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/math>-Technetium: An allotrope with a nonstandard
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β -Technetium, an allotrope with a non-standard volume-pressure relationship

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We report the synthesis and structure of the second allotrope of technetium, β -Tc. Transformative pathways are accessed at extreme conditions using the laser-heated diamond anvil cell and confirmed with *in situ* synchrotron X-ray diffraction and Raman spectroscopy. β -Tc is fully recoverable to ambient conditions, although counter to our DFT calculations predicting a face-centered-cubic lattice, we observe a tetragonal structure ($I4/mmm$) that exhibits further tetragonal distortion with pressure. β -Tc has an expanded volume relative to the hcp ground state phase, that when doped with nitrogen has an unexpected volume lowering. Such anomalous behaviour is possibly indicative of a rare electronic phase transition in a 4d element.

I. INTRODUCTION

Technetium's radioactivity and natural scarcity have led to limited experimental studies, especially at elevated pressures and temperatures. A more complete understanding of technetium would provide valuable insight to many other transition metals given its central position in the transition metal block of the periodic table. Owing to the difficulty in working with technetium, its group-7 neighbor rhenium is often used as a stand-in.[1] Both technetium and rhenium have only one confirmed allotrope, an hcp metallic phase. Hcp Tc is known to be stable to the melt at ambient pressure and to 67 GPa at 300 K;[2, 3] whilst hcp Re is stable against 100s of GPa of compression and predicted to be stable beyond the TPa regime.[4, 5] In contrast, the other group-7 element manganese has 5 reported allotropes. Two of its polymorphs (α and β) have complicated crystal structures, and α -Mn is a well-known antiferromagnet (AFM).[6–8] Another polymorph, γ -Mn, is fcc in its 1368–1406 K stability window,[9] but distorts into a bct phase below its Néel temperature due to its antiferromagnetism.[10, 11] When stabilized at ambient conditions, γ -Mn exhibits an expanded lattice – as much as a 10% increase in atomic volume is observed.[12]

There have been reports of chemical synthesis and purification routes using either thin film grown epitaxially by ion sputtering or thermal decomposition involving Tc that have suggested a cubic (fcc) allotrope.[13, 14] However, these results are treated with caution, as these studies have conflicting and unrepeatable results and their experimental procedures show that they are not within a single component composition. This is further evidenced by conflicting reports of elemental reactions between Tc and anion species e.g. C, N, that all report similar unit cell parameters of approx. 3.98 Å – comparable to the un-

confirmed reports of fcc Tc.[2] For Tc carbides a recent publication refuted the existence of the experimentally reported high temperature cubic phase of TcC based on evolutionary algorithm simulations.[13] It concludes that Tc₆C, the most stable carbide on the convex hull, could not be made, and that the cubic phase observed is a high temperature cubic phase of elemental technetium which becomes thermodynamically stable above 1775 K. Such inconsistencies arise from elemental Tc not found naturally in the earth's crust and its purification being challenging.

In this publication, we unequivocally confirm the existence of the second allotrope of Tc that we designate as β -Tc. β -Tc is made at high temperature, high pressure conditions, and is recoverable to ambient conditions without a substrate. X-ray diffraction (XRD), Raman spectroscopy, and scanning electron microscopy (SEM) measurements imply this is the first realized pure allotrope of Tc with anomalous behavior not previously characterized. Room temperature XRD reveals an expanded volume compared to the ground state hcp phase and a tetragonal distortion; while further compression reveals anomalous volume-pressure relations with a continuous deviation from an fcc motif. Density functional theory (DFT) simulations apt for a simple elemental metal are incongruent with the experimental results, indicating there is a complex underlying electronic behavior to this new allotrope. We have synthesized β -Tc in two different chemical environments, Ar and N₂, and we note differences with their respective structural responses with pressure.

