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## Thermodynamics of technetium: reconciling theory and experiment using density functional perturbation analysis

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The structure, lattice dynamics and thermodynamic properties of bulk technetium were investigated within the framework of density functional theory. The phonon density of states spectrum computed with density functional perturbation theory closely matches inelastic coherent neutron scattering measurements. The thermal properties of technetium were derived from phonon frequencies calculated within the quasi-harmonic approximation (QHA), which introduces a volume dependence of phonon frequencies as a part of the anharmonic effect. The predicted thermal expansion and isobaric heat capacity of technetium are in excellent agreement with available experimental data for temperatures up to ~1600 K.

### Introduction

The basic properties of the radioelement technetium, discovered by Perrier and Segre in 1937,<sup>1</sup> were known by the mid-1970s, from the early studies of its crystallographic structure,<sup>2–9</sup> mechanical properties,<sup>10</sup> superconducting properties,<sup>11,12</sup> electrical resistivity,<sup>13,14</sup> magnetic susceptibility,<sup>14</sup> thermal diffusivity<sup>5,14</sup> and heat capacity.<sup>14,15</sup> Owing to its high critical superconducting transition temperature of  $T_c = 7.85$  K at zero pressure – only second among the elements to that of niobium ( $T_c = 9.26$  K) –, the low-temperature properties of technetium metal have been extensively investigated. This contrasts with the scarcity of high-accuracy data for technetium at higher temperatures. In particular, the lack of reliable experimental and theoretical thermodynamic data above 15 K for crystalline Tc was pointed out by Rard and co-workers.<sup>16,17</sup>

This appears particularly surprising in light of the crucial importance of technetium in the fields of nuclear medicine and nuclear waste management. Indeed, although no stable isotope of technetium exists, the short-lived  $\gamma$ -emitting isotope  $^{99m}\text{Tc}$ , generated from the  $^{99}\text{Mo}$  parent nuclide, is the most commonly used isotope in diagnostic nuclear medicine (~85% of all procedures) due to its optimal nuclear properties as a radioimaging agent ( $t_{1/2} = 6.02$  h,  $\gamma = 142$  keV).<sup>18–20</sup> In addition, its long-lived  $\beta^-$ -emitting isotope,  $^{99}\text{Tc}$  ( $t_{1/2} = 2.13 \times 10^5$  years,  $\beta^- = 294$  keV), is produced in large quantities from the nuclear fuel cycle (with up to 6.1 and 5.9% fission yields from the

fission of  $^{235}\text{U}$  and  $^{239}\text{Pu}$ , respectively) and constitutes an important challenge for nuclear waste storage or disposal and environmental remediation.<sup>21,22</sup>

The first heat-capacity measurements on technetium were made in 1975 by Trainor and Brodsky between 3 and 15 K, using a heat-pulse method designed for use with self-heating samples.<sup>15</sup> The same year, Spitsyn and co-workers obtained heat capacity data, with an estimated uncertainty of ~5%, in the temperature range 950–1580 K, from measurements of heat diffusion through flat technetium samples.<sup>14</sup> Differential scanning calorimetry (DSC) measurements were reported in 1997 by Boucharat<sup>23</sup> between 673 and 1583 K, with a maximum at ~1080 K and a minimum around ~1540 K, and were found to be ~10–20% lower than the data by Spitsyn *et al.*<sup>14</sup> DSC heat-capacity measurements in the range 300–973 K were reported subsequently by van der Laan and Konings<sup>24</sup> for an alloy sample  $^{99}\text{Tc}_{0.85}\text{^{100}Ru}_{0.15}$ , formed by neutron irradiation of pure Tc metal from the same source as Boucharat, and the heat capacity of pure Tc was derived by assuming a zero change of heat capacity upon alloying and a uniform sample composition. However, their estimates based on the empirical Neumann-Kopp rule were ~8% larger than the data of Spitsyn *et al.*<sup>14</sup> in the range 950–973 K. The latest DSC heat-capacity measurements of highly-pure  $^{99}\text{Tc}$  metal were reported by Shirasu and Minato<sup>25</sup> from 323 K up to 1073 K. Their data in the range 950–1073 K were larger by ~1% than the values of Spitsyn *et al.*<sup>14</sup>

In parallel with this experimental effort, several estimates of the thermodynamic properties of  $^{99}\text{Tc}$  were determined with theoretically-based models relying on empirical relationships. As early as 1950, Brewer<sup>26</sup> presented estimated values for the entropy  $S$  or the heat content  $H_T - H_{298}$  of technetium, which

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were used as a basis of more extensive tabulations.<sup>27</sup> In 1989, Krikorian and Lai reported estimates of the heat capacity of Tc using a standard Debye model up to 1500 K.<sup>28</sup> Simultaneously, Guillermet and Grimvall<sup>29</sup> provided estimates for the heat capacity and entropy of technetium from 300 to 4000 K using the concept of “entropy Debye temperature”, which is based on a logarithmic average of phonon frequencies, and an empirical relation between the entropy Debye temperatures of 4d and 5d elements to derive the thermodynamic properties of technetium from the data for rhenium. In 1991, Powers<sup>30</sup> used a methodology similar to the one of Krikorian and Lai,<sup>28</sup> but added a contribution from thermally-induced vacancies to the heat capacity and used a slightly different value of the Debye temperature. Although the heat-capacity estimates predicted by Guillermet and Grimvall<sup>29</sup> and Powers<sup>30</sup> were in close agreement, they remained ~9% larger than the data of Spitsyn *et al.*<sup>14</sup> at 1580 K. Finally, Rard and co-workers<sup>17</sup> re-estimated the heat capacity of Tc metal between 300 and 2400 K using the same method as Guillermet and Grimvall,<sup>29</sup> but utilized the revised thermodynamic data for rhenium provided by Arblaster<sup>31</sup> instead of the data tabulated by Hultgren *et al.*<sup>27</sup> To date, the thermodynamic estimates of Rard *et al.* in the range 298.15–2430 K,<sup>17</sup> based on an empirical relation between the entropy Debye temperatures of Tc and Re, have shown the best overall agreement with the heat-capacity data of Spitsyn *et al.*<sup>14</sup> and Shirasu and Minato.<sup>25</sup>

