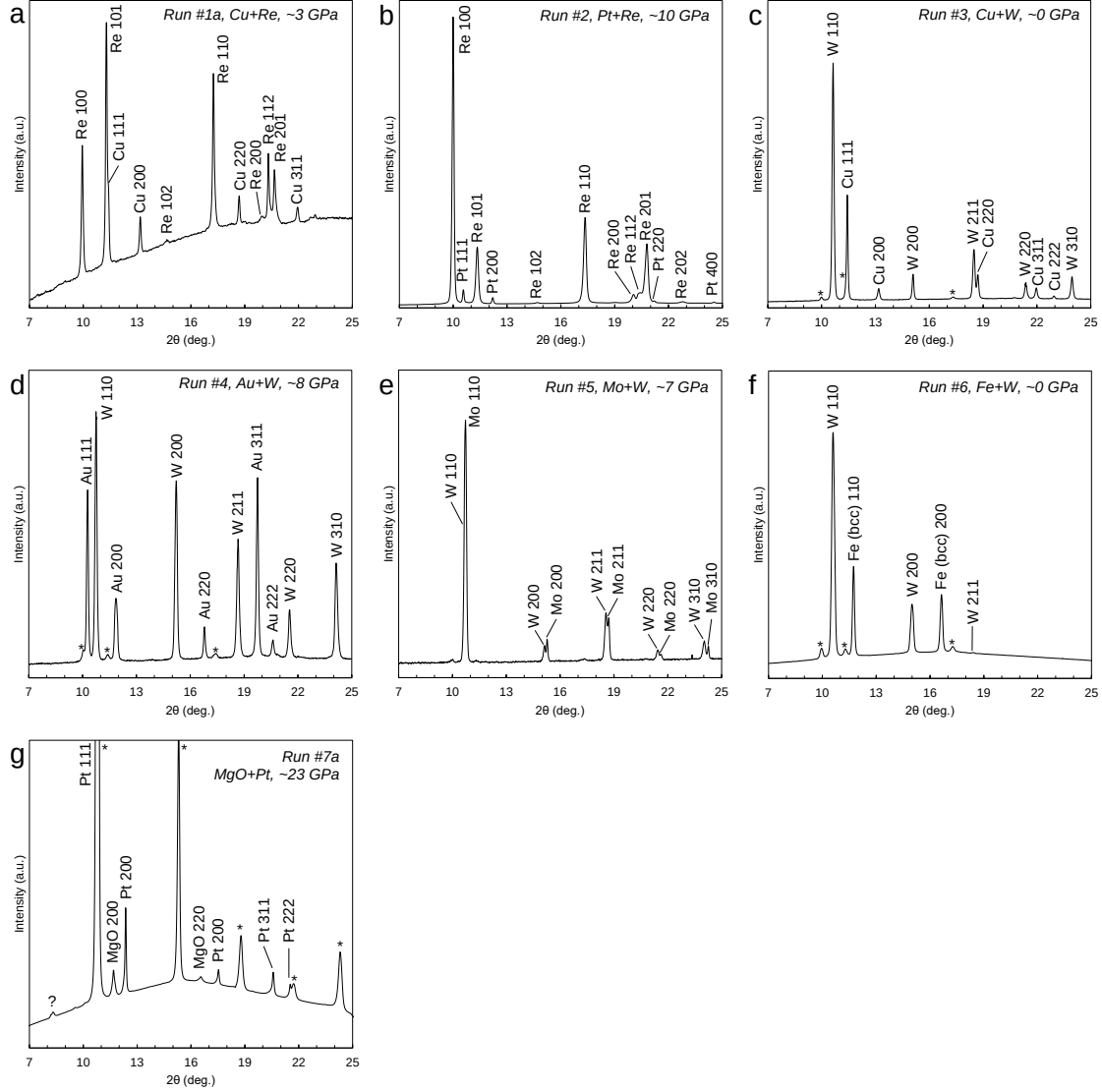


Fig. S3 | Representative XRD profiles of each run at low pressure. a-g XRD of run #1a-#7a, respectively. XRD profiles of runs #1a-#4 and #7a (and #7b, #7c) were measured at SPring-8 BL10XU, and that of runs #5 and #6 were measured at BL37XU. X-ray wavelength of each measurement was $\lambda=0.4135(2)$ (a-b), $0.4153(1)$ (c-d), $0.4137(4)$ (e-f), and $0.41297(7)$ Å (g), respectively. The number in parenthesis is the error at last digit.