II. METHODS

Caution! ⁹⁹Tc is a weak β emitter ($E_{max} = 293$ KeV) with a half-life of 200,000 years and no stable isotopes. Therefore, any manipulation of the material was performed in a posted radio-materials laboratory. All efforts followed locally approved handling and monitoring

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procedures for the specific radioisotope. Details on the containment of samples can be found in the Supplemental Materials.

Hcp Tc metal samples were prepared by UNLV Radiochemistry following the route described in Silva *et al.* [15] NH_4TcO_4 , in a fused quartz boat, was placed in a tube furnace which was flushed with Ar at 300 °C and then ramped to 910 °C. This is followed by steam-reforming thermal reduction of TcO_2 at 910 °C under a wet Ar atmosphere in the presence of activated carbon. This method is shown to consistently produce pure Tc metal as characterized by transmission electron microscopy (TEM) analysis, XRD, and electron energy loss spectrometry (EELS). Poly-crystalline agglomerates of Tc metal were loaded into diamond anvil cells (DAC) with diamonds ranging from 250–600 μm culets and gas loaded with either Ar or N_2 at 1.5 and 3 kbar, respectively. Double sided laser (Nd:YAG $\lambda = 1064\text{ nm}$) heating experiments were performed with *in situ* angle dispersive synchrotron XRD and optical pyrometry measurements at HPCAT, 16-ID-B of the Advanced Photon Source at Argonne National Laboratory ($\lambda = 0.406626\text{ \AA}$). Significant consideration was given to ensure that the laser hot spot, focused X-ray beam, and the defined region of interest sampled by optical pyrometry were all spatially equivalent, and aligned throughout the data acquisition.[16] Thermal radiation from the sample was collected and integrated by plotting light intensity as a function of wavelength and corrected for with a transfer function. Temperature measurements were determined by fitting the thermal emission spectra using Planck’s distribution function for a black-body emitter, assuming a grey-body approximation. Pressure was determined with either the equation of state of Ar or ruby fluorescence.[17, 18] SEM on the recovered sample was performed using a JEOL JSM-6700 field emission FE-SEM. In-house laser (YLF $\lambda = 1070\text{ nm}$) heating experiments were also performed using Raman scattering as a probe. Further details are in the Supplemental Materials.

Plane-wave density functional theory (PW-DFT) [19, 20] simulations were performed with the Vienna *ab initio* simulation package (VASP) version 5.4.4 using the generalized gradient approximation (GGA) functional of Perdew, Burke and Ernzerhof (PBE).[21] The simulations used an evenly spaced Γ -centered k-point grid with 0.2 \AA^{-1} resolution.[22] As the system is metallic, the Brillouin zone was integrated the first order method of Methfessel and Paxton with a width of 0.20 eV .[23] The basis set cutoff energy was 600 eV using the projector augmented wave (PAW) [24] pseudo-potentials formulated for PBE (version 5.4) with valence configurations of $4p^6 5s^2 4d^5$ for Tc (ie. “Tc_pv”), $2s^2 2p^3$ for N, and $2s^2 2p^2$ for C. Energy convergence tolerances for the self-consistent field steps were set to 10^{-9} eV and force convergence tolerances for the geometry optimizations to $10^{-4}\text{ eV \AA}^{-1}$. To minimize the effect of Pulay stress, the volume changing structural optimizations were performed in three parts: two sequential optimizations and

a final single point energy evaluation. Each optimization allowed all degrees of freedom to vary except for when a specific structural constraint was imposed as noted in the text, for instance the c/a ratio along the Bain path.

