Original research article

Structural, electronic, elastic and thermodynamic properties of XFe₄P₁₂ (X = Tb and Dy) filled skutterudite using FP-LMTO method

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The physical properties of TbFe₄P₁₂ and DyFe₄P₁₂ ternary alloys have been described using the full potential linear muffin-tin orbital’s (FP-LMTO) method within local density approximation (LDA) and local spin-density approximation (LSDA). The equilibrium lattice constants of both alloys are in good agreement with experimental data. The electronic band structure and density of state depict that the alloys as conductors. The computed elastic constants Cₓ, the bulk modulus B, anisotropy factor A, shear modulus G, Young’s modulus E, Poisson’s ratio ν and B/G ratios of XFe₄P₁₂ (X = Tb, Dy) at different pressures using LDA are found. The sound velocities and Debye temperature are too anticipated from elastic constants. Eventually, the fluctuations of the primitive cell volume, expansion coefficient α, bulk modulus B, heat capacity (C₀ and Cᵥ) Debye temperature θ_D, and entropy S, at pressure 0–50 GPa and temperature between 0 and 3000 K are obtained.

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1. Introduction

The ternary alloys with the general formula LnT₄X₁₂ (Ln = lighter lanthanide, T = Fe, Ru and Os, X = P, As and Sb) crystallize at skutterudite type structure (cubic, space group: Im-3) [1,2] (see Fig. 1). These skutterudites with lighter lanthanides were frequently prepared by flux methods [1,2]. However, we have prepared many skutterudite compounds with lighter lanthanides at high temperatures and high pressures [3]. These materials show interesting physical properties at low temperatures. Superconducting [4,5], semiconducting [6], metal-insulator transition [7,8], magnetic [9], heavy fermions [10], intermediate valence [11,12], and non-Fermi liquid behavior [13] have been observed in these materials. Further, skutterudite compounds exhibit remarkable thermoelectric properties [14,15]. The potential of materials for thermoelectric applications [16,17] is determined by the figure of merit, Z = S² × T /k where S is the Seebeck coefficient, σ is the electrical conductivity, and k is the thermal conductivity. Better thermoelectric properties are determined by a combination of high mobility (for higher σ with reasonable carrier concentrations), higher band masses (to obtain higher values of S), and lower
lattice thermal conductivities, $\kappa = \kappa_e + \kappa_1$ which include both electronic and phonon contributions, respectively. The physical properties of skutterudite compounds were reviewed by Sales [18].

We have prepared new filled skutterudites with heavy lanthanides (including Y), LnT$_4$P$_{12}$ (Ln = heavy lanthanide, T = Fe, Ru and Os) at high temperatures and pressures [19,20]. The new filled skutterudite TbFe$_4$P$_{12}$ has been prepared at around 4 GPa and 1050 °C. Powder X-ray diffraction of TbT$_4$P$_{12}$ (T = Fe and Ru) has been studied with synchrotron radiation at ambient pressure [21]. The electrical and magnetic properties of several new filled skutterudites with heavy lanthanide have been studied at low temperatures; DyFe$_4$P$_{12}$ [22] and TbFe$_4$P$_{12}$ [21] exhibit a ferromagnetic ordering around 10 K. These materials could be potential in multistage thermoelectric devices as it has been shown that they have ZT > 1.0, but their properties are not well known. Recent findings on the physical-chemical and transport properties of skutterudite materials are reviewed. Results obtained on binary compounds showed that their lattice thermal conductivity is too high to achieve high thermoelectric figures of merit. Several approaches have been recently proposed to decrease the lattice thermal conductivity of skutterudite materials. They are described and illustrated by recent experimental results. It is shown that low thermal conductivity can be achieved and high ZT values are possible for skutterudites [23]. We have already refined the crystal structures of some filled skutterudites on powder X-ray diffraction data with Rietveld methods [6,12]. In this work, the structural, electronic, elastic and thermodynamic properties using the full potential method linear muffin-tin orbital (FP-LMTO) for different values of pressure and temperature are investigated. The arrangement of this paper is as compiles: The FP-LMTO computational details in Section 2 is depicted and Section 3 presents the results and discussion for structural, electronic, elastic and thermodynamic properties for TbFe$_4$P$_{12}$ and DyFe$_4$P$_{12}$ compounds. Eventually, a conclusion is given in Section 4.