Fig. S4

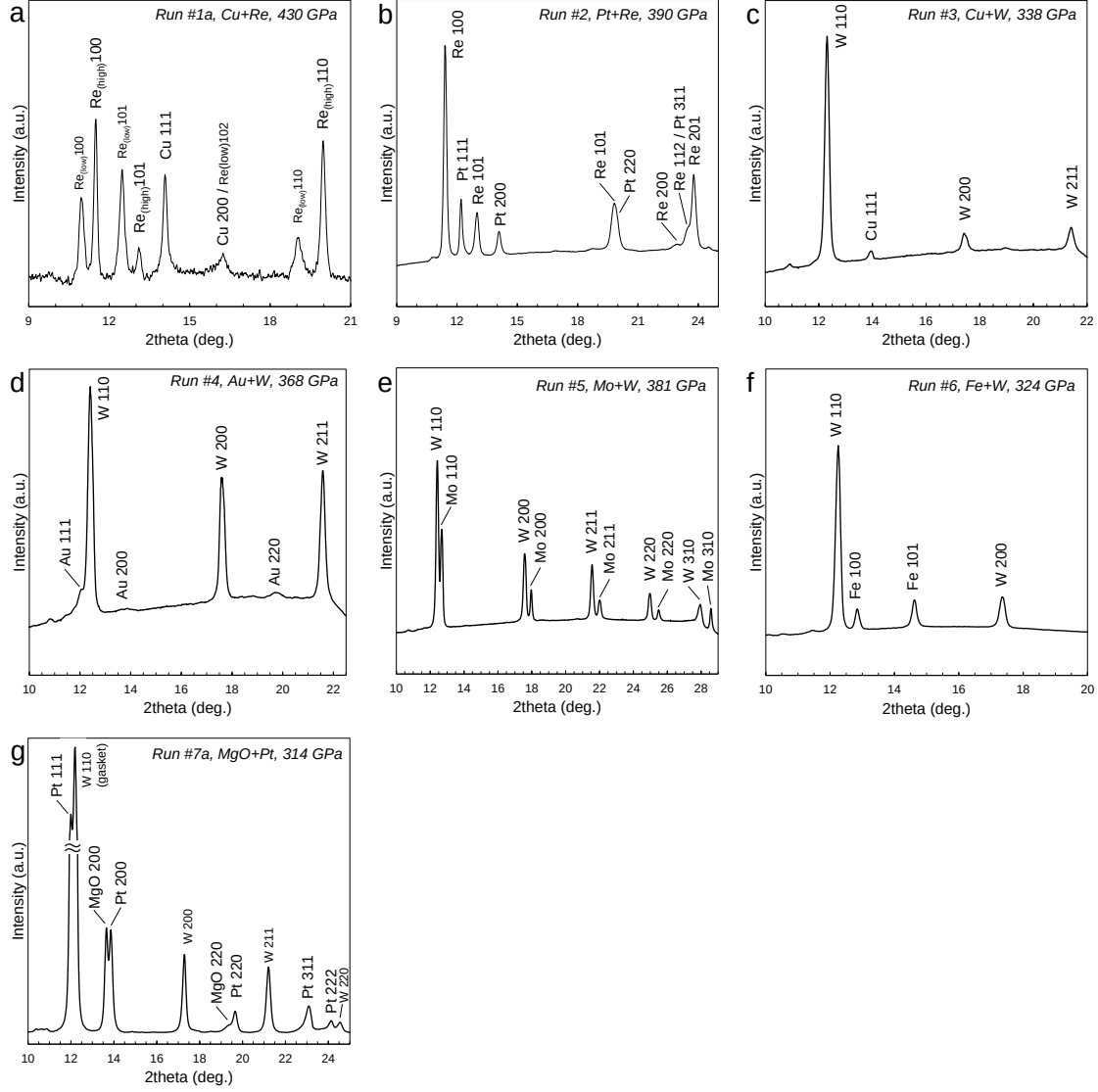


Fig. S4 | Representative XRD profiles of each run at high pressure. a-g XRD of run #1a-#7a, respectively. For run #1a, background profile was subtracted. XRD profiles of runs #1a-#4 and #7a (and #7b, #7c) were measured at SPring-8 BL10XU, and that of runs #5 and #6 were measured at BL37XU. X-ray wavelength of each measurement was $\lambda=0.4135(2)$ (a-b), $0.4153(1)$ (c-d), $0.4137(4)$ (e-f), and $0.41297(7)$ Å (g), respectively. The number in parenthesis is the error at last digit.

