Equation of state for technetium from X-ray diffraction and first-principle calculations

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The ambient temperature equation of state (EoS) of technetium metal has been measured by X-ray diffraction. The metal was compressed using a diamond anvil cell and using a 4:1 methanol-ethanol pressure transmitting medium. The maximum pressure achieved, as determined from the gold pressure scale, was 67 GPa. The compression data shows that the HCP phase of technetium is stable up to 67 GPa. The compression curve of technetium was also calculated using first-principles total-energy calculations. Utilizing a number of fitting strategies to compare the experimental and theoretical data it is determined that the Vinet equation of state with an ambient isothermal bulk modulus of $B_{0T} = 288$ GPa and a first pressure derivative of $B' = 5.9(2)$ best represent the compression behavior of technetium metal.

I. INTRODUCTION

Technetium, the lightest radioelement, exhibits a hexagonal-closed-packed (HCP) structure as a pure element. Nuclear fission reactors produce considerable quantities of ^{99}Tc , which has one of the largest fission yields ($\sim 6\%$) as well as a long half-life ($t_{1/2} = 213\,000$ years, $\beta^- = 293$ keV). Technetium chemistry has been explored for applications in nuclear waste and reprocessing since the 1960's, but a number of fundamental properties of the element remain poorly studied. The phase diagram of metallic technetium is one of the least explored for any transition metal with minimal investigations establishing the structure and properties of technetium metal at high pressures. Accordingly, understanding the pressure and temperature dependence of thermal, mechanical, and electronic properties of technetium is of significance to nuclear waste storage and condensed-matter physics.

Owing to the challenges of studying radioactive elements, previous measurements of pressure-dependent properties of technetium are sparse and are summarized here. In 1955, using an opposed anvil geometry, Bridgman observed the resistance and shear characteristics of technetium up to 10 GPa and found the hcp phase stable with no irregularities.[1] Several studies have shown that the superconducting transition temperature decreases at pressure up to 11 GPa.[2][3][4] For years it has been assumed that nuclear decay is invariant but at least three groups have challenged this belief by showing that the decay constant of $^{99\text{m}}\text{Tc}$ can decrease by 0.023% - 0.046% at 10 GPa.[5–7] For these measurements the compressibility was approximated based on observation made by Waser and Pauling,[5] which resulted in an estimated bulk modulus of 370 GPa. The ambient pressure bulk modulus and other elastic moduli have been determined multiple times by experiments and calculations, Table III, with no reference to how these values or other properties vary under high pressures. In 1989, Guillermet[8] published an extensive review of the thermodynamic properties of technetium and then in 1999 the Nuclear Energy Agency published a report for the Thermodynamic Data Base project on the Chemical Thermodynamics of Technetium[9] which both demonstrate a lack of data on the materials properties of elemental technetium at extreme conditions.

Here we report room-temperature synchrotron diffraction measurements up to 67 GPa and establish an EoS derived from non-hydrostatic high-pressure diffraction experiments. In addition, first-principles total-energy calculations have been carried out to determine the structural properties and compressibility of bulk technetium up to 273 GPa. Our objective is to determine an EoS of technetium and create a baseline for further high pressure studies of technetium metal and relevant systems.

II. METHODS

Caution: Technetium-99 is a weak beta emitter ($E_{\max} = 293$ keV). All manipulations were performed in a radiochemistry laboratory at UNLV designed for chemical synthesis using efficient HEPA-filtered fume hoods, and following locally approved radioisotope handling and monitoring procedures.

Technetium-99 metal was synthesized as polycrystalline aggregates in the radiochemistry laboratory at UNLV as previously described.[10] A modified Mao-Bell cell with a slot opening and a four-post cell with a wide aperture were used. Mao-Bell type cell was configured with two standard brilliant cut diamonds, 300 μm culets. The four-post cell was equipped with one standard and one Boehler-Almax[11] diamond. A grain of technetium no more than 15 μm thick was loaded into a 100-150 μm diameter hole in a rhenium gasket with a 10 μm thick flake of gold (Alfa Aesar 99.8% pure) and then filled with a 4:1 mixture of methanol-ethanol as the pressure transmitting medium. The sample and pressure standard were placed approximately 15 μm apart. Using a micro-focused beam of less than 10 μm , diffraction patterns of the standard were collected independently of the sample. The choice in pressure medium is not ideal for hydrostatic measurements beyond 10 GPa[12] but can yield valuable information when limited in the choice of confining media by safety concerns for handling radioactive material.