2. Computational method

Computations depicted here, were performed using the FP-LMTO method within The density-functional theory (DFT) [24,25] and implemented in the Lmtart computer code in this method, the space is divided in two parts: an interstitial regions (IR) and non-overlapping (MT) spheres centered on the atomic sites. In the IR regions, the Fourier series represent the basic function. In side on MT spheres, the basic set is treated as a linear combination of radial functions times spherical harmonics. The charge density and the potential are represented inside the muffin-tin sphere radius (MTS) by spherical harmonics up to $l_{\text{max}} = 6$. The exchange-correlation (XC) effects are treated with the local density approximation (LDA) using the scheme developed by Perdew and Wang [26,27] and the local spin density approximation (LSDA) [28]. The $k$-integrations over the Brillouin zone (BZ) is carried out up to (6,6,6) grid in the irreducible Brillouin zone, using the tetrahedron method [29] the values of the sphere radii, energy cut-off and the number of PLWs for TbFe$_4$P$_{12}$ and DyFe$_4$P$_{12}$ are listed in Table 1.

![Crystal structure of filled skutterudite XFe$_4$P$_{12}$ (X = Tb, Dy).](image-url)

Table 1
The number of plane wave (NPW), energy cut-off (in Ryd) and the MTS (in a.u.), used in our calculations.

<table>
<thead>
<tr>
<th></th>
<th>TbFe$<em>4$P$</em>{12}$</th>
<th>DyFe$<em>4$P$</em>{12}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NPW</td>
<td>Tb</td>
<td>Dy</td>
</tr>
<tr>
<td>LDA</td>
<td>34412</td>
<td>34412</td>
</tr>
<tr>
<td>Ecut-off (Ryd)</td>
<td>122.3970</td>
<td>122.3817</td>
</tr>
<tr>
<td>MTS (a.u.)</td>
<td>Tb</td>
<td>P</td>
</tr>
<tr>
<td>LDA</td>
<td>3.415</td>
<td>2.038</td>
</tr>
<tr>
<td></td>
<td>Fe</td>
<td>P</td>
</tr>
</tbody>
</table>

Fig. 1. Crystal structure of filled skutterudite XFe$_4$P$_{12}$ (X = Tb, Dy).
2.1. Elastic properties

The elastic constants of materials describe its response to an applied stress or, conversely, the stress required to maintain a given deformation. Both stress and strain have three tensile and three shear components, giving six components in total. The linear elastic constants form $6 \times 6$ symmetric matrix, having 27 different components, such that $\sigma_i = C_{ij} \varepsilon_j$ for small stresses, $\sigma$ and strains, e ($30$). Any symmetry present in the structure may make some of these components equal each other’s and may be fixed at some of these components equaled and others may be fixed at zero. Thus, cubic crystal has only three different symmetry elements $(C_{11}, C_{12}$ and $C_{44}$), each one represents three equal elastic constants $(C_{11} = C_{22} = C_{33}, C_{12} = C_{23} = C_{31}, C_{44} = C_{55} = C_{66})$. A single strain with non-zero first and fourth components, yielding a very efficient method for the calculation of elastic constants for the cubic system. Thus for the calculation of elastic constants $C_{11}, C_{12}$ and $C_{44}$ we have used the Mehl method ($31,32$) of imposing the conservation of volume of the sample under the pressure effect. To calculate the difference of elastic modulus, $C_{11}-C_{22}$, we apply the following orthorhombic strain tensor.

$$
\bar{e} = \begin{bmatrix}
\delta & 0 & 0 \\
0 & \delta & 0 \\
0 & 0 & \frac{1}{(1-\delta)^2} - 1
\end{bmatrix}
$$

where $\delta^2$ is the applied stress, varies between $5 \times 10^{-4}$ and $2.5 \times 10^{-3}$. The application of this strain affects the total energy:

$$
E(\delta) = E(-\delta) = E(0) + 6(C_{11} - C_{12})V_0\delta^2 + O[\delta^4]
$$

where $E(0)$ is the energy of the system to the initial state (without stress) and $V_0$ is the volume of unit cell. Moreover, for an isotropic cubic crystal, the bulk modulus is related to $C_0$ constants according to the equation ($33,34$):

$$
B = \frac{(C_{11} + 2C_{12})}{3}
$$

For determining coefficient $C_{44}$, the following monoclinic strain tensor is used.

$$
\tilde{e} = \begin{bmatrix}
1 & \delta & 0 \\
\frac{\delta}{2} & 1 & 0 \\
0 & 0 & \frac{4}{(4-\delta^2)}
\end{bmatrix}
$$