Fig. S5

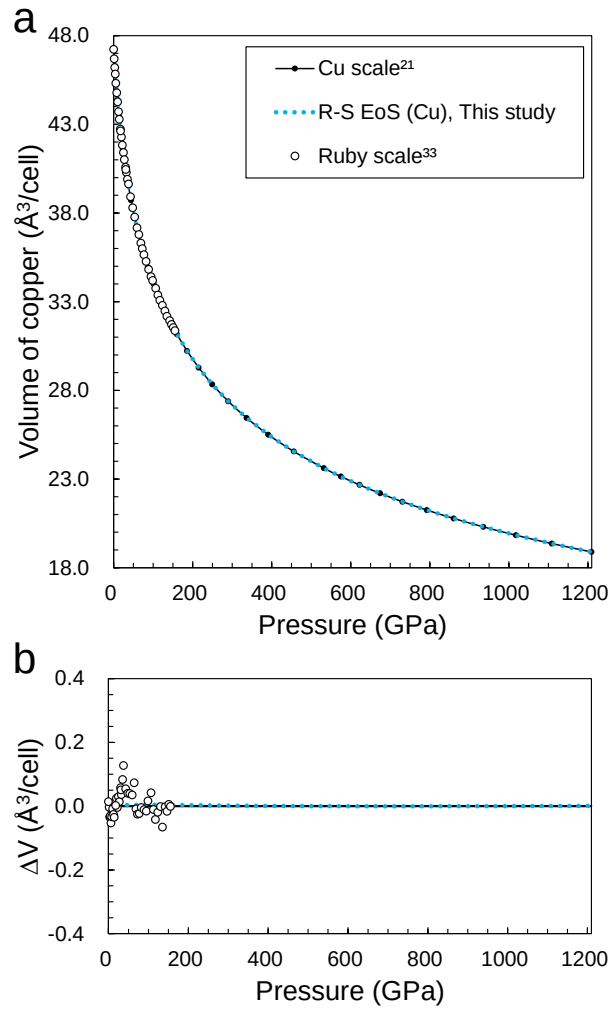


Fig. S5 | Comparison of the Cu scale²¹ and R-S EoS of Cu and ISSP-Ruby2020²⁴. **a** Compression curve of copper up to 1.2 TPa. Solid and blue-dotted curves are the copper scale²¹ and R-S EoS of Cu, respectively. Solid circles are P-V data of Cu scale used in the R-S EoS fitting. Open circles are the experimental result of static compression study³³ calibrated by Ruby scale, which is not included in R-S EoS fitting. Here Ruby scale's pressure are recalculated by IPPS-Ruby2020²⁴. **b** the volume differences relative to Cu scale²¹. The symbols and curves are the same in Figure S5a. Source data is available in Table S14.