Angular-dispersive X-ray powder diffraction data of technetium and gold in a diamond-anvil cell was obtained at beamlines 16-ID-B and 16-BM-D of the High Pressure Collaborative Access Team (HPCAT) at the Advanced Photon Source (APS). In order to prevent dispersal of radioactive material in the case of diamond failure, mylar windows were added to the DAC containment. At each beamline, diffraction patterns were collected with a MAR345 image plate with incident monochromatic beams of 29.200 keV and 33.169 keV X-rays. The sample to detector distances were calibrated with CeO_2 (SRM 674b), then the two-dimensional images were integrated and corrected for distortions using FIT2D.[13] Rietveld refinements were performed using Topaz4.

First-principles total-energy calculations were performed using spin-polarized density functional theory, as implemented in the Vienna Ab initio Simulation Package (VASP).[14] The exchange-correlation energy was calculated using the generalized gradient approximation[15] (GGA) with the parametrization of Perdew and Wang[16] (PW91). This functional was found to correctly describe the geometric parameters and properties of technetium bulk and cluster structures.[17][18]

The interaction between valence electrons and ionic cores was described by the Projector Augmented Wave (PAW) method.[19][20] The Tc $4p^6 5s^2 4d^5$ electrons were treated explicitly as valence electrons in the Kohn-Sham (KS) equations and the remaining cores were represented by PAW pseudopotentials. The core radii of the PAW potential for Tc is 2.75. The KS equations were solved using the blocked Davidson iterative matrix diagonalization scheme followed by the residual vector minimization method. The plane-wave cutoff energy for the electronic wave functions was set to 500 eV. The technetium HCP crystal structure was optimized with periodic boundary conditions applied using the conjugate gradient method, accelerated using the Methfessel-Paxton Fermi-level smearing[21] with a Gaussian width of 0.1 eV. The total energy of the molecular system and Hellmann-Feynman forces acting on atoms were calculated with convergence tolerances set to 10^{-3} eV and 0.01 eV/ $\text{\AA}$, respectively.

Structural optimization was carried out using the Monkhorst-Pack special k -point scheme[22] with a $11 \times 11 \times 11$ mesh for integration in the Brillouin zone (BZ). For each compression state, the c/a ratio optimization of the lattice parameters was performed at constant volume.

FIG. 1. A representative series of diffraction patterns of technetium up to 67 GPa. Three low angle peaks were contributed from the sample containment.

TABLE I. Compression data of technetium. The estimated standard deviation of lattice parameters is lower than 0.0008 Å and the pressure uncertainty is lower than 2 GPa.

P_{Au} (GPa)	a (Å)	c (Å)	V (Å ³ /atom)	a_{Au} (Å)	P_{DFT} (GPa)	V_{DFT} (Å ³ /atom)
0.08	2.7404	4.3993	14.31	4.0779	0.0	14.50
0.32	2.7390	4.3984	14.29	4.0760	1.2	14.45
0.39	2.7388	4.3980	14.28	4.0755	4.6	14.29
0.47	2.7386	4.3979	14.28	4.0748	12.1	13.98
2.12	2.7355	4.3865	14.21	4.0620	20.4	13.67
2.44	2.7347	4.3841	14.20	4.0596	29.5	13.37
2.63	2.7343	4.3830	14.19	4.0582	39.7	13.07
2.89	2.7336	4.3813	14.18	4.0563	50.7	12.78
3.08	2.7334	4.3817	14.18	4.0548	63.1	12.49
3.26	2.7327	4.3804	14.16	4.0535	76.6	12.21
3.61	2.7316	4.3784	14.15	4.0510	91.5	11.93
3.94	2.7305	4.3782	14.13	4.0486	108.0	11.65
4.18	2.7301	4.3770	14.13	4.0470	125.9	11.38
4.9	2.7276	4.3743	14.09	4.0423	145.6	11.12
5.6	2.7259	4.3710	14.06	4.0370	167.1	10.85
5.8	2.7256	4.3694	14.06	4.0357	190.4	10.60
6.0	2.7254	4.3677	14.05	4.0344	215.9	10.34
6.2	2.7251	4.3667	14.04	4.0333	243.4	10.09
6.4	2.7247	4.3666	14.04	4.0318	273.2	9.85
7.4	2.7215	4.3628	13.99	4.0256		
7.7	2.7213	4.3599	13.98	4.0232		
8.0	2.7203	4.3598	13.97	4.0215		
12.3	2.7078	4.3432	13.79	3.9957		
13.1	2.7061	4.3398	13.76	3.9912		
14.8	2.7030	4.3345	13.71	3.9823		
16.5	2.6971	4.3231	13.62	3.9731		
17.7	2.6962	4.3229	13.61	3.9672		
22.2	2.6881	4.3095	13.48	3.9455		
31.3	2.6692	4.2729	13.18	3.9070		
32.7	2.6648	4.2711	13.13	3.9014		
36.0	2.6574	4.2564	13.02	3.8891		
40.1	2.6479	4.2435	12.88	3.8745		
43.7	2.6436	4.2355	12.82	3.8624		
46.0	2.6406	4.2280	12.77	3.8551		
48.4	2.6346	4.2254	12.70	3.8474		
51.8	2.6317	4.2120	12.63	3.8372		
57.4	2.6214	4.1982	12.49	3.8210		
62.0	2.6161	4.1868	12.41	3.8084		
63.6	2.6138	4.1823	12.37	3.8041		
67.1	2.6054	4.1775	12.28	3.7948		

