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Improving equations of state calibrations in the toroidal DAC—The case study of molybdenum



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ABSTRACT

We report an updated isothermal equation of state (EoS) of molybdenum (Mo) obtained by compression in beveled and toroidal diamond-anvil cells (DACs). For an improved compression environment, we developed a copper (Cu) pressure-transmitting medium (PTM) for the toroidal diamond-anvil cell samples, as it is a soft metal compared to Mo with a well calibrated EoS. A Ne PTM was used for the conventional beveled DAC samples. The unit-cell volumes of Mo were measured to 336(1) GPa in the Cu PTM and 231.2(6) GPa in the Ne PTM at room temperature. We additionally calculated elastic stiffness and compliance constants and evaluated the uniaxial stress of Mo and Cu with pressure. A new EoS for Mo is presented from data collected in all sample environments and compared to our theoretical predictions as well as previous compression studies of Mo. The (200) lattice plane of Mo produced the lowest volumes across the pressure range of this study for all compression environments, suggesting that it is less affected by nonhydrostatic stresses in the DAC compared to the other observed diffraction planes. The presented Mo EoS is compatible with extrapolations of EoS fits of Mo in helium (He) within ~1% at 330 GPa. Results from this work demonstrate that compressing a sample in a softer metal in the toroidal DAC can improve the compression environment and result in measured sample volumes comparable to those collected in noble-gas media at multi-megabar conditions.

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INTRODUCTION

Molybdenum (Mo) has drawn interest in numerous static, dynamic, and theoretical high pressure–temperature studies. Given the stability of Mo in a simple body-centered cubic (bcc) structure to multi-megabar pressures, it has been utilized as a diamond-anvil cell (DAC) standard for equations of state (EoS) and ruby fluorescence calibrations.^{1–9} In shock experiments, bcc Mo has been utilized as a standard for high impedance materials and for thermal EoS corrections.^{10–12} Mo is a group 6d-transition metal and exhibits key industrial properties, including high strength, hardness, and ambient melting temperature as well as low thermal expansion. From a fundamental condensed-matter physics standpoint, these properties are interesting to track under extreme compression conditions. Despite predictions of a potential high-pressure phase transformation of Mo to hexagonal-closed packed (hcp) and face-centered cubic (fcc) lattices,^{13–18} Mo has been experimentally observed in the bcc structure to at least 400 GPa under room

temperature static compression⁷ and into the multi-terapascal range under shock conditions.^{10,19}

Equations of state of Mo have been calibrated under static compression⁷ to 410 GPa and under ramp compression¹⁹ to 1000 GPa. At 400 GPa, the utilization of these two scales would produce differences in pressure of ~20 GPa (5%). This difference between DAC and dynamic compression EoS calibrations may be, in part, attributable to the external pressure scales chosen for DAC EoS calibrations, the reduction of dynamic compression data to 300 K, and the lack of hydrostaticity in the compression environment under static and dynamic loadings. To contribute to the improvement of EoS calibrations in the DAC at multi-megabar conditions, here we aim to focus on the optimization of the sample compression environment in the DAC for reliable volume measurements at these ultrahigh pressures. Noble gases, such as neon (Ne) and helium (He), are thought to provide the most ideal compression environment in the DAC, with helium being the closest to hydrostatic.²⁰ At present, an Mo EoS has

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only been measured in He up to 122 GPa,²¹ requiring extensive extrapolation to utilize this calibration at multi-megabar conditions. Uniaxial stress values determined for Mo in the DAC also increase by a factor of 4 up to 24 GPa,⁶ suggesting that the measured volumes of Mo may be strongly affected by nonhydrostatic stresses at more extreme pressures, and that nonhydrostatic EoS calibrations of Mo may not be reliable. Correction for the uniaxial stress of Mo under nonhydrostatic loading in the DAC is also complicated by the anomalous elastic properties of Mo.^{7,22–24} Directly improving the compression environment of Mo in the DAC is likely the optimal way to construct a static Mo EoS scale that is applicable to multi-megabar conditions.

The toroidal diamond-anvil cell (tDAC) can achieve pressures under static compression above 300 GPa, but improving the compression environment in the tDAC is difficult. The small tDAC sample chamber ($\sim 4\text{--}6\text{ }\mu\text{m}$ diameter) presents a great challenge for embedding micrometer-sized samples in soft media (i.e., noble gases and alkali halides). However, this may be aided by surrounding the sample in a metal that can be precisely fabricated and loaded in controlled volumes and that is softer and lower in shear strength compared to the rhenium (Re) gasket and the Mo sample material. Copper (Cu) is a promising candidate, as it is relatively compressible ($K_0 = 133\text{ GPa}$)^{25,26} with a low ambient shear strength ($\tau_r = 2.65\text{ GPa}$).²⁷ By comparison, the ultra-sonically derived isothermal ambient bulk modulus (K_0) of Mo and Re is 261²⁸ and 360 GPa,²⁹ respectively. Cu remains in the fcc structure to at least 1.15 TPa,³⁰ and it exhibits low yield stress to multi-megabar conditions.^{20,31,32} Cu is commonly used as a pressure calibrant to ultrahigh pressures,^{31–34} and multiple Cu EoS scales have been calibrated up to 1 TPa using static and dynamic techniques.^{20,30,35,36} Cu could, therefore, serve the dual purpose of a pressure-transmitting medium (PTM) and a pressure calibrant in the tDAC. In comparison with the soft alkali halides, Cu can also be purchased as μm -scale spheres or μm -thick foils such that controlled volumes of Cu at maximum density can be placed into the μm -scale tDAC sample chamber.

Here, we explore the compressibility of Mo embedded in a Cu PTM to 336 GPa in the tDAC and in a Ne PTM up to 231 GPa with the standard beveled DAC. We calibrate an EoS for bcc Mo to a Cu pressure scale and compare it to our theoretically derived Mo EoS and to previous studies. This work extends the calibration of Mo in a noble-gas medium by $>100\text{ GPa}$ and in a soft environment, more broadly, by $>200\text{ GPa}$ compared to previous DAC studies.^{8,21} We also calculated elastic constants for Mo and Cu as functions of pressure and utilized these moduli to characterize the uniaxial stress experienced by these materials in the sample chamber at extreme conditions.

METHODS

Experimental methods

Six compression experiments were conducted on Mo, four in the tDAC with a Cu PTM and two standard beveled anvil experiments with a Ne PTM. One cell was also probed at ambient conditions on standard diamond anvils to obtain a zero-pressure volume of Mo. For all experiments, the LLNL-type membrane DAC³⁷ was used. Toroidal diamond anvils were milled using the focused-ion

beam (FIB) (LLNL) from Type IIa 30/300 μm beveled anvils (Almax EasyLab) to produce toroidal profiles following Ref. 38 with central culets ranging from 9 to 15 μm diameter. Mo foils were used as sample material (Goodfellow, 99.9%, metal basis) and Cu spheres (Goodfellow, 99.9% metal basis) were employed to fabricate the medium around the Mo sample. Re gaskets were indented to $\sim 9\text{--}12\text{ }\mu\text{m}$ thick prior to milling a sample chamber with the FIB. A 5–6 μm diameter sample chamber was first milled into the Re, and then the chamber was filled with Cu spheres and compressed until the Cu uniformly filled the hole. A final 3–4 μm diameter hole was then milled into the Cu and filled with a Mo cylinder sandwiched between two smaller Cu spheres. The cylinders of the Mo foils were milled with the FIB to diameters matching the 3–4 μm diameter sample chambers. With this, the final sample configuration consisted of Mo fully encased in Cu [Figs. 1(a)–1(c)]. Two samples were also prepared on Type 1a 75/300 μm beveled anvils (Almax EasyLab) to create a Ne compression environment for comparison to sample compression in Cu [Fig. 1(b)]. For these samples, a Re gasket was indented to $\sim 15\text{ }\mu\text{m}$ thick and prepared with a $\sim 40\text{ }\mu\text{m}$ diameter hole. At the center of the sample chamber, $\sim 10\text{ }\mu\text{m}$ diameter disks of Mo foils and Cu foils (5 μm thick, Goodfellow, 99.97%) were placed on top of each other. The sample was then loaded with a 99.999% pure Ne gas at a pressure of $<0.2\text{ GPa}$. An experimental summary of the samples run in this work is provided in Table I.

