

Anisotropic Debye-Waller Factors and Debye Temperatures in Hexagonal Close-Packed Elements: A Comprehensive Compilation and Analysis

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Abstract

In this study, we have investigated the anisotropic behavior of Debye-Waller factors (DWFs) and Debye temperatures (DTs) in three distinct materials: hexagonal rhenium (Re), osmium (Os), and thallium (Tl). We conducted a comparative analysis, aligning our experimental data on directional Debye temperatures with theoretical calculations. This exercise provided valuable insights into the concurrence between practical and theoretical approaches, thereby offering a critical evaluation of the accuracy and reliability of theoretical predictions. For hexagonal close-packed (hcp) structures, deviations from the ideal c/a ratio of 1.633 reveal the nuanced interplay of forces along the hexagonal axis. In hcp metals, including our subjects, two principal DWFs, Ba and Bc, correspond to the 'a' and 'c' crystallographic directions. The relationship between these factors and atomic amplitudes offers profound insights into interatomic bonding, with the Bc/Ba ratio typically exceeding 1 for c/a ratios straying from the ideal 1.633 value. This study advances our understanding of anisotropic properties in hcp metals, sheds light on the structural nuances of the materials examined, and contributes significantly to crystallography, materials science, and solid-state physics.

Keywords: X-ray diffraction, Debye temperature, hcp element vacancy formation energy.

INTRODUCTION

Osmium's monocrystal elastic constants are of great interest for several reasons. Among the 30 d-electron transition metals, we only lack monocrystal elastic constants for two elements: La (Lanthanum) and Os (Osmium). This absence of data is shocking, considering that Osmium is known to possess the highest hardness of any metallic element. Current research in material science often focuses on hardness. The hardness of a material is closely related to its elastic constants. Previous research has explored the connections between anisotropy and physical properties, with notable contributions from Tynan et al. [1] in their work on "Deuterium retention and thermal conductivity in ion-beam displacement-damaged tungsten," and R.J. Olsen et al [2] in their investigation of "defect clusters in ion-irradiated Ni and NiCo using diffuse X-ray scattering and electron microscopy."

However, it is worth noting that these discussions have yet to explicitly delve into the anisotropy of Debye-Waller factors (DWFs). It is important to emphasize that DWFs can indeed manifest anisotropy in crystals characterized by anisotropic structures.

In the case of hexagonal crystals, like the ones discussed here, there are typically two principal DWFs denoted as Ba and Bc, which are associated with the 'a' and 'c' crystallographic directions, respectively. Gopi Krishna et al. [3], Shankarnarayana et al. [4], and Sirdeshmukh et al.

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[5] have compiled data on directional DWFs for various hexagonal close hcp elements, providing valuable insights into their anisotropic properties. Singh et al. [6] have also performed theoretical calculations to determine directional X-ray Debye temperatures for several hcp metals. They have compared their calculated results with experimental data, contributing to a better understanding of these materials. Osmium, in particular, has garnered considerable attention due to its exceptional properties. Pantea et al. [7, 8] conducted experiments to determine the elastic constants of Osmium and subsequently calculated its Debye Temperatures (DTs) using these low-temperature elastic constants.

Furthermore, their research delved into the variations in Osmium's computed Debye temperature values, a subject of interest due to the different calculation methods employed. In a separate study, Debye et al. [9] reported Debye Temperature values derived from theoretically obtained elastic constant data, considering varying applied pressures. This research expanded our understanding of how external pressure influences the Debye temperature characteristics of Osmium. These studies collectively contribute valuable insights into the determination and variations of DTs in Osmium, providing a comprehensive perspective on the subject matter from both experimental and theoretical angles. It is essential to highlight the current absence of X-ray data concerning the Amplitudes of Vibration (AV) and DT for the elements Re, Os, and Tl. Therefore, the primary aim of this communication is to present the outcomes of an X-ray investigation that sought to ascertain the AVs and their corresponding DTs for Re, Os, and Tl. These results are poised to offer invaluable insights into the AV properties of these materials, effectively bridging a critical gap in our comprehension of their physical characteristics. The metallic samples used in this study were procured from a commercial source and were initially small ingots. Meticulously, these ingots were transformed into fine filings using a jeweler's file. This filing procedure was conducted with precision to ensure accurate results. Subsequently, the filings underwent further refinement by passing through a 325 mesh screen.

The X-ray measurements were executed using a Philips 3020 diffractometer equipped with a proportional counter, employing CuK α radiation. Operating parameters for the X-ray tube were set at 40 kV and 25 mA, with all measurements conducted under ambient room temperature conditions. This rigorous methodology underpins our efforts to contribute new data regarding the AV and DT of these elemental materials, adding depth to our understanding of their fundamental physical properties.