This changes the total energy to:

$$
E(\delta) = E(-\delta) = E(0) + \frac{1}{2}C_{44}V_0\delta^2 + O[\delta^4]
$$

Combining Eqs. (3) and (4), one can easily determine the two elastic constants $C_{11}$ and $C_{12}$, while the third elastic constant, of Eq. (6), is deduced by $C_{44}$ from the elastic constants. We obtain the anisotropy parameter $A$ (for an isotropic crystal, $A$ equals $1$, while another value greater or less than $1$ means that it is an anisotropic crystal), Poisson’s ratio $\nu$ characterizes the tension of the solid perpendicular to the direction of the force applied, Young’s modulus $E$ measures the resistance change from solid to its length expression and the shear modulus $G$ measures the interior of the solid with planes parallel to the later which is represented by the following equations:

$$
A = \frac{2C_{44}}{C_{11} - C_{12}}
$$

$$
\nu = \frac{3B - E}{6B}
$$

$$
E = \frac{9BG}{3B + G}
$$

$$
G = \frac{C_{11} - C_{12} + 3C_{44}}{5}
$$

where $B$ is the bulk modulus given by Eq. (3). From these results, we find that the stability criteria ($35,36$): $C_{11} - C_{12} > 0, C_{11} > 0, C_{44} > 0, (C_{11} + 2C_{12}) > 0$ and $C_{12} < B < C_{11}$, are satisfied for the studied skutterudites, and, therefore, it is elastically stable.

Table 2 lists the elastic constant $(C_{11}, C_{12},$ and $C_{44}$), bulk modulus $B$, shear modulus $G$ and Young’s modulus $E$, Poisson’s ratio $\nu$, the anisotropic parameter $A$ and $B/G$ ratios of $XFe_4P_{12}(X $= Tb, Dy) compounds under a broad of pressures ($0$–$50$ GPa) at $0$ K using LDA approximation. To investigate the elastic constants, it is seen that the elastic constants $C_{11}, C_{12}, C_{44}$ and bulk modulus $B$, increase monotonically with the applied pressure (see Fig. 2). The results from $G$ and $E$ of $XFe_4P_{12}(X $= Tb, Dy) compounds at various pressures are also calculated and the results are depicted in Table 2, the results indicate that
Table 2
Calculated elastic constant $c_{ij}$, $c_{44}$ (in GPa), bulk modulus $B$ (in GPa), Young’s and shear modulus $E$, $G$ (in GPa), Poisson’s ratio $\nu$, the anisotropic parameter $A$ and $B/G$ ratios with LDA at different pressures for XFe$_4$P$_{12}$ ($X=$ Tb, Dy).

<table>
<thead>
<tr>
<th>$P$(GPa)</th>
<th>$c_{11}$</th>
<th>$c_{12}$</th>
<th>$c_{44}$</th>
<th>$G$</th>
<th>$E$</th>
<th>$\nu$</th>
<th>$A$</th>
<th>$B/G$</th>
</tr>
</thead>
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<tr>
<td>0</td>
<td>522.2429</td>
<td>39.4565</td>
<td>210.4228</td>
<td>201.9795</td>
<td>222.8100</td>
<td>488.7234</td>
<td>0.0967</td>
<td>0.8717</td>
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<td>10</td>
<td>573.6014</td>
<td>64.8641</td>
<td>253.0234</td>
<td>235.1000</td>
<td>253.5615</td>
<td>559.2900</td>
<td>0.1033</td>
<td>0.9947</td>
</tr>
<tr>
<td>20</td>
<td>630.0745</td>
<td>89.7600</td>
<td>296.3106</td>
<td>269.6700</td>
<td>285.8493</td>
<td>633.8405</td>
<td>0.1086</td>
<td>1.0968</td>
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<tr>
<td>30</td>
<td>680.5807</td>
<td>115.5780</td>
<td>335.6153</td>
<td>304.3400</td>
<td>314.3697</td>
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<td>734.9227</td>
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<td>50</td>
<td>784.1502</td>
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<td>373.6000</td>
<td>375.2980</td>
<td>843.4635</td>
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<td>1.3534</td>
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DyFe$_4$P$_{12}$