Room-temperature compression experiments were carried out at Argonne National Lab, High-Pressure Collaborative Access Team (HPCAT) Sector 16, beamline 16 ID-B and at Deutsches Elektronen-Synchrotron, PETRA-III Extreme Conditions Beamline (ECB), beamline P02.2. At HPCAT, samples were probed with an x-ray beam of wavelength $\lambda = 0.406626\text{ }\text{\AA}$ at $1.5 \times 2.3\text{ }\mu\text{m}$ at full width at half maximum (FWHM). The sample-detector geometry was calibrated to a CeO_2 powder standard, and diffraction was collected on a Pilatus detector. At P02.2, samples were probed with an x-ray beam of wavelength $\lambda = 0.4851\text{ }\text{\AA}$ at $750 \times 800\text{ nm}^2$ at FWHM also with the sample-detector geometry calibrated to a CeO_2 powder standard following Ref. 39. Diffraction was collected on a Perkin-Elmer detector. Samples were compressed under membrane compression, and diffraction data were collected and monitored during all experiments using Dioptas⁴⁰ and processed post-experimentally using in-house OriginC codes (e.g., peak fitting and indexing, P - V calculations, line-shift analysis).

Sample pressure was tracked using the volume calculated based on diffraction from the Cu (111) lattice plane, as it was observed with the highest intensity across this study. At peak pressures, calculating pressure from fitting multiple Cu diffraction peaks results in a pressure difference of $<1\%$. The Cu pressure scale from Ref. 35 with $V_0 = 11.810\text{ }\text{\AA}^3/\text{at}$, $K_0 = 133\text{ GPa}$, and $K'_0 = 5.30(2)$ was used in this study, because it was calibrated to the same ruby scale as the Mo EoS from Ref. 21 that we compare our results to frequently in this work. The Mo EoS calibrated by Ref. 21 is the current highest-pressure calibration for Mo in a helium PTM and is utilized here as a reference for compression data collected under nearly ideal compression conditions. Applying this scale to our data does require significant extrapolation to $>300\text{ GPa}$, and calibration of our Cu data to dynamic scales^{26,36} that exceed the pressure range of this study is also discussed in the supplementary material (Text S1). Additionally,

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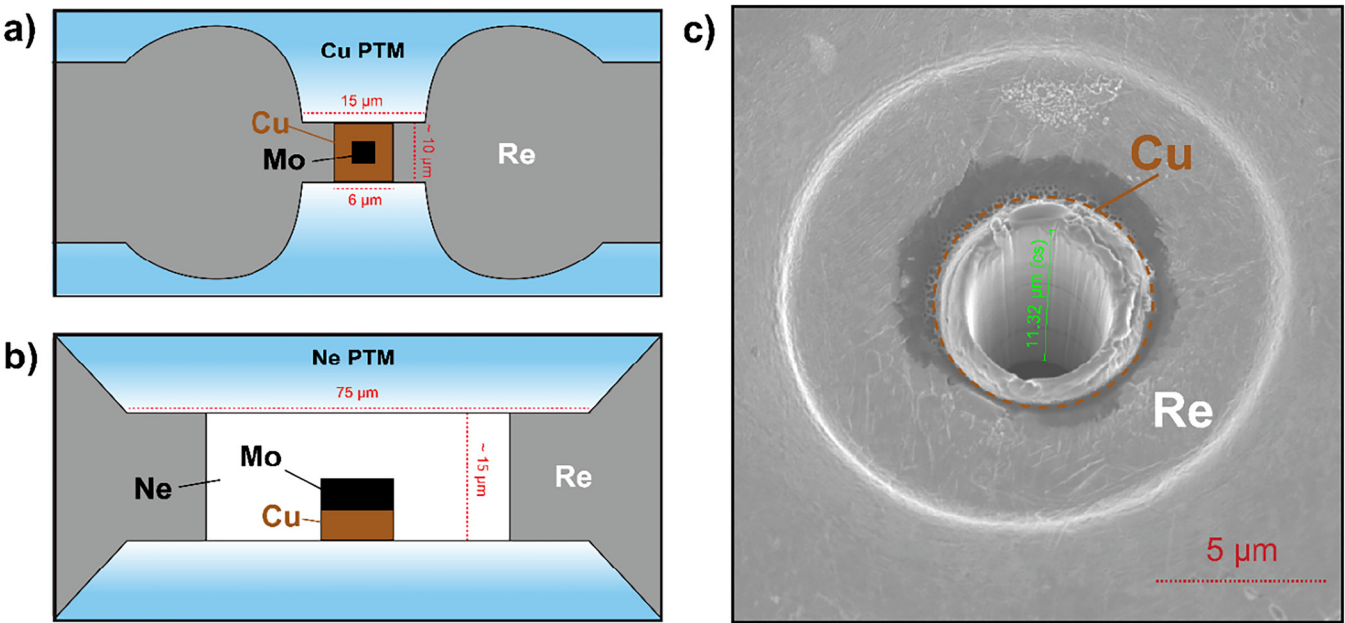


FIG. 1. Sample and PTM preparation schematics for the Mo experimental runs in this study with (a) a Cu PTM in the toroidal DAC and (b) a Ne PTM in the conventional beveled DAC. (c) A scanning-electron microscopy image of a Re gasket prepared for the Cu PTM toroidal loadings. This image was collected at the stage in preparation where the initial 6 μm diameter gasket hole was filled with copper and re-milled with a 4 μm diameter hole for subsequent Cu–Mo–Cu layered loading.

for each diffraction pattern collected, the Cu volumes indexed from the (111) lattice plane are provided in Tables S1–S6 of the [supplementary material](#) and can be calibrated to other EoSs as preferred. The volumes of Mo were calculated individually from the (110), (200), (211), and (220) diffraction planes and compared for each sample based on which diffraction planes were observed across the entire pressure range of each experiment study (Table I). For sample stress-state evaluation, the difference in lattice volumes calculated from these lattice planes was used.

Theoretical methods

We additionally applied density-functional theory (DFT) to explore the EoS, phase stability, and elasticity of Mo. For comparison,

we evaluated the elastic moduli for Cu as well. One fundamental assumption in DFT is the exchange and correlation effect of the electrons. Here, we are applying the Perdew–Burke–Ernzerhof for solids (PBEsol) formulation of the exchange and correlation energy functional,⁴¹ as it is generally good for *d*-transition metals,⁴² including Mo and Cu. Our implementation of DFT is an all-electron full-potential linear muffin-tin orbitals (FPLMTO) method.⁴³ These calculations do not suffer from any pseudopotential approximation, utilized in plane-wave techniques, that can break down at high pressure. To ensure a good representation of the electronic structure, we include 3d4s4p semi-core states with 5s5p4d4f valence states, all with different tail energies in a common energy window to allow for hybridization. Spin–orbit coupling is included but discarded for the *p*-states following Ref. 44. For the elastic constants, we applied the

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TABLE I. Sample details for each Mo experiment run in this study. Sample pressures were determined based on the volume of Cu calculated from the (111) lattice plane and using the Cu EoS reported by Ref. 35.