Fig. S6

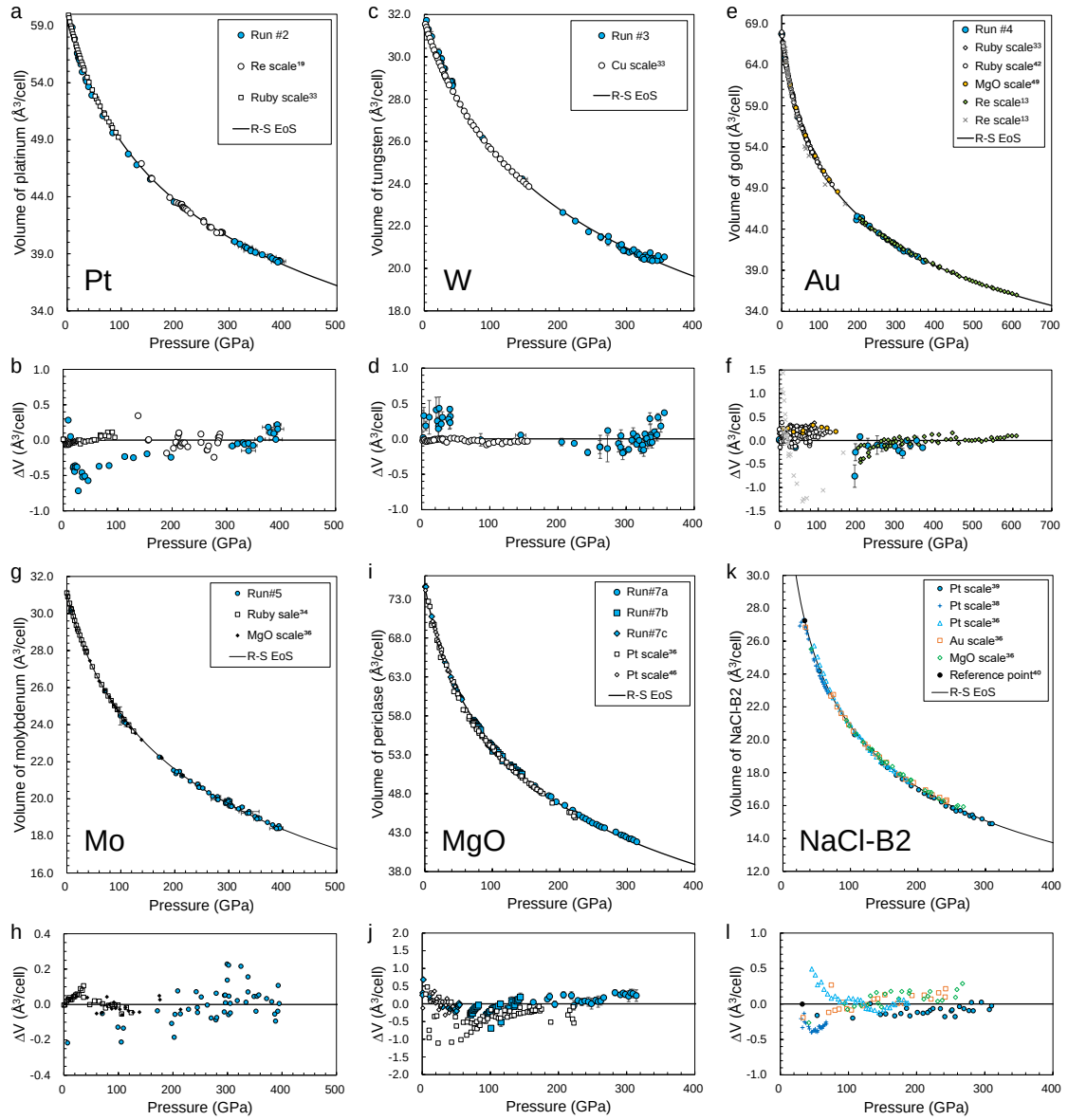


Fig. S6 | Compression curves of platinum (Pt), tungsten (W), gold (Au), molybdenum (Mo), periclase (MgO) and sodium chloride (NaCl-B2 phase). a,c,e,g,i,k (upper panels) Compression data and R-S EoS of Pt, W, Au, Mo, MgO and NaCl-B2, respectively. b,d,f,h,j,l (lower panels) Volume differences of the data relative to each R-S EoS. Each symbol is the same as the one in the figure for the respective compression curve. In (e) and (f), because the low-pressure data below 200 GPa of Dewaele et al.¹³ shows large deviation from the EoS which is thought to be caused by the inhomogeneous stress distribution during the rapid pressure increase in Stage II of the t-DAC experiment, these data (crosses) was excluded for the Au R-S EoS fitting.

Fig. S7

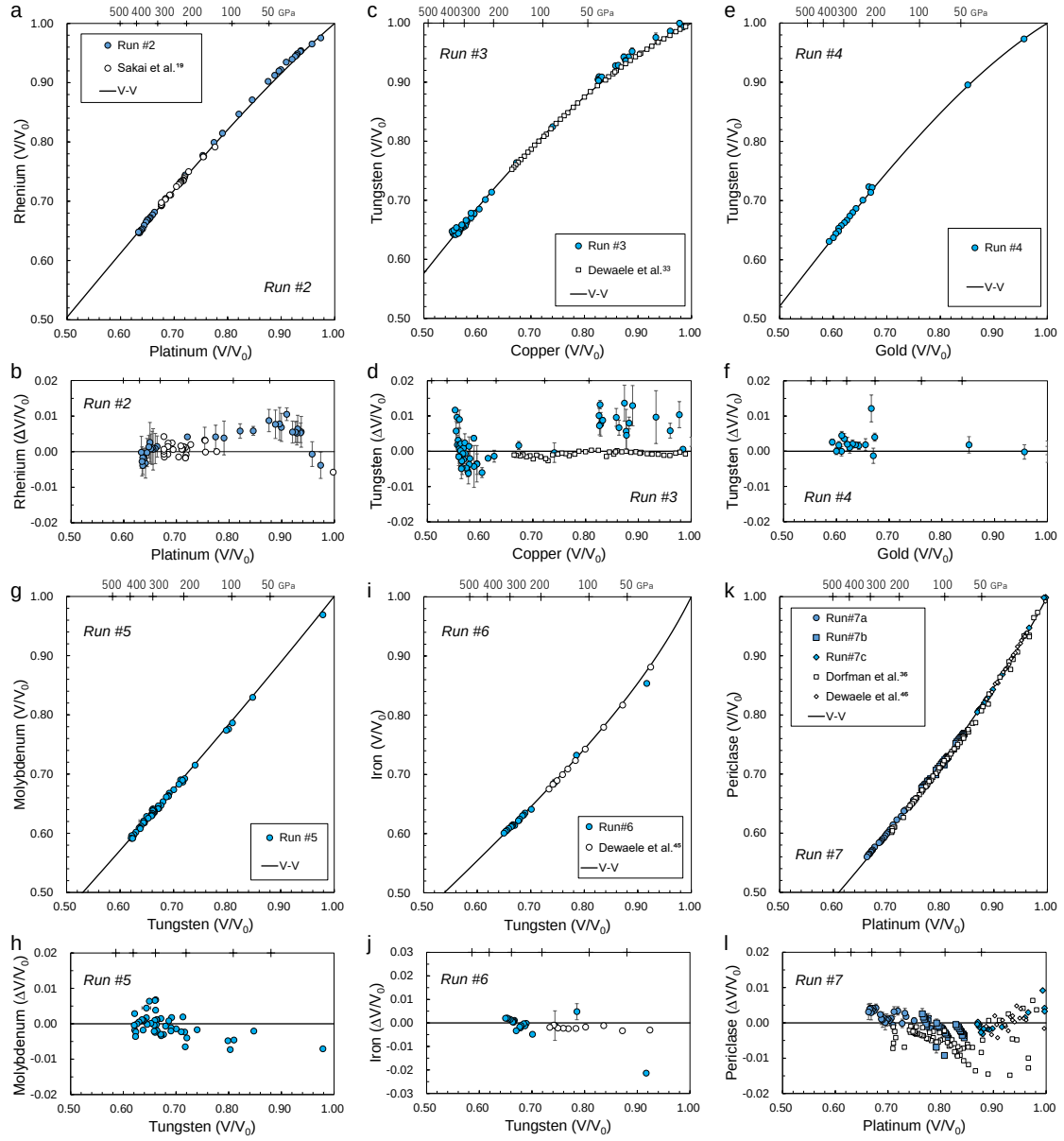


Fig. S7 | Volume-Volume relations of run #2-#7abc. a,c,e,g,i,k (upper panels) V-V data observed in each run and the V-V relation curve obtained from R-S EoSs. Crosses at the top of the figure are pressure markers corresponding to 50-500 GPa based on the EoS of this study. b,d,f,h,j,l (lower panels) The relative volume difference from the V-V curve for vertical axis's material of upper panel.