In this work, the crystal structure, lattice dynamics and thermodynamic properties of bulk technetium were investigated within the framework of density functional theory. To the best of our knowledge, this study represents the first attempt to calculate the thermodynamic properties of technetium metal from first-principles methods. Details of our computational approach are provided in the next section, followed by a discussion of our results and conclusions.

## Computational methods

First-principles total energy calculations were performed using density functional theory, as implemented in the Vienna *Ab initio* Simulation Package (VASP).<sup>32</sup> The exchange–correlation energy was calculated within the generalized gradient approximation<sup>33</sup> (GGA), with the parameterization of Perdew, Burke, and Ernzerhof (PBE).<sup>34</sup> Standard functionals such as the PBE functional were found in previous studies to correctly describe the structural parameters and properties of various crystalline structures characterized experimentally.<sup>35–39</sup>

The interaction between valence electrons and ionic cores was described by the projector augmented wave (PAW) method.<sup>40,41</sup> The Tc 4p<sup>6</sup>5s<sup>2</sup>4d<sup>5</sup> electrons were treated explicitly as valence electrons in the Kohn–Sham (KS) equations and the remaining core electrons together with the nuclei were represented by PAW pseudopotentials. The KS equation was solved using the blocked Davidson<sup>42</sup> iterative matrix diagonalization scheme. The plane-wave cutoff energy for the electronic

wave functions was set to 500 eV, ensuring the total energy of the system to be converged to within 1 meV per atom.

The crystal structure was optimized with periodic boundary conditions applied. Ionic relaxation was carried out using the quasi-Newton method and the Hellmann–Feynman forces acting on atoms were calculated with a convergence tolerance set to 0.01 eV Å<sup>−1</sup>. Structural optimization and properties calculations of the unit cell were carried out using the Monkhorst-Pack special *k*-point scheme<sup>43</sup> with a 11 × 11 × 9 mesh for integrations in the Brillouin zone (BZ). The tetrahedron method with Blöchl corrections<sup>44</sup> was used for BZ integrations. Ionic and cell relaxations of the crystal structure were performed simultaneously, without symmetry constraints.

A 2 × 2 × 2 supercell was constructed from the optimized unit cell, and relaxed with a 5 × 5 × 3 *k*-point mesh for use in lattice dynamics calculations. Utilizing the optimized supercell as an initial guess, additional force relaxation calculations were carried out on an additional support grid for the evaluation of the augmentation charges, with forces converged to within 10<sup>−6</sup> eV Å<sup>−1</sup> and projection operators evaluated in reciprocal space. The forces were computed using density functional perturbation theory (DFPT) with VASP at the GGA/PBE level and phonon frequencies were calculated. Further analysis from a set of phonon calculations in the vicinity of the computed equilibrium crystal structure was carried out to obtain thermal properties at constant pressure (*e.g.*, Gibbs free energy, isobaric heat capacity, enthalpy and Gibbs energy functions) within a quasi-harmonic approximation (QHA). The QHA utilized in this study introduces a volume dependence of phonon frequencies as a part of anharmonic effect.<sup>45</sup>

## Results and discussion

### Crystal structure

The unit cell of bulk technetium optimized with DFT at the GGA/PBE level crystallizes in the hexagonal closed-packed structure (space group *P6<sub>3</sub>/mmc*, IT no.; 194 *Z* = 2), with lattice parameters: *a* = *b* = 2.756 Å, *c* = 4.398 Å (*a/c* = 0.626);  $\alpha = \beta = 90.0^\circ$ ,  $\gamma = 120.0^\circ$ ; *V* = 28.934 Å<sup>3</sup>. These results are in good agreement with the experimental crystallographic values of *a*<sub>0</sub> = 2.7409 ± 0.0035 Å and *c*<sub>0</sub> = 4.3987 ± 0.0034 Å (*a/c* = 0.6231 ± 0.0004) at ambient temperature and pressure recommended by Rard *et al.*,<sup>17</sup> based on the average of the measurements of Mooney<sup>2</sup> and Spitsyn *et al.*,<sup>9</sup> as well as with other experimental determinations (*cf.* Table 1).

