

## PAPER

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# Mechanical and thermodynamical properties of hexagonal compounds at optimized lattice parameters from two-dimensional search of the equation of state

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We have calculated the mechanical and thermodynamical properties of selected hexagonal structures by using the optimized lattice parameters (*a* and *c*) from two-dimensional (2D) search of the equation of state (EOS) within the appropriate exchange–correlation functional. To overcome the deficiency of density functional theory (DFT) for compounds with localized electrons, a PBE + *U* approximation was used with our calculated effective *U* parameter. For calculating the elastic constants of hexagonal structure, the Hex-elastic package was used which is compatible with the highly accurate all electron full-potential (Linearized) augmented plane-wave plus local orbital [FP-(L)APW + lo] method as implemented in the WIEN2k code. The obtained results of the 2D-search of the EOS for the optimized lattice parameters (*a* and *c*) are in good agreement with the experimental data. This method clearly shows its superiority compared to the 1D-search of the EOS method. Furthermore, the obtained elastic constants by using the optimized lattice parameters (*a* and *c*) from the 2D-search, were in good agreement with the available experimental data and better than the previous theoretical calculations. Our calculations show that the PBE + *U* approximation improves the results for elastic constants. Consequently, we can claim the following predictions; first, we suggest the value of Poisson's ratio as a boundary condition to predict the type of bonds. Second, we make a one-to-one correspondence between two quantities, shear modulus and *C*<sub>55</sub>. Third, we predict the stiffness of the material from the Debye temperature and average sound velocity.

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## Introduction

Nowadays with increasing computational power, there is much effort and growing interest in the field of elastic constants and improving the search method to find the equation of state, especially for hexagonal compounds with two degrees of freedom, *i.e.* volume and  $\frac{c}{a}$  changes. Elastic constants link the stress to strain and distinguish the elastic and plastic regimes due to the elastic stability criteria. In turn, these parameters can describe the response of crystals to external forces on solid materials by using first principle calculations<sup>1–8</sup> due to their technological important properties such as stiffness, hardness, and brittle/ductility. Moreover, other mechanical properties such as Voigt, Reuss, and Hill bulk moduli, shear and Young's moduli as well as Poisson's ratio<sup>3,9</sup> are estimated from elastic

coefficients. They also make a connection with thermodynamical properties such as transverse and longitudinal sound velocities, specific heat, Debye temperature, and melting point.<sup>9</sup> In addition, based on the calculated elastic constants, we are able to define the elastic anisotropy ratio, which is an important physical quantity for the structural phase stability of crystal structures.<sup>9</sup> Based on these evidences one can conclude that the calculation of elastic constants for solid materials, is very attractive and important. Therefore, elastic constants can be the physical quantities for evaluating of accuracy and validity for the employed methods, thus the elastic constants can be a level of accuracy for the employed method, especially based on density functional theory (DFT), one of the most accurate schemes for the band structure calculations.

Besides, to find the elastic constants at zero-pressure based on the energy approach,<sup>10</sup> we have to calculate the optimized volume from EOS, because of  $C_{ij} \propto \frac{1}{V_0} \left. \frac{\partial^2 E}{\partial \delta^2} \right|_{\delta=0}$ . Usually for hexagonal compounds with two degrees of freedom, EOS is calculated with constant  $\frac{c}{a}$  ratio (1D-search of EOS) while in our research to find the elastic constants of hexagonal compounds, we are interested to improve the method of search for evaluation EOS and calculate the optimized volume with 2D-search of

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EOS.<sup>11</sup> In this regards, we use 2D optimize package<sup>12</sup> and apply the appropriate exchange–correlation functional. To overcome the deficiency of DFT for the compounds with localized electrons, we apply PBE + *U* approximation using our calculated *U* parameter.

## Theoretical background

In following, a brief summary of theoretical background for the field of elastic constants calculations, 2D-search of EOS and the calculation of effective Hubbard *U* parameter have been reviewed.

### Elastic constants

Elastic constants are defined by Taylor expansion of the total energy  $E(V, \delta)$  of the lattice distortion ( $R'$ ) with respect to a small strain ( $\delta$ ) of the lattice, where  $R'$  is expressed by  $R$ , the matrix of Bravais lattice vectors of hexagonal symmetry, multiplied by a symmetric distortion matrix, *i.e.* ( $R' = R \times D$ ). In Voigt notation, the symmetric distortion matrix is written as:

$$D = \begin{pmatrix} 1 + \delta_1 & \frac{\delta_6}{2} & \frac{\delta_5}{2} \\ \frac{\delta_6}{2} & 1 + \delta_2 & \frac{\delta_4}{2} \\ \frac{\delta_5}{2} & \frac{\delta_4}{2} & 1 + \delta_3 \end{pmatrix} \quad (1) \quad \text{and}$$

We express the energy of strained system by a Taylor expansion in the distortion parameters.

$$E(V, \delta) = E(V_0, 0) + V_0 \left( \sum_{i=1}^6 \tau_i \delta_i + \frac{1}{2} \sum_{i=1}^6 \sum_{j=1}^6 C_{ij} \delta_i \delta_j + o(\delta^3) \right) \quad (2)$$

$\tau_i$  are related to the strain on the crystal,  $C_{ij}$  are elastic constants and  $V_0$  is the volume of unstrained hexagonal system.

Since hexagonal compounds, have five independent elastic constants, called  $C_{11}$ ,  $C_{12}$ ,  $C_{13}$ ,  $C_{33}$ , and  $C_{55}$  (ref. 13) ( $C_{55} = C_{44}$ ), therefore, we need five different strains to determine these elastic constants. The five distortions that are used in the Hex-elastic package<sup>14</sup> along with energy equations are described as below:

$$D_1 = \begin{pmatrix} 1 + \delta & 0 & 0 \\ 0 & 1 + \delta & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad (3)$$

$$E(V, \delta) = E(V_0, 0) + V_0 \delta (\tau_1 + \tau_2) + V_0 ((C_{11} + C_{12}) \delta^2 + O(\delta^3)) \quad (4)$$

$$D_2 = \begin{pmatrix} \left( \frac{1 + \delta}{1 - \delta} \right)^{\frac{1}{2}} & 0 & 0 \\ 0 & \left( \frac{1 - \delta}{1 + \delta} \right)^{\frac{1}{2}} & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad (5)$$

$$E(V, \delta) = E(V_0, 0) + V_0 ((C_{11} - C_{12}) \delta^2 + O(\delta^3)) \quad (6)$$

$$D_3 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 1 & 1 + \delta \end{pmatrix} \quad (7)$$

$$E(V, \delta) = E(V_0, 0) + V_0 \delta (\tau_3) + V_0 \left( C_{33} \frac{\delta^2}{2} + O(\delta^3) \right) \quad (8)$$

$$D_4 = \begin{pmatrix} 1 & 0 & \delta \\ 0 & 1 & 0 \\ \delta & 1 & 1 \end{pmatrix} \quad (9)$$

$$E(V, \delta) = E(V_0, 0) + V_0 \delta (\tau_5) + V_0 (2C_{55} \delta^2 + O(\delta^3)), \quad C_{55} = C_{44} \quad (10)$$

$$D_5 = \begin{pmatrix} (1 + \delta)^{-\frac{1}{3}} & 0 & 0 \\ 0 & (1 + \delta)^{-\frac{1}{3}} & 0 \\ 0 & 0 & (1 + \delta)^{\frac{2}{3}} \end{pmatrix} \quad (11)$$

$$E(V, \delta) = E(V_0, 0) + V_0 \left( C_{ZZ} \frac{\delta^2}{9} + O(\delta^3) \right) \quad (12)$$

$$C_{ZZ} = C_{11} + C_{12} + 2C_{33} - 4C_{13} \quad (13)$$

Using the calculated elastic constants, other structural properties such as bulk ( $B$ ), shear ( $S$ ) and Young's ( $E$ ) moduli and dimensionless Poisson's ratio  $\nu$  ( $BSE\nu$ ) are estimated based on Voigt, Reuss, and Hill's approximations.<sup>15–17</sup> For hexagonal structure, the above parameters are given by following equations;

$$B_V = \frac{1}{9} (2C_{11} + C_{33}) + \frac{2}{9} (C_{12} + 2C_{13}) \quad (14)$$

$$B_R = \frac{1}{(2S_{11} + S_{33}) + 2(2S_{12} + 2S_{13})} \quad (15)$$

$$B_H = \frac{B_V + B_R}{2} \quad (16)$$

$$S_V = \frac{1}{15} (2C_{11} + C_{33} - 2C_{13} - C_{12}) + \frac{1}{5} (2C_{55} + C_{66}),$$

$$C_{66} = \frac{C_{11} - C_{12}}{2} \quad (17)$$

$$S_R = \frac{15}{4(2S_{12} + S_{33}) - 4(S_{12} + 2S_{13}) + 3(2S_{55} + S_{66})} \quad (18)$$

$$S_H = \frac{S_V + S_R}{2} \quad (19)$$

$$E = \frac{9BS}{3B + S} \quad (20)$$

$$\nu = \frac{3B - 2S}{2(3B + S)} \quad (21)$$

where  $C_{ij}$  and  $S_{ij}$  denote the elastic constants and elastic compliances, respectively.

