Electronic structures and thermodynamic properties of HfAl$_3$ in L1$_2$, D0$_{22}$ and D0$_{23}$ structures

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Abstract: To better understand the relative stability and bonding characteristics of the L1$_2$, D0$_{22}$ and D0$_{23}$ structures for HfAl$_3$, the formation enthalpies, electronic structures and thermodynamics properties were investigated by first-principles calculations. The agreement of calculated equilibrium lattice parameters and formation enthalpies with experimental results indicates the reliability of this work. The order of structural stability is D0$_{23}$>D0$_{22}$>L1$_2$. The results of densities of states, atomic Mulliken charge and bond population support the best structural stability for D0$_{23}$ structure. Variations of thermodynamic properties with temperature were predicted via phonon frequencies calculation. The enthalpy, entropy, free energy of D0$_{23}$ structure change more quickly than those of the other two structures. The Debye temperatures of L1$_2$, D0$_{22}$ and D0$_{23}$ structures are 399, 407 and 416 K, respectively. The volume thermal expansions for HfAl$_3$ increase exponentially at the low temperature, whereas the thermal expansion coefficients increase linearly at the high temperature.

Key words: first principles calculations; HfAl$_3$; electronic structure; thermodynamics properties

1 Introduction

The early-transition-metal trialuminides TMAl$_3$ (TM=Sc, Ti, Zr, Hf, etc) have been attracted great interest due to their low densities, high melting points and low oxidation resistances. These trialuminides are being investigated to be used as single phase high-temperature structural materials and as precipitation strengtheners in two-phase aluminum alloys [1]. In these trialuminides, TiAl$_3$, VAl$_3$, NbAl$_3$ and TaAl$_3$ crystallize in the tetragonal D0$_{22}$ structure, while ZrAl$_3$ embodies in the tetragonal D0$_{23}$ structure [2,3]. ScAl$_3$ and YAl$_3$ are found to be the cubic L1$_2$ structure at high temperature [2,3]. As an important adding element to increase the recrystallization resistance and structural stability of aluminum alloys, Hf makes the extruded aluminum alloys meet the demand of tolerant of high temperature by forming HfAl$_3$ dispersoids [4]. HfAl$_3$ crystallizes in the D0$_{23}$ structure at low temperature, the D0$_{22}$ structure at high temperature [5] and the metastable L1$_2$ structure [1].

Due to the lack of sufficient number of slip systems for the D0$_{23}$ structure, the L1$_2$ structure has been proved experimentally that it is more ductile than the D0$_{22}$ structure [6]. Accordingly, the L1$_2$-trialuminate alloys are more likely to be suitable in structural applications [7]. By rapid solidification of supersaturated Al-rich solid solutions [8–11], chill casting and gas atomization [12,13], and mechanical alloying [1,14], the metastable L1$_2$-HfAl$_3$ had been prepared. However, the L1$_2$-HfAl$_3$ may transform to D0$_{22}$ or D0$_{23}$ structures during the heating process: a transformation of L1$_2$ to D0$_{23}$ at 750 °C had been observed [1].

Few theoretical and experimental works have been reported on HfAl$_3$ compounds. Only their structural properties, phase stability and bulk moduli have been considered. The D0$_{22}$ unit cell consists of two L1$_2$ cubes stacked along z direction with a [1/2 1/2 0] antiphase shift between the cubes, while the D0$_{23}$ structure consists of a stacking of four L1$_2$ cubes with the same antiphase shift every two cubes [15]. The order of relative
stabilities of L12, D022, and D023 structures in the HfAl3 compounds from their formation enthalpies is D023 > D022 > L12 [15]. The reported isothermal bulk modules of these HfAl3 compounds indicate that the value for each structure is very close to each other [15,16]. To our best knowledge, theoretical investigations on electronic structures and thermodynamic properties of HfAl3 are still scarce. The reason of difference in stability for these HfAl3 is still not clear. Additionally, in ordered intermetallics, physical and mechanical properties depend strongly on the nature of the bonding between atomic species.

In this work, to better understand the relative stability, bonding characters and thermodynamic properties of the L12, D022 and D023 structures HfAl3, we performed calculations of the formation enthalpy, electronic structures and phonon dispersions of HfAl3 in three different crystal structures using the density-functional theory (DFT) as implemented in the first-principles calculations with the generalized gradient approximation (GGA). Such structural stability and electronic structure studies can provide guidance in other TM trialuminides as well.