III. RESULTS AND DISCUSSION

Hcp Tc was observed to be stable during laser heating from near ambient to pressures below 4 GPa and to temperatures up to and post-quenching the melt. A typical XRD pattern of the hcp Tc starting material before laser heating is shown in Figure 1. All peaks can be attributed to either hcp Tc or the inert Ar medium. While heating above 4 GPa at temperatures around 1500 K, hcp Tc was seen to transform to a new allotrope, β -Tc. The transformation is marked by the appearance of a new set of Bragg peaks. β -Tc is fully recoverable to ambient conditions (XRD pattern and Rietveld fit of recovered sample in Supplemental Materials). Figure 1 contrasts the Le Bail refinements of the XRD patterns of hcp and β -Tc at 4.5 GPa and ambient temperature. Hcp Tc was fit with a previously determined $P6_3/mmc$ structure with starting values of $a=2.7409\text{ \AA}$ and $c=4.3987\text{ \AA}$.[25] β -Tc can be indexed at this pressure by a tetragonal space group $I4/mmm$ with atoms on the 2a Wyckoff position, $a=2.806(1)\text{ \AA}$, and $c=3.965(5)\text{ \AA}$. This new allotrope persists upon successive laser heating up to 2800 K at pressures between 10–30 GPa.

The transformation into β -Tc can also be observed through Raman spectroscopy. The doubly degenerate E_{2g} phonon is the only Raman active optical mode of hcp Tc,[26] observed here at 135 cm^{-1} at ambient conditions. The bct structure of β -Tc has a single atom primitive unit cell ergo no allowed optical Raman modes, leading to a featureless spectrum shown in the inset of Figure 1. No evidence of other modes were observed across the full Raman spectral range, indicating that no other elements are present in significant enough concentration to provide a spectroscopic signature.

Using *in situ* XRD, the stability of the Tc allotropes were mapped as a function of both pressure and temperature, as summarized in Figure 2. Below the critical transformation pressure of $\sim 4\text{ GPa}$, the hcp allotrope of Tc is stable — even after quenching from the melt. Above this critical pressure, the phase boundary is very steep and the transition temperature has no pressure dependence. The boundary was challenging to map above this pressure as the phase transformation process was observed to be sluggish. The data representative of β -Tc in Figure 2 are shown only when a single phase was confirmed by XRD. The phase stabilities clearly demonstrate that the non-hcp allotrope can only be obtained through high temperature coupled with high pressure.

The metastable recoverability to ambient conditions of the β -Tc phase is confirmed by XRD Rietveld analysis. Safety protocols do not allow for decompression of a radioactive sample during an experiment conducted at the

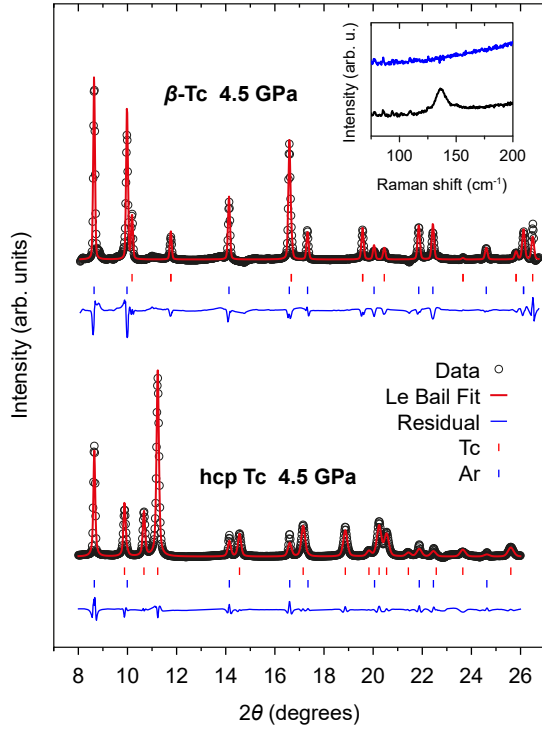


FIG. 1. XRD patterns of a Tc at room temperature pre (hcp, bottom) and post (β -Tc, top) laser heating. Black open circles are the experimental data, the Le Bail refinement is shown in red, and the residual is shown in blue. All peaks were attributed to Ar or Tc; tick marks for each phase shown below peaks. Inset: Raman spectrum of a room temperature Tc sample pre (hcp, black) and post (β -Tc, blue), laser heating.