Since Voigt and Reuss equations (VRe) represent the upper and lower limits of  $BSE\nu$  properties,<sup>17</sup> hence thermodynamical properties such as average sound velocity ( $v_m$ ) which is consist of the longitudinal ( $v_l$ ) and transversal ( $v_t$ ) sound velocities and Debye temperature ( $\theta_D$ ) are calculated by using Hill scheme<sup>17</sup> which is average of VRe, and by using following equations;

$$v_l = \left( \frac{3B_H + 4S_H}{3\rho} \right)^{\frac{1}{2}}, \quad v_t = \left( \frac{S_H}{\rho} \right)^{\frac{1}{2}} \quad (22)$$

$$v_m = \left[ \frac{1}{3} \left( \frac{2}{v_l^3} + \frac{1}{v_t^3} \right) \right]^{-\frac{1}{3}} \quad (23)$$

$$\theta_D = \frac{h}{k_B} \left( \frac{3}{4\pi V_a} \right)^{\frac{1}{3}} v_m \quad (24)$$

where  $h$  is Plank's constant,  $k_B$  is the Boltzmann's constant,  $V_a$  is the atomic volume and  $\rho$  is mass density of material.

## Two dimensional search

In this research, we performed a convenient volume and  $\frac{c}{a}$  structure optimization by using 2Doptimize package<sup>12</sup> for hexagonal compounds. That means to find the optimized lattice parameters (**a** and **c**) we have performed at least 25 self-consistent calculations.

In this package, firstly for each volume we find the optimized  $\frac{c}{a}$  ratio, then we select a set of  $\frac{c}{a}$  changes and then by using the following equation:

$$E(X) = a_0 + a_1X + \dots + a_nX^n \quad (n = 2, 3, 4) \quad (25)$$

( $n$  and  $x$  represent the order of fitting and  $\frac{c}{a}$  ratio, respectively) we find the best  $\frac{c}{a}$  ratio for each volume in the way that the energy has minimum value.

In the next step, we would have a set of energy values and volumes at optimized  $\frac{c}{a}$  ratio and then by using the included supported equation of states, *i.e.* EOS2, Murnaghan and Birch–Murnaghan, the minimum total energy and the equilibrium volume are calculated.

After that, to find  $\frac{c}{a}$  ratio at the equilibrium volume, 2Doptimize package fits the optimized  $\frac{c}{a}$  ratios for each volume on the polynomial.

$$\text{coa}(v) = b_0 + b_1v + \dots + b_nv^n \quad (n = 2, 3, 4) \quad (26)$$

Where  $\text{coa}$  and  $v$  denote the  $\frac{c}{a}$  ratio and volume, respectively.

Finally, 2Doptimize package calculates optimized  $\frac{c}{a}$  ratio at the optimized volume, by using the above equation.

Table 1 The calculated effective Hubbard  $U$  parameter for Gd, Tb,  $\text{Gd}_2\text{In}$  and MnAs

Compound	$U_{\text{eff}}$	
Gd	0.500	
Tb	0.250	
MnAs	0.073	
$\text{Gd}_2\text{In}$	$\text{Gd}_I$	$\text{Gd}_{II}$
	0.500	0.510

## Effective Hubbard $U$ parameter

In order to calculate the effective Hubbard  $U$  parameter, we have used the method of Anisimov and Gunnarsson,<sup>18</sup> which is based on the Linearized Muffin-Tin Orbital (LMTO) basis set. Since this method cannot be used within the LAPW method, Madsen and Novák<sup>19</sup> moved the localized electrons from valence to core states to avoid of hybridization.

In practice, in this method we make a  $2 \times 2 \times 2$  supercell with one impurity site. Then, by using the following equation

$$U_{\text{eff}} = \varepsilon_{d/f}^{\uparrow} \left( \frac{n+1}{2}, \frac{n}{2} \right) - \varepsilon_{d/f}^{\uparrow} \left( \frac{n+1}{2}, \frac{n}{2} - 1 \right) - \varepsilon_F \left( \frac{n+1}{2}, \frac{n}{2} \right) + \varepsilon_F \left( \frac{n+1}{2}, \frac{n}{2} - 1 \right) \quad (27)$$

we performed two calculations, and after that, we moved the localized electrons from valence to core states and eliminated them from valence states by increasing linearization energy at a very high value. In the above equation  $n$  is number of localized electrons at impurity site,  $\varepsilon_{d/f}^{\uparrow}$  and  $\varepsilon_F$  are the spin up eigenvalue of localized electron (d or f electrons) and Fermi energy, respectively, the spin up eigenvalue, are weighted as a function of spin up relativistic quantum number. The calculated effective Hubbard  $U$  parameter for MnAs, Gd,  $\text{Gd}_2\text{In}$  and Tb compounds were listed in Table 1.

## Details of calculations

The first-principles calculations of mechanical and thermodynamical properties presented in this paper, were performed using Hex-elastic package<sup>14</sup> based on the second-order derivative ( $E''(\delta)$ ) of the polynomial fit of energy ( $E = E(\delta)$ ) vs. strains, at zero strain ( $\delta = 0$ ), which is completely compatible with WIEN2k package.<sup>20</sup> The WIEN2k is an *ab initio* full potential linearized augmented plane wave (FP-LAPW) plus local orbital method for calculating the electronic ground state of the periodic systems based on DFT.

In this procedure, the unit cell volume is divided into the non-overlapping atomic spheres around each atom with Muffin-Tin radius ( $R_{\text{mt}}$ ) and the remaining is interstitial area. Two different types of basis functions are used in these regions. In the atomic spheres, the wave functions are expanded into atomic orbitals and the maximum angular momentum of this basis function is set to  $l_{\text{max}} = 9/10$ , while in the interstitial region, a plane-wave basis set is used and the convergence of this basis set is checked by a cutoff parameter  $R_{\text{mt}}K_{\text{max}} = 8/9$

where  $R_{\text{mt}}$  is the smallest atomic sphere radius in the unit cell. Updating the positions, were done until forces drop below 1 mRy per bohr during elastic constants calculations. To treat the exchange–correlation functional, we used the improved generalized gradient approximation (PBE)<sup>21</sup> which is the recommended option<sup>11,22</sup> except for Re, Ru, and Os compounds,<sup>11</sup> in which we applied WC<sup>23</sup> instead of the PBE functional. Moreover, we used PBE +  $U$  approximation for MnAs, Gd, Gd<sub>2</sub>In and Tb compounds to overcome the deficiency of DFT for the compounds with localized electrons.

## Result and discussion

### Two-dimensional calculation

In the first step of these calculations, we have performed 1D and 2D-search of EOS for Tm within PBE functional (see Fig. 1). It shows that the effect of 2D-search, *i.e.* a convenient volume and  $\frac{c}{a}$  structure optimization, is important. As one can see from Fig. 1, 2D-search of EOS, predicts the smaller optimized volume and lower energy rather than 1D-search of EOS for Tm metal, which is consistent with experimental volume.<sup>11</sup>

In Fig. 2, we have compared the optimized volume, energy and bulk modulus for some hexagonal compounds with 2D and 1D-search of EOS.

Fig. 2 shows that the 2D-search of EOS, predicts the optimized energy lower than 1D-search. However, this difference may be negligible but as can be seen from Fig. 2, these differences can influence the optimized volume and bulk modulus. Consequently, the accuracy of DFT which is achieved by using 2D-search of EOS is much better than that obtained by 1D-search.

Therefore, in order to increase the accuracy of the elastic constants calculations, we have calculated the cell parameters of the investigated compounds using 2D-search of EOS, which are listed in Table 2 along with previous theoretical results and the experimental data to seek meaning comparison.<sup>11,24–35</sup>

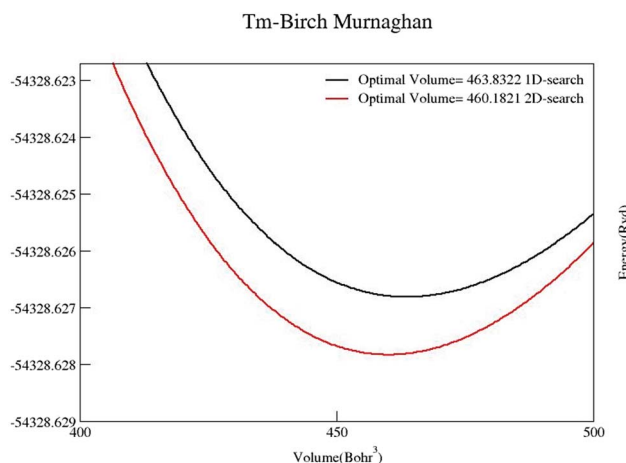


Fig. 1 1D and 2D-search of EOS for hexagonal Tm-metal within PBE exchange–correlation approximation.

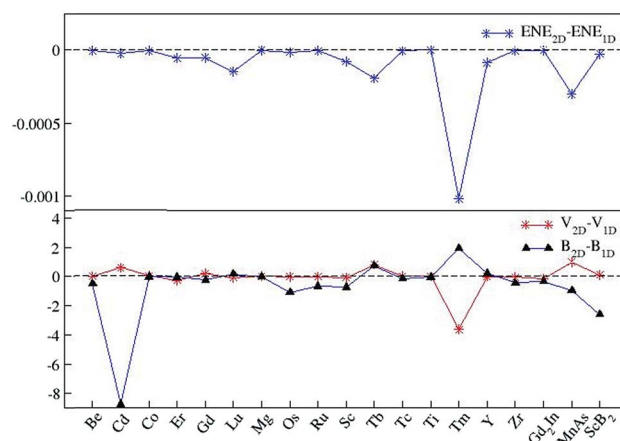


Fig. 2 difference between the optimized energy (in Ry), volume (bohr<sup>3</sup>) and bulk modulus (in GPa) with 1D and 2D-search of EOS for some hexagonal compounds.

### Elastic constants calculation

The complete sets of zero-pressure and zero-temperature single crystal's elastic constants of hexagonal compounds are calculated by using Hex-elastic package<sup>14</sup> at their optimized lattice constants from 2D-search of EOS. These are listed in Table 2, in comparison with available experiments and previous theoretical calculations.