2 Methods and computational details

2.1 First-principles method

In the present work, the first principles calculations based on density functional theory (DFT) implemented in Cambridge sequential total energy package (CASTEP) code [17] were carried out to investigate the formation enthalpies and electronic structures. Ultra soft pseudo-potential (USPP) was employed to indicate the interactions between ionic core and valence electrons. The generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) parameterization [18] was used to describe the exchange correlation energy. Valence electrons included in this work for distinct atoms were Al 3s23p1 and Hf 5s25p65d66s2. After convergence tests, the k-points were 20×20×20, 20×20×12 and 20×20×6 for L12-HfAl3, D022-HfAl3 and D023-HfAl3, respectively, and the cutoff energy for plane wave expansions was set as 500 eV.

The phonon calculations were performed by using the linear response method applied Norm-conserving pseudo-potential. The k-point meshes of 12×12×12, 12×12×8 and 12×12×4 were applied along with the cutoff energy of 500 eV for L12, D022 and D023 structures, respectively. The thermodynamic properties of HfAl3 were obtained via the resultant phonon dispersion.

2.2 Thermodynamics properties

Based on the phonon calculations, the enthalpy (H), free energy (F), heat capacity (Cv) and entropy (S) as functions of temperature at the finite temperature can be computed. The vibrational contributions to the thermodynamic parameters were evaluated by the Debye’s quasi-harmonic approximation (QHA) [19,20]:

\[
H(T) = E_{tot} + E_p + \int \frac{h\omega}{\exp[h\omega/(kT)] - 1} F(\omega)d(\omega) \tag{1}
\]

\[
F(T) = E_{tot} + E_p + kT \int \ln[1 - \exp[-h\omega/(kT)]]F(\omega)d(\omega) \tag{2}
\]

\[
C_v(T) = k \int \frac{[h\omega/(kT)]^2 \exp[h\omega/(kT)]}{\exp[h\omega/(kT)] - 1} F(\omega)d(\omega) - k \int [1 - \exp[-h\omega/(kT)]]F(\omega)d(\omega) \tag{3}
\]

\[
S(T) = k \int \frac{h\omega/(kT)}{\exp[h\omega/(kT)] - 1} F(\omega)d(\omega) - k \int [1 - \exp[-h\omega/(kT)]]F(\omega)d(\omega) \tag{4}
\]

where \(E_{tot}\) is the total energy of the system, \(E_p\) is the zero point vibrational energy, \(\omega\) is the phonon vibration frequency, \(F(\omega)\) is phonon density of state, \(k\) and \(h\) are Boltzmann’s constant and Planck’s constant, respectively.

The Debye temperatures \(\Theta_D\) can be estimated from the heat capacity \(C_v\) by the following equations [21]:

\[
C_v(T) = 9nk \left(\frac{T}{\Theta_D}\right)^3 \int_0^{\Theta_D/T} x^4 \exp(x) \frac{dx}{(\exp(x) - 1)^2} \tag{5}
\]

\[
x = \frac{h\omega}{kT} \tag{6}
\]

where \(n\) is the number of atoms in the molecule.

From the obtained phonon dispersion, the thermal expansion coefficients for HfAl3 are calculated by the Debye–Grüneisen model [22]:

\[
\beta = \frac{\gamma C_v}{BV} \tag{7}
\]

\[
\gamma = -\frac{d(ln \Theta(V))}{d(ln V)} \tag{8}
\]

where \(\beta\) is the volume thermal expansion coefficient; \(\gamma\), \(C_v\), \(B\) and \(V\) are Grüneisen parameter, heat capacity, bulk modulus and volume, respectively; \(\Theta(V)\) is the Debye temperature. The bulk modules of these HfAl3 compounds used in the Eq. (7) are quoted from the reported values [16].

3 Results and discussion

3.1 Structural stability

The initial crystal structures of HfAl3 in L12, D022 and D023 structures are illustrated in Fig. 1. The calculated structural parameters, together with the
experimental values [23–25], are listed in Table 1. It is found from Table 1 that the calculated lattice parameters agree very well with the available experimental data, whose average deviation is less than 1%. This provides a confirmation that the present utilized computational methodology is suitable and reliable.

To investigate the structural stability, the formation enthalpy ($\Delta H$) was calculated by the following expression:

$$\Delta H = \frac{1}{4} [E_{\text{total}} - (E_{\text{Hf}}^{\text{bulk}} + 3E_{\text{Al}}^{\text{bulk}})]$$  (9)