Fig. S8

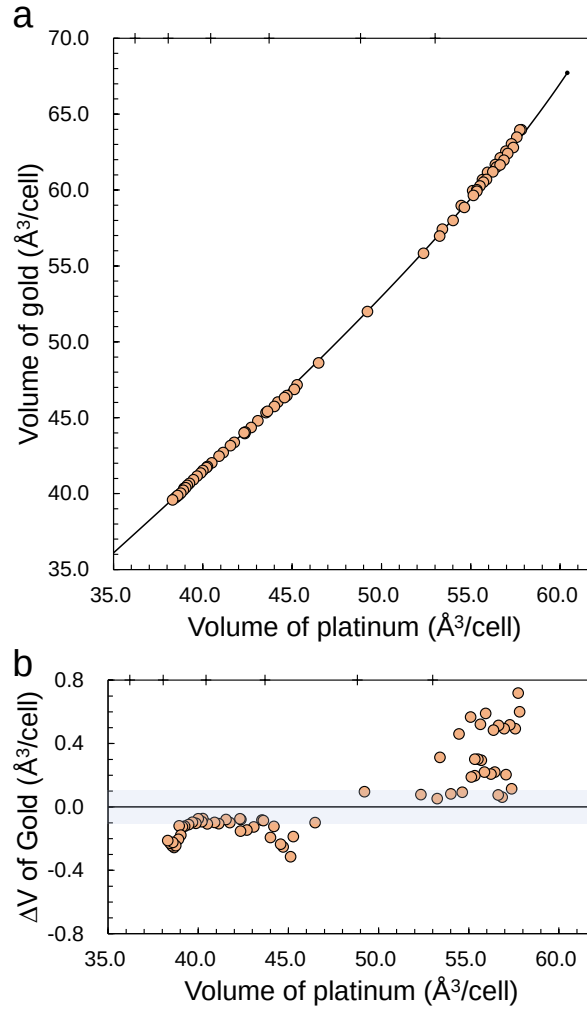


Fig. S8 | Volume-Volume relations of Au-Pt and the compression data⁵⁵. a Solid curve shows the V-V relationship between Au and Pt calculated from present R-S EoSs. Circles are the result of the simultaneous compression of Au and Pt by using t-DAC reported by Zurkowski et al.⁵⁵.

Fig. S9

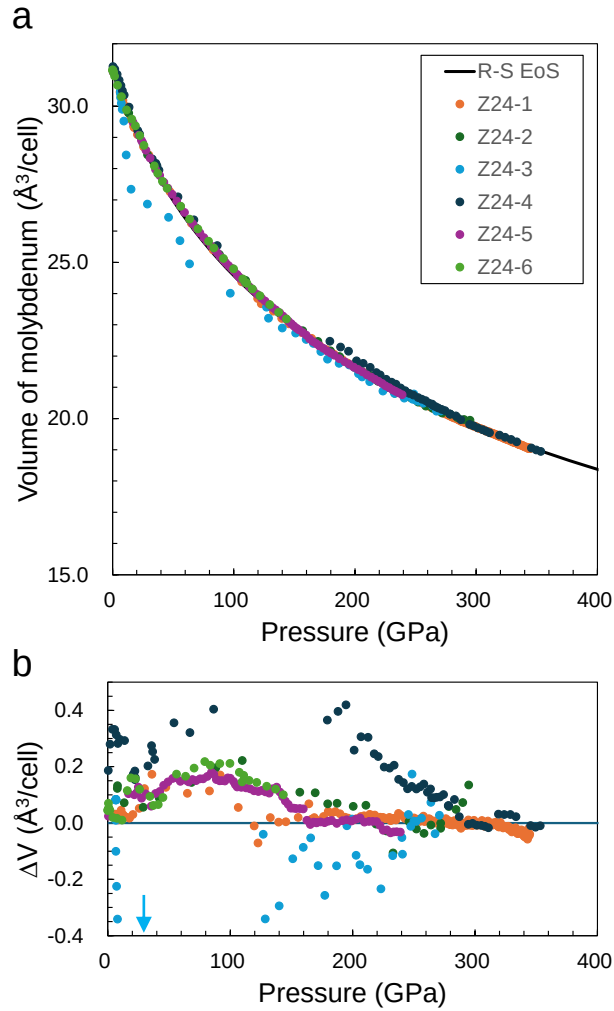


Fig. S9 | Compression curve of molybdenum comparing with the compression data of Zurkowski et al.⁵⁶ **a** Solid curve shows the R-S EoS of molybdenum of this study. Z24-1~6 are the compression data of copper and molybdenum (run1-4, t-DAC; run5-6, Ne pressure medium) in Zurkowski et al.⁵⁶ Here pressure values are recalculated by using the copper scale²¹. **b** the volume differences relative to the R-S EoS. The symbols are the same in Figure S9a. Arrow means that some data points exist at the out range of the figure in run Z24-3.