By using first-principle calculations and elastic constants, it is possible to estimate the technological important properties such as stiffness, hardness, brittle/ductility and type of bonds for crystal structures.

A material behaves as a brittle (ductility) if the  $\frac{B}{S}$  ratio is less (more) than 1.75.<sup>8</sup> The sign of Cauchy pressure ( $C_{12} - C_{55}$ ) can be used to predict the type of bonds. Usually, the Cauchy pressure of compounds with more dominant covalent (ionic) bonds is negative (positive).<sup>7</sup> On the other hand, the value of Poisson's ratio can be used to predict the type of bonds. Stiffness is resistance to deformation forces. Young's modulus, as the ratio of stress and strain, is representative of the stiffness. It means that the greater the value of Young's modulus ( $E$ ), the stiffer the material is. Hardness is related to how much the material is resistant to the shape changes. There are two representatives for it; (i) bulk modulus, which is related to the resistance against the volume changes and (ii) shear modulus, which is related to the resistance against the reversible deformations. Therefore, it is clear that shear modulus can be a better predictor for hardness.<sup>8</sup>

In this paper for each compound, we defined a word like "MJNK" where M stands for I (ionic) or C (covalent) bonds based on the Cauchy pressure prediction, J for B (brittle) or D (ductility) and N (K) stands for  $H_n$  ( $S_m$ ) where  $H$  ( $S$ ) means hardness (stiffness) and index  $n$  ( $m$ ) shows the ordering of compound in terms of hardness, based on the shear modulus calculation, (stiffness-using Young's modulus) in this research. Moreover at the end of this section, we will check the ordering of compound in terms of hardness by using new offered Vickers

**Table 2** The calculated *a*-lattice and *c*-lattice constants in unit of Angstrom within PBE exchange–correlation potentials except for Re, Ru and Os compounds which we applied WC instead of the PBE functional, in comparison with experimental data and the previous theoretical results obtained from different methods of calculations, bold fonts are our calculations

Solid	Symmetry	<i>a</i>	<i>c</i>	Other		Exp.	
				<i>a</i>	<i>c</i>	<i>a</i>	<i>c</i>
Sc	194 ( <i>P63/mmc</i> )	<b>3.3048</b>	<b>5.2057</b>	3.2600 <sup>a</sup>	4.9100 <sup>a</sup>	3.3100 <sup>b</sup>	5.2761 <sup>b</sup>
Y	194 ( <i>P63/mmc</i> )	<b>3.6580</b>	<b>5.6728</b>	3.5900 <sup>a</sup>	5.3500 <sup>a</sup>	3.6500 <sup>b</sup>	5.7342 <sup>b</sup>
Ti	194 ( <i>P63/mmc</i> )	<b>2.9346</b>	<b>4.6617</b>	2.9700 <sup>a</sup>	4.8000 <sup>a</sup>	2.9500 <sup>b</sup>	4.6800 <sup>b</sup>
Zr	194 ( <i>P63/mmc</i> )	<b>3.2331</b>	<b>5.1710</b>	2.9900 <sup>a</sup>	5.5700 <sup>a</sup>	3.2300 <sup>b</sup>	5.1500 <sup>b</sup>
Tc	194 ( <i>P63/mmc</i> )	<b>2.7517</b>	<b>4.4104</b>	2.7200 <sup>a</sup>	4.3400 <sup>a</sup>	2.7400 <sup>b</sup>	4.3950 <sup>c</sup>
Re	194 ( <i>P63/mmc</i> )	<b>2.7585</b>	<b>4.4599</b>	2.7800 <sup>a</sup>	4.3900 <sup>a</sup>	2.7600 <sup>b</sup>	4.4576 <sup>b</sup>
Ru	194 ( <i>P63/mmc</i> )	<b>2.7015</b>	<b>4.2736</b>	2.6800 <sup>a</sup>	4.2600 <sup>a</sup>	2.7100 <sup>b</sup>	4.2768 <sup>c</sup>
Os	194 ( <i>P63/mmc</i> )	<b>2.7357</b>	<b>4.3248</b>	2.7500 <sup>a</sup>	4.3100 <sup>a</sup>	2.7400 <sup>b</sup>	4.3200 <sup>b</sup>
Gd	194 ( <i>P63/mmc</i> )	<b>3.6402</b>	<b>5.8258</b>			3.6400 <sup>c</sup>	5.7803 <sup>c</sup>
Tb	194 ( <i>P63/mmc</i> )	<b>3.5851</b>	<b>5.7809</b>			3.6000 <sup>c</sup>	5.6919 <sup>c</sup>
MnAs	194 ( <i>P63/mmc</i> )	<b>3.6822</b>	<b>5.4987</b>	3.8400 <sup>d</sup>	5.6832 <sup>d</sup>	3.7238 <sup>e</sup>	5.7045 <sup>e</sup>
TiB <sub>2</sub>	191 ( <i>P6/mmm</i> )	<b>3.0340</b>	<b>3.2346</b>	3.0292 <sup>f</sup>	3.2198 <sup>f</sup>	3.0320 <sup>g</sup>	3.2290 <sup>g</sup>
AgB <sub>2</sub>	191 ( <i>P6/mmm</i> )	<b>3.0212</b>	<b>4.0659</b>	2.9860, 2.9940, 3.0000, 3.0340 <sup>h</sup>	4.0430, 4.0510, 3.4930, 4.0850 <sup>h</sup>	3.0000 <sup>i</sup> , 3.0700 <sup>j</sup>	3.2400 <sup>i</sup> , 3.1800 <sup>j</sup>
Gd <sub>2</sub> In	194 ( <i>P63/mmc</i> )	<b>5.4546</b>	<b>6.7981</b>			5.1390 <sup>k</sup> , 5.4130 <sup>l</sup>	6.6600 <sup>k</sup> , 6.7500 <sup>l</sup>

<sup>a</sup> Ref. 24 TB calculation. <sup>b</sup> Ref. 25 and 26. <sup>c</sup> Ref. 11. <sup>d</sup> Ref. 27 GGA calculation. <sup>e</sup> Ref. 28. <sup>f</sup> Ref. 29 PBE calculation. <sup>g</sup> Ref. 30. <sup>h</sup> Ref. 31. <sup>i</sup> Ref. 32. <sup>j</sup> Ref. 33. <sup>k</sup> Ref. 34. <sup>l</sup> Ref. 35.

hardness and correlation between ductile/brittle and ionic/covalent concepts.

Our calculated elastic constants for Sc are summarized in Table 3, in comparison with available experimental data.<sup>36–42</sup> To

the best of our knowledge no theoretical value for the elastic constants of scandium available in literature, hence our results can serve as a reference for future investigations. We should emphasize that our calculated results agree well with

**Table 3** The calculated elastic constant ( $C_{ij}$  in GPa), Bulk modulus ( $B$ ), Shear modulus ( $S$ ) and Young's modulus ( $E$ ) in Voigt (V)–Reuss (R)–Hill (H) approximations (in GPa), Poisson's ratio ( $\nu$ ), transverse elastic wave velocity ( $\nu_t$  in  $\text{m s}^{-1}$ ), longitudinal elastic wave velocity ( $\nu_l$  in  $\text{m s}^{-1}$ ), average wave velocity ( $\nu_m$  in  $\text{m s}^{-1}$ ) and Debye temperature ( $\theta_D$  in K) for Sc, Y, and Ti compounds in comparison with available experimental and theoretical data, this work (bold)