Since it was reported experimentally that polycrystalline Tc films thinner than 15 nm adopt the face-centered cubic (FCC) structure with *a*<sub>0</sub> = 3.68 Å,<sup>48</sup> relaxation calculations were also carried out with VASP for bulk Tc crystallizing in the FCC structure. An equilibrium lattice parameter of *a* = 3.87 Å was obtained for the FCC arrangement, however, the HCP structure for bulk Tc is slightly more energetically favorable by ~0.1 eV per atom than the FCC, consistent with previous calculations at the GGA/PW91 level of theory.<sup>49</sup> Therefore, the remainder of

**Table 1** Structural unit-cell parameters of HCP bulk technetium

Lattice parameters (Å)			Ref.
<i>a</i>	<i>c</i>	<i>a/c</i>	
2.756	4.398	0.626	This study
2.735 ± 0.002	4.388 ± 0.002	0.6233	Mooney <sup>2</sup>
2.743 ± 0.002	4.400 ± 0.002	0.6234	Lam <i>et al.</i> <sup>3</sup>
2.7415 ± 0.002	4.400 ± 0.002	0.6231	Muller <i>et al.</i> <sup>4</sup>
2.7414	4.3997	0.6231	Baker <sup>5</sup>
2.740	4.398	0.6230	Trzebiatowski <sup>6</sup>
2.743	4.400	0.6234	Koch <i>et al.</i> <sup>7</sup>
2.7407 ± 0.0002	4.3980 ± 0.0002	0.6232	Marples <i>et al.</i> <sup>8</sup>
2.73	4.39	0.622	Spitsyn <i>et al.</i> <sup>9</sup>
2.740 ± 0.002	4.399 ± 0.004	0.6229	Giorgi <sup>16</sup>
2.7375	4.3950	0.6228	Haines <i>et al.</i> <sup>47</sup>
2.7409 ± 0.0035	4.3987 ± 0.0034	0.6231 ± 0.0004	Rard <i>et al.</i> <sup>17</sup>

the present study will focus solely on the HCP bulk structure of technetium.

### Thermodynamic properties

The forces exerted on atoms of the equilibrium structure of bulk technetium were computed using density functional perturbation theory (DFPT) with VASP at the GGA/PBE level of theory and phonon frequencies were derived. Phonon analysis was performed at constant equilibrium volume at 0 K; the computed and measured phonon density of states (PDOS) spectra,  $F(\omega)$ , are shown in Fig. 1.

The calculated PDOS exhibits two major peaks: a wide one with a maximum at  $\omega = 16.5$  meV and a narrow one centered at  $\omega = 25.0$  meV. These peak positions are in good agreement with the inelastic coherent neutron scattering measurements on a technetium foil made by Zakharov *et al.*<sup>50</sup> using a time-of-flight spectrometer, who reported maxima at  $\omega = 16.0 \pm 0.5$  meV and  $\omega = 27.0 \pm 1.0$  meV at  $T = 300$  K. The slight shift

between the narrow peak positions calculated at 0 K and measured at room temperature can be ascribed to the anomalous long-wavelength phonon frequencies of the longitudinal optical (LO) branch of HCP bulk Tc. This peculiar temperature dependence of the LO phonons in superconducting HCP transition metals originates from the splitting of doubly degenerate electron bands near the Fermi level by lattice distortion.<sup>51,52</sup>

Further analysis from a set of phonon calculations in the vicinity of the computed equilibrium crystal structure was carried out to obtain thermal properties at constant pressure (e.g., the Gibbs free energy and the isobaric heat capacity) within a quasi-harmonic approximation (QHA). The QHA mentioned here introduces a volume dependence of phonon frequencies as a part of anharmonic effect.<sup>45</sup> A temperature effect can be added to the total energy of the system through the phonon contribution to the Helmholtz free energy,  $F_{\text{phonon}}$ , calculated at constant volume as a function of the temperature  $T$  using the formula:

$$F_{\text{phonon}}(T) = \frac{1}{2} \sum_{\mathbf{q}, \nu} \hbar \omega_{\mathbf{q}, \nu} + k_B T \sum_{\mathbf{q}, \nu} \ln[1 - e^{-\beta \hbar \omega_{\mathbf{q}, \nu}}] \quad (1)$$

where  $\mathbf{q}$  and  $\nu$  are the wave vector and band index,  $\hbar$  is the reduced Planck constant,  $\hbar \omega_{\mathbf{q}, \nu}$  is the energy of a single phonon with angular frequency  $\omega_{\mathbf{q}, \nu}$ ,  $k_B$  is the Boltzmann constant,  $T$  is the temperature of the system, and  $\beta = (k_B T)^{-1}$ .

In order to determine the thermal properties at constant pressure, a transformation is necessary to introduce a volume dependence of the thermodynamic functions. The Gibbs free energy can be defined at a constant pressure by the transformation:

$$G(T, P) = \min_V [U(V) + F_{\text{phonon}}(T; V) + PV], \quad (2)$$

where  $\min_V$  [function of  $V$ ] corresponds to a unique minimum of the expression between brackets with respect to the volume  $V$ ,  $U$  is the total energy of the system, and  $P$  is the pressure.  $U(V)$  and  $F_{\text{phonon}}(T; V)$  were calculated and the thermodynamic functions of the right-hand sides of the equation above were fitted to the integral forms of the third-order Birch–Murnaghan and Vinet equation of state (EoS). The third-order Birch–Murnaghan isothermal EoS is expressed as:<sup>53,54</sup>