where $E_{\text{total}}$ is the total energy of HfAl$_3$, $E_{\text{Hf}}^{\text{bulk}}$ and $E_{\text{Al}}^{\text{bulk}}$ are the total energy of a Hf atom and an Al atom in the bulk state. A more negative formation enthalpy corresponds to a better structural stability. The calculated formation enthalpies of the HfAl$_3$ compounds, together with the available experimental and other theoretical data [16,26], are also listed in Table 1. From Table 1, the formation enthalpies in our work are in good agreement with the ab initio approach and experiment, and the difference in formation enthalpy between our results and reported values is less than 1 kJ/mol. The order of formation enthalpy is D0$_{23}$<D0$_{22}$<L1$_2$. This suggests that the order of structural stabilities of L1$_2$, D0$_{22}$, and D0$_{23}$ structure is D0$_{23}$>D0$_{22}$>L1$_2$, which is in good agreement with the report in Ref. [15]. Actually, D0$_{23}$-HfAl$_3$ is a stable phase at the temperature below 650 °C, while D0$_{22}$-HfAl$_3$ is a stable phase at the temperature higher than 650 °C [27]. When metastable L1$_2$-HfAl$_3$, which is detected in Al–Hf bilayers, is heated, it transforms either in D0$_{22}$ or D0$_{23}$ structures depending on the temperature [23]. It must be noted that, in the experiment, the transformation of L1$_2$ to D0$_{23}$ at 750 °C was observed, but the transformation of D0$_{23}$ to D0$_{22}$ by heating at higher temperatures was not found [1].

### 3.2 Electronic structures

The densities of states, including total and partial densities of states (TDOS and PDOS), in terms of the chemical bonding in HfAl$_3$ compounds were investigated to understand the structural stability. The results of densities of states are plotted in Fig. 2. One can see that the total densities of states for all structures have a similar shape characterized by the presence of pseudogap near the Fermi level ($E_F$) for HfAl$_3$ compounds. The right part of the TDOS corresponds to nonbonding states, while the left part refers to bonding states. In the L1$_2$ structure, $E_F$ lies on the right of the minimum of TDOS, whereas in D0$_{22}$ structure the $E_F$ locates on the left of the maximum of the TDOS. The $E_F$ of D0$_{23}$ structure exactly situates at the pseudogap. The TDOS values at the $E_F$ for L1$_2$, D0$_{22}$, and D0$_{23}$ structures are 1.74, 1.33 and 1.13 electron/eV per unit cell, respectively. It is interesting to compare the TDOS and formation enthalpies of L1$_2$, D0$_{22}$ and D0$_{23}$ structures that the most negative formation enthalpy corresponds to the lowest TDOS value at the $E_F$. This suggests that D0$_{23}$ structure with the low TDOS value can more easily reaches the maximum band-filling state than D0$_{22}$ and L1$_2$ structures, resulting in the most stable compound for D0$_{23}$-HfAl$_3$.

It can be seen in the PDOS that the left part of the TDOS ranging from –6 to 0 eV for HfAl$_3$ compounds are contributed by a strong hybridization between Hf 5d states and Al 3p states. As a result, the strong Hf–Al atomic bonds form. The Hf d-DOSs at the $E_F$ for L1$_2$, D0$_{22}$ and D0$_{23}$ structures are 0.73, 0.73 and 0.56 electron/eV formula unit, respectively. The Al p-DOSs at the $E_F$ for L1$_2$, D0$_{22}$ and D0$_{23}$ structures are 0.63, 0.48 and 0.41 electron/eV per unit cell, respectively. The decreasing DOS will result in an increase in the degree

### Table 1 Calculated and experimental lattice parameters and formation enthalpies for HfAl$_3$ compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Present</th>
<th>Experiment</th>
<th>α/Å</th>
<th>β/Å</th>
<th>γ/Å</th>
<th>Present</th>
<th>ab initio [16]</th>
<th>Experiment [26]</th>
<th>ΔH/(kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L1$_2$-HfAl$_3$</td>
<td>4.096</td>
<td>4.080 [23]</td>
<td></td>
<td></td>
<td></td>
<td>−36.454</td>
<td>−36.828</td>
<td></td>
<td></td>
</tr>
<tr>
<td>D0$_{22}$-HfAl$_3$</td>
<td>3.946</td>
<td>3.928 [24]</td>
<td>8.924</td>
<td></td>
<td>8.888</td>
<td>−38.991</td>
<td>−38.649</td>
<td></td>
<td></td>
</tr>
<tr>
<td>D0$_{23}$-HfAl$_3$</td>
<td>4.002</td>
<td>3.989 [25]</td>
<td>17.226</td>
<td></td>
<td>17.155</td>
<td>−39.224</td>
<td>−39.632</td>
<td>−40.6±0.8</td>
<td></td>
</tr>
</tbody>
</table>
of hybridization as it has already seen in TiM (M=Fe, Co, Ni) compounds [28]. Thus, the degree of hybridization of the d–p states between Hf and Al atoms increases. In other words, the strength of the d–p bond increases from L1₂, D₀₂₂ to D₀₂₃ structures. Therefore, the stability of the compounds decreases in the order of L₁₂< D₀₂₂< D₀₂₃ because of the degeneracy of the d–p states at the E₉.