Sample	PTM	DAC type	Culet diameter (μm)	Mo (<i>hkl</i>) observed to peak pressures	Maximum pressure (GPa)	Beamline
tDAC-Cu1	Cu PTM	Toroidal	15	110, 200, 211, 220	328(1)	16 ID-B
tDAC-Cu2	Cu PTM	Toroidal	15	110, 200, 211	283.1(8)	P02.2
tDAC-Cu3	Cu PTM	Toroidal	15	110, 200, 211	266.1(8)	P02.2
tDAC-Cu4	Cu PTM	Toroidal	9	110	336(1)	P02.2
DAC-Ne1	Ne PTM	Beveled	75/300	110, 200, 211, 220	231.2(6)	P02.2
DAC-Ne2	Ne PTM	Beveled	75/300	110, 200, 211	160.1(4)	P02.2
Amb-DAC	None	Standard	300	110, 200, 211, 220, 310	0.0001	P02.2

same approach as Ref. 45, but for the band-structure calculation, we included ~ 8000 k points in the irreducible part of the Brillouin zone for the integrations in the reciprocal space. DFT has been shown to reliably predict elastic moduli, particularly for high-symmetry phases, such as cubic phases, and it has been shown that the quality of the DFT results for EoS does not worsen with increasing pressure.⁴⁶

RESULTS AND DISCUSSION

The P - V relation of Mo calibrated to Cu pressure to 336 GPa

Selected diffraction patterns of tDAC compression of Mo encased in Cu from sample tDAC-Cu1 are shown in Fig. 2. High intensity diffraction from bcc Mo and fcc Cu is observed to the highest pressures. Lower intensity peaks of hcp Re are also picked up from the gasket by the tails of the x-ray beam (Fig. 2). No doublet peaks of Mo, Cu, or Re are observed, as has been reported in previous toroidal and double-stage compression studies.^{31,38,47} This is likely because sample tDAC-Cu1, run at HPCAT, contained a culet diameter that was nominally the size of the x-ray beam tail. All other samples run in this study utilized a nano-focused x-ray beam at the P02.2 beamline with an x-ray tail within the culet diameter as well. Therefore, in all experiments, the tails of the x-ray beam did not interact with the torus of the anvils that experienced significantly lower pressures.³⁸ As shown in Fig. 2, the Mo signal is much stronger compared to the Re signal such that the overlap of the Mo (110) and Re (101) does not limit our ability to measure the Mo (110) lattice plane spacing. Additionally, diffraction from Mo and Re could be differentiated in these experiments by texturing, as the signal from Mo typically consisted of spotty rings

originating from larger grains, while the Re produced low-intensity uniform rings from the fine-grained gasket material (Fig. 2). Based on our DFT calculations, bcc Mo is predicted to be stable to 650 GPa (Fig. S1 in the supplementary material), in agreement with our experimental observations of bcc Mo to >300 GPa (Fig. 2).

Diffraction from Mo (110) and Cu (111) was observed in all samples up to 336(1) GPa, while the signal from the (200), (211), and (220) Mo planes was observed up to 328(1) GPa (Table I). Based on previous nonhydrostatic compression studies of Mo,⁷ the (200) lattice plane of Mo is the least affected by deviatoric stress in the DAC compared to other lattice planes of Mo. Therefore, Fig. 3 shows the evolution of the atomic volume of Mo calculated based on the (200) lattice planes with Cu-derived pressure observed in samples tDAC-Cu1, tDAC-Cu2, tDAC-Cu3, and DAC-Ne1 up to 328(1) GPa. These were then compared to the *ab initio* Mo EoS, which was determined using our present DFT calculations (Fig. 3). As shown in Table I, sample tDAC-Cu4 compressed to 336(1) GPa, but signal from the sample was weak at multi-megabar conditions, and only the (110) peak of Mo could be tracked across the entire pressure range. As such, the evolution of Mo (110) volumes with pressure up to 336(1) GPa is also provided in Fig. S2 of the supplementary material.

The experimentally determined Mo volumes show a smoothly decreasing trend with pressure (Fig. 3). Overall, the Mo data collected in Ne and Cu do not exhibit significant deviations, suggesting that the Ne and Cu media redistribute the uniaxial stress in the sample chamber to similar degrees. Compared to the computationally determined Mo EoS, the experimental data exhibit excess Mo volumes up to ~ 175 GPa. Above these pressures, the experimental and theoretical

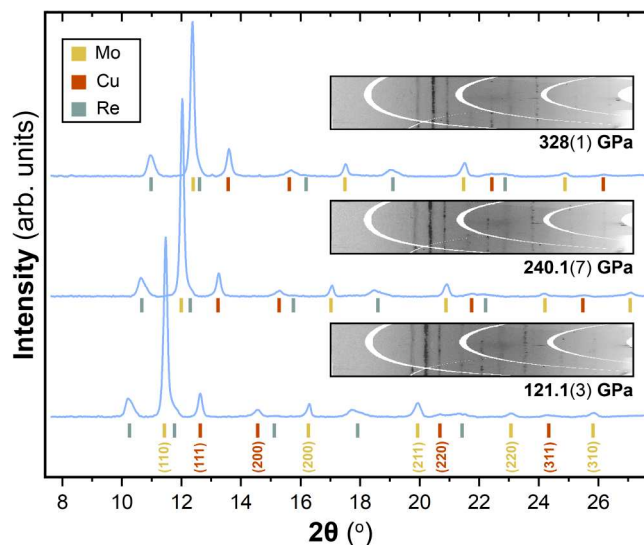


FIG. 2. Azimuthally integrated diffraction patterns ($\lambda = 0.406626$ Å) from sample tDAC-Cu1 up to 328(1) GPa with the diffraction angles of Mo (yellow), Cu (red), and Re (gray) identified. Miller indices for Mo and Cu are included. For each 1D pattern, a portion of the caked diffraction image is included as an insert.

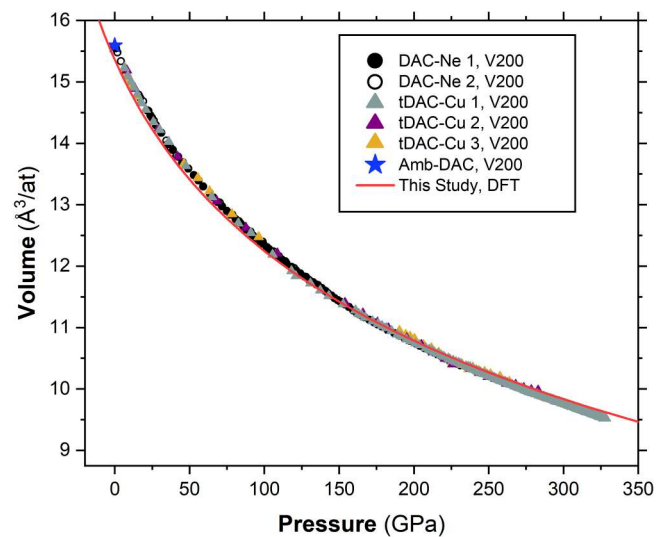


FIG. 3. Volumes of Mo calculated from the (200) lattice plane plotted with pressure determined from Cu³⁵ [$V_0 = 11.810$ Å³/at, $K_0 = 133$ GPa, $K'_0 = 5.30$ (2)]. P - V data for Mo samples embedded in Cu and embedded in Ne are included. An equation of state determined using DFT is drawn via the red solid line.