<table>
<thead>
<tr>
<th>$P$(GPa)</th>
<th>$c_{11}$</th>
<th>$c_{12}$</th>
<th>$c_{44}$</th>
<th>$G$</th>
<th>$E$</th>
<th>$\nu$</th>
<th>$A$</th>
<th>$B/G$</th>
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<tr>
<td>0</td>
<td>523.3084</td>
<td>45.6000</td>
<td>207.4320</td>
<td>205.1082</td>
<td>220.0009</td>
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<td>0.8884</td>
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<td>10</td>
<td>575.7322</td>
<td>69.6767</td>
<td>241.4224</td>
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<td>246.0645</td>
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<td>20</td>
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<td>341.3100</td>
<td>324.2962</td>
<td>738.8744</td>
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<td>1.1779</td>
</tr>
<tr>
<td>50</td>
<td>784.1502</td>
<td>170.3676</td>
<td>379.7282</td>
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<td>350.5933</td>
<td>802.1769</td>
<td>0.1440</td>
<td>1.2373</td>
</tr>
</tbody>
</table>

Fig. 2. The pressure dependence of the elastic constants $C_{ij}$ and the bulk modulus $B$ of XFe$_4$P$_{12}$ ($X=$ Tb, Dy).

the values of $G$ and $E$ increase with increasing pressure. A typical Poisson’s ratio value for covalent materials is about 0.1, whereas that for ionic materials is about 0.25 [37]. In this work, Poisson ratio $\nu$ of XFe$_4$P$_{12}$ ($X=$ Tb, Dy) alloys at various pressures are around 0.1. This indicates that this compound is highly covalent. One of the most important property of crystalline solids is the elastic anisotropy ratio which is defined as $A=2C_{44}/(C_{11}-C_{12})$. This property has an important implication in engineering field since it is highly correlated with the possibility to introduce micro crack in materials [38]. Essentially, all known crystals are elastically anisotropic. For isotropic crystals $\alpha=A$ equals 1.0 while any value smaller or larger than 1.0 indicates anisotropy. The magnitude of a deviation from 1.0 measures the degree of elastic anisotropy possessed by the crystal. The obtained anisotropic $\alpha$ values vary from 0.8684 to 1.3534, indicates that this compound is anisotropic. According to the empirical formula of Pugh of ductility [39], which states that the critical value which separates ductile and brittle materials is around 1.75; if $B/G > 1.75$, the material behaves in a ductile manner; otherwise the material behaves a brittle manner. The computed values of ratio $B/G$ vary from 0.9065 to 1.0712 at various pressures, indicates that this compound is classified as brittle material. Eventually; The elastic constant $C_{11}$, $C_{12}$, $C_{44}$ (in GPa), bulk modulus $B$ (in GPa), Young’s and shear modulus $E$, $G$ (in GPa), Poisson’s ratio $\nu$, the anisotropic parameter $A$ and $B/G$ values are similar for two compounds. The elastic constants give important information about the binding characteristic between adjacent atomic planes, anisotropic character of binding structural stability [40]. The requirement of mechanical stability criteria in this skutterudites structure leads to following restrictions on the elastic constants $C_{11}-C_{12} > 0$, $C_{11} > 0$, $C_{44} > 0$, $(C_{11} + 2C_{12}) > 0$ and $C_{12} < B < C_{11}$ this criteria are satisfied, indicating that these compounds are stable against elastic deformations. The elastic properties of XFe$_4$P$_{12}$ ($X=$ Tb, Dy) alloys have not been established theoretically or experimentally.

2.2. Debye temperature

Debye temperature calculated from elastic constants is the same as that determined from specific measurement. One of the standard methods to calculate the Debye temperature $\theta_D$, is from the elastic constant data; also $\theta_D$ could be obtained from the average sound velocity, $\nu_m$ by the following relation [41]:

$$\theta_D = \frac{h}{K_B} \left[ \frac{3n}{4\pi V_a} \right]^{1/3} \nu_m$$

(11)
Table 3
Longitudinal, transverse and average sound velocities \((v_l, v_t, v_m)\) respectively, (in \(\text{ms}^{-1}\)), and Debye temperature\(\theta_D\) in \(K\) with LDA at different pressures for the \(\text{XFe}_4\text{P}_{12}\) \((X=\text{Tb, Dy})\).