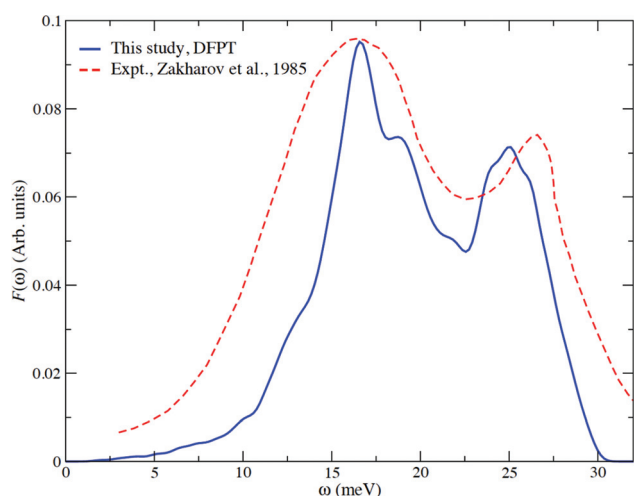
$$P(V) = \frac{3K_0}{2} \left[ \left( \frac{V_0}{V} \right)^{\frac{7}{3}} - \left( \frac{V_0}{V} \right)^{\frac{5}{3}} \right] \left\{ 1 + \frac{3}{4} (K'_0 - 4) \left[ \left( \frac{V_0}{V} \right)^{\frac{2}{3}} - 1 \right] \right\}, \quad (3)$$

where  $P$  is the uniform hydrostatic pressure,  $V_0$  is the reference volume,  $V$  is the deformed volume, and the bulk modulus and its first derivative with respect to the pressure are given by:

$$K_0(T) = -V \left( \frac{\partial P}{\partial V} \right)_{P=0} \quad \text{and} \quad K'_0(T) = \left( \frac{\partial K}{\partial P} \right)_{P=0}. \quad (4)$$

The universal Vinet<sup>55</sup> EoS is expressed as:

$$P(V) = 3K_0 \frac{(1-x)}{x^2} \exp \left[ \frac{3}{2} (K'_0 - 1)(1-x) \right], \quad (5)$$



**Fig. 1** Phonon density of states (PDOS) spectrum of technetium computed with density functional perturbation theory (DFPT) at the GGA/PBE level (solid curve), along with the inelastic coherent neutron scattering measurements of Zakharov *et al.*<sup>50</sup> (dashed curve).

where

$$x = \left( \frac{V}{V_0} \right)^{\frac{1}{3}}. \quad (6)$$

The bulk moduli computed at 0 K with the third-order Birch–Murnaghan and Vinet EoS are  $K_0 = 303$  and 304 GPa ( $K'_0 = 4.5$  and 4.6), respectively, in close agreement with the experimental value of  $306 \pm 6$  GPa for polycrystalline technetium obtained by ultrasonic velocity measurements.<sup>56</sup> Softening of the bulk modulus occurs as the temperature increases up to room temperature, with estimates of 286 and 288 GPa ( $K' = 4.5$  and 4.6) predicted at 298 K with the Birch–Murnaghan and Vinet EoS, respectively, *i.e.* slightly above the experimental value of  $281 \pm 6$  GPa for polycrystalline Tc.<sup>56</sup> Since only minor differences exist between the data fitted to the integral forms of the third-order Birch–Murnaghan and Vinet EoS, results presented in the following will be limited to the Vinet EoS.

Fig. 2 shows the variation of the Helmholtz free energy as a function of the volume per technetium atom computed within the QHA with density functional perturbation theory (DFPT), at the GGA/PBE level, from 0 to 2400 K by step of 100 K. The thermodynamic functions fitted to the Vinet EoS are represented by solid blue curves and the equilibrium volume at a given temperature  $T$  is obtained by minimizing the Helmholtz free energy with respect to  $V$ ; the local minimum of each free energy curve in Fig. 2 is indicated by a red cross.

By increasing the temperature, the volume dependence of the phonon free energy changes, hence the equilibrium volume changes at each given temperature: this is considered as thermal expansion under this QHA approximation. The computed thermal expansion of technetium is shown in Fig. 3, along with the experimental dilatometer data reported by Shirasu and Minato.<sup>57</sup> The calculated values of  $\Delta L/L_0$  are in excellent agreement (*i.e.* within less than 0.1%) with available

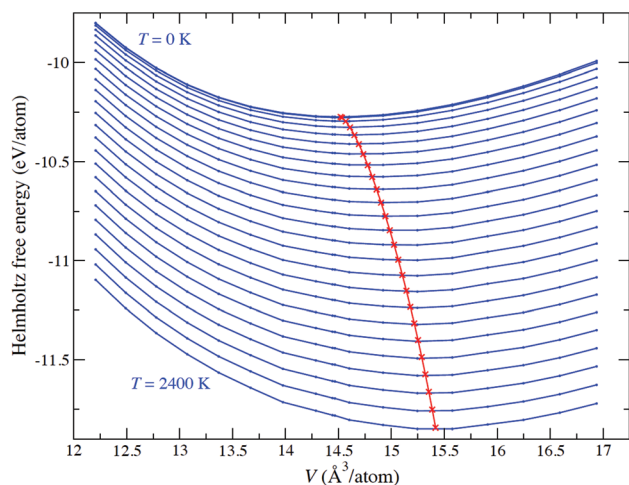


Fig. 2 Helmholtz free energy as a function of the volume per technetium atom computed with density functional perturbation theory (DFPT) at the GGA/PBE level from 0 to 2400 K, by step of 100 K. The local minimum of each free energy curve is indicated by a red cross.