Fig. S10

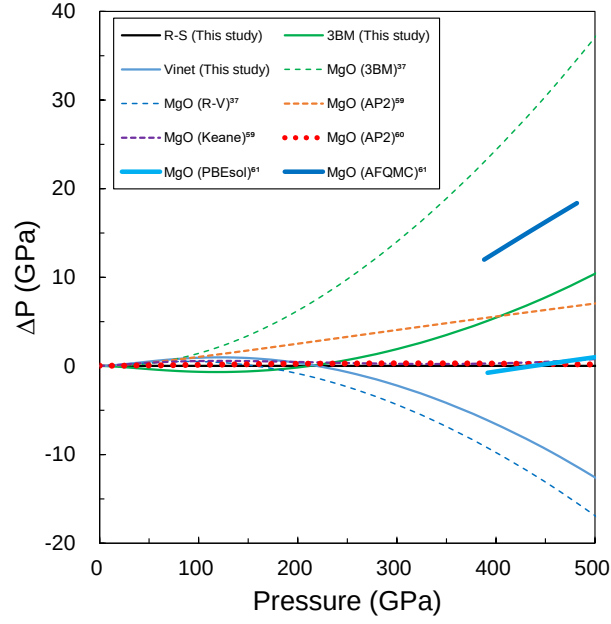


Fig. S10 | EoS comparison between MgO scales. The vertical axis shows pressure difference between the present R-S EoS and each MgO EoS. The *ab initio* results of Zhang et al.⁶¹ are the results at temperature of 0 K. EoS parameters for AP2 and Keane EoS (Tange, unpub.) can be found in Sakai et al.⁵⁹. The AP2 EoS model⁶⁰ (Red dotted curve) is the EoS corrected using statically compressed data up to 250 GPa³⁶.

Fig. S11

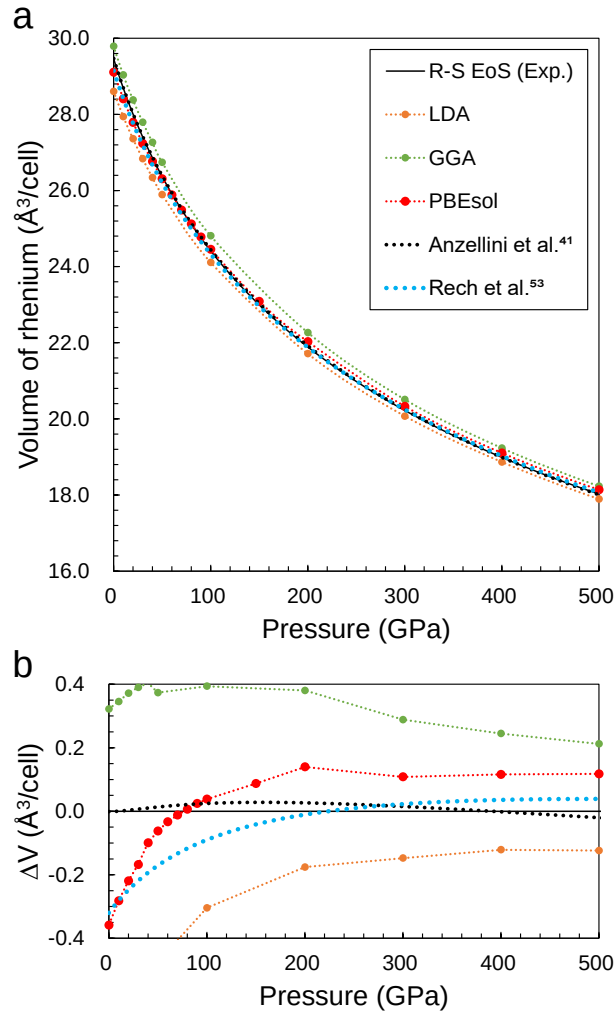


Fig. S11 | Comparison of rhenium equations of state between experiment and theory.
a Orange, green, and red symbols and dotted curves are the results of *ab initio* calculations (LDA, GGA, PBEsol) of this study, respectively. Each symbol position corresponds to the calculated raw data point at 0 K. The parameters of each EoS are summarized in Table S10. **b** The volume difference from the R-S EoS. Symbols are the same in (a).