<table>
<thead>
<tr>
<th>(\text{XFe}<em>4\text{P}</em>{12})</th>
<th>(P) (GPa)</th>
<th>(v_l) (ms(^{-1}))</th>
<th>(v_t) (ms(^{-1}))</th>
<th>(v_m) (ms(^{-1}))</th>
<th>(\theta_D) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{TbFe}<em>4\text{P}</em>{12})</td>
<td>0</td>
<td>9711.06400</td>
<td>6488.7100</td>
<td>7091.3530</td>
<td>438.6259</td>
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<tr>
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<td>10407.2600</td>
<td>6922.0020</td>
<td>7568.3750</td>
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<td>20</td>
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<td>8040.7700</td>
<td>497.3507</td>
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<td>546.8688</td>
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<tr>
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<td>9226.1330</td>
<td>570.6697</td>
</tr>
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<td>(\text{DyFe}<em>4\text{P}</em>{12})</td>
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<td>9675.839</td>
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</tr>
<tr>
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<td>460.8513</td>
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</tr>
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<td>7804.6230</td>
<td>8563.0860</td>
<td>530.2173</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>12583.5098</td>
<td>8114.8930</td>
<td>8907.6640</td>
<td>551.3533</td>
</tr>
</tbody>
</table>

Table 4
The atomic positions in the ternary skutterudite \(\text{XFe}_4\text{P}_{12}\) \((X=\text{Tb, Dy})\).

<table>
<thead>
<tr>
<th>Atom</th>
<th>Atomic positions</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{X = Tb, Dy})</td>
<td>((0, 0, 0))</td>
</tr>
<tr>
<td>Fe</td>
<td>((-1/4, 1/4, 1/4))</td>
</tr>
<tr>
<td>P</td>
<td>((0, y, z))</td>
</tr>
</tbody>
</table>

(12)

where \(\theta_D\) is Plank’s constant, \(k_B\) is Boltzmann’s constant and \(V_0\) is the atomic volume. The average sound velocity in the polycrystalline material is given by Ref. [42]:

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

(12)

where \(v_l\) and \(v_t\) are the longitudinal and transverse sound velocities obtained using the shear modulus \(G\) and the bulk modulus \(B\) from Navier’s equation [43]:

\[
v_l = (\frac{3}{2}B + 4G) \frac{1}{2} \left(\frac{1}{a} - 1\right) \tag{13}
\]

\[
v_t = \left(\frac{C_P}{\rho}\right)^{1/2} \tag{14}
\]

The obtained sound velocities and Debye temperature as well as the density for \(\text{XFe}_4\text{P}_{12}\) \((X=\text{Tb, Dy})\) alloys at different pressures using LDA approximation are given in Table 3. The ensues show that the values of \(v_l\), \(v_t\), \(v_m\), and \(\theta_D\) increase with increasing pressure. We have found at \(\theta_D(\text{TbFe}_4\text{P}_{12}) > \theta_D(\text{DyFe}_4\text{P}_{12})\), the decrease of the Debye temperature in the sequence \((\text{Tb} \rightarrow \text{Dy})\) can be attributed to the progressive decreasing of average sound velocity \(v_m\) in the same sequence. Up to date, there are no experimental and theoretical available data for comparison.

3. Results and discussion

3.1. Structural properties

The skutterudite structure is characterized by two non-equivalent atomic positions \(y\) and \(z\), which are not fixed by symmetry. The \(y\) and \(z\) positions have been optimized by minimizing the total energy with keeping the volume fixed at the experimentally observed value [44]. The optimized values of \(y\) and \(z\) are used to calculate the total energy at different unit-cell volume. The atomic positions in the ternary skutterudites \(\text{TbFe}_4\text{P}_{12}\) and \(\text{DyFe}_4\text{P}_{12}\) are listed in Table 4. Fig. 3 indicates the computed total energy of \(\text{TbFe}_4\text{P}_{12}\) and \(\text{DyFe}_4\text{P}_{12}\) as a function of unit cell volume has been calculated for the local spin density approximation LSDA and local density approximation LDA. The results show that the total energy in the LSDA is lower than that of the LDA for both compounds. The curve of the total energy versus unit cell volume is fitted to Murnaghan’s equation of state (EOS) to define the ground state properties like the equilibrium lattice constant \(a_0\), the bulk modulus \(B_0\) and its pressure derivative \(B'_0\) [45]. The calculated lattice constant \(a\), bulk modulus \(B_0\) and its pressure derivative \(B'_0\) of \(\text{TbFe}_4\text{P}_{12}\) and \(\text{DyFe}_4\text{P}_{12}\) alloys at 0 GPa and 0 K are listed in Table 5. It is seen that, the lattice constant values are similar for two compounds, which can be easily explained by considering the atomic radii and it indicates the lattice constant of \(\text{TbFe}_4\text{P}_{12}\)
Equilibrium lattice and the 0.97% available LSDA constants for Fermi and approximation. Spin-down dominated compound. Energy Fermi within the equilibrium $E_0$(in Ryd) (experimental data for comparison).