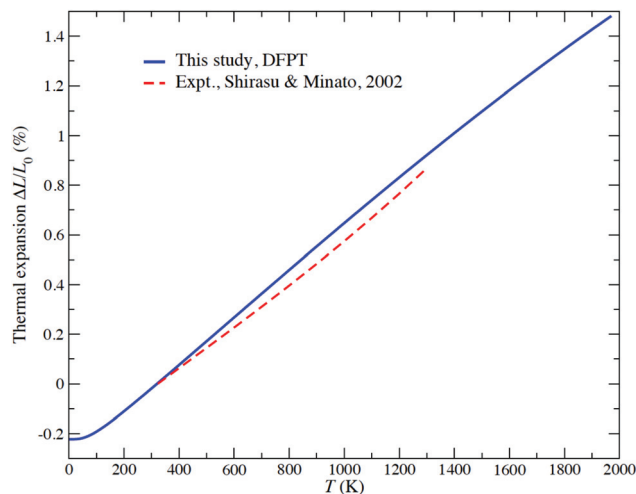


Fig. 3 Thermal expansion of technetium calculated at the DFPT/GGA/PBE level of theory. For the sake of comparison with the experimental data of Shirasu and Minato,<sup>57</sup> a reference length  $L_0 = V_0^{1/3}$  corresponding to  $T = 323$  K was adopted.

measurements, where the length  $L_0$  ( $L = V^{1/3}$ ) corresponds to a reference temperature of  $T = 323$  K.

The resulting thermal variation of the Gibbs free energy calculated with the QHA using eqn (2) is shown in Fig. 4.

The lattice contribution to the isobaric heat capacity was then derived as a function of the temperature from the Gibbs free energy according to:

$$C_p^{\text{vib}}(T, P) = -T \frac{\partial^2 G(T, P)}{\partial T^2}, \quad (7)$$

where the pressure is set to a reference of  $P = 1$  bar corresponding to the standard state usually adopted in calorimetric data.<sup>58</sup>

Owing to the metallic nature of technetium, the contribution associated with the conduction electrons to the heat

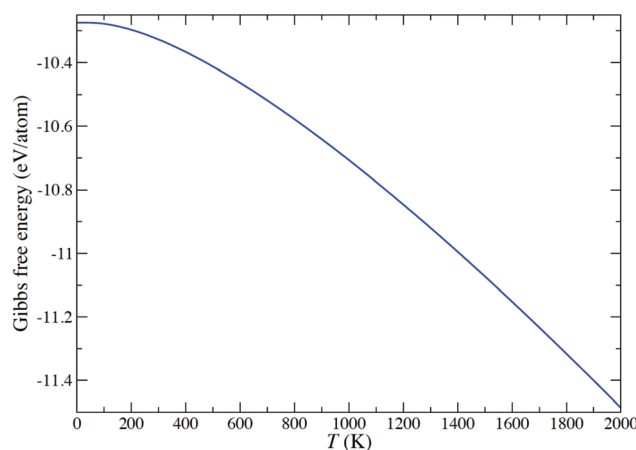


Fig. 4 Thermal evolution of the Gibbs free energy of technetium computed with DFPT at the GGA/PBE level of theory.



capacity has to be taken into account, in addition to the lattice vibration contribution. The electronic heat capacity of a free-electron Fermi gas at low temperature is given by:<sup>59</sup>

$$C_P^{\text{el}}(T) = \frac{2\pi^2}{3} k_B^2 N(E_F)(1 + \lambda)T = \gamma_0(1 + \lambda)T, \quad (8)$$

where  $N(E_F)$  is the electronic density of state (DOS) per electron spin at the Fermi level, and  $\lambda$  is the electron-phonon enhancement parameter. The present DOS calculation yielded a value of  $N(E_F) = 7.99$  states per atom, spin and Rydberg, in good agreement with the low-temperature experimental value<sup>29</sup> of 7.39 states per atom per spin per Ry and with the previous theoretical estimates of 7.62–9.45,<sup>60</sup> 8.28,<sup>61</sup> and 6.82 states per atom per spin per Ry.<sup>62</sup> The electron-phonon enhancement parameter  $\lambda = 0.68$  derived at low-temperature by Guillermet and Grimvall from the McMillan formula should vanish for  $T \gtrsim \theta^S/3 \approx 107$  K,<sup>59</sup> where the entropy Debye temperature  $\theta^S$  was estimated to be  $320 \pm 3$  K for technetium.<sup>29</sup> Therefore, adopting the approach proposed by Guillermet and Grimvall,<sup>29</sup> the electronic contribution to the heat capacity used in this study was the low-temperature experimental estimate<sup>15</sup>  $C^{\text{el}}(T) = (4.3 \times 10^{-3} T) \text{ J K}^{-1} \text{ mol}^{-1}$  reduced by a factor of  $(1 + \lambda) = 1.68$  to account for the suppression of the electron-phonon interaction above  $T \gtrsim \theta^S/3$ .