	Sc		Y			Ti		
	PBE	Exp. ( $T = 27^\circ\text{C}$ ) ( $T = 303\text{ K}$ )	PBE	Other	Exp. ( $T = 27^\circ\text{C}$ )	PBE	Other	Exp.
$C_{11}$	<b>92.87</b>	99.30 <sup>a,b</sup> , 98.10 <sup>c</sup> , 98.60 <sup>d</sup>	<b>77.43</b>	80.60 <sup>i</sup>	77.90 <sup>a,c</sup>	<b>174.08</b>	175.00 <sup>j</sup>	160.00 <sup>a,b</sup> , 162.40 <sup>k</sup>
$C_{12}$	<b>31.73</b>	39.70 <sup>a,b</sup> , 45.70 <sup>c</sup> , 44.80 <sup>d</sup>	<b>23.85</b>	18.40 <sup>i</sup>	29.20 <sup>a,c</sup>	<b>88.25</b>	82.60 <sup>j</sup>	90.00 <sup>a,b</sup> , 92.00 <sup>k</sup>
$C_{13}$	<b>30.06</b>	29.40 <sup>a,b</sup> , 29.40 <sup>c</sup> , 29.50 <sup>d</sup>	<b>21.29</b>	27.10 <sup>i</sup>	21.00 <sup>c</sup> , 20.00 <sup>a</sup>	<b>76.01</b>	74.70 <sup>j</sup>	66.00 <sup>a,b</sup> , 69.00 <sup>k</sup>
$C_{33}$	<b>90.60</b>	107.00 <sup>a,b</sup> , 105.10 <sup>c</sup> , 106.20 <sup>d</sup>	<b>80.94</b>	88.10 <sup>i</sup>	76.90 <sup>a,c</sup>	<b>189.24</b>	196.00 <sup>j</sup>	181.00 <sup>a,b</sup> , 180.70 <sup>k</sup>
$C_{55}$	<b>31.41</b>	27.70 <sup>a,b</sup> , 27.20 <sup>c</sup> , 27.50 <sup>d</sup>	<b>22.39</b>	31.10 <sup>i</sup>	24.70 <sup>c</sup> , 24.30 <sup>a</sup>	<b>43.27</b>	41.80 <sup>j</sup>	46.50 <sup>a,b</sup> , 46.70 <sup>k</sup>
$B_V$	<b>51.11</b>		<b>40.96</b>			<b>113.10</b>		
$B_R$	<b>51.09</b>	56.60 <sup>c</sup> , 56.70 <sup>d</sup> , 55.87 <sup>e</sup>	<b>40.96</b>	43.80 <sup>i</sup>	41.20 <sup>c</sup> , 41.18 <sup>e</sup>	<b>113.10</b>	112.10 <sup>j</sup>	105.00 <sup>a,b</sup> , 105.13 <sup>e</sup>
$B_H$	<b>51.10</b>		<b>40.96</b>			<b>113.10</b>		
$S_V$	<b>30.98</b>		<b>25.60</b>			<b>45.70</b>		
$S_R$	<b>30.97</b>	30.60 <sup>e</sup> , 29.10 <sup>c</sup>	<b>25.29</b>		25.60 <sup>c</sup> , 25.40 <sup>e</sup>	<b>45.19</b>	41.00 <sup>j</sup>	43.40 <sup>a,b,e</sup>
$S_H$	<b>30.97</b>		<b>25.45</b>			<b>45.45</b>		
$E_V$	<b>77.31</b>		<b>63.57</b>			<b>120.83</b>		
$E_R$	<b>77.30</b>	77.60 <sup>e</sup> , 74.40 <sup>c</sup>	<b>62.92</b>		63.50 <sup>c</sup> , 63.20 <sup>e</sup>	<b>119.64</b>	109.70 <sup>j</sup>	162.90 <sup>a,b</sup> , 114.40 <sup>e</sup>
$E_H$	<b>77.30</b>		<b>63.24</b>			<b>120.23</b>		
$\nu_V$	<b>0.247</b>		<b>0.241</b>			<b>0.321</b>		
$\nu_R$	<b>0.247</b>	0.268 <sup>e</sup> , 0.279 <sup>c</sup>	<b>0.243</b>		0.243 <sup>c</sup> , 0.244 <sup>e</sup>	<b>0.323</b>	0.337 <sup>j</sup>	0.318 <sup>a,b</sup> , 0.319 <sup>e</sup>
$\nu_H$	<b>0.247</b>		<b>0.242</b>			<b>0.323</b>		
$\theta_D$	<b>363.04</b>	346.00 <sup>f</sup> , 360.00 <sup>g</sup> , 355.00 <sup>d</sup>	<b>245.39</b>		248.00 <sup>f</sup>	<b>405.91</b>		420.00 <sup>f</sup>
$V_t$	<b>3196.06</b>		<b>2380.22</b>			<b>3152.69</b>		
$V_l$	<b>5520.22</b>		<b>4083.26</b>			<b>6163.52</b>		
$V_m$	<b>3547.36</b>		<b>2640.24</b>			<b>3531.84</b>		

<sup>a</sup> Ref. 36. <sup>b</sup> Ref. 37. <sup>c</sup> Ref. 38. <sup>d</sup> Ref. 41. <sup>e</sup> Ref. 42. <sup>f</sup> Ref. 39. <sup>g</sup> Ref. 40. <sup>i</sup> Ref. 43 LMTO: full potential linear muffin-tin orbital method. <sup>j</sup> Ref. 44 PBE calculations. <sup>k</sup> Ref. 45.

experimental data.<sup>36–42</sup> Our calculations  $\left(\frac{B_H}{S_H} = 1.65\right)$  result show that the Sc is a brittle material, however this value is near to 1.75, while experiments predict that it behaves as a ductile  $\left(\frac{B}{S} = 1.86/1.94\right)$ . This inconsistency can be considered from the fact that our calculations are at zero temperature, while the experiments are at 303 K. Therefore, our PBE calculations result shows that the Sc behaves as an IBH<sub>4</sub>S<sub>4</sub> material at zero-temperature. Future experimental work will testify our calculated results.

In Table 3, we have compared our results of Y compound with the computational data of Fast *et al.*<sup>43</sup> obtained by using full potential linear Muffin-Tin orbital (LMTO) method and experimental data.<sup>36,38,39,42</sup> One can see that our results agree well with the experimental data and much better than Fast *et al.*<sup>43</sup> calculations. Our Cauchy pressure ( $C_{12} - C_{55} > 0$ ) within PBE predicts that for Y, ionic bonds are more dominant which is consistent with the prediction of Cauchy pressure using experimental elastic constants. While previous theoretical calculations predict that, the sign of Cauchy pressure is negative, it means that for Y, covalent bonds are more dominant. Therefore, our results within PBE, define Y as an IBH<sub>2</sub>S<sub>2</sub> material. Our

calculated elastic constants within PBE for Ti compound are given in Table 3 along with previous theoretical calculations and experimental data. It is clear that our results are in very good agreement with the experimental data<sup>36,37,39,42,45</sup> in comparison to the previous calculations.<sup>44</sup> Therefore, our calculations within PBE exchange–correlation, predict that, Ti behaves as an IDH<sub>7</sub>S<sub>8</sub> material. Table 4, presents the simulated calculations of the elastic constants for Zr compound along with the experimental data and the previous theoretical calculations. Our results agree well with the both previous experimental and theoretical calculations.<sup>38,46–53</sup> In addition we have calculated Debye temperature of Zr, which show very good agreement with experimental data. Our results predict that Zr as a ductile material within PBE, and predict ionic nature for the bonds (IDH<sub>6</sub>S<sub>6</sub>), while the Poisson's ratio 0.332 (see ref. 31) predicts that Zr exhibit metallic bonding which is consistent with the experimental data (0.35). The calculated results of Tc within PBE were listed in Table 4 in comparison with available experimental and theoretical data.<sup>38,43,54</sup> Our calculated bulk modulus is better than the previous calculations and show good agreement with experimental data. To our knowledge, there are no experimental and theoretical data for Debye temperature of Tc. We hope that, our results provide a useful reference for future

**Table 4** The calculated elastic constant ( $C_{ij}$  in GPa), Bulk modulus ( $B$ ), Shear modulus ( $S$ ) and Young's modulus ( $E$ ) in Voigt (V)–Reuss (R)–Hill (H) approximations (in GPa), Poisson's ratio ( $\nu$ ), Transverse elastic wave velocity ( $\nu_t$  in  $\text{m s}^{-1}$ ), longitudinal elastic wave velocity ( $\nu_l$  in  $\text{m s}^{-1}$ ), average wave velocity ( $\nu_m$  in  $\text{m s}^{-1}$ ) and Debye temperature ( $\theta_D$  in K) for Zr and Tc compounds in comparison with available experimental and theoretical data, this work (bold)

	Zr		Exp.	Tc		
	PBE	Other		PBE	Other	Exp.
$C_{11}$	<b>145.28</b>	141.10 <sup>a</sup> , 153.10 <sup>b</sup> , 139.40 <sup>c</sup> , 142.00 <sup>d</sup> , 147.90 <sup>e</sup> , 151.50 <sup>f</sup> , 152.00 <sup>g</sup>	144.00 <sup>h</sup>	<b>525.41</b>	611.70 <sup>k</sup>	
$C_{12}$	<b>63.86</b>	67.60 <sup>a</sup> , 63.40 <sup>b</sup> , 71.30 <sup>c</sup> , 71.00 <sup>d</sup> , 66.30 <sup>e</sup> , 71.80 <sup>f</sup> , 74.00 <sup>g</sup>	74.00 <sup>h</sup>	<b>229.73</b>	218.70 <sup>k</sup>	
$C_{13}$	<b>66.46</b>	64.30 <sup>a</sup> , 76.50 <sup>b</sup> , 66.30 <sup>c</sup> , 71.00 <sup>d</sup> , 66.20 <sup>e</sup> , 66.10 <sup>f</sup> , 63.20 <sup>g</sup>	67.00 <sup>h</sup>	<b>184.72</b>	207.50 <sup>k</sup>	
$C_{33}$	<b>165.39</b>	166.90 <sup>a</sup> , 171.20 <sup>b</sup> , 162.70 <sup>c</sup> , 147.00 <sup>d</sup> , 182.70 <sup>e</sup> , 160.60 <sup>f</sup> , 153.30 <sup>g</sup>	166.00 <sup>h</sup>	<b>596.32</b>	645.00 <sup>k</sup>	
$C_{55}$	<b>27.51</b>	25.80 <sup>a</sup> , 22.40 <sup>b</sup> , 25.50 <sup>c</sup> , 8.00 <sup>d</sup> , 39.20 <sup>e</sup> , 34.10 <sup>f</sup> , 33.20 <sup>g</sup>	33.00 <sup>h</sup>	<b>160.02</b>	196.60 <sup>k</sup>	
$B_V$	<b>94.39</b>			<b>316.16</b>		
$B_R$	<b>93.97</b>			<b>316.04</b>	348.60 <sup>k</sup>	281.00 <sup>l</sup>
$B_H$	<b>94.18</b>			<b>316.10</b>		
$S_V$	<b>36.42</b>			<b>163.44</b>		
$S_R$	<b>34.76</b>			<b>161.33</b>		123.00 <sup>l</sup>
$S_H$	<b>35.59</b>			<b>162.39</b>		
$E_V$	<b>96.81</b>			<b>418.25</b>		
$E_R$	<b>92.84</b>			<b>413.62</b>		
$E_H$	<b>94.83</b>			<b>415.93</b>		
$\nu_V$	<b>0.329</b>			<b>0.279</b>		
$\nu_R$	<b>0.335</b>		0.35 <sup>i</sup>	<b>0.281</b>		0.310 <sup>l</sup>
$\nu_H$	<b>0.332</b>			<b>0.280</b>		
$\theta_D$	273.77		290.00 <sup>j</sup>	517.27		
$V_t$	<b>2345.11</b>			<b>3798.88</b>		
$V_l$	<b>4678.12</b>			<b>6880.01</b>		6220.00 <sup>i</sup> (in $T = 25^\circ\text{C}$ )
$V_m$	<b>2630.37</b>			<b>4233.05</b>		

<sup>a</sup> Ref. 46. <sup>b</sup> Ref. 47 FP-LMTO calculation. <sup>c</sup> Ref. 48 DFT calculation. <sup>d</sup> Ref. 49 TB calculation. <sup>e</sup> Ref. 50 EAM calculation. <sup>f</sup> Ref. 51 MEAM calculation. <sup>g</sup> Ref. 52 MEAM calculation. <sup>h</sup> Ref. 53. <sup>i</sup> Ref. 38. <sup>j</sup> Ref. 39. <sup>k</sup> Ref. 43 LMTO calculation. <sup>l</sup> Ref. 54.

experimental works and theoretical studies. Our calculation predicts that dominant bonds for Tc, are ionic which agree with the previous prediction using elastic constants.<sup>43</sup> Our calculations exhibit that Tc behaves as a ductile material, which is consistent with the experimental data.<sup>54</sup> Therefore, based on our PBE calculations, Tc is an IDH<sub>10</sub>S<sub>10</sub> material.

