Original Research

Interplay Between Acoustic Properties of Technetium and Nitrides

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Abstract

We study the interplay comprehensive computation of second- and third- order elastic constants using Lennard-Jones potential and then velocities and attenuation of acoustics waves in hexagonal structured Tc and TcN subnitride. The comparison of these computed results has been made with available theoretical and experiment results. The orientation dependent acoustic velocity has been also evaluated to study the anisotropic behaviour of these compounds. The inconsistent behaviour of angle-dependent velocities is associated to the action of second order elastic constants. The average sound velocity is a direct consequence of Debye temperature, specific heat and thermal energy density of these compounds. The mechanical properties of Tc are better than those of Technetium nitride, because technetium has high ultrasonic velocities and low attenuation. Obtained results, together with other well known physical properties, may expand future prospects for the applications and study of these materials.

Keywords: Elastic constants; longitudinal waves; surface waves; ultrasonic velocity.

1. Introduction

Many compounds of the transition elements have certain properties which are not possessed by other compounds, due to the presence of the partially-filled shells of the d electrons in the transition-element ions. Because of interesting magnetic, superconducting, mechanical, acoustical and structural properties, they are materials of fundamental importance for magnetic storage devices, superconductors and in the semiconductor industry [1,2]. Transition-metal nitrides have received increasing theoretical and experimental attention owing to their outstanding mechanical, thermal, optoelectronic, semiconducting, magnetic or superconducting properties, which can be used advantageously in a variety of technological applications [3-7].

Technetium is the only radioactive transition-metal, occurs mainly in spent nuclear fuel. The practical difficulties of working with a radioactive rare material have so far hampered studies of technetium solid state physics [8,9]. The zero temperature equation of state and elastic constants of pure Tc have been calculated in a study of bcc, fcc and hcp structures [10], and the stability of several more complex structures has been explored in a similar work [11]. These studies verify the stability of the hcp structure for Tc. It was found that the Tc compounds are also potential high hardness materials. A similar study compared the properties of transition metal mononitrides [12]. Several authors have presented results of electronic structure calculations for 4d-transition-metal-nitrides from different view points [13-15]. There are many theoretical studies investigating the elastic and mechanical properties of 4d and 5d transition metal nitrides, including ones of specific compositions and structures that demonstrate extraordinary properties. These include the studies on technetium nitrides by Liang et al [16].

There are three types of acoustic mode lattice vibration: one longitudinal acoustic and two transverse acoustical for hexagonal and cubic structured materials [17,18]. Hence, there are three types of acoustic wave velocities for each direction of
propagation of wave, which are well related to second order elastic constants. But all the three type of orientation dependent acoustic wave velocity of technetium and its nitride are not reported in literature. Therefore in this paper, we have calculated the three types of acoustic wave velocities of hexagonal structured technetium and its nitride at room temperature for each direction of propagation of wave using the second order elastic constants that are important for surface and structural study of these compounds. The six second order elastic constants (SOEC) and ten third order elastic constants (TOEC) are calculated using Lenard-Jones Potential that is many body interaction potential. The calculated ultrasonic parameters are discussed with related thermo physical properties for the characterization of the chosen compounds. The obtained results are interesting for the characterization of these materials.

2. Theory

The second \((C_{ij})\) and third \((C_{ijk})\) order elastic constants of material are defined by following expressions.

\[
C_{ij} = \frac{\partial^2 U}{\partial e_i \partial e_j}; \quad \text{I o r}\; J = 1,\ldots,6 \quad (1)
\]

\[
C_{ijk} = \frac{\partial^2 U}{\partial e_i \partial e_j \partial e_k}; \quad \text{I o r} J o r K = 1,\ldots,6 \quad (2)
\]

where, \(U\) is elastic energy density , \(e_i \equiv e_{ij} (i\ or\ j = x, y, z, I=1,\ldots,6)\) is component of strain tensor. Eqs. (1) and (2) leads six second and ten third order elastic constants (SOEC and TOEC) for the hexagonal structure materials [19,20].

\[
\begin{align*}
C_{11} &= 24.1 p^4 C' \\
C_{12} &= 5.918 p^4 C' \\
C_{13} &= 1.925 p^6 C' \\
C_{33} &= 3.464 p^8 C' \\
C_{44} &= 2.309 p^4 C' \\
C_{66} &= 9.851 p^4 C' \\
C_{111} &= 126.9 p^2 B + 8.853 p^4 C' \\
C_{112} &= 19.168 p^2 B - 1.61 p^4 C' \\
C_{113} &= 1.924 p^4 B + 1.155 p^6 C' \\
C_{123} &= 1.617 p^2 B - 1.155 p^4 C' \\
C_{133} &= 3.695 p^6 B \\
C_{155} &= 1.539 p^4 B \\
C_{144} &= 2.309 p^4 B \\
C_{344} &= 3.464 p^6 B \\
C_{222} &= 101.039 p^2 B + 9.007 p^4 C' \\
C_{333} &= 5.196 p^2 B \\
\end{align*}
\]  

where \( p = c/a: \) axial ratio; \( C' = \chi a / p^5; \) \( B = \psi a^3 / p^3; \)

\[
\chi = (1/8) \{ nb_0 (n-m)\} / \{ a^{n+4} \} \quad \psi = -\chi / (6 a^2 (m+n+6));
\]

\( m, n = \text{integer quantity}; b_0 = \text{Lennard Jones parameter}. \)

The anisotropic behaviour of the material can be understood with the knowledge of ultrasonic velocity because the velocity is related to the second order elastic constants14.