The DFPT/QHA results for the isobaric heat capacity of technetium, with and without the electronic contribution, are displayed in Fig. 5, along with available experimental data and predictions from theoretically-based models. The present calculations show that  $C_P^{\text{el}}$  is nearly negligible below  $\sim 160$  K and steadily increases with temperature and accounts for *ca.* 3 and 16% of the total isobaric heat capacity,  $C_P(T) = C_P^{\text{el}} + C_P^{\text{vib}}$ , at 298 and 2000 K, respectively. Let us note that the computed lattice contribution to the isobaric heat capacity  $C_P^{\text{vib}}$  is close to the experimental data of Boucharat,<sup>23</sup> while the calculated

total heat capacity is in excellent agreement with the experimental data of Shirasu and Minato<sup>25</sup> (*i.e.* overestimating DSC data by 1.8–0.5% in the range 323–1073 K) and Spitsyn *et al.*<sup>14</sup> (*i.e.* overestimating data derived from heat-diffusion measurements by 1.2–0.9% in the range 950–1580 K). The predicted  $C_P$  values between 298.15 K and  $\sim 1600$  K also agree within less than 1% with the data recommended by Rard *et al.*<sup>17</sup> based on an empirical scaling of the entropy Debye temperatures of Tc and Re; a maximum relative difference of 2.3% is found at 2400 K, near the melting temperature. The QHA methodology used in this study is expected to be accurate up to a temperature of  $\sim (2/3)T_m = 1620$  K, where the melting point of technetium is  $T_m = 2430 \pm 30$  K.<sup>29</sup> The predictions of van der Laan and Konings<sup>24</sup> consistently overestimate the present results by 2.7 to 7.2% between 300 and 973 K, while the models of Guillermet and Grimvall<sup>29</sup> and Powers<sup>30</sup> systematically overestimate (underestimate) our predictions above (below)  $\sim 490$  and  $\sim 515$  K, respectively. At 298.15 K, the computed  $C_P$  value of  $25.07 \text{ J mol}^{-1} \text{ K}^{-1}$  is close to the value of  $24.88 \text{ J mol}^{-1} \text{ K}^{-1}$  recommended by Rard *et al.*<sup>17</sup> At 2400 K, near the estimated melting temperature of Tc, the computed total and lattice heat capacities  $C_P$  and  $C_P^{\text{vib}}$  are 33.04 and  $26.94 \text{ J mol}^{-1} \text{ K}^{-1}$ , slightly above the Dulong–Petit asymptotic value,  $C_P = 3R = 24.94 \text{ J mol}^{-1} \text{ K}^{-1}$ , where  $R$  is the universal gas constant. This stems from the fact that the heat capacity of real solids has anharmonic corrections to the Dulong–Petit value of strictly harmonic lattice vibrations.

While  $C_P(T)$  values are measured directly in experiments and calculated directly from eqn (7) and (8) in this study, the model used by Guillermet and Grimvall<sup>29</sup> and Rard and co-workers<sup>17</sup> obtained the heat capacity by differentiation of the entropy since:

$$\frac{C_P}{T} = \left( \frac{\partial S}{\partial T} \right)_P, \quad (9)$$

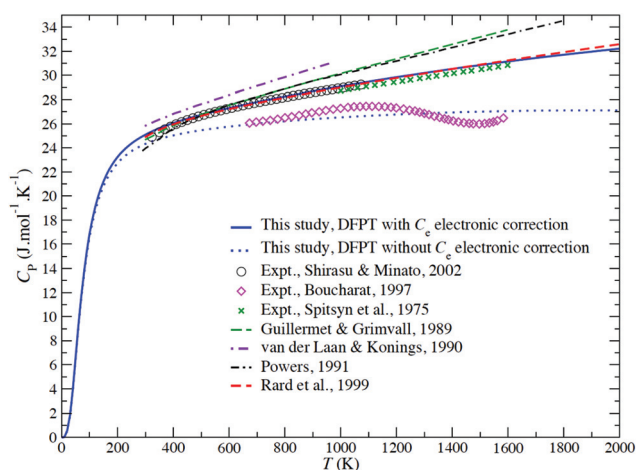
where the entropy  $S = S^{\text{vib}} + S^{\text{el}}$  includes both lattice vibration and electronic contributions;  $S^{\text{el}}$  can be obtained using a similar approach as discussed previously in eqn (8) for  $C^{\text{el}}$ , *i.e.*  $S^{\text{el}} = \gamma_0 T$ , where  $\gamma_0$  is related to the low-temperature heat capacity. In their approach, the vibrational entropy  $S^{\text{vib}}$  can be represented by an “entropy Debye temperature”,  $\theta^S$ .<sup>63</sup> This parametrization of entropy data allows for anharmonic effects and does not imply the limitations inherent in the standard Debye model at high temperatures. The actual vibrational entropy is related to  $\theta^S(T)$  by the formula

$$S^{\text{vib}}(T) = S_D \left( \frac{T}{\theta^S} \right), \quad (10)$$

where  $S_D$  is the entropy expression of a standard Debye model. Due to the anharmonicity, the phonon frequencies  $\omega_{q,v}$  change with the temperature, hence  $\theta^S$  is temperature dependent.

In the model used by Guillermet and Grimvall<sup>29</sup> and Rard and co-workers,<sup>17</sup>  $\theta^S$  is obtained from the formula

$$\theta^S = \frac{\hbar}{k_B} \left( \frac{k_c}{M} \right)^{1/2}, \quad (11)$$



**Fig. 5** Thermal evolution of the isobaric heat capacity of technetium calculated at constant atmospheric pressure with DFPT at the PBE/GGA level of theory. The experimental data of Shirasu and Minato,<sup>25</sup> Boucharat,<sup>23</sup> and Spitsyn *et al.*<sup>14</sup> are also shown, along with predictions using various models.<sup>17,24,29,30</sup>

where  $k_e$  is a parameter with the dimension of a force constant and  $M$  is the atomic mass, in conjunction with the empirical relation<sup>59</sup> between 4d and 5d transition metals of the same group in the periodic table:

$$\frac{k_e^{4d}}{k_e^{5d}} = 0.76 \pm 0.02, \quad (12)$$

which is expected to be valid irrespective of the crystal structure adopted by 4d and 5d transition metals. The differences between the  $C_p$  results of Guillermet and Grimvall<sup>29</sup> and Rard and co-workers<sup>17</sup> (Fig. 5) arise essentially from the different values of  $\theta^s(T)$  derived for Tc using eqn (10)–(12) from the experimental Re entropy data reported by Hultgren *et al.*<sup>27</sup> and by Arblaster,<sup>31</sup> respectively.