APS, so all data was collected upon increasing pressure. Samples were decompressed and recovered once back at UNLV for further study. The Rietveld refinement of this recovered phase however showed some discrepancy between experimental and calculated peak intensities for the 112/200 and 103/211 peaks, yet the overall fit is very good with $wRp = 9.4\%$ and $R = 4.5\%$. Surprisingly, the measured ambient volume of the new tetragonally indexed phase ($15.92 \text{ \AA}^3/\text{Tc}$, $a=2.829(6) \text{ \AA}$, $c=3.99(1) \text{ \AA}$) is significantly larger than the $14.31 \text{ \AA}^3/\text{Tc}$ volume of the hcp phase.[3] This volume difference is also large compared to previous shock simulations where the predicted fcc structure has an ambient volume much closer to that of the hcp phase, $14.501 \text{ \AA}^3/\text{Tc}$. [27]

The measured larger unit cell volume of the β -Tc phase, compared to the ambient hcp phase is a fascinating observation that demands further thought (Figure 3a). A major chemical concern is whether the laser heating protocol is in fact leading to undesired Tc-carbide formation, leading to this observed volume expansion. To address this, we conducted these experiments 12 times, using laser heating methods over short timescales of 1-2 seconds to minimize any thermal build up and the promotion of carbon diffusion from the diamond anvils. Our SEM and Raman spectroscopy measurements on recov-

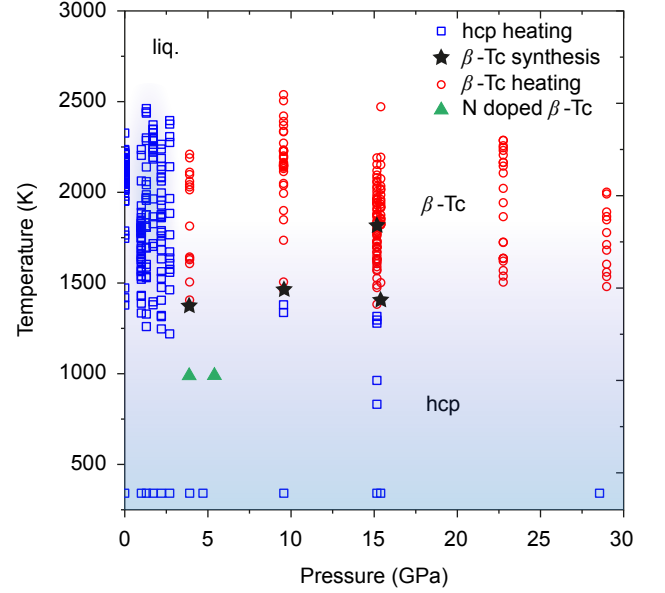


FIG. 2. Diagram showing the phase stability domains of hcp and β -Tc. The open markers represent a pressure-temperature condition where a single phase of hcp (squares) or bct (circles) could be confirmed by XRD. Stars indicate a point where the hcp-bct transformation was observed. Data at 15 GPa and 1800 K representing the transformation of β -Tc was uncharacteristically high due to a jump in temperature during laser heating, yet it is shown for completeness. Triangles indicate the P,T conditions where N doped β -Tc is formed.

ered samples revealed no presence of carbide formation. Also, there is no known eutectic between Tc and C, and the most modern evolutionary algorithm simulations predict that Tc carbide is not energetically favorable. In the case of Fe-C, it is important to note that the volume-carbon content relation for the bcc phase results in a volume lowering compared to the pure element.[28]