Single elastic constants for Re within WC<sup>23</sup> exchange–correlation are listed in Table 5. Currently, there is no theoretical calculation of single elastic constants are available in the literature. Our calculated elastic constants, agree well with the experimental data<sup>25,36,39,42,43,45</sup> especially our calculated Debye temperature.<sup>39</sup> Table 5 exhibit that Re is a ductile and stiff material and also predicts that the dominant bonds are ionic (IDH<sub>11</sub>S<sub>11</sub>).

The simulated elastic constants of Ru using FPLAPW-WC are listed in Table 5 in comparison with theoretical LMTO calculations<sup>43</sup> and experimental measurements.<sup>25,39,42</sup> It is clear that our results are in good agreement with the experimental data and better than previous calculations. Our  $\frac{B_H}{S_H}$  ratio (1.56) and experimental value (1.63), suggest that Ru behaves as a brittle material. The present value of Young's and shear moduli are high, therefore it is suggested that Ru is stiffer and hardness. These results within WC exchange–correlation, suggest that Ru should be considered as a CBH<sub>12</sub>S<sub>12</sub> material, while the Poisson's ratio 0.236 (see ref. 31 and reference therein) predicts that Ru exhibit ionic bonding which is consistent with the experimental elastic constants prediction. The elastic constants of Os

along with previous theoretical calculations are listed in Table 5. Our results within WC exchange–correlation are in reasonable agreement with previous calculations.<sup>42,43</sup> However, our calculated  $C_{55}$  is 312.7 GPa, while the previous calculated value was 162.2 GPa.<sup>43</sup> This difference leads to the different signs of Cauchy pressure ( $C_{12} - C_{55}$ ) for our results than the previous calculations.<sup>43</sup> Therefore, our (previous<sup>43</sup>) results predict that covalent (ionic) bonds are more dominant for Os compound, while the Poisson's ratio 0.221 (see ref. 31 and reference therein) predicts that Os exhibit ionic bonding.

Our results predict that  $C_{13} > C_{12}$  while the previous one indicated  $C_{12} > C_{13}$ . The calculated Bulk, Shear and Young's moduli, suggest that Os should be a brittle, stiff and hard material (CBH<sub>14</sub>S<sub>14</sub>).

Based on the data gathered in Table 6, it is clear that the effect of Hubbard  $U$  parameter correction, improves the result of gadolinium towards the experimental ones.<sup>36–39</sup> Prediction of Cauchy pressure ( $C_{12} - C_{55}$ ) and Poisson's ratio within PBE and PBE +  $U$  approximation about the type of bonds, are similar (for Gd, ionic bonds are more dominant)  $C_{12} < C_{55}$  PBE and PBE +  $U$  approximations predict that Gd is a brittle material but PBE +  $U$  approximation ( $\frac{B_H}{S_H} = 1.57$ ) predicts that it is more brittle than PBE approximation ( $\frac{B_H}{S_H} = 1.68$ ). The higher value of shear modulus within PBE +  $U$  approximation indicates that Gd is harder than that obtained within PBE approximation. The higher value of Young's modulus with Hubbard  $U$  correction

**Table 5** The calculated elastic constant ( $C_{ij}$  in GPa), Bulk modulus ( $B$ ), Shear modulus ( $S$ ) and Young's modulus ( $E$ ) in Voigt (V)–Reuss (R)–Hill (H) approximations (in GPa), Poisson's ratio ( $\nu$ ), transverse elastic wave velocity ( $\nu_t$  in  $\text{m s}^{-1}$ ), longitudinal elastic wave velocity ( $\nu_l$  in  $\text{m s}^{-1}$ ), average wave velocity ( $\nu_m$  in  $\text{m s}^{-1}$ ) and Debye temperature ( $\theta_D$  in K) for Re, Ru, and Os compounds in comparison with available experimental and theoretical data, this work (bold)

	Re			Ru			Os		
	WC	Other	Exp.	WC	Other	Exp.	WC	Other	Exp.
$C_{11}$	<b>649.00</b>		634.40 <sup>a</sup> , 616.00 <sup>b</sup>	<b>622.52</b>	701.00 <sup>d</sup>	563.00 <sup>e</sup>	<b>816.26</b>	894.50 <sup>c</sup>	
$C_{12}$	<b>269.39</b>		266.00 <sup>a</sup> , 273.00 <sup>b</sup>	<b>202.99</b>	169.20 <sup>d</sup>	188.00 <sup>e</sup>	<b>225.23</b>	249.20 <sup>c</sup>	
$C_{13}$	<b>187.64</b>		202.00 <sup>a</sup> , 206.00 <sup>b</sup>	<b>179.81</b>	187.40 <sup>d</sup>	168.00 <sup>e</sup>	<b>256.13</b>	245.60 <sup>c</sup>	
$C_{33}$	<b>678.16</b>		701.10 <sup>a</sup> , 683.00 <sup>b</sup>	<b>724.57</b>	774.50 <sup>d</sup>	624.00 <sup>e</sup>	<b>914.98</b>	1016.40 <sup>c</sup>	
$C_{55}$	<b>184.95</b>		169.10 <sup>a</sup> , 161.00 <sup>b</sup>	<b>212.42</b>	240.00 <sup>d</sup>	181.00 <sup>e</sup>	<b>312.70</b>	162.20 <sup>c</sup>	
$B_V$	<b>362.83</b>			<b>343.87</b>			<b>446.94</b>		
$B_R$	<b>362.43</b>	447.30 <sup>c</sup>	372.00 <sup>d</sup> , 365.25 <sup>e</sup>	<b>342.98</b>	368.80 <sup>d</sup>	310.92 <sup>e</sup> , 320.80 <sup>d</sup>	<b>444.92</b>	476.10 <sup>c</sup> , 411.89 <sup>e</sup>	418.00 <sup>d</sup>
$B_H$	<b>362.63</b>			<b>343.42</b>			<b>445.93</b>		
$S_V$	<b>200.71</b>			<b>220.72</b>			<b>304.85</b>		
$S_R$	<b>197.69</b>		178.80 <sup>e</sup>	<b>219.13</b>		191.10 <sup>e</sup>	<b>304.38</b>	275.20 <sup>e</sup>	
$S_H$	<b>199.20</b>			<b>219.93</b>			<b>304.61</b>		
$E_V$	<b>508.38</b>			<b>545.46</b>			<b>745.14</b>		
$E_R$	<b>501.83</b>		461.10 <sup>e</sup>	<b>541.98</b>		475.80 <sup>e</sup>	<b>743.56</b>	675.20 <sup>e</sup>	
$E_H$	<b>505.11</b>			<b>543.72</b>			<b>744.35</b>		
$\nu_V$	<b>0.266</b>			<b>0.235</b>			<b>0.222</b>		
$\nu_R$	<b>0.269</b>		0.290 <sup>e</sup>	<b>0.236</b>		0.245 <sup>e</sup>	<b>0.221</b>	0.227 <sup>e</sup>	
$\nu_H$	<b>0.267</b>			<b>0.236</b>			<b>0.221</b>		
$\theta_D$	<b>416.08</b>		416.00 <sup>f</sup>	<b>582.94</b>		555.00 <sup>f</sup>	<b>502.37</b>		467.00 <sup>f</sup>
$V_t$	<b>3076.93</b>			<b>4206.67</b>			<b>3676.42</b>		
$V_l$	<b>5464.27</b>			<b>7157.37</b>			<b>6148.81</b>		
$V_m$	<b>3423.22</b>			<b>4662.72</b>			<b>4068.39</b>		

<sup>a</sup> Ref. 45. <sup>b</sup> Ref. 36. <sup>c</sup> Ref. 43 LMTO calculation. <sup>d</sup> Ref. 25. <sup>e</sup> Ref. 42. <sup>f</sup> Ref. 39.

indicates that Gd is stiffer than that obtained within PBE prediction. Therefore, comparing the results of PBE +  $U$  approximation for Gd with results of other compounds within different exchange–correlation, indicate Gd as an IBH<sub>1</sub>S<sub>1</sub> material. According to Table 6 (Tb compound) we can observe that PBE +  $U$  approximation improves the obtained elastic constants towards the experimental data.<sup>39,42,55</sup> Concerning the changes of other parameters, we obtain that the effect of Hubbard  $U$  parameter is so important for Tb (see Table 6). The effective Hubbard  $U$  parameter changes the order of  $C_{12} > C_{55}$  (PBE) to  $C_{12} < C_{55}$  (PBE +  $U$ ). This means that PBE exchange–correlation predicts that ionic bonds are more dominant for Tb, while Hubbard  $U$  correction (PBE +  $U$  approximation) changes it from ionic to covalent bonds.