In the present study, however, the vibrational contribution to the entropy,  $S^{\text{vib}}$ , was computed directly from phonon frequencies, obtained with DFPT at constant equilibrium volume, using the expression:

$$S^{\text{vib}}(T) = -k_B \sum_{q,v} \ln[1 - e^{-\beta \hbar \omega_{q,v}}] - \frac{1}{T} \sum_{q,v} \frac{\hbar \omega_{q,v}}{e^{\beta \hbar \omega_{q,v}} - 1}, \quad (13)$$

As shown in Fig. 6, the entropy for Tc calculated using eqn (13) and the electronic contribution  $S^{\text{el}}$  is in good overall agreement with values recommended by Rard *et al.*<sup>17</sup> At 298.15 K, the computed value of 33.77 J mol<sup>−1</sup> K<sup>−1</sup> is ~3.8% larger than the recommended value of Rard and co-workers (*i.e.* 32.50 J mol<sup>−1</sup> K<sup>−1</sup>). This room-temperature value predicted with DFPT is in excellent agreement (*i.e.* within 0.8%) with the value of 33.5 J mol<sup>−1</sup> K<sup>−1</sup> reported by a number of studies.<sup>26,27,64–67</sup> At higher temperatures, this entropy difference reduces up to ~1053 K and above this temperature the computed entropy becomes smaller than the recommended values by up to ~2.0% at 2400 K (*i.e.* 90.54 J mol<sup>−1</sup> K<sup>−1</sup> vs. 92.40 J mol<sup>−1</sup> K<sup>−1</sup> for the recommended value). The entropy increases steadily with tempera-

ture as a result of the larger number of microstates in the system,  $W$ , which in turn increases logarithmically the entropy according to Boltzmann's entropy formula,  $S = k_B \log(W)$ .

In order to derive the enthalpy function,  $(H_T - H_{298.15})T^{-1}$ , and the Gibbs energy function,  $-(G_T - H_{298.15})T^{-1}$ , the thermal evolution of the isobaric heat capacity of technetium calculated from DFPT was fitted using nonlinear least-squares regression to a Haas–Fisher-type polynomial, *i.e.*,

$$C_p(T) = a + bT + cT^{-2} + dT^{-0.5} + eT^2, \quad (14)$$

with the resulting optimized coefficients in the temperature range  $T = 190$ – $1620$  K given in Table 2.

The enthalpy function was then computed by analytical integration of the fit to the isobaric heat capacity using the formula:

$$(H_T - H_{298.15})T^{-1} = \int_{298.15}^T (a + bT + cT^{-2} + dT^{-0.5} + eT^2) dT. \quad (15)$$

The Gibbs energy function was then computed using the following expression:

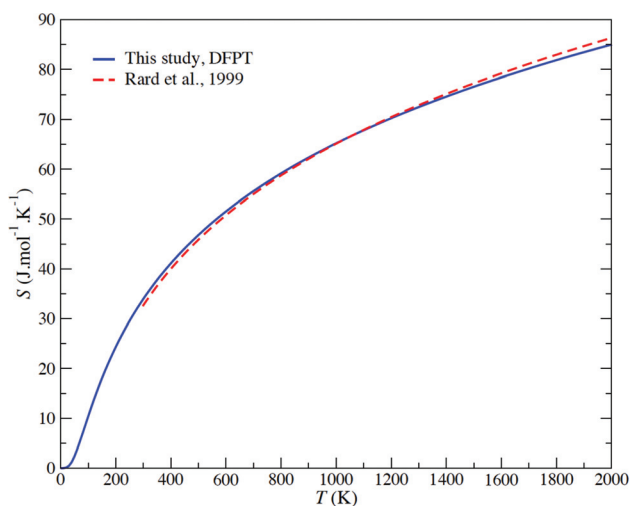
$$-(G_T - H_{298.15})T^{-1} = S - (H_T - H_{298.15})T^{-1}, \quad (16)$$

where the entropy  $S$  includes both lattice vibration and electronic contributions. The enthalpy function and Gibbs energy

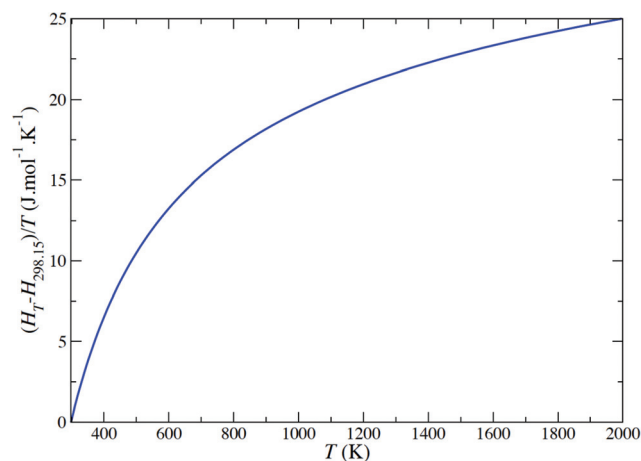
**Table 2** Coefficients of the Haas–Fisher heat capacity polynomial  $C_p(T)$  for technetium calculated using DFPT. The range of validity of the fit is 190–1620 K

$a \times 10$ ( $T^0$ )	$b \times 10^{-3}$ ( $T$ )	$c \times 10^5$ ( $T^{-2}$ )	$d \times 10$ ( $T^{-0.5}$ )	$e \times 10^{-7}$ ( $T^2$ )	SSD <sup>a</sup>
2.456	5.247	−1.0729	3.775	−7.240	0.01

<sup>a</sup> Sum of squared differences between calculated and fitted data.