Figure 3a plots experimental pressure/volume data of β -Tc synthesized in Ar and N_2 environments along with that of the hcp phase [3] and the DFT optimized hcp, fcc, and bct phases. Compression of β -Tc reveals that the tetragonal distortion present at ambient pressure becomes more pronounced with pressure. From 0–16 GPa, the tetragonal distortion hovers around $\Delta=0.004$ ($c/a=1.410$). Above 16 GPa there is a sudden increase in the tetragonal distortion, becoming $\Delta=0.013$ ($c/a=1.401$) at 29 GPa. This is clearly observed in our XRD experiments through peak shifts that are inconsistent with a cubic structure and a peak splitting of the 200 and 211 peaks (Figure 3b left panel) with compression. Critically, at the high temperatures where β -Tc is formed, the lattice is indexed as fcc and there is no observation of peak splitting observed at ambient temperature. It is not common for fcc-like metals to tetragonally distort with compression, nor has such a distortion been predicted for

significantly reduced atomic volumes (see Table I). At ambient pressure the optimized bct structure retains its tetragonal distortion, while at the elevated pressure it reverts to an fcc structure with $c/a=\sqrt{2}$. For comparison, the DFT optimized fcc structures are also displayed in Table I, and they are consistent with those previously evaluated by DFT for an fcc Tc phase.[13, 27, 29] As a rudimentary structural survey provides no insight into the large atomic volume and tetragonal distortion observed for β -Tc, it is worth exploring the potential energy landscapes surrounding known transformations of an fcc metal. Along the Bain transformation path from bcc to fcc (in a $tI2$ representation) [30] in Figure 5a there is only a single energetic minimum around the fcc structure which has a sigmoidal increase in energy towards the bcc structure ($c/a=1$). This increase becomes steeper with pressure explaining why the 4.5 GPa optimization of the experimental bct structure resorts to an fcc structure. There is little volume variance for the optimized structures along the Bain path, with the atomic volume capping at its largest value ($14.6 \text{ \AA}^3/\text{Tc}$ at 0 GPa) for a c/a of 0.9. While the atomic volume is at its lowest around the fcc structure, it is simply too small anywhere along the Bain path (within the chosen electronic structure methodology) to explain what is observed experimentally for β -Tc synthesized in a non-interacting Ar environment.

As the Bain path indicates that no tetragonal modification of an fcc structure is favorable within the electronic structure method chosen, one can look to alternative modifications of the fcc structure to explain the experimental observations. One alternative is distortions of the angles between the lattice vectors of the fcc $hR1$ primitive unit cell. Such rhombohedral distortions give rise to vanadium's $\text{bcc} \rightarrow hR1 \rightarrow hR1 \rightarrow \text{bcc}$ phase progression with pressure.[31–33] It should be noted that at lower pressures a tetragonal or rhombohedral modification of an fcc structure would be indistinguishable in the experimental XRD data, but over the full pressure range the tetragonally distorted structure is shown to be correct. Tracing the variation of the energy with respect to the rhombohedral angle of $hR1$ Tc (Figure 5b) shows that once again the fcc structure ($\alpha=60^\circ$) is the lowest energy structure at all pressures evaluated. The rhombohedral distortion landscape has a global minima about the fcc structure that increases to a local maximum around the simple cubic (sc) structure ($\alpha=90^\circ$), evolving into a much sharper local minimum about the body-centered cubic structure ($\alpha=109.47^\circ$). The only marked change to the relative energetics with pressure along this pathway is an increasing unfavorability of the sc structure; the relative stability of the bcc phase varies by only $\sim 1 \text{ meV/Tc GPa}^{-1}$. The atomic volumes are found to vary greatly with rhombohedral distortion between the bcc and fcc structures, where regardless of pressure the structures near $\alpha=90^\circ$ become larger than those observed experimentally for β -Tc. They are also 9-12% larger than the predicted fcc/bcc structures.