On the basis of mode of atomic vibration, there are three types of velocities (longitudinal, quasi shear and shear) in acoustical region [21]. These velocities vary with the direction of propagation of wave from the unique axis of hexagonal structured crystal [22]. The ultrasonic velocities as a function of angle between direction of propagation and unique axis for hexagonal structured materials are [23]:

\[
\begin{align*}
V_1^2 &= (C_{33} \cos^2 \theta + C_{11} \sin^2 \theta + C_{44} \\
&+ \{C_{11} \sin^2 \theta - C_{33} \cos^2 \theta \\
&+ C_{44} (\cos^2 \theta - \sin^2 \theta) \}^2 \\
&+ 4 \cos^2 \theta \sin^2 \theta (C_{13} + C_{44})^{1/2} \} / 2 \rho \\
\end{align*}
\]

\[
\begin{align*}
V_5^2 &= (C_{33} \cos^2 \theta + C_{11} \sin^2 \theta \\
&+ C_{44} - \{C_{11} \sin^2 \theta - C_{33} \cos^2 \theta \\
&+ C_{44} (\cos^2 \theta - \sin^2 \theta) \}^2 \\
&+ 4 \cos^2 \theta \sin^2 \theta (C_{13} + C_{44})^{1/2} \} / 2 \rho \\
\end{align*}
\]

\[
\begin{align*}
V_5^2 &= (C_{44} \cos^2 \theta + C_{66} \sin^2 \theta) / \rho \\
\end{align*}
\]

where \( V_1, V_5, \) and \( V_5 \) are longitudinal, quasi shear and pure shear wave ultrasonic velocities. Variables \( \rho \) and \( \theta \) represent the density of the material and angle with the unique axis of the crystal respectively. The Debye temperature (TD) is an important physical parameter for the characterization of materials, which is well related to the Debye average velocity \((V_D)\).

\[
T_D = \frac{h V_D (6 \pi^2 n_a)^{1/3}}{K_B} \quad (7)
\]

where \( h = \) quantum of action and is equal to Planck’s constant divided by \( 2\pi; \) \( K_B = \) Boltzmann Constant; \( n_a = \) atom concentration.

3. Results and Discussions

The unit cell parameters ‘a’ (basal plane parameter) and ‘p’ (axial ratio) for \( Tc \) and \( TcN \) are 2.75, 2.83 and 1.60, 2.00 [24] respectively. The value of \( m \) and \( n \) for chosen materials are 6 and 7. The values of \( b_0 \) for these materials are \( 1.5 \times 10^{64} \) and \( 1.6 \times 10^{64} \text{ erg cm}^7 \) respectively. The SOEC and TOEC have been calculated for these materials using Eq. (3) and are presented in Table 1.
Table 1 Second and third order elastic constants (SOEC and TOEC) & bulk modulus (B) in the unit of GPa of materials at room temperature.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>$C_{11}$</th>
<th>$C_{12}$</th>
<th>$C_{13}$</th>
<th>$C_{33}$</th>
<th>$C_{44}$</th>
<th>$C_{66}$</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tc</td>
<td>521</td>
<td>128</td>
<td>149</td>
<td>828</td>
<td>171</td>
<td>206</td>
<td>302</td>
</tr>
<tr>
<td>TcN</td>
<td>533</td>
<td>191</td>
<td>188</td>
<td>882</td>
<td>177</td>
<td>225</td>
<td>342</td>
</tr>
<tr>
<td>[24] Tc</td>
<td>478</td>
<td>198</td>
<td>212</td>
<td>480</td>
<td>131</td>
<td>298</td>
<td></td>
</tr>
<tr>
<td>[24] TcN</td>
<td>492</td>
<td>197</td>
<td>260</td>
<td>714</td>
<td>175</td>
<td>334</td>
<td></td>
</tr>
<tr>
<td>[25] TcN</td>
<td>554</td>
<td>224</td>
<td>263</td>
<td>639</td>
<td></td>
<td>385</td>
<td></td>
</tr>
</tbody>
</table>