Fig. S12

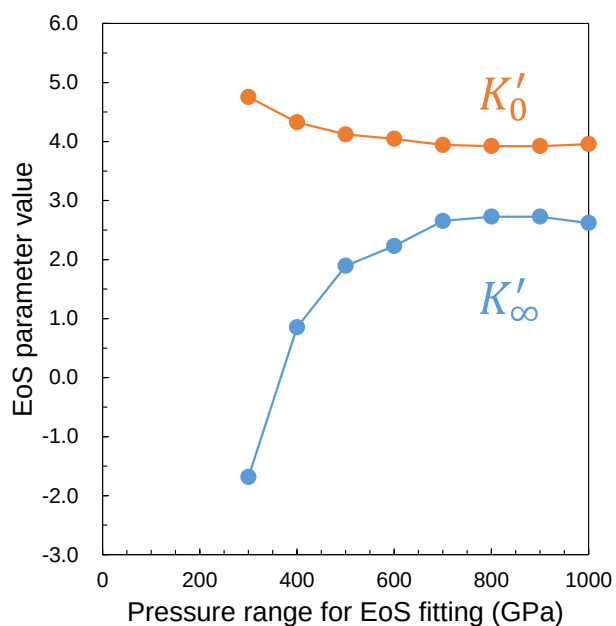


Fig. S12 | Pressure range dependency of EoS parameter. Orange and blue circles are obtained R-S EoS parameter value for K'_0 and K'_∞ , respectively. The P-V data of the *ab initio* calculation (PBEsol) was used here. Pressure range means the maximum pressure of P-V data set for EoS fitting. For example, ‘pressure range = 700’ indicates that the data from 0 to 700 GPa are used for EoS fitting. The fitting parameters of each pressure range data are summarized in Table S11.

Fig. S13

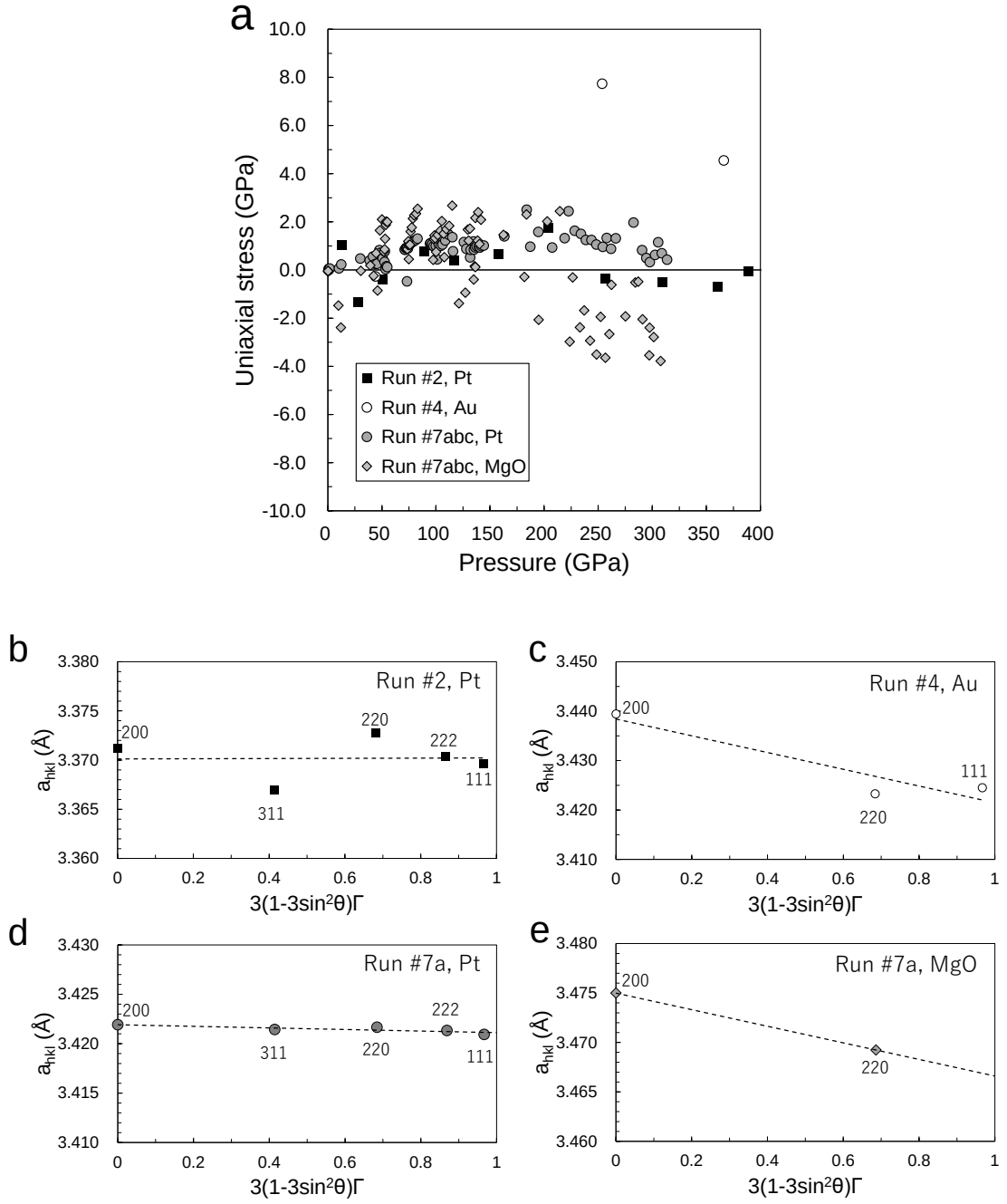


Fig. S13 | Uniaxial stress analysis. **a** uniaxial stress of platinum (Pt), gold (Au) and magnesium oxide (MgO) in run #2, #4 and #7abc. **b-e** Gamma plot of Pt in run #2 (**b**), Au in run #4 (**c**), MgO in run #7a (**d**) and Pt in run #7a (**e**) at highest pressure condition.