Figures 1a, 1b and 1c depict the X-ray Diffraction (XRD) patterns for Re, Os, and Tl, respectively. These patterns were acquired through slow scans conducted at an intensity measurement speed of 0.51/min. We employed the ASTM data for indexing to identify and label the diffraction patterns accurately. For the analysis of Re, we utilized the following reflections: 100, 002, 102, 110, 103, 112, 201, 004, 202, 104, 203, and 210. In the case of Os, the reflections considered were 100, 101, 102, 110, 103, 112, 201, 004, 202, 104, and 203. For Tl, a broader set of reflections was employed, including 100, 002, 101, 102, 110, 103, 200, 112, 004, 202, 104, 203, 114, 105, 204, 300, and 213. It's important to note that any additional reflections observed in the diffraction patterns suggest the presence of impurities. Readers are referred to prior publications for further insights into the sample preparation process, instrumental conditions utilized for intensity recording, and the specific corrections applied [1, 10]. These details provide a comprehensive understanding of the methodologies employed in this analysis.

EXPERIMENTAL

In this current study, the calculated values are linked to the anisotropic DWFs and DTs of hexagonal rhenium (Re), Osmium (Os), and thallium (Tl) using X-ray integrated intensities. The experiments were executed using a Philips 3020 powder diffractometer with a proportional counter. Filtered CuK α radiation was employed at room temperature, and adjustments were made to account

for thermal diffuse scattering. The text notes that the observed anisotropy in these parameters is negligible, considering experimental errors. This suggests that the crystals of these elements do not exhibit significant directional variations in their vibrational properties. The comparison of observed directional Debye temperatures with values obtained through theoretical calculations plays a crucial role in validating experimental results and evaluating measurement accuracy. The text underscores the estimation of vacancy formation energies for Re, Os, and Tl through a correlation with X-ray Debye temperature, offering insights into the stability of their crystal lattices. Notably, Osmium garners significant interest due to its exceptional hardness, compounded by the absence of monocrystal elastic constants, which are vital for studying mechanical properties, including hardness. It highlights the anisotropic nature of DWFs, describing atomic vibration amplitudes in crystals. In hexagonal crystals such as Re, Os, and Tl, two principal DWFs correspond to the 'a' and 'c' crystallographic directions. Previous research conducted by various authors on hcp elements like titanium, zirconium, ruthenium, thulium, and hafnium contributes significantly to understanding anisotropy in DWFs and DTs. Osmium, in particular, attracts substantial attention due to its extraordinary properties, likely stemming from its hardness and unique characteristics, making it a focal point in contemporary research. The text draws attention to the variations in DT values for Osmium derived from diverse methods, encompassing experimental and theoretical approaches. It is imperative to note that the text underscores the absence of available X-ray data about vibration amplitudes and DTs for rhenium, Osmium, and thallium, underscoring the profound significance of the ongoing investigation. The experimental determination of vibrational properties in specific hexagonal metals sheds light on their inherent anisotropy. It highlights the pivotal role of these findings in materials science research.

ANALYSIS OF DATA

For HCP structure. The integrated intensity of Bragg reflection as follows.

$$I_0 = I_c \exp\{- (4\pi \sin\theta/\lambda)^2 [\langle u^2 \rangle \cos^2\psi + \langle u_c^2 \rangle \sin^2\psi]\} \quad (1)$$

C constant, I_c calculated intensity. $\langle u^2 \rangle$ and $\langle u_c^2 \rangle$ are the vibrational amplitudes of vibration, ψ is the angle between the diffraction vector and the hexagonal axis. The calculated intensity I_c is given by

$\langle u^2 \rangle$ and $\langle u_c^2 \rangle$ are obtained from a least squares analysis of the logarithmic form of Eq. (1). From these, the directional DWFs B_a and B_c were obtained from the equations

$$B_a = 8\pi^2 \langle u_a^2 \rangle, B_c = 8\pi^2 \langle u_c^2 \rangle \quad (2)$$

The mean DWF \bar{B} is given by

$$\bar{B} = (2B_a + B_c)/3 \quad (3)$$

The directional DTs θ_a , θ_c and mean DT, θ_M were obtained from B_a , B_c and \bar{B} , are given by,

$$\begin{aligned} \bar{B} &= (6h^2/M k_B \theta_M) W(X) \\ B_a &= (6h^2/M k_B \theta_c) W(X) \\ B_c &= (6h^2/M k_B \theta_c) W(X) \end{aligned} \quad (4)$$

The function $W(X)$ is given by

$$W(X) = [\phi(X)/X + (1/4)], \quad (5)$$

$X = \theta_M/T$, T is the temperature of the crystal and $\phi(X)$ is the Debye function.