**Fig. 6** Thermal evolution of the entropy of technetium computed with DFPT at the GGA/PBE level along with the semi-empirical values of Rard *et al.*<sup>17</sup>



**Fig. 7** Thermal evolution of the enthalpy function of technetium calculated at the DFPT/GGA/PBE level of theory.

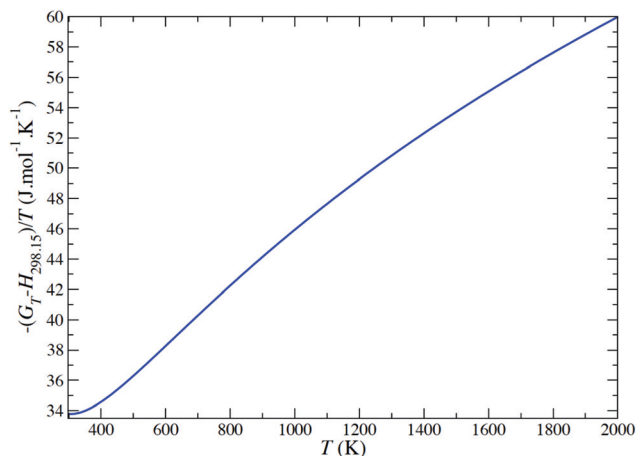


Fig. 8 Thermal evolution of the Gibbs energy function of technetium calculated at the DFPT/GGA/PBE level of theory.

function computed using eqn (15) and (16) are shown in Fig. 7 and 8, respectively.

## Conclusions

The structure, lattice dynamics and thermodynamic properties of bulk technetium were investigated from first-principles using density functional theory. The predicted crystallographic parameters for HCP Tc bulk are in good agreement with XRD data and the phonon frequencies and the simulated density of states spectrum computed with density functional perturbation theory closely match available inelastic coherent neutron scattering measurements. The bulk moduli computed at 0 K with the third-order Birch–Murnaghan and Vinet EoS are  $K_0 = 303$  and  $304$  GPa, respectively, in close agreement with the experimental value of  $306 \pm 6$  GPa for polycrystalline technetium obtained by ultrasonic velocity measurements. Softening of the bulk modulus occurs as the temperature increases up to room temperature, with estimates of  $286$  and  $288$  GPa predicted at  $298$  K with the Birch–Murnaghan and Vinet EoS, respectively, *i.e.* slightly above the experimental value of  $281 \pm 6$  GPa for polycrystalline Tc.

The thermal properties of technetium were derived from phonon frequencies calculated within the quasi-harmonic approximation (QHA), which introduces a volume dependence of phonon frequencies as a part of the anharmonic effect. The predicted thermal expansion agrees within less than  $0.1\%$  with available measurements.

The calculated isobaric heat capacity is in excellent agreement with the experimental data of Shirasu and Minato (*i.e.* overestimating DSC data by  $1.8$ – $0.5\%$  in the range  $323$ – $1073$  K) and Spitsyn *et al.* (*i.e.* overestimating data derived from heat-diffusion measurements by  $1.2$ – $0.9\%$  in the range  $950$ – $1580$  K). The predicted isobaric heat capacity values between  $298.15$  K and  $\sim 1600$  K also agree within less than  $1\%$  with the data recommended by Rard *et al.* based on an empirical scaling of the entropy Debye temperatures of Tc and Re; a

maximum relative difference of  $2.3\%$  is found at  $2400$  K, near the melting temperature. The present calculations also show that the electronic contribution to the heat capacity is nearly negligible below  $\sim 160$  K and steadily increases with temperature and accounts for *ca.*  $3$  and  $16\%$  of the total isobaric heat capacity at  $298$  and  $2000$  K, respectively.

The entropy for Tc calculated from phonon frequencies is in good overall agreement with values recommended by Rard *et al.* At  $298.15$  K, the computed value of  $33.77$  J mol $^{-1}$  K $^{-1}$  is  $\sim 3.8\%$  larger than the recommended value of Rard and co-workers (*i.e.*  $32.50$  J mol $^{-1}$  K $^{-1}$ ). This room-temperature value predicted with DFPT is in excellent agreement (*i.e.* within  $0.8\%$ ) with the value of  $33.5$  J mol $^{-1}$  K $^{-1}$  reported by a number of studies. At higher temperatures, this entropy difference reduces up to  $\sim 1053$  K and above this temperature the computed entropy becomes smaller than the recommended values by up to  $\sim 2.0\%$  at  $2400$  K (*i.e.*  $90.54$  J mol $^{-1}$  K $^{-1}$  vs.  $92.40$  J mol $^{-1}$  K $^{-1}$  for the recommended value).

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