Fig. S14

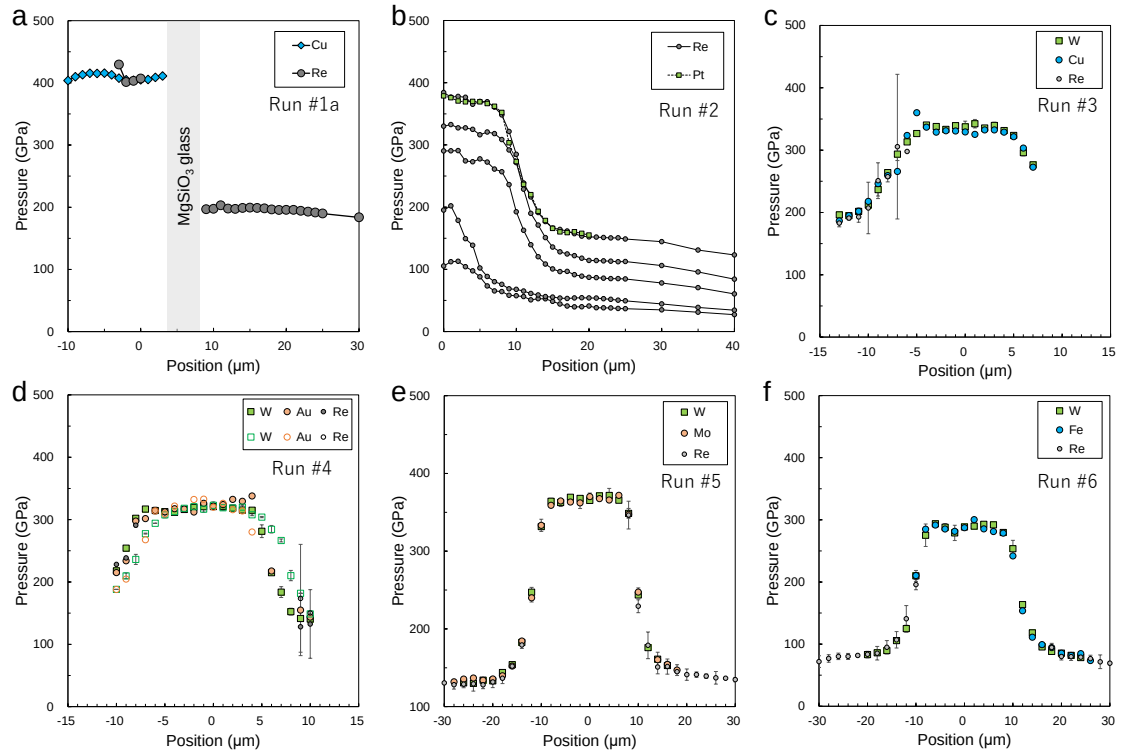


Fig. S14 | Pressure distribution in t-DAC experiments, run #1a-#6. a-f Pressure distribution in run #1a, #2, #3, #4, #5 and #6, respectively. Pressure was calculated based on present study's EoSs. In run #1a, no XRD peak was observed at MgSiO_3 position. Five cases of the pressure distribution during compression in run #2 are shown in (b). Culet size is $20\ \mu\text{m}$ for both run #1a and #2. In (d), Solid symbols are pressure distribution along the Y-axis, and open symbols are that along the Z-axis, respectively.

Supplementary method of the *ab initio* calculation

Our computations are based on the density-functional theory^{73,74} within the local density approximation (LDA)^{75,76}, the generalized gradient approximation (GGA)⁷⁷, and its extended form, PBEsol⁷⁸. The valence electron configuration for the pseudopotential was treated as $5s^25p^65d^56s^2$. The kinetic-energy cutoff of 80 Ry was applied to all the calculations. A $12 \times 12 \times 8$ uniform k -points grid was sampled on the irreducible wedges of the first Brillouin zone of the *hcp* structure. The temperature effect on the electronic structure was approximately included by Fermi-Dirac smearing for the electronic configurations under the ground state. We confirmed that these calculation conditions produced a sufficient total energy convergence of less than 1 mRy/Re. The structural optimization was performed until the residual stress became less than 0.01 GPa. All the calculations were carried out using the QUANTUM ESPRESSO distribution⁷⁹.

Supplementary References

- [73]P. Hohenberg and W. Kohn, *Phys. Rev.* **136**, B864 (1964).
- [74]W. Kohn and L. J. Sham, *Phys. Rev.* **140**, A1133 (1965).
- [75]D. M. Ceperley and B. J. Alder, *Phys. Rev. Lett.* **45**, 566 (1980).
- [76]J. P. Perdew and A. Zunger, *Phys. Rev. B* **23**, 5048 (1981).
- [77]J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
- [78]J. P. Perdew, A. Ruzsinszky, G. I. Csonka, O. A. Vydrov, G. E. Scuseria, L. A. Constantin, X. Zhou, and K. Burke, *Phys. Rev. Lett.* **100**, 136406 (2008).
- [79]P. Giannozzi *et al.*, *J. Phys.: Condens. Matter* **21**, 395502 (2009).