PBE +  $U$  approximation predicts that Tb is harder than the PBE prediction. The higher value of Young's modulus within PBE +  $U$  approximation predicts that Tb is stiffer than the prediction of PBE. Hubbard  $U$  correction predicts that Tb is more brittle than PBE. Therefore, comparison of our results within PBE +  $U$  approximation with other compounds within different exchange–correlations for Tb, indicate that Tb behaves as a CBH<sub>3</sub>S<sub>3</sub> material. We have calculated the mechanical and thermodynamical properties of Gd<sub>2</sub>In intermetallic compound within PBE and PBE +  $U$  approximations. According to the results of Gd<sub>2</sub>In (Table 6) we can conclude that the effect of Hubbard potential on variation of the elastic constants is important. The Hubbard  $U$  correction leads the order of  $C_{11}$  and  $C_{33}$  changes from  $C_{11} < C_{33}$  to  $C_{11} > C_{33}$ , however this small

change could be due to numerical errors in calculations. PBE and PBE +  $U$  approximations predict that Gd<sub>2</sub>In is a brittle material but PBE ( $\frac{B_H}{S_H} = 1.55$ ) predicts that Gd<sub>2</sub>In is more brittle than PBE +  $U$  prediction ( $\frac{B_H}{S_H} = 1.65$ ). The higher value of Young's modulus with Hubbard  $U$  parameter makes Gd<sub>2</sub>In stiffer than PBE prediction. PBE and PBE +  $U$  approximations predict that ionic bonds are more dominant for Gd<sub>2</sub>In ( $C_{12} > C_{55}$ ), *i.e.* the prediction of PBE and PBE +  $U$  about type of bonds are the same. Thus, in this research Gd<sub>2</sub>In behaves as an CBH<sub>5</sub>S<sub>5</sub> material.

Our results for TiB<sub>2</sub> are listed in Table 7 along with experimental data,<sup>56–59</sup> and previous calculations.<sup>31,60</sup> It is clear that our results are in very good agreement with experimental data and much better than previous calculations. Our  $\frac{B_H}{S_H} = 0.97$  ratio show that TiB<sub>2</sub> behaves as a brittle material, which is consistent with experimental prediction and better than previous calculations. The high value of Young's and shear moduli, define TiB<sub>2</sub> as a stiff and hard material. Therefore, in this research, TiB<sub>2</sub> behaves as a CBH<sub>13</sub>S<sub>13</sub> material within PBE.

The obtained results of AgB<sub>2</sub> are listed in Table 7. Kwon *et al.*<sup>61</sup> reported that AgB<sub>2</sub> is a potential candidate for high Tc superconductors which confirm by several studies.<sup>31–33,62–65</sup> We were interested to study this compound since Shein and Ivanovskii<sup>31</sup> reported that it is mechanically unstable ( $C_{55} < 0$ ) using elastic constants calculation, whereas Ozisik *et al.*<sup>66</sup>

**Table 6** The calculated elastic constant ( $C_{ij}$  in GPa), Bulk modulus ( $B$ ), Shear modulus ( $S$ ) and Young's modulus ( $E$ ) in Voigt (V)–Reuss (R)–Hill (H) approximations (in GPa), Poisson's ratio ( $\nu$ ), transverse elastic wave velocity ( $v_t$  in  $\text{m s}^{-1}$ ), longitudinal elastic wave velocity ( $v_l$  in  $\text{m s}^{-1}$ ), average wave velocity ( $v_m$  in  $\text{m s}^{-1}$ ) and Debye temperature ( $\theta_D$  in K) for Gd, Tb, and Gd<sub>2</sub>In compounds in comparison with available experimental data, this work (bold)

Gd	Gd				Tb			Gd <sub>2</sub> In	
	PBE	PBE + $U$	Other	Exp. ( $T = 27^\circ\text{C}$ )	PBE	PBE + $U$	Exp.	PBE	PBE + $U$
$C_{11}$	<b>63.82</b>	<b>70.00</b>		67.83 <sup>a,b,c</sup>	<b>55.46</b>	<b>73.79</b>	68.55 <sup>f</sup>	<b>91.59</b>	<b>105.36</b>
$C_{12}$	<b>25.65</b>	<b>23.13</b>		25.59 <sup>a,b,c</sup>	<b>17.07</b>	<b>20.27</b>	24.65 <sup>f</sup>	<b>46.34</b>	<b>35.36</b>
$C_{13}$	<b>14.03</b>	<b>18.23</b>		20.73 <sup>a,b,c</sup>	<b>15.00</b>	<b>18.12</b>	22.40 <sup>f</sup>	<b>17.03</b>	<b>26.29</b>
$C_{33}$	<b>68.58</b>	<b>72.08</b>		71.23 <sup>a,b,c</sup>	<b>62.03</b>	<b>75.18</b>	73.30 <sup>f</sup>	<b>94.76</b>	<b>104.11</b>
$C_{55}$	<b>17.59</b>	<b>21.55</b>		20.77 <sup>a,b,c</sup>	<b>16.77</b>	<b>24.14</b>	21.60 <sup>f</sup>	<b>36.70</b>	<b>27.99</b>
$B_V$	<b>33.74</b>	<b>36.81</b>			<b>29.68</b>	<b>37.31</b>		<b>48.75</b>	<b>54.52</b>
$B_R$	<b>33.68</b>	<b>36.80</b>		37.90 <sup>a,b,c</sup>	<b>29.64</b>	<b>37.31</b>	38.79 <sup>f</sup>	<b>48.16</b>	<b>54.42</b>
$B_H$	<b>33.71</b>	<b>36.80</b>			<b>29.66</b>	<b>37.31</b>		<b>48.45</b>	<b>54.48</b>
$S_V$	<b>20.35</b>	<b>23.47</b>			<b>18.94</b>	<b>26.09</b>		<b>32.38</b>	<b>33.32</b>
$S_R$	<b>19.70</b>	<b>23.29</b>		21.80 <sup>a,b,c</sup>	<b>18.69</b>	<b>25.98</b>	22.40 <sup>f</sup>	<b>30.06</b>	<b>32.63</b>
$S_H$	<b>20.03</b>	<b>23.38</b>			<b>18.81</b>	<b>26.03</b>		<b>31.22</b>	<b>32.98</b>
$E_V$	<b>50.83</b>	<b>58.07</b>			<b>46.84</b>	<b>63.48</b>		<b>79.52</b>	<b>83.05</b>
$E_R$	<b>49.46</b>	<b>57.70</b>		54.80 <sup>a,b,c</sup>	<b>46.34</b>	<b>63.25</b>	56.30 <sup>f</sup>	<b>74.66</b>	<b>81.58</b>
$E_H$	<b>50.15</b>	<b>57.90</b>			<b>46.59</b>	<b>63.36</b>		<b>77.10</b>	<b>82.32</b>
$\nu_V$	<b>0.248</b>	<b>0.237</b>			<b>0.236</b>	<b>0.216</b>		<b>0.228</b>	<b>0.246</b>
$\nu_R$	<b>0.255</b>	<b>0.238</b>		0.259 <sup>a,b,c</sup>	<b>0.239</b>	<b>0.217</b>	0.258 <sup>f</sup>	<b>0.241</b>	<b>0.250</b>
$\nu_H$	<b>0.252</b>	<b>0.237</b>			<b>0.238</b>	<b>0.216</b>		<b>0.234</b>	<b>0.248</b>
$\theta_D$	<b>164.32</b>	<b>177.27</b>	175 <sup>d</sup>	182 (in $T = 0\text{K}$ ) <sup>e</sup>	<b>157.17</b>	<b>184.45</b>	170 ± 11 <sup>d</sup> , 176.00 <sup>e</sup>	<b>209.70</b>	<b>216.00</b>
$V_t$	<b>1601.13</b>	<b>1730.13</b>			<b>1514.49</b>	<b>1881.54</b>		<b>1954.09</b>	<b>2012.71</b>
$V_l$	<b>2780.86</b>	<b>2950.02</b>			<b>2583.42</b>	<b>2963.13</b>		<b>3319.30</b>	<b>3477.59</b>
$V_m$	<b>1777.99</b>	<b>1918.08</b>			<b>1676.07</b>	<b>1970.42</b>		<b>2165.61</b>	<b>2234.01</b>

<sup>a</sup> Ref. 38. <sup>b</sup> Ref. 36. <sup>c</sup> Ref. 37. <sup>d</sup> Ref. 55. <sup>e</sup> Ref. 39. <sup>f</sup> Ref. 42.