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trends cross over (Figs. 3 and S2 in the [supplementary material](#)). One reason for the difference between our experimental and computational results is likely related to the fact that the DFT results from this work underestimate the room-temperature equilibrium ($P=0$) atomic volume that we measured experimentally. Another source of this discrepancy may also be due to thermal expansion in the experimental data that is measured at room-temperature, while no thermal correction is applied here to the zero kelvin DFT results.

For a more detailed investigation of the compression environment of the Mo samples in Cu and Ne, the differences in Mo volumes determined from the (110), (200), (211), and (220) lattice planes of Mo for the Cu and Ne PTM sample configurations are shown in Fig. 4. Uniaxial stress from the anvils can produce anisotropic compression in a polycrystal sample, as each lattice plane is uniquely affected. Overall, samples tDAC-Cu1, DAC-Ne1, and DAC-Ne2 show significantly less scattered compared to samples tDAC-Cu2 and tDAC-Cu3, and most of the data exhibit volume deviations within 1% of each other (Fig. 4). Just comparing the Mo data collected in the Cu PTM, samples tDAC-Cu2 and tDAC-Cu3 exhibit volume deviations of up to $\pm 2\%$, while sample tDAC-Cu1 exhibits volume deviations only up to $\pm 0.75\%$ for all lattice planes (Fig. 4). The Mo data collected in the Ne PTM also show little scatter with volume deviations of at most 1% (Fig. 4). The tDAC-Cu1 volume residuals evolve more uniformly with pressure compared to the other Cu PTM samples and follow the trends of the Ne PTM data (Fig. 4). We interpret these behaviors to reveal that the Mo sample in tDAC-Cu1 was likely embedded in a more uniform Cu environment compared to the tDAC-Cu2 and tDAC-Cu3 samples (Fig. 4).

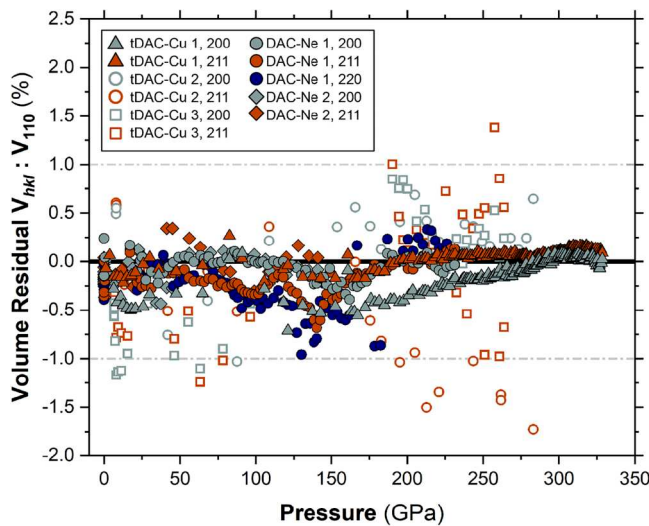


FIG. 4. Percent volume residuals for the volumes of Mo calculated from the (200), (211), and (220) lattice planes of Mo compared to that of the (110) lattice plane for all samples run in this study. A reference line at 0 is included to highlight the data with negative versus positive volume residuals. Reference dashed-dotted lines are also placed at 1 and -1 to emphasize that most of the V_{200} , V_{211} , and V_{220} volumes are within 1 vol. % percent of V_{110} .

Examining our data (Fig. 4), despite the scatter observed from the tDAC-Cu2 and tDAC-Cu3 samples, tDAC-Cu1, DAC-Ne1, and DAC-Ne2 do show that the (200) lattice volumes are predominantly smaller or nominally the same as the (110) lattice volumes. Our data do, therefore, support Ref. 7 that the (200) lattice plane of Mo produces values closer to the hydrostatic measurements in the DAC²¹ by comparison to the (110) lattice plane reported in a non-hydrostatic environment. However, the volume differences determined from the (200) and (110) lattice planes are small (within $\sim 1\%$ of each other) suggesting that our Cu tDAC compression environment performed similarly to the beveled-DAC with a Ne compression environment.

Evaluation of the elasticity of bcc Mo with pressure

Due to the symmetry of the structure, the C_{11} , C_{12} , and C_{44} elastic stiffness constants for a cubic crystal system govern the three independent modes of crystal's elastic deformation. The C_{11} axial compression modulus represents axial stress resulting in strain parallel to that axis, the C_{12} dilation modulus represents stress that produces strain along a normal axis, and the C_{44} shear modulus represents shear stress resulting in shear strain along a face. The elastic anisotropy factor (S), defined as

$$S = 1/(C_{11} - C_{12}) - 1/(2C_{44}) \quad (1)$$

is a representation of cubic crystal anisotropy under compression. S corresponds to the difference between the crystal shear along the (110) by a stress parallel to $[1-10]$ and crystal shear along the (100) by a stress parallel to $[010]$.⁴⁸

Utilizing DFT, we calculated the Mo and Cu elastic stiffness constants and the elastic anisotropy factor up to 680 GPa (Table II; Table S7 in the [supplementary material](#); Fig. 5; Fig. S3 in the [supplementary material](#)). The evolution of the Mo elastic stiffness tensor and the elastic anisotropy factor is compatible with the values reported in previous first principles, radial diffraction, and ultrasonic studies^{6,28,49,50} (Fig. 5). The rate at which the C_{12} constant is increasing for Mo is greater than the rate of change of the C_{11} constant, suggesting that Mo is becoming axially more compressible relative to the dilational deformation. In other words, the tetragonal shear constant, $C' = (C_{11} - C_{12})$, is decreasing, suggesting that bcc is approaching a phase transition at some higher pressure. C' scales well with the energy difference between the bcc and fcc phases.⁴⁵ Based on the DFT work conducted in this study, this

TABLE II. Elastic stiffness constants of Mo calculated using DFT up to 682 GPa.

P (GPa)	C_{11} (GPa)	C_{12} (GPa)	C_{44} (GPa)	S (GPa ⁻¹)
1	468	160	104	-1.56×10^{-3}
34	651	266	148	-7.81×10^{-4}
86	890	417	204	-3.37×10^{-4}
163	1194	628	276	-4.48×10^{-5}
277	1592	932	370	1.64×10^{-4}
442	2089	1366	465	3.08×10^{-4}
682	2701	2015	581	5.97×10^{-4}