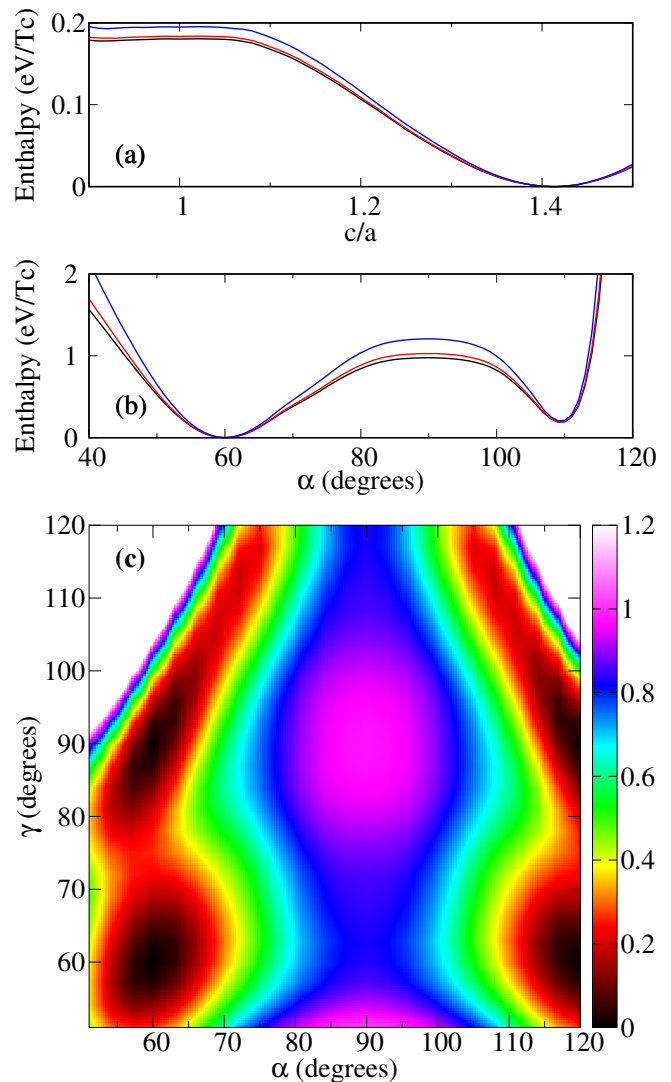


FIG. 5. (a) Enthalpy variation of the DFT optimized $tI2$ structures along the Bain path at 0 GPa (black), 5 GPa (red), and 25 GPa (blue). (b) Enthalpy variation of the DFT optimized $hR1$ structures with α at 0 GPa (black), 5 GPa (red), and 25 GPa (blue). (c) Heat map of the per atom enthalpy variation of a 0 GPa modified $hR1$ structure where $a=b=c$ but $\alpha=\beta \neq \gamma$. All enthalpies are relative to the fcc Tc structure, ie. $c/a=\sqrt{2}$ for $tI2$ or $\alpha=\beta=\gamma=60^\circ$ for $hR1$.

The 0 GPa energy landscape in Figure 5c expands on the analysis of a rhombohedral distortion by accounting for the 1-atom primitive cell of the bct structure taking on a lowered $hR1$ -like symmetry with $a=b=c$ but $\alpha=\beta \neq \gamma$ ($\alpha \approx 119.9^\circ$ and $\gamma \approx 90.1^\circ$ for the experimental structures shown in Table I). The fcc structure appears at four points on the plotted landscape (α, γ : $60, 60$; $60, 90$; $120, 60$; and $120, 90$), and it is always the lowest energy structure regardless of pressure (5 GPa plot in the Supplemental Materials). The Bain path as represented in Figure 5c (between $\alpha=120^\circ$, $\gamma=90^\circ$ and $\alpha=\gamma=109.47^\circ$) is the domain of greatest stability aside from the broad