III. RESULTS & DISCUSSION

Representative diffraction patterns measured over the pressure range of this work are shown in Figure 1. The mylar windows contributed three reflections to each diffraction pattern at $2\theta = 6.4^\circ, 8.6^\circ, 10.9^\circ$; these reflections were excluded from the final refinements. Eight reflections belonging to the sample were identified in the region of $2\theta = 10^\circ - 30^\circ$. At each pressure, seven peaks were observed which index to gold. The sample pressure was determined using the EoS parameters recommended by Takemura and Dewaele,[23] $B_0 = 167$ GPa, and $B'_0 = 5.9(1)$. No correction was applied to the pressure. Uncertainty in the pressure was estimated to be less than 2% over this pressure range.[24] The measured P-V data points are presented in Table I and plotted in Figure 3a.

A 4:1 mixture of methanol-ethanol is commonly used as a quasi-hydrostatic medium and is reported to provide hydrostatic conditions up to 10.5 GPa.[12,25] In a nonhydrostatic environment each crystallite experiences different stress conditions. The micro-stress may be estimated from the broadening of the diffraction peaks[26] and the Young's modulus.[8] Figure 2 shows the evolution of the micro-stress as a function of pressure. Below 9 GPa, when the medium is a fluid, there is no significant change in micro-stress. Once the medium is solid, the stress profile displays three domains: strongly increasing up to 22 GPa, invariant from 22 to 40 GPa and then gradually increasing beyond 40 GPa. The considerable amount of micro-stress, at these pressures introduces uncertainty into lattice parameters and consequently the equation of state.

FIG 2. Micro-stress in the technetium sample as a function of pressure as determined following the procedure from Anzellini et al.[26] using the Young's modulus determined by Love et al.[27]

In light of the variation of micro-stress with pressure, two pressure ranges were considered in determining the EoS, 0-10 GPa and 0-67 GPa. The first range is in the hydrostatic regime for this pressure medium and the second is the full pressure range of this study. Using the software package EoSfit7GUI[28] the data was fit to a third-order Birch-Murnaghan and Vinet EoS at each step in the analysis. For the low pressure range the 2nd and 3rd order equations are used, while only the 3rd order equations are considered for the full pressure range. Given the strong correlation between the bulk modulus and its pressure derivative it would be preferable to independently determine the bulk modulus and its pressure derivative. In a recent study of the gold pressure standard[23], the ambient-pressure bulk modulus was fixed to a value that the literature agreed upon from several experimental methods, and then the pressure derivative was refined against the high pressure diffraction data. Without a surplus of values to compare from multiple experimental techniques we used the sole published value determined from ultrasonic data. The estimated uncertainties reported in parenthesis include contributions from the pressure determination, lattice parameters determination and the quality of the fitting of the PV data. Fitting errors are defined at the 95% confidence level.[28]

The EoS parameters for the hydrostatic pressure range refined using the second order Vinet equation are $V_0 = 14.301(4)$ Å³/atom, $B_0 = 333(8)$ GPa and for Birch-Murnaghan equation are $V_0 = 14.305(4)$ Å³/atom, $B_0 = 321(8)$ GPa. The refined EoS parameters are $V_0 = 14.307(7)$ Å³/atom $B_0 = 310(20)$ GPa, $B'_0 = 6(6)$ for both the third order Vinet and Birch-Murnaghan equations. The data from the full pressure range was fit with all parameters free obtaining $V_0 = 14.310(4)$ Å³/atom $B_0 =$