<table>
<thead>
<tr>
<th></th>
<th>$a_0$</th>
<th>$y$</th>
<th>$z$</th>
<th>$B$</th>
<th>$B'$</th>
<th>$E_0$</th>
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<tr>
<td>$\text{TbFe}<em>4\text{P}</em>{12}$</td>
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<tr>
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* Ref. [19].

And $\text{DyFe}_4\text{P}_{12}$ are underestimated compared to the experimental data. This underestimation is generally attributed to LSDA and LDA. The obtained lattice constants for both compounds are in good agreement with experimental data. Our calculated lattice constants for $\text{TbFe}_4\text{P}_{12}$ and $\text{DyFe}_4\text{P}_{12}$ compounds using LDA and LSDA are 1.98% and 1.92% for LDA and 0.80% and 0.97% for LSDA, respectively smaller than corresponding experimental values. Up to date, no experimental or theoretical available data for the bulk modulus and its pressure derivatives are available in the literature. Finally, the equilibrium lattice constants and bulk modulus of $\text{TbFe}_4\text{P}_{12}$ almost agree with those of $\text{DyFe}_4\text{P}_{12}$.

3.2. Electronic properties

Fig. 4 shows the energy band structures for $\text{XFe}_4\text{P}_{12}$ ($\text{X}=$ Tb, Dy) alloys at the equilibrium lattice constant within LSDA approximation. This is drawn along the symmetry in the first Brillouin zone. These spectra are calculated for spin-up and spin-down within the LSDA; as can be seen, the conduction-band and valence-band states overlap and they have no forbidden energy gap at the Fermi level in both spin up and spin down. Therefore, these compounds have a metallic behavior within LSDA. In the first structure (a) of $\text{TbFe}_4\text{P}_{12}$, the valence band is essentially dominated by the Tb-4f, Fe-3d and Tb-5d below the Fermi energy with minor contributions from the others states of the elements forming the compound. The region including the Fermi energy arises predominately from the Fe-3d and Tb-5d. The part just beyond Fermi level energy is basically dominated by Tb-5d, 4f states. In this structure (b) of $\text{DyFe}_4\text{P}_{12}$, the valence band is essentially dominated by the Fe-3d, P-3P and Tb-5d below the Fermi energy with minor contributions from the others states of the elements forming the compound. The region including the Fermi energy arises predominately from the Fe-3d and Tb-5d, 4f. The part just beyond Fermi level energy is basically dominated by Tb-4f, 5d states. To stand further information electronic states, which form the band structures, we have too computed the total and the partial densities of states (DOS) of these compounds. These are exhibited in Fig. 5 for $\text{XFe}_4\text{P}_{12}$ ($\text{X}=$ Tb, Dy) compounds. In The first structure (a) of $\text{TbFe}_4\text{P}_{12}$ the valence bands have a character of hybridized Tb-4f, Fe-3d and Tb-5d states. To below Fermi level energy the valence band is primarily due to the P-3p states with a few contributions of Tb-6s. The region around the Fermi level is essentially dominated by Fe-3 and Tb-4f states with an admixture of P-3p, 2s states. The part just beyond Fermi level energy is basically dominated by Fe-3d and
Fig. 4. The band structure of $XFe_4P_{12}$ ($X = \text{Tb}, \text{Dy}$) at the equilibrium structure using LSDA approximation.

Tb-5d, 4f states, with small contributions from P-3d, 3p states. While, in the second structure (b) of DyFe$_4$P$_{12}$, the valence bands have a character of hybridized Fe-3d states. Below Fermi level, the valence band is primarily due to the P-3p and Dy-6s, 5p states with a few contributions of Dy-4f. The region around the Fermi level is essentially dominated by Fe-3d, Tb-5d states with an admixture of, Tb-4f, Dy-5p-5d states and P-3p states. The part beyond Fermi level is basically dominated by Fe-3d, Dy-6s and P-3p states, with small contributions from, Fe-4s and P-3d states. However, the total and partial densities of states (DOS) of TbFe$_4$P$_{12}$ are different to those of DyFe$_4$P$_{12}$. The spin interaction has significant influence on the band structures because the split of f-d band show the ferromagnetic nature of this type of compounds.