basin about the conventional *hR1* fcc primitive unit cell, yet none of those structures thusly represented are stable or large enough to explain the experimental observations. Furthermore, the phonon band structure for fcc Tc at 0 and 5 GPa have no apparent Kohn anomalies (see Supplemental Materials) which are attributed to vanadium's distorted phase progression.[32, 34, 35] Peierls instabilities have been attributed to symmetry breaking distortions away from higher symmetry structures in known elemental systems like β -Sn, γ -Se, A17 P, and A7 P.[36–40] However, DFT optimizations of these structures for Tc either produced higher energies or resorted to the fcc structure itself, and attempts to refine the XRD data with these structures yielded worse fits of the data. Thus, within the weak electron correlation description of the GGA no common distortion is predicted to occur to explain the observations on β -Tc.

The previously discussed simulations continually produced structures with volumes too low compared to the experimental results, which is surprising as the PBE functional employed is well-known to typically overestimate the volume ($\leq 5\%$) of a system as may be seen in the comparison between the simulated and experimental volumes of the hcp phase in Figure 3a. On-atom electron localization through increased electron correlation effects is one possibility that could increase the atomic volumes, as it is known that with increased volume the individual atoms will tend towards a free-atom limit.[41] Screened on-site Coulomb interactions in the form of a Hubbard “+U” correction is one technique that can be used to correct an overly weak description of electron correlation in some density functionals and increase on-site localization of charge density.[42] We evaluated the ability of a single-parameter DFT+U applied to the Tc *d* electrons to determine if including such electron correlation effects could remedy the under-prediction of the volumes by the conventional GGA.[43, 44] The Hubbard parameter was determined using a linear response approach [45] giving $U_{\text{eff}}=2.95$ eV for the ambient hcp phase of Tc and $U_{\text{eff}}=3.15$ eV for the XRD determined ambient bct β -Tc structure, so a median value of $U_{\text{eff}}=3.05$ eV was used in the simulations. As with the pure GGA simulations, the GGA+U simulations underestimate the volume compared to the experimentally determined values with the predicted ambient fcc structure actually decreasing in volume by $0.03 \text{ \AA}^3/\text{Tc}$ in both the *tI2* and *hR1* representations. No new minima are observed with GGA+U along the Bain or rhombohedral transformation pathways. There is just a lowering of the energy penalty to adopt a non-fcc structure, ie. both the bcc and sc phases became more stable by ~ 0.08 eV/Tc in their 0 GPa *hR1* representations. As every simulation run gave similar results whether or not a Hubbard correction was included, one can ascertain that slightly stronger electron correlations than described by PBE are alone not the cause for the curious properties observed for this new Tc allotrope.

The effect of introducing varying amounts of nitrogen in the octahedral sites of an ambient pressure fcc Tc lat-

tice was performed using DFT to determine if doping could explain what was observed for the synthesis of β -Tc in N_2 . At the 3.5 wt% N level of doping, Tc_4N maintains a cubic structure with a volume beyond what was measured ($16.1 \text{ \AA}^3/\text{Tc}$). A step down in concentration to Tc_8N produces a $15.2 \text{ \AA}^3/\text{Tc}$ fcc Tc sublattice, close to what was measured experimentally and suggesting a dopant concentration of 1.8 wt% (11 atom%) N. However, the limits of detection for the EDX measurements are estimated to be slightly lower than this concentration (discussed in Supplemental Materials). By a concentration below the estimated limit of detection, 0.5 wt% (3 atom%), the DFT optimized cell remains cubic but is only $14.7 \text{ \AA}^3/\text{Tc}$, well below the measured value of the samples produced in N_2 . While DFT does indicate that N doping can cause the structures observed for synthesizing β -Tc in N_2 , the coarse agreement with experiment suggests that like β -Tc formed in Ar there is something more complicated occurring than can be predicted with a simple metallic picture.