309(7) GPa and $B'_0 = 4.7(4)$ for the Vinet equation and $V_0 = 14.309(4)$ Å³/atom, $B_0 = 309(7)$ GPa and $B'_0 = 4.6(4)$ for the Birch-Murnaghan equation. For the combined X-ray and Ultrasonic analysis, the isothermal bulk modulus was fixed at $B_0 = 288$ GPa, the converted value from the adiabatic bulk moduli determined from the ultrasonic measurement.[27,29] For the Vinet equation this yielded values of $V_0 = 14.320(2)$ Å³/atom, $B_0 = 288$ GPa and $B'_0 = 5.9(2)$ for the Birch-Murnaghan equation and $V_0 = 14.320(2)$ Å³/atom, $B_0 = 288$ GPa and $B'_0 = 5.8(2)$.

The calculated volumes of technetium in hcp packing show a continuous decrease up to 273 GPa. The choice in functional has been previously demonstrated to work reliably for technetium-containing structures.[18] While the volumes are systematically overestimated by about 1.3%, the compressibility is in good agreement with the experimental data. A similar fitting method was applied here as for the XRD data. The refined values from the Vinet EoS are $V_0 = 14.49(2)$ Å³/atom, $B_0 = 304(1)$ GPa and $B'_0 = 4.6(2)$.

Table II. Summary of EoS parameters for experimental hydrostatic and nonhydrostatic pressure ranges and the theoretical compression curve using the Vinet and Birch-Murnaghan equation of state with all parameters free and with the bulk modulus fixed at the ultrasonic result, 288 GPa[27].

EoS Type	Vinet 2	BM 2	Vinet 3	BM 3	Vinet 3	BM 3	Vinet 3	BM 3	Vinet 3	BM 3
Max Pressure	10 GPa (XRD)		10 GPa (XRD)		67 GPa (XRD)		67 GPa (US+XRD)		273 GPa (DFT)	
V_0	14.301(4)	14.305(4)	14.307(7)	14.307(7)	14.310(4)	14.309(4)	14.320(2)	14.320(2)	14.49(1)	14.48(2)
B_0	333(8)	321(8)	310(30)	310(30)	309(7)	309(7)	288	288	304(1)	314(2)
B'_0	-	-	6(6)	6(6)	4.7(4)	4.6(4)	5.9(2)	5.8(2)	4.57(2)	4.18(3)

EoS parameters are compared by pressure range, and EoS type in Table II. There is no appreciable difference between the quality of the fit or the resulting parameters between the two EoS forms except in the case of the 2nd order equations in the hydrostatic domain. Hydrostatic data is preferred for EoS determination, but the total compression in this range is only ~3%, which is inadequate to define the parameters of a 3rd order EoS. The hydrostatic data fits an unreasonably stiff model at high pressures, Figure 3b. Finally, the difference between observed and predicted pressure shows a random distribution as can be seen in the difference plot of Figure 3c. As expected the spread in the data under hydrostatic conditions is considerably lower than that at higher pressures. At low pressures the difference is less than 0.4 GPa while over the entire pressure range the spread is four times greater.

There are a number of factors that need to be taken into consideration when evaluating our equation of state for technetium. First, analysis of the two pressure ranges offer different interpretations for the compressibility of technetium with the hydrostatic range indicating that the bulk modulus is greater than 320 GPa while the nonhydrostatic data suggest that it is less than 310 GPa. While a larger pressure range alone does not automatically improve the equation of state, it is necessary to achieve a sufficiently large compression in order to estimate the bulk modulus and begin to refine higher order parameters. The pressure range achieved in the diffraction experiment under hydrostatic conditions resulted in a compression of ~3% while the maximum compression for the experiment was ~15%. The conflict between the need for larger compression and hydrostatic conditions is a challenge for incompressible material such as technetium.

Over the years, bulk moduli of most elements, including technetium, have been repeatedly revised, reflecting the challenges associated with these measurements. The selection listed in Table III is representative of recent work on technetium. The consensus is that the bulk modulus is just under 300 GPa. In this study a compression curve was produced from DFT methods, which when fit to an equation of state agrees well with the diffraction data. Previously, using the same GGA/PW91 methodology, the bulk modulus was reported to be 298 GPa[18]. The difference between these is due to the previous work making a determination via elastic constants while the more recent is a fitting of the structural evolution.