The elastic constants of the material are important, since they are related to hardness and therefore of interest in applications where mechanical strength and durability are important. Also, the second order elastic constants are used for the determination of the ultrasonic attenuation and related parameters. The calculated SOEC are some different than the others [24,25] while they are same orders. Actually Week et al. [24] has based first principle calculations using gradient-corrected density functional theory to evaluate elastic constants, which is quite different from present approach. Also Y. Liang et al. [25] have based on first-principles calculations by the BSTATE code using the plane-wave pseudo potential method and employing the local-density approximation LDA. Also the bulk modulus (B) for these compounds can be calculated with the formula $B = 2(C_{11} + C_{12} + 2C_{13} + C_{33})/9$. The evaluated $B$ for these compounds is presented in Table 1. The obtained Bulk moduli are of the same [24]. It is obvious from Table 1 that, there is good agreement between the present and reported theoretical/experimental bulk modulus and second order elastic constants of Tc and TcN [24, 25]. Thus our theoretical approach for the calculation of second order elastic constants for hexagonal structured materials at room temperature is well justified. However, third order elastic constants are not compared due to lack of data in the literature but the negative third order elastic constants are found our previous papers for hexagonal structure materials [19,20,22,23]. Hence applied theory for the evaluation of higher order elastic constants is justified.

The computed orientation dependent ultrasonic wave velocities and Debye average velocities at 300 K are shown in Figs.1–4. Figs.1–3 show that the velocities $V_L$ and $V_{S1}$ have minima and maxima respectively at 45° with the unique axis of the crystal while $V_{S2}$ increases with the angle from the unique axis. The combined effect of SOEC and density is reason for abnormal behaviour of angle dependent velocities.

![Fig. 1. $V_L$ vs angle with unique axis of crystal](image1)

![Fig. 2. $V_{S1}$ vs angle with unique axis of crystal](image2)
The nature of the angle dependent velocity curves in the present work is found similar as that for heavy rare-earth metals, third group nitrides, laves-phase compounds and other hexagonal wurtzite structured materials [19, 20, 22, 23, 26]. The chosen compounds have shown similar properties with their crystal structure. Thus the angle dependencies of the velocities in these materials are justified.

Figs.1–3 indicates that the magnitude of acoustical velocity is larger for technetium and smaller for \(\text{TcN}\). The respective smaller magnitude of acoustical velocity in \(\text{TcN}\) is due to its higher gravitational density.

Debye average velocity (\(V_D\)) of technetium and its nitride is increasing with the angle and has maxima at 55° at 300 K (Fig. 4). Since \(V_D\) is calculated using \(V_L, V_{S1}\) and \(V_{S2}\) [18, 22], therefore the angle variation of \(V_D\) is influenced by the constituent ultrasonic velocities. The maximum \(V_D\) at 55° is due to a significant increase in longitudinal and pure shear (\(V_{S2}\)) wave velocities and a decrease in quasi-shear (\(V_{S1}\)) wave velocity. Thus it can be concluded that when a sound wave travels at 55° with the unique axis of these crystals then the average sound wave velocity is maximum.

Thus the preset average sound velocity directly correlates with the Debye temperature, specific heat and thermal energy density of these materials. The Debye average velocity has a minimum value for technetium in comparison to technetium nitride compound along every direction of propagation (Fig. 4). This indicates that technetium is much stable than \(\text{TcN}\) due to the large average sound velocity [23].

It can be seen that from Figs. 1–4 technetium has maximum velocity and its nitride has least velocity for all angles of the crystals. Since ultrasonic attenuation \(A \propto V^{-3}\) [27, 28] and velocity is the largest for \(\text{Tc}\) among its nitride thus the attenuation \(A\) should be smallest and material should be most ductile. The minimum ultrasonic attenuation for \(\text{Tc}\) justifies its quite stable hexagonal structure state. Also \(\text{Tc}\) has minimum elastic constants and bulk modulus among its nitride. Hence technetium is more ductile, stable and contains few defects in the crystal structure in comparison to other compounds.

The ratio \(A= 4 \; C_{44} / (C_{11}+ C_{33} - 2C_{13})\) is the measure of elastic anisotropy in the crystal. The value of \(A\) for \(\text{Tc}\) and \(\text{TcN}\) is 0.651 and 0.681 respectively. A comparison of these anisotropy values with those of \(\text{GaN, AlN, InN}\) (III group nitride-semiconductor) [29, 30] implies that the elastic anisotropy of these materials is lower than the III group nitrides. Hence, by proposing a low value of anisotropy, these materials favour instability in comparison to those of III group nitrides.

4. Conclusions

The paper presents the study of theory of higher order elastic constants is justified for the hexagonal structured technetium and its nitrides. All elastic constants and density are mainly the affecting factor for anomalous behaviour of ultrasonic velocity in these compounds. Although, the nature of angle dependency of acoustical velocity in these materials is quite similar to that of laves phase compounds and third group nitrides but they favour instability due to lower anisotropy. All elastic constants and density are mainly the affecting affecting factor for anomalous behaviour of acoustical velocity in these materials. The average sound velocity is a direct consequence of Debye temperature, specific heat and thermal energy density of these compounds. The mechanical properties of technetium are better than of its nitride, because \(\text{Tc}\) has high ultrasonic velocities and low attenuation.
References