Similar doping evaluations were done with carbon as the dopant, and in each case the carbon doped cell is slightly larger than its nitrogen doped counterpart. Carbon doping can be eliminated as a cause for the behavior observed for β -Tc synthesized in Ar as it would've required a concentration of nearly Tc_4C to obtain the volumes observed. A concentration that high is stoichiometric and should be detectable by XRD,[13] in addition there is no detectable Raman signature that must arise from a solid with more than one element type in its primitive unit cell. Additionally, Ar is an inert PTM and highly unlikely to dope a sample in the same way, especially as it is very large compared to β -Tc with a 4.3 GPa, 300 K fcc lattice constant of 4.7 \AA (ie. an atomic volume of 25.98 \AA^3) and a kinetic diameter of 3.542 \AA . [46, 47]

In this light, β -Tc is best considered as a high temperature phase of Tc. Although the shallow laser heating skin depth doesn't allow for a reliable volume of hcp Tc at high temperature, our thermal (isobaric) volumetric trends seem to roughly follow those previously detailed.[29, 48] Our most reliable high temperature structural refinement of β -Tc in Ar (9.7 GPa, 2147 K) is fcc with a volume of $15.6 \text{ \AA}^3/\text{Tc}$, whereas the hcp phase is roughly $15.0 \text{ \AA}^3/\text{Tc}$ at a similar temperature (0.1 GPa, 2263 K). Such an entropically favorable $\sim 5\%$ increase in atomic volume is not unheard of for transitions into high temperature phases. For instance, the atomic volume increases by 4% for the α -Mn to β -Mn transition at 1 atm,[49] and 1-2% for ε -Fe to γ -Fe between 52 and 86 GPa.[50] Additionally, the prismatic hcp to fcc transition in Ti exhibits a 14.2-19.5% volume increase.[51]

Furthermore, it is our hypothesis that β -Tc exhibits magnetic ordering, wherein the high temperature fcc structure is paramagnetic and it tetragonally distorts into the bct structure as it crosses its Néel temperature somewhere above 300 K.[41, 52, 53] Preliminary DFT+U simulations support this hypothesis with AFM type-I ordering similar to γ -Mn (with spins anti-parallel along

the [001] easy axis) being the most energetically favorable magnetic/non-magnetic configuration in the experimental bct structures and their similarly dimensioned fcc counterparts.[10, 11] Likewise, the volume contraction of high temperature β -Tc compared to ambient is likely analogous to Cr, which exhibits a volume contraction as it is heated through the first-order AFM to paramagnetic (PM) transition.[54] While an antiferromagnetic, high temperature phase can explain many of the volume anomalies observed for β -Tc, further experimental developments are needed for confirmation.

IV. CONCLUSIONS

In conclusion, we have synthesized a metastable tetragonal allotrope of Tc using high temperature and high pressure conditions that is fully recoverable to ambient conditions. β -Tc tetragonally distorts at room temperature, evident from the splitting of the 200 and 211 XRD peaks. The tetragonal distortion becomes more pronounced with increased pressure indicating a pressure-volume response quite dissimilar to what should be expected for a conventional fcc elemental phase, in particular for a 4d transition metal whose behavior could be anticipated to be nearly free electron-like. DFT simulations using the generalized gradient approximation are unable to fully explain the behavior observed for the new allotrope, further confirming the phase is more complicated than a conventional fcc metal. The behavior of β -Tc has likely been previously overlooked because of this non-standard behavior, and we are working towards a concrete theoretical and experimental identification of

the cause of this behavior. Samples of β -Tc synthesized in N_2 instead of Ar have a slightly different behavior, remaining cubic when quenched to ambient. The volumetric response and DFT simulations indicate the samples produced in N_2 are β -Tc doped to a concentration upwards of Tc_8N , although a deeper understanding of the anomalous behavior of the samples produced in Ar will likely change this value. We suspect that previously reported but hard to replicate compounds like TcC or $TcN_{0.75}$ are likely β -Tc stabilized by impurities such as carbon, oxygen, or nitrogen.[13, 55, 56]

V. ACKNOWLEDGMENTS

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