**Table 7** The calculated elastic constant ( $C_{ij}$  in GPa), Bulk modulus ( $B$ ), Shear modulus ( $S$ ) and Young's modulus ( $E$ ) in Voigt (V)–Reuss (R)–Hill (H) approximations (in GPa), Poisson's ratio ( $\nu$ ), transverse elastic wave velocity ( $\nu_t$  in  $\text{m s}^{-1}$ ), longitudinal elastic wave velocity ( $\nu_l$  in  $\text{m s}^{-1}$ ), average wave velocity ( $\nu_m$  in  $\text{m s}^{-1}$ ) and Debye temperature ( $\theta_D$  in K) for  $\text{TiB}_2$  and  $\text{AgB}_2$  compounds in comparison with available experimental and theoretical data, this work (bold)

$\text{TiB}_2$				$\text{AgB}_2$	
$\text{TiB}_2$	PBE	Other	Exp.	PBE	other
$C_{11}$	<b>655.34</b>	670.90 <sup>a</sup> , 651.00 <sup>b</sup>	690.00 <sup>c</sup> , 660.00 <sup>d</sup> , 672.00 <sup>e</sup> , 654.40 <sup>f</sup>	<b>270.64</b>	220.90 <sup>a</sup> , 370.20 <sup>g</sup>
$C_{12}$	<b>63.46</b>	64.00 <sup>a</sup> , 76.00 <sup>b</sup>	410.00 <sup>c</sup> , 48.00 <sup>d</sup> , 40.00 <sup>e</sup> , 48.98 <sup>f</sup>	<b>198.04</b>	253.70 <sup>a</sup> , 95.70 <sup>g</sup>
$C_{13}$	<b>101.77</b>	100.90 <sup>a</sup> , 115.00 <sup>b</sup>	320.00 <sup>c</sup> , 93.00 <sup>d</sup> , 125.00 <sup>e</sup> , 95.25 <sup>f</sup>	<b>74.89</b>	82.50 <sup>a</sup> , 62.90 <sup>g</sup>
$C_{33}$	<b>458.59</b>	472.90 <sup>a</sup> , 461.00 <sup>b</sup>	440.00 <sup>c</sup> , 432.00 <sup>d</sup> , 224.00 <sup>e</sup> , 458.10 <sup>f</sup>	<b>204.46</b>	173.50 <sup>a</sup> , 210.40 <sup>g</sup>
$C_{55}$	<b>262.55</b>	266.60 <sup>a</sup> , 259.00 <sup>b</sup>	250.00 <sup>c</sup> , 260.00 <sup>d</sup> , 232.00 <sup>e</sup> , 262.60 <sup>f</sup>	<b>119.27</b>	−42.40 <sup>a</sup> , 7.70 <sup>g</sup>
$B_V$	<b>255.92</b>			<b>160.15</b>	
$B_R$	<b>251.38</b>	262.00 <sup>b</sup>	417.00 <sup>c</sup> , 244.00 <sup>d</sup> , 247.50 <sup>f</sup>	<b>146.37</b>	148.40 <sup>g</sup>
$B_H$	<b>253.65</b>			<b>153.26</b>	
$S_V$	<b>264.36</b>			<b>81.50</b>	
$S_R$	<b>258.45</b>	255.00 <sup>b</sup>	169.00 <sup>c</sup> , 262.00 <sup>d</sup> , 264.30 <sup>f</sup>	<b>60.08</b>	48.40 <sup>g</sup>
$S_H$	<b>261.40</b>			<b>70.79</b>	
$E_V$	<b>589.94</b>			<b>209.03</b>	
$E_R$	<b>577.44</b>	578.00 <sup>b</sup>	446.00 <sup>c</sup> , 579.00 <sup>d</sup> , 584.70 <sup>f</sup>	<b>158.55</b>	130.90 <sup>g</sup>
$E_H$	<b>583.69</b>			<b>184.03</b>	
$\nu_V$	<b>0.115</b>			<b>0.282</b>	
$\nu_R$	<b>0.117</b>	0.130 <sup>b</sup>	0.323 <sup>c</sup> , 0.104 <sup>d</sup> , 0.106 <sup>f</sup>	<b>0.319</b>	0.353 <sup>g</sup>
$\nu_H$	<b>0.116</b>			<b>0.299</b>	
$\theta_D$	<b>1216.17</b>	1204.50 <sup>b</sup>	989.00 <sup>c</sup> , 1211.00 <sup>d</sup> , 1217.00 <sup>f</sup>	<b>490.68</b>	408.40 <sup>g</sup>
$V_t$	<b>7642.57</b>	7545.00 <sup>b</sup>	7660.00 <sup>f</sup>	<b>3252.82</b>	2688.00 <sup>g</sup>
$V_l$	<b>11599.80</b>	11585.90 <sup>b</sup>	11245.00 <sup>f</sup>	<b>6084.10</b>	5637.00 <sup>g</sup>
$V_m$	<b>8367.34</b>	8272.40 <sup>b</sup>	8350.00 <sup>f</sup>	<b>3633.27</b>	3023.00 <sup>g</sup>

<sup>a</sup> Ref. 31 GGA calculation. <sup>b</sup> Ref. 60. <sup>c</sup> Ref. 56. <sup>d</sup> Ref. 57. <sup>e</sup> Ref. 58. <sup>f</sup> Ref. 59. <sup>g</sup> Ref. 66 PBE calculation.

suggested that it is mechanically stable owing to the  $C_{55}$  positive value 7.7 GPa. Our calculated elastic constants, using lattice parameters from 2D-search, are positive which suggests that this compound is mechanically stable which is consistent with Ozisik *et al.* calculations. The present value of  $C_{55}$  for  $\text{AgB}_2$  (119.27 GPa) is much higher than the Ozisik *et al.*<sup>66</sup> calculation (7.7 GPa) which indirectly, is a hardness predictor. It means our results show that  $\text{AgB}_2$  is much hardness. Ozisik *et al.* calculations predict  $\frac{B}{S} = 3.01$ <sup>66</sup> for  $\text{AgB}_2$  compound which is more ductile than our calculation  $\frac{B_H}{S_H} = 2.16$ . The comparison of Young's modulus between Ozisik<sup>66</sup> and our calculations, demonstrate that  $\text{AgB}_2$  is stiffer than our calculations. Therefore, our results within PBE suggest that  $\text{AgB}_2$  is an  $\text{IDH}_9\text{S}_9$  material. These differences can be considered from the fact that our calculations are using lattice parameters from 2D-search. Future experimental work will testify our calculated results. The obtained ferromagnetic-results of MnAs, along with experimental data in the paramagnetic state at 303 K (ref. 67) for seeking comparison, are given in Table 8. The effect of Hubbard  $U$  parameter, changes the order of elastic constants from  $C_{12} < C_{13} < C_{55} < C_{33} < C_{11}$  to  $C_{13} < C_{12} < C_{55} < C_{33} < C_{11}$  when we move from PBE  $\rightarrow$  PBE +  $U$ . It is observed that PBE +  $U$  approximation, improves the obtained bulk modulus toward experimental values.<sup>68</sup> The Hubbard  $U$  correction does not change the prediction of Cauchy pressure ( $C_{12} - C_{55}$ ) and Poisson's ratio regarding the type of bonds. Both of PBE and PBE +  $U$  predict ionic bonds are more dominate for MnAs compound ( $C_{12} > C_{55}$ ).

**Table 8** The calculated elastic constant ( $C_{ij}$  in GPa), Bulk modulus ( $B$ ), Shear modulus ( $S$ ) and Young's modulus ( $E$ ) in Voigt (V)–Reuss (R)–Hill (H) approximations (in GPa), Poisson's ratio ( $\nu$ ), transverse elastic wave velocity ( $\nu_t$  in  $\text{m s}^{-1}$ ), longitudinal elastic wave velocity ( $\nu_l$  in  $\text{m s}^{-1}$ ), average wave velocity ( $\nu_m$  in  $\text{m s}^{-1}$ ) and Debye temperature ( $\theta_D$  in K) for ferromagnetic MnAs-compound in comparison with available experimental and theoretical data, this work (bold)

MnAs	PBE	PBE + $U$	Other	Exp.
$C_{11}$	<b>109.80</b>	<b>116.51</b>		40.00 <sup>a</sup>
$C_{12}$	<b>42.72</b>	<b>55.37</b>		8.00 <sup>a</sup>
$C_{13}$	<b>43.38</b>	<b>15.97</b>		10.00 <sup>a</sup>
$C_{33}$	<b>138.43</b>	<b>108.82</b>		110.00 <sup>a</sup>
$C_{55}$	<b>69.47</b>	<b>88.55</b>		34.00 <sup>a</sup>
$B_V$	<b>68.55</b>	<b>57.38</b>		
$B_R$	<b>67.81</b>	<b>55.87</b>		36 <sup>b</sup>
$B_H$	<b>68.18</b>	<b>56.63</b>		
$S_V$	<b>49.73</b>	<b>57.30</b>		
$S_R$	<b>44.59</b>	<b>46.41</b>		
$S_H$	<b>47.16</b>	<b>51.86</b>		
$E_V$	<b>120.15</b>	<b>128.97</b>		
$E_R$	<b>109.72</b>	<b>109.04</b>		
$E_H$	<b>114.98</b>	<b>119.19</b>		
$\nu_V$	<b>0.207</b>	<b>0.125</b>		
$\nu_R$	<b>0.230</b>	<b>0.174</b>		
$\nu_H$	<b>0.218</b>	<b>0.149</b>		
$\theta_D$	<b>346.29</b>	<b>360.48</b>	254.40 <sup>c</sup>	
$V_t$	<b>2657.19</b>	<b>2786.26</b>		
$V_l$	<b>4429.63</b>	<b>4339.20</b>		
$V_m$	<b>2939.57</b>	<b>3060.01</b>		

<sup>a</sup> Ref. 67 measured at 303 K and in the paramagnetic state. <sup>b</sup> Ref. 68 measured at 273 K. <sup>c</sup> Ref. 55.

Hubbard  $U$  correction makes MnAs more brittle than PBE prediction. PBE +  $U$  approximation predicts that MnAs is more hard (see the value of shear modulus in Table 8) than PBE prediction. The higher value of Young's modulus within PBE +  $U$  approximation, predicts that MnAs is stiffer than the PBE prediction. Therefore, in this work we recognize MnAs as a CBH<sub>8</sub>S<sub>7</sub> material.