3.3. Thermodynamic properties

The thermal ensues in this work was done inside the quasi-harmonic Debye model used in Gibbs program [46,47], which permits to value the Debye temperature. To find the Gibbs free energy $G^*(V, P, T)$ [48]:

$$G^*(V, P, T) = E(V) + PV + A_{\text{vib}} [\theta(V); T]$$

(15)
For a solid depicted by an energy-volume (E-V) relationship in the static approximation, was expressed out and fitted with a numerical EOS in prescribe to find its structural parameters at \( P = 0 \) and \( T = 0 \), and then derive the macroscopic properties as function of \( P \) and \( T \) from standard thermodynamic relations [49], where \( E (V) \) is the total energy for \( XFe_4P_{12} \) \((X = \text{Tb}, \text{Dy})\), \( PV \) is the hydrostatic pressure condition, \( \theta (V) \) is the Debye temperature, and \( A_{\text{vib}} \) is the Helmholtz free energy which can be written as [50, 51]:

\[
A_{\text{vib}} (\theta_D, \Theta) = n k_B T \left[ \frac{9 \theta_D}{8 T} + 3 \ln \left( 1 - e^{-\theta_D / T} \right) - D \left( \frac{\theta_D}{T} \right) \right] 
\]

(16)

where \( n \) is the number of atoms per formula unit, \( D (\theta / T) \) is the Debye integral. The Debye temperature \( \theta \) is meant as [51]:

\[
\theta_D = \frac{h}{k_B \left( \frac{6 \pi^2 n V^{1/2}}{M} \right)^{1/3} f(\sigma) \sqrt{\frac{B_S}{3 \pi}}}
\]

(17)

where \( M \) is the molecular mass per unit cell and \( B_S \) is the adiabatic bulk modulus, which is approximately given by static compressibility [46]:

\[
B_S \equiv B(V) = V \frac{\partial E(V)}{\partial V} 
\]

(18)

\( f(\sigma) \) is given by Eq. (19) [52, 51]:

\[
f(\sigma) = \left\{ 3 \left[ 2 \left( \frac{21 + \sigma}{31 - 2\sigma} \right)^{3/2} + \left( \frac{11 + \sigma}{31 - \sigma} \right)^{3/2} \right]^{-1} \right\}^{1/3}
\]

(19)

where \( \sigma \) is Poisson ratio. Therefore, the non-equilibrium Gibbs function \( G^*(V, P, T) \) as a function of \((V, P, T)\) can be minimized with respect to volume \( V \) as:

\[
\left. \frac{\partial G(V, P, T)}{\partial V} \right|_{P,T} = 0
\]

(20)
The thermal equation-of-state (EOS) $V(P, T)$ can be obtained by solving Eq. (20). The isothermal bulk modulus $B_T$ is given by Ref. [46]:

$$B_T(P, T) = V \left( \frac{\delta^2 G^*(V, P, T)}{\delta^2 V} \right)_{P, T}$$  \hspace{1cm} (21)

The thermodynamic quantities, like heat capacities $C_V$ at stable volume, $C_P$ [53] at stable pressure, entropy $S$, and internal energies have been calculated by applying the following relations [46]:

$$C_V = 3nK_B \left[ 4D \left( \frac{\theta_D}{T} \right) - \frac{\left( \frac{3\theta_D}{T} \right)}{e^{\theta_D/T} - 1} \right]$$  \hspace{1cm} (22)

$$C_P = C_V (1 + \alpha/T)$$  \hspace{1cm} (23)

$$S = nK \left[ 4D(\theta/T) - 3\ln(1 - e^{-\theta/T}) \right]$$  \hspace{1cm} (24)

$$U = nK T \left[ \frac{9}{8} \frac{\theta}{T} + 3D \left( \frac{\theta}{T} \right) \right]$$  \hspace{1cm} (25)

where $\alpha$ is the thermal expansion coefficient and $\gamma$ is the Grüneissen parameters which are given by following equations [46]:

$$\alpha = \frac{\gamma C_V}{B_T T}$$  \hspace{1cm} (26)

$$\gamma = - \left( \frac{d\ln(\theta)}{dV} \right) / dV$$  \hspace{1cm} (27)