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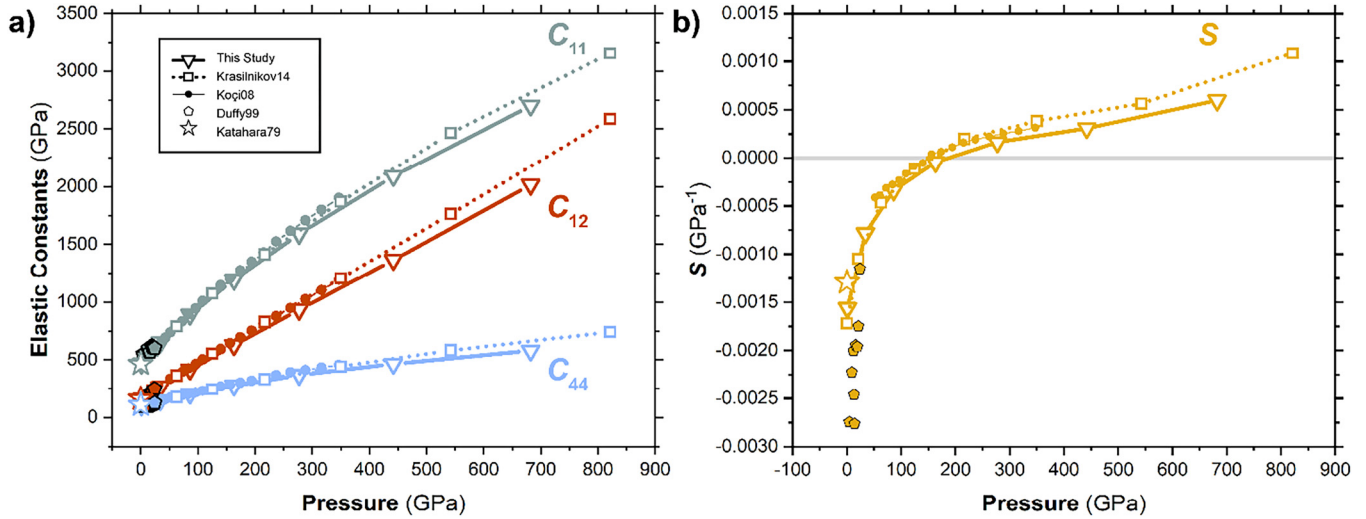


FIG. 5. Evolution of the Mo (a) elastic stiffness constants C_{11} (gray), C_{12} (red), C_{44} (blue) and (b) elastic anisotropy factor (gold) calculated using DFT in this study (triangles), compared to (50) (squares), (49) (filled circles), (6) (pentagons), and (28) (stars).

behavior is likely related to the bcc–fcc transition predicted in Mo around 650 GPa (Fig. S1 in the [supplementary material](#)).

Notably, up to ~ 180 GPa, the S value for Mo is negative, indicating that Mo is less resistant to shear along the cell face relative to the cell diagonal. At 180 GPa, $S = 0$, and Mo is isotropic, and above 180 GPa, the S values for Mo are positive such that Mo is more resistant to shear along the cell face vs the cell diagonal. This change in sign of S is not unique to this study and is compatible with previous measurements and calculations of Mo elasticity^{6,28,49,50} [Fig. 5(b)].

We additionally modeled the directional dependence of the elastic modulus (stress/strain) for Mo and Cu with pressure using the ELATE software⁵¹ (Figs. S4 and S5 in the [supplementary material](#)). At ambient conditions, Mo exhibits higher compressibility along the cell diagonals, such as the family of $[hk0]$ and $[hkl]$ planes for the cubic cell (Fig. S4 in the [supplementary material](#)). Upon pressurization, the compression behavior of Mo evolves as compression along the axial directions of the cell increases. At the pressure where the elastic modulus for Mo is isotropic ($S = 0$, ~ 180 GPa), the volumetric representation of the elastic modulus is spherical (Fig. S4 in the [supplementary material](#)), and beyond these pressures, Mo is softer along the cell faces relative to the cell edges and corners (Fig. S4 in the [supplementary material](#)). In contrast, Cu exhibits a higher ratio of stress to strain along the cell edges and corners up to 680 GPa, and the behavior is enhanced with increasing pressure (Fig. S5 in the [supplementary material](#)).

Evaluation of the stress-state of bcc Mo and fcc Cu to 336 GPa

Utilizing the calculated elasticity data, we then aimed to quantify the uniaxial stress experienced by Mo and Cu up to

336 GPa and further evaluate the differences between the Ne and Cu sample environments. We considered the differences in d-spacings measured for the (110), (200), (211), and (220) lattice planes of Mo and the (111), (200), and (220) lattice planes of Cu. For Mo and Cu, we fit a third order polynomial to the evolution of elastic constants with pressure (Table II; Table S7 in the [supplementary material](#); Fig. 5; Fig. S3 in the [supplementary material](#)).

Following the model developed by Refs. 22 and 23, the nonhydrostatic cubic lattice parameter for a given lattice plane, a_{hkl} , can be written as

$$a_{hkl} = M_0 + M_1 [3\Gamma(1 - 3\sin^2\theta)], \quad (2)$$

with

$$\Gamma_{hkl} = (h^2k^2 + k^2l^2 + h^2l^2)/(h^2 + k^2 + l^2)^2. \quad (3)$$

Given the experimentally determined a_{hkl} , Miller indices (hkl), and half of the Bragg scattering angle (2θ), M_0 and M_1 can be determined from the intercept and slope, respectively, of Eq. (2). Once M_1 and M_0 are determined at each pressure, the following equation can be applied to approximate the uniaxial stress, t , with pressure,

$$M_1 = -a_p(\alpha St/3). \quad (4)$$

The term a_p is the uniaxial-stress-corrected lattice parameter, and it has been approximated as M_0 for the calculation of the uniaxial stress in previous studies.^{31,32,34,52} The α term is a correction factor usually in the range of 0–1 representing the contributions of uniform stress ($\alpha = 0$) and uniform strain ($\alpha = 1$) conditions.

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Interestingly, previous studies^{7,24,53} conclude that an α factor between 1 and 2 is appropriate for materials with a negative elastic anisotropy factor, S . Based on the values determined for Mo in this study and from previous studies^{6,28,49,50} [Fig. 5(b)], the S values for Mo are negative to ~ 180 GPa and become positive above these

pressures. The α term for Mo should, therefore, be in the range of 1–2 up to 180 GPa and ≤ 1 above 180 GPa. By comparison, for fcc metals, such as gold (Au) and silver (Ag), an $\alpha = 1$ has been used to calculate a conservative uniaxial stress correction.^{31,52} For the Cu in our sample, it is likely that an α value of unity is reasonable, as it is an fcc metal with similar properties as Au and Ag.

Figure 6 visualizes the value αt for both Mo and Cu. Regarding Mo, when $\alpha = 1$, Figs. 6(a) and 6(b) are unchanged and can be viewed as the maximum uniaxial stress values. For $\alpha = 2$, all values in Figs. 6(a) and 6(b) would be divided in half. All data in Fig. 6(a) show significant scatter with large αt values irrespective of the α value applied. Additionally, between ~ 100 and ~ 250 GPa, the αt values for Mo extend asymptotically to $+\infty$ with the discontinuity centered around 180 GPa [Fig. 6(b)]. The asymptotic nature of the data in the 100–250 GPa range is attributable to the fact that calculating t from Eq. (4) requires a division by S , and in this pressure region, S is approaching or equal to zero [Fig. 5(b)]. Therefore, a differing model must be applied to accurately calculate uniaxial stress for materials with an elastic anisotropy factor that is near zero and for materials that are isotropic or evolve through an isotropic state under compression (Fig. S4 in the supplementary material).