The DT is, $\theta_M = XT$, Where T is the temperature.

RESULTS AND DISCUSSION

The consequence of a crystal's structure is evident in the anisotropy displayed by its physical properties. The structural characteristics and the degree of anisotropy in these properties are

contingent upon the interatomic forces acting among the constituent atoms within the crystal lattice. In the hcp structure, the ideal c/a ratio is 1.633. Any deviation from this perfect value signifies a discrepancy in the relative strength of forces along the directions parallel and perpendicular to the hexagonal axis. A higher c/a ratio implies weaker muscles along the hexagonal axis, whereas a lower ratio suggests more vital details along this axis compared to the perpendicular direction. Anisotropy is a characteristic feature of these factors in anisotropic crystals. Consequently, hexagonal metals exhibit two principal Debye-Waller factors, denoted as B_a and B_c , corresponding to the 'a' and 'c' crystallographic directions. Table 1 provides values for B_c and B_a in several hcp metals, incorporating data obtained from the current investigation results.

The DWF and atomic amplitude relationship is intricately tied to interatomic bonding within a crystal lattice. Accordingly, the B_c/B_a ratio should be greater than 1 for metals exhibiting c/a ratios more significant than the ideal value of 1.633. Conversely, for metals with c/a ratios closely approximating 1.633, the B_c/B_a ratio should be approximately 1. Table 1 presents values for B_c and B_a and the c/a ratios for various hcp metals, including Re, Os, and Tl. Notably, significant departures from the ideal c/a value of 1.633 are observed only in the cases of Cd and Zn. The B_c/B_a values in these two crystals substantially exceed 1, indicating a pronounced deviation in the interatomic forces along the 'c' and 'a' crystallographic directions. In all other instances, where the c/a ratio is approximately 1.633, the B_c/B_a values also hover around 1. Any minor deviations where B_c/B_a slightly exceeds one while c/a values are somewhat less than 1.633 can likely be attributed to errors in the Debye-Waller factors. Notably, these deviations need more significant implications.

To visually represent this relationship, Figure 2 illustrates a clear trend in the B_c/B_a ratio increasing as the c/a ratio moves further from the ideal value of 1.633.

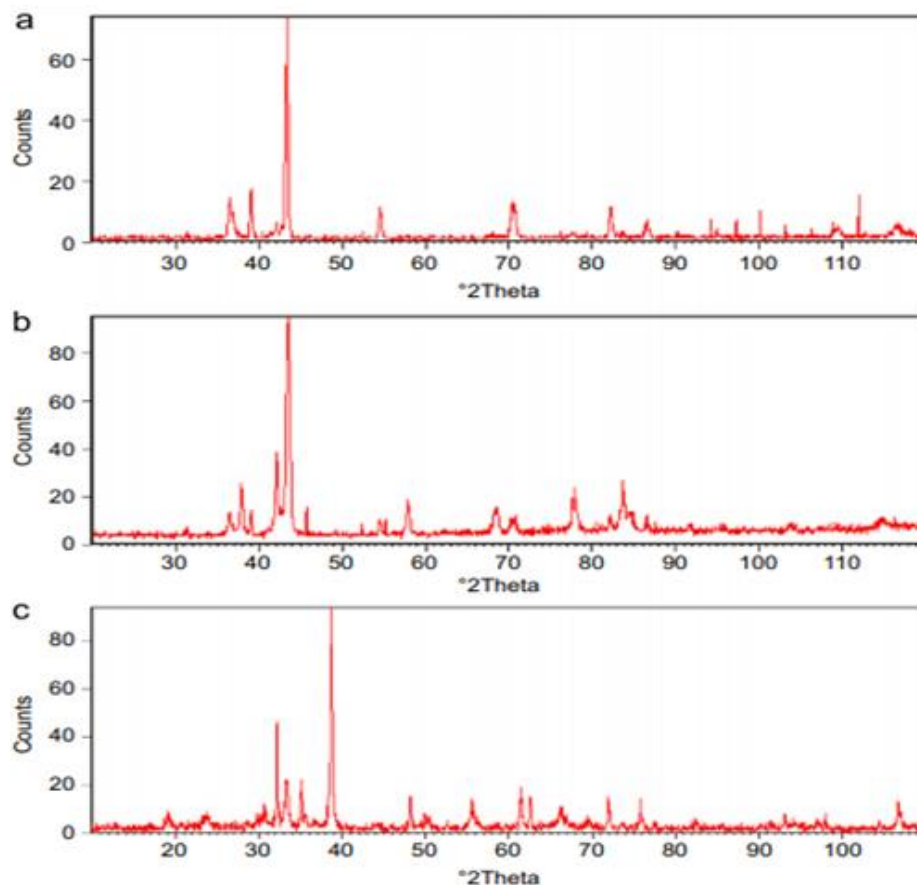


Figure 1. X-ray diffraction pattern of (a) Re, (b) Os and (c) Tl.