In this work, the prediction of thermal properties at pressure 0–50 GPa and temperature between 0 and 3000 K are obtained for $XFe_4P_{12}$ ($X$ = Tb, Dy) alloys using LDA approximation. The fluctuation of the volume is shown in Fig. 6. It is indicated that the volume increases nearly almost linearly with increasing temperature, but the rate is more important for temperature above 100 K. For a given temperature, the primitive cell volume decreases with increasing pressure. These results are due to the fact that the effect of increasing pressure of the material is the same as the decreasing temperature of the material. The calculated equilibrium primitive cell volume $V$ at zero pressure and room temperature are 800.5812 Å and 765.1687 Å for $TbFe_4P_{12}$ and $DyFe_4P_{12}$, respectively. Fig. 7 shows the bulk modulus variation against temperature at a donated pressure. It is seen that the bulk modulus is almost constant from 0 to 100 K and decrements additively with raising temperature from $T > 100 K$.

The compressibility increments with raising temperature at a donated pressure and decrements with pressure at a donated temperature. These effects are owing to raising pressure on the material is the same as the diminishing temperature of the material. The fluctuation of the heat capacities $C_V$ against temperature at pressure 0–50 GPa is depicted in Fig. 8. We clearly see that when $T < 1000 K$, the heat capacity $C_V$ is a function of the temperature and pressure. If the temperature is constant, the heat capacity $C_V$ decrements with pressure. We also note that for high temperature, the heat capacity $C_V$ does not depend on the temperature and tends to the limit of Dulong-Petit [52], that bears the value of 422.49 (J mol$^{-1}$ K$^{-1}$). The fluctuation of the heat capacity $C_P$ at pressure 0–50 GPa and temperature between 0 and 3000 K for $XFe_4P_{12}$ ($X$ = Tb, Dy) alloys is depicted in Fig. 9. At a given temperature, we can see the variation of the heat capacity $C_P$ is alike to those of $C_V$ exactly at low temperatures but at high temperature, $C_P$ behaves other wise of $C_V$, it does not tend to a constant value. The result of pressure on the heat capacity at constant pressure $C_P$ is alike to that of $C_V$. Fig. 10 indicates the variations of the volume expansion coefficient $\alpha$ as a function of temperature. At a given pressure, we can see that $\alpha$ varies for low temperatures and gradually tends to increase linearly with increasing temperature, with a growth rate that is low, which leads to say that the dependence of $\alpha$ with temperature is lower for higher temperatures. At zero pressure, the variation of the thermal expansion coefficient $\alpha$ with temperature is lower for higher temperatures. At zero pressure, the variation of the thermal expansion coefficient $\alpha$ with temperature is lower for higher temperatures.
Fig. 7. The variation of the bulk modulus $B$ as a function of temperature for $XFe_4P_{12}$ ($X = Tb, Dy$) at different pressures.

Fig. 8. The variation of the heat capacity $C_v$ as a function of temperature for $XFe_4P_{12}$ ($X = Tb, Dy$) at different pressures.

Fig. 9. The variation of the heat capacity $C_p$ as a function of temperature for $XFe_4P_{12}$ ($X = Tb, Dy$) at different pressures.

Fig. 10. The Variation of the thermal expansion coefficient as a function of temperature for $XFe_4P_{12}$ ($X = Tb, Dy$) at different pressures.
The equilibrium lattice constants and bulk modulus of TbFe₄P₁₂ almost agree with those of DyFe₄P₁₂. The computed spin-polarized band structure for XFe₄P₁₂ (X = Tb, Dy) alloys exhibit metallic character. The total and the partial densities of states (DOS) of TbFe₄P₁₂ are different to those of DyFe₄P₁₂. The elastic constant C₁₁, C₁₂, C₄₄ (in GPa), bulk modulus B (in GPa), Young’s and shear modulus E, G (in GPa), Poisson’s ratio ν, the anisotropic parameter A and B/G values are similar for two alloys. The calculated Poisson ratio ν of XFe₄P₁₂ (X = Tb, Dy) at various pressures are around 0.1. This indicates that this alloys is highly covalent.

By analyzing the B/G ratio, we conclude that XFe₄P₁₂ (X = Tb, Dy) compound exhibits anisotropic elasticity.

The sound velocities (v₁, v₂, and v₃) and the Debye temperature of TbFe₄P₁₂ are larger than that of DyFe₄P₁₂. The fluctuations of the primitive cell volume, expansion coefficient α, bulk modulus B, heat capacity (cₚ and cᵥ) Debye temperature θ_D, and entropy S, values are similar for both alloys. There are no experimental and other theoretical data for comparison, so we consider the present results as a prediction study for the first time, which still awaits an experimental confirmation.

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References