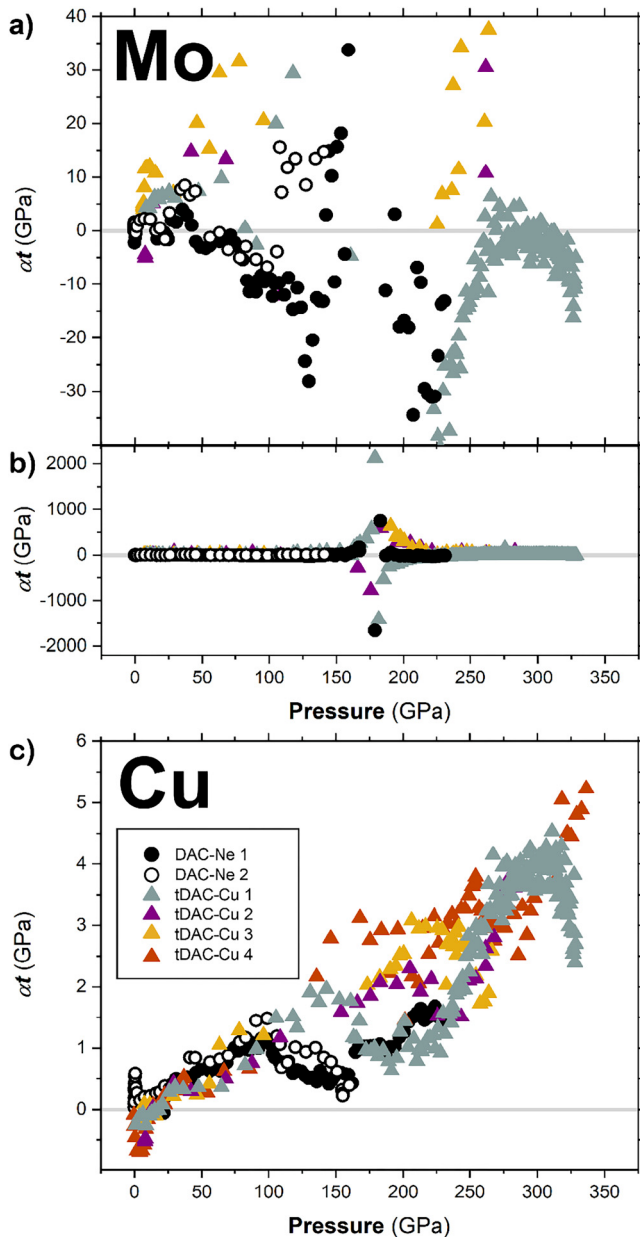


FIG. 6. (a) Calculated αt for Mo with pressure. (b) Calculated αt for Mo with pressure showing a larger αt range to highlight the evolution of αt for Mo to $+\infty$ as S approaches 0 at 180 GPa. (c) Calculated αt values for Cu with pressure.

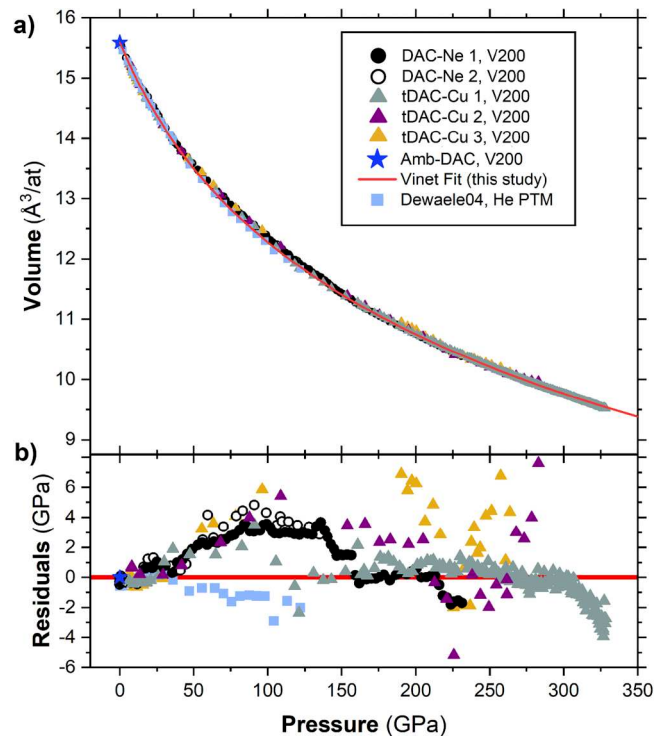


FIG. 7. (a) Indexed Mo volumes from the (200) lattice plane for all samples run in this study. A Vinet equation of state fit, with measured $V_0 = 15.592(1) \text{ Å}^3/\text{at}$, K_0 fixed to 261 GPa²⁸ and $K' = 4.061(3)$ is given by the red line (EoS 1 in Table III). Mo data from Ref. 21 measured in a He PTM (blue squares) is included for comparison. (b) Pressure residuals for each dataset in relation to the Vinet fit.

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As α for Cu is likely unity, Fig. 6(c) also represents the uniaxial stress values for Cu. The Cu uniaxial stress data exhibit little scatter and show an increasing trend with pressure up to ~ 5 GPa at 336 GPa [Fig. 6(c)]. The range of uniaxial stress values calculated here is compatible with previous toroidal DAC observations of Cu under compression.^{31,32} These uniaxial stress values are indistinguishable for the samples where the Cu chip was surrounded by Ne and for the samples where Cu was under nonhydrostatic compression as the PTM in the tDAC. Based on these results, Cu is a viable metal PTM for studies of harder metals, such as Mo, as Cu does not support significant deviatoric stress up to multi-megabar pressures under noble-gas and nonhydrostatic compression conditions.

EoS of Mo calibrated to 328 GPa

Since the established DAC uniaxial stress correction^{22,23} is complicated for Mo due to its elastic properties, the lattice volumes of Mo determined from the (200) lattice plane to 328(1) GPa will be utilized here to calibrate EoSs. These volumes are a closer approximation to an ideal hydrostatic state compared to the (110) lattice volumes, as they consistently produce lower volumes closer to the volumes of Mo measured in He²¹ (Fig. 4, Fig. 7). A Vinet EoS⁵⁴ was then fit to our Mo (200) volumes calibrated to the Cu

pressure following the form:

$$P = 3K_0\{[1 - (V/V_0)^{1/3}]/(V/V_0)^{2/3}\}e^{3/2(K'-1)(1-(V/V_0)^{1/3})}. \tag{5}$$

Several EoSs were fit to our data and are shown in Table III and Table S8 in the supplementary material. We fit two EoSs to the data collected on tDAC-Cu1, tDAC-Cu2, tDAC-Cu3, DAC-Ne1, and DAC-Ne2 calibrated to the DAC Cu scale from Ref. 35 (Table III). In all cases, our measured ambient volume of Mo [15.592(1) Å³/at] determined from amb-DAC was utilized and held fixed. Then, a Mo EoS was derived with the zero-pressure bulk modulus, K_0 , held to the ultrasonically determined isothermal value of 261 GPa,²⁸ and a second EoS was derived allowing K_0 to be fit (Table III). The pressure derivative to the bulk modulus, K' , was fit in all EoSs (Table III). Throughout the remainder of this work, EoS 1 from Table III will be applied. This EoS utilizes the Cu scale from Ref. 35 that was calibrated to the same ruby as the Mo EoS measured in He from Ref. 21. Given the focus of this work, this fit represents the most direct comparison of the behaviors of Mo in He, Ne, and Cu PTMs. Additional Mo EoS fits are provided in Table S8 of the supplementary material whereby the dynamic Cu scales from Refs. 26 and 36 are applied, and a discussion of the differences between them is given in Text S1 of the supplementary material.