Table 1. *c/a* ratio and the ratio B_c/B_a for h.c.p. metals

Element	a	c	<i>c/a</i>	B_a (Å ²)	B_c (Å ²)	B_c/B_a	Ref
Be	2.2866	3.5833	1.57	0.599	0.541	0.90312	[b]
Cd	2.9789	5.6177	1.89	1.15	3.04	2.6435	[b]
Dy	3.5840	5.6680	1.58	0.81	0.89	1.0988	[a]
Er	3.5500	5.5900	1.57	0.57	0.73	1.2807	[c]
Gd	3.6290	5.7960	1.59	0.80	0.88	1.1	[a]
Hf	3.1967	5.0578	1.59	0.41	0.41	1	[e]
Ho	3.5773	5.6158	1.57	0.96	0.97	1.0104	[b]
Lu	3.5031	5.5509	1.58	0.86	0.97	1.1279	[a]
Mg	3.2093	5.2103	1.62	1.34	1.58	1.1791	[b]
Os	2.7353	4.3191	1.58	0.09	0.10	1.1111	[f]
Re	2.7600	4.4580	1.61	0.11	0.12	1.0910	[f]
Ru	2.7039	4.2817	1.58	0.14	0.15	1.0714	[e]
Sc	3.3090	5.2733	1.59	0.72	0.73	1.0139	[d]
Tb	3.6010	5.6936	1.58	0.67	0.71	1.0597	[d]
(a)Ti	2.9500	4.6860	1.59	0.54	0.48	0.8889	[e]
Tl	3.4566	5.5248	1.60	2.08	2.03	0.9760	[f]
Tm	3.5375	5.5546	1.57	0.82	0.84	1.0244	[e]
Y	3.6474	5.7306	1.57	0.83	0.80	0.9639	[a]
Zn	2.6648	4.9467	1.86	0.82	2.04	2.4878	[b]
Zr	3.2320	5.1470	1.59	0.52	0.51	0.9808	[e]

[a] Gopi Krishna et al, [b] Gopi Krishna and Sirdeshmukh (1998), [c] Gopi Krishna (1985), [d] Gopi Krishna (1988), [e] Shankarnarayana (2002), [f] present work

Table 2. Values of Debye-Waller factor and Debye temperature of Re, Os and Tl

Parameter	<i>c/a</i>	B_c (Å)	B_a (Å)	q_c (K)	q_a (K)	q_M (K)	q (K)	E_r (eV)
Re	1.61	0.12(1)	0.11(1)	412(8)	415(2)	413(2)	421	5
Os	1.58	0.10(1)	0.09(1)	441(2)	444(2)	443(2)	437	5.59
Tl	1.6	2.01(12)	2.08(7)	86(6)	90(8)	88(8)	79	0.39

Table 2 presents the obtained values for the Debye-Waller factor, Debye temperature (θ), and *c/a* ratios for Re, Os, and Tl. For comparison, Table 2 also includes values of Debye temperature derived from the Kopp-Neumann relation. The *c/a* ratios closely align with the ideal value of 1.63 for hcp elements. When considering the margin of error, it becomes evident that the anisotropy in the vibration amplitudes is minimal. Consequently, the directional Debye-Waller factors and Debye temperatures display only slight anisotropy, which aligns with the findings of Sirdeshmukh et al. [5] in their study of several hexagonal metals. Their research revealed that significant anisotropy occurs primarily in cases where the *c/a* ratio deviates significantly from the ideal value of 1.633. It's essential to emphasize that substantial deviations from B_c/B_a values exceeding one are observed solely in Cd and Zn crystals, where the *c/a* ratio notably diverges from 1.633. In all other cases, where the *c/a* ratio approximates 1.63, B_c/B_a values are also near 1. Instances where B_c/B_a is marginally greater than one while *c/a* values are slightly less than 1.633 can be attributed to errors in the Debye-Waller factors, and these deviations lack significance. To illustrate this relationship visually, Figure 2 presents a graph showing a discernible trend of B_c/B_a increasing as the *c/a* ratio moves further away from the ideal value of 1.633.