At ambient conditions, rhenium and technetium are isostructural and rhenium is commonly used as a nonradioactive technetium homolog that can provide valuable insights on the behavior of technetium. The equation of state of rhenium has been extensively studied by X-ray diffraction up to the highest achievable static pressures[30] and nevertheless disagreement in the EoS parameters persists.[26] The effects of non-hydrostatic compression on EoS parameters are widely debated in the high pressure community and the need for an accurate description of the stress state of the sample and pressure gauge is paramount to reliable pressure determination. Experimental results for rhenium from ultrasonic, Hugoniot, and isothermal data agree that the room temperature bulk modulus is 350-376 GPa[26,30–37] with greater spread in the first pressure derivative values. For both metals, a range of values has been established without an unambiguous solution. It is clear that the similarities between rhenium and technetium hold true at extreme conditions and that their compression behaviors are sensitive to stress conditions, sample preparation, and diagnostic technique. The differences seen in EoS parameters for technetium are therefore not surprising and within expectation.

a) EOS of technetium

b) EOS of technetium

c) Pressure Difference

FIG. 3. Pressure-volume data of Tc. a) A comparison of the Vinet equation of state of technetium up to 67 GPa with a fixed bulk modulus and refined. b) Comparison of compressibility from DFT calculations and experimentally determined EoS up to 300 GPa with the equation of state refined from hydrostatic and nonhydrostatic conditions extrapolated out to 300 GPa. Uncertainties are smaller than the symbol size c) Pressure difference between experimental pressure and the respective equations of state. Orange squares for fixed bulk modulus and red circles for the refined bulk modulus.

TABLE III. Comparison of B_o and B'_o of technetium

B_o (GPa)	B'_o	Method ^c	Reference
288		Ultrasonic (E)	Love <i>et al.</i> (Ref. [27])
281		Phonon Dispersion Curves (E)	Guillermet and Grimvall (Ref. [8])
296.3		Pseudopotentials (C)	Baria <i>et al.</i> (Ref. [38])
297		Muffin-tin Orbital Theory (C)	Walzer (Ref. [39])
295		Metallic Electron-Gas Model (C)	Wojciechowski (Ref. [40])
298		GGA/PW91 (C)	Weck <i>et al.</i> (Ref. [18])
304(1) ^a	4.6(2) ^a	GGA/PW9 (273 GPa) ^b (C)	Current Work
309(7) ^a	4.7(4) ^a	XRD (67 GPa) ^b (E)	Current Work
288 ^d	5.9(2) ^a	US+XRD (67 GPa) ^b (E)	Current Work

^aThe value in parenthesis presents the uncertainty.

^bThe value in parenthesis represents the maximum pressure

^cThe letters E and C denote experimental and computational methods

^dFixed to value determined by ultrasonic measurement

An accurate determination of the bulk modulus of technetium will solidify our understanding of the trends describing the 4d transition metals. The bulk moduli of the transition metals are plotted against the number of d electrons in Figure 4. Manganese, 3d⁵, represents a minimum in the bulk moduli. This minimum is not seen in rhenium for the 5d metals and is suggested to be at technetium for the 4d metals. Theoretical studies of the transition metals[38–40] suggest that the half-filled d-shell corresponds to a softening for the 4d to a smaller degree than what is seen in the 3d metals. The nonhydrostatic X-ray data suggest that this effect is smaller than previously estimated while the combined data suggest the opposite, that the effect is stronger.

FIG. 4. The bulk moduli of the transition metals are plotted with respect to their period as a function of d-electrons. Bulk moduli presented are from two computational studies looking at all of the transition metals with an unfilled d-shell.[38,40]

IV. CONCLUSION

An analysis of the equation-of-state for technetium has been performed from X-ray diffraction data, ultrasonic measurements and DFT calculations. The study produced three equations of state to consider for technetium which agree

very well in the experimental pressure range. The EoS refined from only the diffraction data yielded the best match to theory but the fit using the fixed bulk moduli give the best representation of the physical behavior of technetium metal, $B_o = 288$ GPa and $B'_o = 5.9(2)$. We have confirmed that the HCP phase is stable up to 67 GPa. Nonhydrostatic behavior is observed at high pressures but did not prevent a quality fit from being obtained for the equation of state as is evident from the low average difference in the calculated pressure. This equation of state is considered a reliable description of technetium compression behavior within the bounds reported here. To further our understanding of the pressure-dependent behavior of technetium and periodic trends of transition metals it would be beneficial to investigate the effects of temperature and pressure on the structural properties of technetium under hydrostatic conditions up to higher pressures.

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