TABLE III. Vinet equation of state parameters for Mo determined from this study and previous studies.^{5,7,8,19,21,28,55,56} Bold values in the table were fixed during the EoS fitting.

EoS	Study	Datasets	Fitting type	V_0 (Å ³ /atom)	K_0 (GPa)	K'	Calibrant	Max P (GPa)	Method
1 ^a	This study	V200, DAC-Ne 1,2; tDAC-Cu 1,2,3	Vinet	15.592(1)^b	261^c	4.061(3)	Cu ^d	328(1)	XRD-DAC
2	This study	V200, DAC-Ne 1,2; tDAC-Cu 1,2,3	Vinet	15.592(1)^b	275.4(8)	3.80(1)	Cu ^d	328(1)	XRD-DAC
3	This study	...	Vinet	15.357(2)	279.0(3)	4.177(3)	...	384	DFT
	Dewaele <i>et al.</i> ²¹	He PTM	Vinet	15.558	261	4.05(2)	Ruby ^e	122	XRD-DAC
	Dewaele <i>et al.</i> ²¹	He PTM	Vinet	15.558	272(2)	3.68(6)	Ruby ^e	122	XRD-DAC
	Akahama <i>et al.</i> ⁷	No PTM, V_{200}	Vinet	15.58(1)	262(5)	4.55(16)	Pt ^f	410	XRD-DAC
	Katahara <i>et al.</i> ²⁸		Vinet		260.8	4.46			Ultrasonic
	Vohra and Ruoff ⁵	No PTM	BM3		262.8	3.949			XRD-DAC
	Litasov <i>et al.</i> ⁵⁵	4–5 diffraction lines	Vinet	15.57(1)	260(1)	4.21(5)	MgO, Au ^g	31	XRD-MAP
	Zeng <i>et al.</i> ⁵⁶	...	BM	15.97	263.33	4.21	...		DFT
	Huang <i>et al.</i> ⁸	Ne PTM	BM	15.61(4)	273(15)	3.6(4)	MgO ^h	80	XRD-DAC
	Wang <i>et al.</i> ¹⁹	...	Vinet		261	4.4(2)	...	1 TPa	XRD-ramp

^aEoS used in Figs. 7 and 8.
^bAmbient volume was determined from diffraction collected on Amb-DAC in this study. The error on the volume is included here, but the ambient volume was held fixed in the EoS fitting.
^cAcoustic value from Ref. 28.
^dCu pressures calibrated to the DAC Cu scale from Ref. 35 that is in turn calibrated to their updated ruby scale.
^eRuby pressures reported based on an updated scale from Ref. 35.
^fPt pressure calibrated to Ref. 57.
^gMgO and Au EoS calibrated in Ref. 55.
^hMgO pressure calibrated to Ref. 58.

In Table S8 of the [supplementary material](#), different components of our datasets were isolated and fit to an EoS to evaluate the differing behaviors of the Cu and Ne PTMs among our samples. When the ambient bulk modulus is fixed to the ultrasonic value,²⁸ the EoS fit to all our Mo data utilizing the DAC Cu scale from Ref. 35 produces a K' value of 4.061(3) (EoS 1, Table III). By comparison, fitting an EoS only to the subset of this Mo data that were collected in a Ne PTM produces a K' of 4.100(10) and fitting an EoS to the subset of these Mo data collected in Cu PTM data produces a K' of 4.058(3) (Table S8 in the [supplementary material](#)). The EoS I (Table III) fit to all our datasets is, therefore, within error identical to EoS fit to our Mo data collected in a Cu PTM (Table S8 in the [supplementary material](#)). The EoS fit to the Mo data collected in Ne produces an $\sim 1\%$ larger K' value compared to that fit to the data collected in Cu. Our Mo data collected in Ne do appear stiffer in the 1–150 GPa range, which may be related to the fact that the Mo data in Cu were collected on toroidal anvils that undergo significant elastic deformation in this pressure range and often produce lower sample volumes in this region.^{31,59} However, removing the tDAC data in the 50–150 GPa range does not change the Cu PTM EoS for Mo, resolving that the K' value fit in our EoS I in Table III is related to the constraints placed by the multi-megabar measurements in the Cu PTM.

Figure 7(a) shows the evolution of Mo (200) volumes from samples tDAC-Cu1, tDAC-Cu2, tDAC-Cu3, DAC-Ne1, and DAC-Ne2 with pressure compared to the Vinet Mo EoS of the combined dataset (EoS 1, $V_0 = 15.592 \text{ \AA}^3/\text{at}$, $K_0 = 261 \text{ GPa}$, $K' = 4.061$) (Table III). Pressure residuals of all data compared to the Vinet fit are within $\pm 8 \text{ GPa}$ up to 328 GPa [Fig. 7(b)], and pressure residuals for the samples likely containing optimized Ne and Cu compression environments (tDAC-Cu1, DAC-Ne1, DAC-Ne2) exhibit pressure

residuals within $\pm 5 \text{ GPa}$ up to 328 GPa. In Fig. 7, Mo data from Ref. 21 are included as a reference dataset in a He PTM. The Mo data collected in He (Ref. 21) trend slightly lower in volume with pressure compared to our datasets, which may reflect the softer nature of He vs Ne and Cu, but the Vinet EoS fit to our combined Cu PTM and Ne PTM data for Mo is still compatible within 3 GPa of the data from Ref. 21 up to 122 GPa [Fig. 7(b)].

Comparing Mo EoSs from this study and several previous DAC,^{7,8,21} multi-anvil press (MAP),⁵⁵ dynamic compression,^{5,19} ultrasonic,²⁸ and DFT studies⁵⁶ with the DAC study in He from Ref. 21, Fig. 8 shows the deviation in pressures calculated from each of the reported EoSs. Of these previous studies (Table III), our experimentally determined equation of state calibrated to the DAC Cu scale from Ref. 35 (EoS 1, Table III) predicts pressures within 4 GPa of the extrapolated hydrostatic Mo EoS²¹ at 330 GPa [Fig. 8(a); Fig. S6 in the [supplementary material](#)]. Since our EoS I fit is dominated by the Mo data collected in a Cu PTM in the tDAC, these pressure residuals suggest an agreement within $\sim 1\%$ between the Mo EoS derived in a He PTM²¹ and the Mo EoS derived in a Cu PTM in the tDAC when ultimately calibrated to the same ruby gauge.

The DAC EoS of Mo calibrated to Pt by Ref. 7 went to similarly high pressures (410 GPa) as this study, but the reported EoS differs significantly from our EoS [Fig. 8(a)]. This is likely related to the platinum (Pt) scale from Ref. 57 used in the study by Ref. 7 because recalibration of the Pt volumes from Ref. 7 to a relevant DAC Pt scale³⁵ results in better agreement between our Mo EoS and that of Ref. 7. The other DAC, ultrasonic, and multi-anvil studies^{8,28,55} were extrapolated from much lower pressures ($<100 \text{ GPa}$) and/or were calibrated to differing pressure scales, which may attribute to their divergence from the hydrostatic EoS when extrapolated above a megabar (Fig. 8). Our computationally