The directional DTs obtained in this study exhibit a similar order of magnitude to those derived from theoretical calculations utilizing elastic constant data by Singh et al. [6]. However, it's worth noting that directional Debye temperatures are not available for Os, precluding a direct comparison. For comparison purposes, we have included the DT (θ_D) values obtained from specific heat data and elastic constant data [11]. These values offer an alternative perspective on Debye temperature

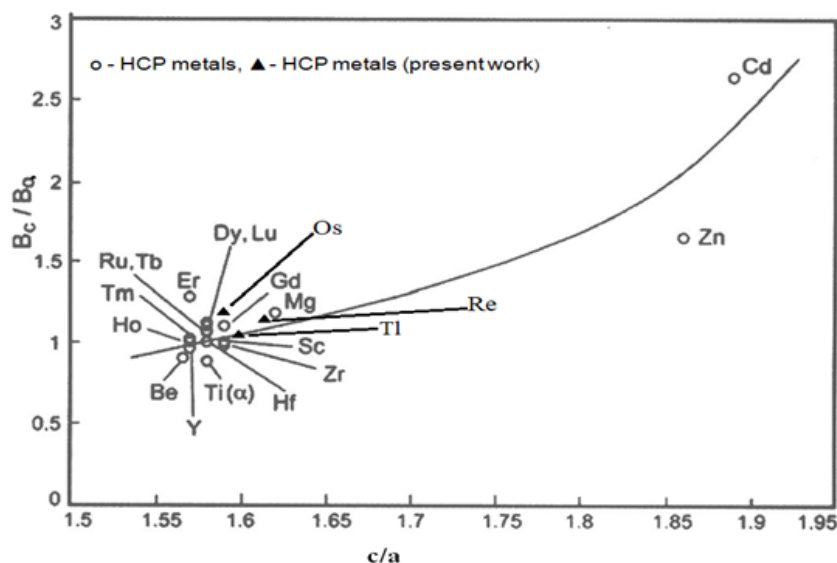


Figure 2. Plot of B_c/B_a vs. axial ratio (c/a) for hcp metals

estimation. Additionally, we've incorporated Debye temperature values reported by Pantea et al. [7, 8] and Deng et al. [9] for osmium, further enriching the comparative analysis. The importance of θ_M (Debye temperature in this study) for Re, Os, and Tl aligns well with those obtained from specific heat and elastic constant data. However, it's essential to note that precise concordance between θ_M and θ_D , θ_E (Debye temperatures from specific heat and flexible regular data, respectively) may not always be expected, as they rely on different methodologies and data sources. The values of vacancy formation energies (VFEs) are invaluable in comprehending diffusion mechanisms in pure metals, with the vacancy mechanism being predominant in most cases. In light of this, our study has sought to estimate the energy of VFE (E_f) for Re, Os, and Tl, contributing to a deeper understanding of their diffusion behavior.

Geeta Krishna [10], Gschneidner Jr [11] and Glyde [12] derived the following relation between the VFE and the DT (q) of a solid;

$$E_f = A(k/h)^2 M\theta^2 a^2 \quad (6)$$

The validity of Equation (6) has been confirmed through verification across several fcc, bcc, and hcp metals [13–16] Purushotham [17–32]. As a result, the X-ray DTs obtained in our current study have been applied to estimate VFEs for Re, Os, and Tl. These estimated values for VFEs for Re, Os, and Tl are also provided in Table 1. It's important to note that experimental values of E_f for these elements are unavailable for direct comparison.

CONCLUSIONS

In this study, the anisotropic DWFs and DTs of hexagonal rhenium (Re), osmium (Os), and thallium (Tl) were determined using X-ray integrated intensities. Within the constraints of experimental errors, the study observed that the anisotropy in the DWFs and DTs for Re, Os, and Tl is minimal. This suggests that these elements' crystals do not exhibit significant directional variation in their vibrational properties.

- The results indicate that the experimental values align reasonably well with the theoretical values, further validating the accuracy of the measurements and theoretical models.
- The research estimated the VFEs for Re, Os, and Tl. VFEs are crucial for understanding diffusion mechanisms in pure metals, and their estimation adds valuable insights into the behavior of these elements.
- The study's significance lies in its novelty, as it presents the first-ever results on the X-ray determination of directional VA, DWFs, and DTs for Re, Os, and Tl. These findings expand

our knowledge of these elements' physical properties.

This study provides valuable insights into the vibrational properties of hexagonal rhenium, osmium, and thallium through the determination of DWFs and DTs. The minimal anisotropy observed in these parameters, along with the successful comparison with theoretical calculations, enhances our understanding of the behavior of these elements at the atomic level. Additionally, the estimation of VFEs contributes to our comprehension of diffusion mechanisms in pure metals.

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