Previous studies show that correlation between hardness and shear modulus is not always valid for a large variety of materials as discussed in ref. 69. The new research of Chen *et al.*<sup>69</sup> shows that the calculated Vickers hardness ( $H_v$ ) as  $H_v = 2(k^2S)^{0.585} - 3$  ( $k = S/B$ ,  $S$ -shear and  $B$ -bulk modulus) is a better prediction of hardness than shear modulus. This motivated us to check the hardness of materials in this research by using shear modulus ( $S$ ) and Vickers hardness ( $H_v$ ). The ordering of compound in terms of hardness (PBE +  $U$  results were used) using our shear modulus calculation (low to high) is as Gd, Y, Tb, Sc, Gd<sub>2</sub>In, Zr, Ti, MnAs, AgB<sub>2</sub>, Tc, Re, Ru, Ti<sub>2</sub>B, and Os. While our Vickers hardness calculation predicts it as Zr, Ti, Gd, Y, Sc, Gd<sub>2</sub>In, Tb, AgB<sub>2</sub>, Tc, MnAs, Re, Ru, Os, and Ti<sub>2</sub>B.

The previous analysis<sup>70</sup> on the elastic properties revealed that  $\frac{S}{B}$  ratio (Pugh's modulus, it can define as  $\frac{B}{S}$  (ref. 8 and 31)) and revised Cauchy pressure  $\frac{1}{E}(C_{12} - C_{55})$  ( $E$ -Young modulus) are well correlated to a hyperbolic criterion to recognize the ductile to brittle properties for a large materials of cubic symmetry. This means that there is a correlation between ductility/brittle and metallic/covalent concepts.<sup>70</sup> We could find (see Fig. 6) this correlation between ductility/brittle and ionic/covalent concepts for our hexagonal compounds except for Sc, Y, Gd, and Gd<sub>2</sub>In at zero temperature (PBE +  $U$  results were used) which for them our results predict brittle materials and ionic bonds. However, using the mechanism proposed by the previous analysis<sup>70</sup> these materials are not exceptions. From Fig. 6, we can see that the Sc, Y, Gd and Gd<sub>2</sub>In are close to the transformation zone. So, we realize that the mechanism

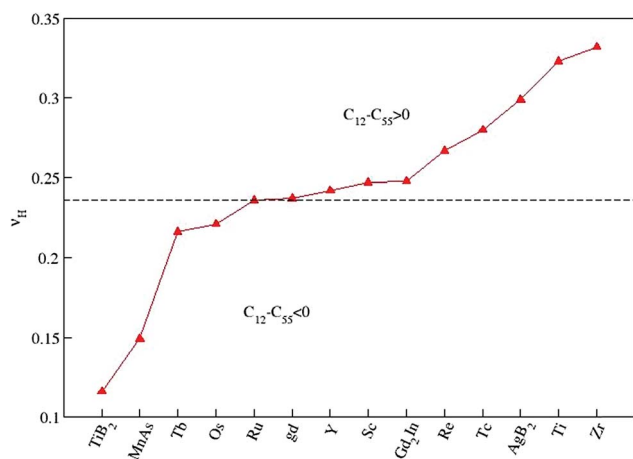


Fig. 3 Comparison of the sign of Cauchy pressure and the Poisson's ratio for considered hexagonal compounds. The results of PBE +  $U$  approximation were used for Gd, Tb, MnAs and Gd<sub>2</sub>In.

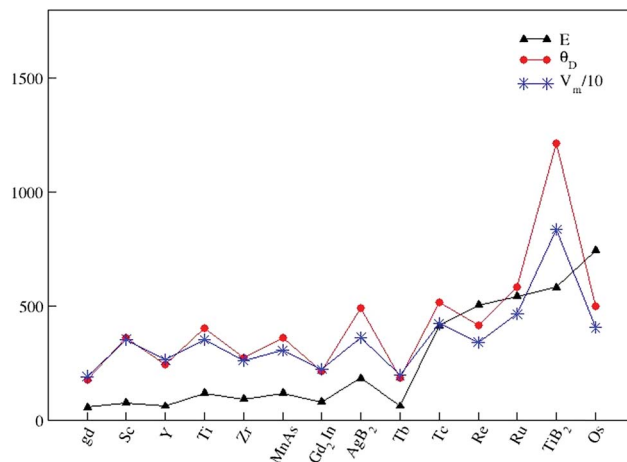


Fig. 4 Comparison of the behavior of Young's modulus (in GPa), Debye temperature (in K) and average sound velocity (in  $\text{m s}^{-1}$ ) for the considered compounds. The results of PBE +  $U$  approximation were used for Gd, Tb, MnAs and Gd<sub>2</sub>In.

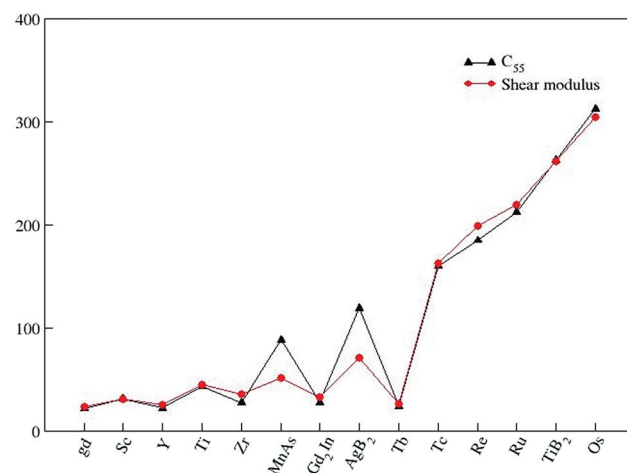


Fig. 5 Comparison of two quantities  $C_{55}$  and shear modulus (in GPa) for the considered hexagonal compounds. The results of PBE +  $U$  approximation were used for Gd, Tb, MnAs and Gd<sub>2</sub>In.

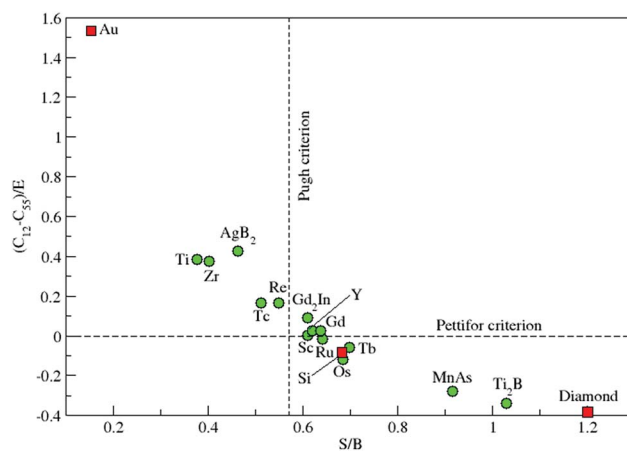


Fig. 6 The correlation between ductile/brittle and types of bond. Au is typical metallic and exhibits the most ductile and plastic materials while the Si and diamond are typical covalent bond materials and diamond is known as the hardest material.

proposed in the previous report<sup>70</sup> can be also suitable for the hexagonal compounds.

Based on the previous report<sup>70</sup>, it is interesting to see that the correlation between ductile/brittle and ionic/covalent concepts derived from the hexagonal compounds can provide us a more clear insight to the relationship between hardness and Pugh's modulus. This means that Pugh's modulus ratio as  $\left(\frac{S}{B}\right)$  seems to mirror the hardness of materials *i.e.* hardness increases with increasing Pugh's modulus. For example, the ordering of hardness using shear modulus for Ru and Os will be as Ru, Ti<sub>2</sub>B, Os while from Fig. 6, using Pugh's modulus, it will be as Ru, Os. In the above, we completed this discussion using Vickers hardness.

Moreover our results show that the Poisson's ratio (to predict the type of bonds) follows the  $\frac{B}{S}$  ratio (to predict brittle/ductility of materials) trend. This can again emphasize that there is a correlation between type of bonds and brittle/ductility of materials.

## Prediction

The sign of Cauchy pressure ( $C_{12} - C_{55}$ ) can be used to predict the type of bonds. Usually, the Cauchy pressure of compounds with more dominant covalent (ionic) bonds is negative (positive).<sup>7</sup> On the other hand, the value of Poisson's ratio can be used to predict the type of bonds.<sup>8</sup>

If we compare the sign of Cauchy pressure and the value of Poisson's ratio, we can offer the typical value of  $\nu = 0.236$  as a limit to determine the type of bonds (see Fig. 3). The present value of 0.236, derived from the Cauchy pressure, as a limit to determine the type of bonds is in good agreement with the previous results (see ref. 31 and reference therein).

Stiffness is resistance to deformation forces. Young's modulus, as the ratio of stress and strain, is representative of the stiffness. It means that the greater the value of Young's modulus ( $E$ ), the stiffer the material is. Fig. 4 shows that, Debye temperature and average sound velocity can be considered as a stiffness predictor, generally. However, we do not see this behavior for Re and Os elements. Hardness is related to how much the material is resistant to the shape changes. There are two representatives; (i) bulk modulus, which is related to the resistance against the volume changes and (ii) shear modulus, which is related to the resistance against the reversible deformations. Therefore, shear modulus can be a better predictor for hardness.<sup>8</sup> Fig. 5 shows that shear modulus follows the  $C_{55}$  trend. Therefore, we can usually obtain a larger shear modulus is mainly due to its larger  $C_{55}$ .

## Conclusions

We performed the 2D-search of EOS to find the optimized lattice parameters ( $a$  and  $c$ ) for hexagonal compounds. By using these parameters, we calculated the zero-pressure and zero-temperature mechanical and thermodynamical properties of the considered compounds. Our results are in very good

agreement with experimental data and are better than the previous theoretical calculations. Our results show that the effect of Hubbard  $U$  parameter improves the results of elastic constants calculations. Our results based on the shear modulus calculation predict that Gadolinium (Osmium) has the smallest (highest) value of hardness and stiffness in this research. We offered the typical value of  $\nu = 0.236$  for Poisson's ratio as a limit to determine the type of bonds. It was observed the Debye temperature or average sound velocity could be used as a stiffness predictor.

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