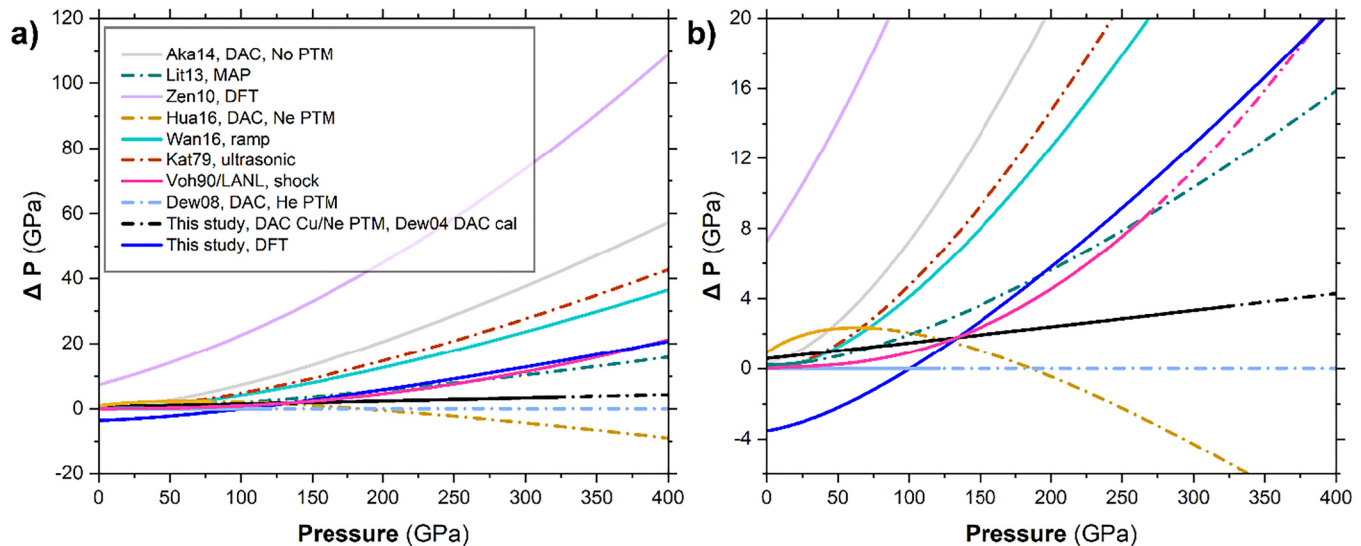


FIG. 8. (a) Pressure differences between the Mo EoS calibrated in a He PTM from Ref. 21, the current experimentally determined EoS, the current computationally determined EoS and the EoS fits from (5), (7), (19), (28), (55), (56). (b) Zoomed in version of (a) showing the finer details of the pressure differences among these studies. For the references listed in Table III that did not provide a V_0 value, a $V_0 = 15.558 \text{ \AA}^3/\text{at}$ from Ref. 60 was utilized for general comparison in these plots.

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determined EoS for Mo is in relative agreement with the reduced shock Mo scale⁵ and predicts excess pressures of around ~ 11 GPa at 330 GPa compared to our experimental EoS (Fig. 8). Our computational results, however, are in closer agreement to our experimental results and the Mo data in He²¹ compared to previous Mo EoS determined by DFT.⁵⁶ The Mo EoS determined from ramp compression up to 1 TPa¹⁹ also exhibits higher pressures compared to our results. Interestingly, we find that if we calibrate our Mo EoS to a Cu EoS reduced from ramp compression,³⁶ then our Mo EoS agrees with ramp compression Mo EoS from Ref. 19 (Fig. S6 in the [supplementary material](#)). Additionally, if we calibrate our Mo EoS to a Cu scale dominated by reduced from shock compression data,²⁶ we obtain a Mo EoS compatible with the reduced shock Mo EoS reported by Ref. 5 and references therein. Further discussion of these trends is provided in Text S1 of the [supplementary material](#).

Of these previous studies, the results from our experimental measurements of Mo encased in Cu and Ne under compression to 328 GPa are the most compatible with the Mo volumes collected in a He PTM in standard anvils when applying related pressure scales.^{21,35} The current experimental results demonstrate that fully encapsulating high-strength metals, such as Mo, in a softer metal such as Cu dramatically improves the compression conditions in the tDAC to multi-megabar conditions, and the EoS fits offer a reliable ultrahigh-pressure calibration. Results from this work are broadly applicable to all materials compressed in the tDAC that are stiffer than Cu.

CONCLUSIONS

In this work, toroidal configurations were developed to fully encase Mo samples in Cu. Cu is a soft metal that does not support significant deviatoric stress under uniaxial compression, and it has a well calibrated EoS. These factors make Cu a reasonable candidate for a solid pressure-transmitting medium and pressure calibrant in the tDAC. The atomic volumes of Mo were probed while fully encased in Cu to 336 GPa in the tDAC and encased in Ne to 231 GPa on standard anvils. For comparison, the volumes and elastic moduli of Mo were also calculated with pressure using DFT methods. Utilizing the elastic moduli and experimentally measured lattice volumes of Mo and Cu, we evaluated the uniaxial stress experienced by Mo and Cu to 336 GPa. We found that Cu supports a uniaxial stress of up to 5 GPa under nonhydrostatic loading to 336 GPa. We also found that this uniaxial stress model cannot be applied to Mo because Mo compresses through an isotropic state at 180 GPa. Since the Mo (200) lattice plane produced the smallest atomic volumes for all PTMs utilized, an EoS was calibrated to our Mo (200) volumes with Cu pressure as the closest approximation to the hydrostatic value. The Mo EoS measured from our data collected in a Cu PTM and a Ne PTM agree within 1%, with the Cu PTM data producing lower K' fits. The pressures predicted from the EoS calibrated to our combined datasets [$V_0 = 15.592(1)$, $K_0 = 261$ GPa, $K' = 4.061(3)$] agree with extrapolations of hydrostatic Mo EoSs within $\sim 1\%$ at 330 GPa. These results highlight that copper dramatically redistributed the stresses in the tDAC under compression to multi-megabar conditions such that the Mo volumes measured are consistent with Mo measurements in Ne and He.

SUPPLEMENTARY MATERIAL

See the [supplementary material](#) that contains a discussion of the differing Cu scales applicable to this study. It also provides tables of the measured Cu and Mo volumes from each sample, the calculated Cu elastic constants with pressure, and additional EoS fittings to the Mo data. It includes figures depicting the calculated structural stability of Mo with pressure, P - V data for Mo calculated from the (110) plane, the elastic stiffness constants of Cu, volumetric representations of the elastic stiffness tensor with pressure for Mo and Cu, and comparisons of the Mo EoS fits utilizing differing Cu pressure scales.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

C. C. Zurkowski: Conceptualization (lead); Data curation (lead); Formal analysis (lead); Investigation (lead); Methodology (lead); Project administration (equal); Visualization (lead); Writing – original draft (lead); Writing – review & editing (lead). **R. E. Lim:** Formal analysis (supporting); Software (supporting); Visualization (supporting); Writing – review & editing (supporting). **O. S. Pardo:** Data curation (supporting); Writing – review & editing (supporting). **E. F. O'Bannon III:** Project administration (supporting); Supervision (supporting); Writing – review & editing (supporting). **K. Glazyrin:** Funding acquisition (equal); Methodology (supporting); Resources (supporting); Software (supporting). **P. Söderlind:** Formal analysis (equal); Investigation (equal); Methodology (equal). **Z. Jenei:** Conceptualization (supporting); Funding acquisition (lead); Methodology (supporting); Project administration (equal); Resources (lead); Supervision (equal); Writing – review & editing (supporting).

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DATA AVAILABILITY

The data used to obtain the results and conclusions presented in this work are provided in the main text and the [supplementary material](#). Additional data analysis related to this paper may be provided upon request to the corresponding authors.

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