Table 2 lists the atomic Mulliken charge and bond population results of L₁₂, D₀₂₂ and D₀₂₃ HfAl₃ compounds. It is clear that Hf atoms loss electrons and Al atoms get electrons. The number of electrons transferred from Hf to Al in D₀₂₃ structure is 0.68 (0.17×4), which is larger than those in L₁₂ (0.21×1=0.21) and D₀₂₂ (0.12×2=0.24) structures. This indicates that the Hf—Al bonds in D₀₂₃ structure are stronger than those in L₁₂ and D₀₂₂ structures. From Table 2, the calculated bond populations are positive, suggesting that the Hf—Al bonds are characterized as covalent. The greater Hf—Al bond population and shorter Hf—Al bond length in D₀₂₃ structure mean that covalent features are stronger in D₀₂₃ structure than those in L₁₂ and D₀₂₂ structures.

The metallicity of the HfAl₃ compound can be calculated by Ref. [29].

\[ f_{m} = 0.026 D_{f}/n_{e} \quad (10) \]

where \( D_{f} \) is the DOS value at \( E_{F} \), \( n_{e} \) is the valence electronic density of the cell and can be obtained from \( n_{e} = N/V_{cell} \) (\( N \) is the total number of valence electrons and \( V_{cell} \) is the cell volume). The calculated values of \( f_{m} \) for L₁₂, D₀₂₂ and D₀₂₃ structures are 0.2393, 0.1645 and 0.0911, respectively. This means that the metallic feature of bonding is in a decreasing order from L₁₂ to D₀₂₃ structures.

To further reveal the covalent feature, the charge density difference, which can directly reflect the bonding characteristics [30], was investigated in this work. The results are plotted in Fig. 3. The contours are plotted from \(-0.04 \text{ e/Å}^{3}\) to \(0.04 \text{ e/Å}^{3}\) with \(0.02 \text{ e/Å}^{3}\) interval. From Fig. 3, the extremely localized nature of electronic charge between Hf and Al atoms in these HfAl₃ shows their strong covalent characters. Due to the individualized nature of charge among Al atoms, as a result, the bonding between Al and Al is metallic. Obviously in Fig. 3, the charge density of Al site is more negative than that of Hf site, indicating that there is electron transfer from Hf atom to Al atom. The number of electrons transferred has been discussed in the Mulliken population analysis. The bonding charges in L₁₂ mainly locate at the tetrahedral interstices along the \([111]\) direction, whereas in D₀₂₃ it locates along the \([112]\) direction. This is because of the Hf-d hybridization around its local field leading by the nearest-neighbor
Table 2 Atomic Mulliken charge and bond population analysis of HfAl$_3$ compounds

<table>
<thead>
<tr>
<th>Structure</th>
<th>Atom</th>
<th>Charge number</th>
<th>Electron number</th>
<th>Bond</th>
<th>Population</th>
<th>Length/Å</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>s</td>
<td>p</td>
<td>d</td>
<td>Total</td>
<td>Al$_{1c}$—Hf (3)</td>
</tr>
<tr>
<td>L1$_2$</td>
<td>Hf1:1a</td>
<td>0.31</td>
<td>0.15</td>
<td>3.33</td>
<td>3.79</td>
<td>0.21</td>
</tr>
<tr>
<td></td>
<td>Al3:3c</td>
<td>1.08</td>
<td>1.99</td>
<td>0</td>
<td>3.07</td>
<td>-0.07</td>
</tr>
<tr>
<td>D0$_{22}$</td>
<td>Hf1:2a</td>
<td>0.33</td>
<td>0.28</td>
<td>3.27</td>
<td>3.88</td>
<td>0.12</td>
</tr>
<tr>
<td></td>
<td>Al1:2b</td>
<td>1.12</td>
<td>1.77</td>
<td>0</td>
<td>2.89</td>
<td>0.11</td>
</tr>
<tr>
<td></td>
<td>Al2:4d</td>
<td>1.08</td>
<td>2.04</td>
<td>0</td>
<td>3.12</td>
<td>-0.12</td>
</tr>
<tr>
<td>D0$_{23}$</td>
<td>Hf1:4e</td>
<td>0.29</td>
<td>0.22</td>
<td>3.32</td>
<td>3.83</td>
<td>0.17</td>
</tr>
<tr>
<td></td>
<td>Al1:4c</td>
<td>1.07</td>
<td>2.04</td>
<td>0</td>
<td>3.11</td>
<td>-0.11</td>
</tr>
<tr>
<td></td>
<td>Al2:4d</td>
<td>1.08</td>
<td>2.01</td>
<td>0</td>
<td>3.09</td>
<td>-0.09</td>
</tr>
<tr>
<td></td>
<td>Al3:4e</td>
<td>1.10</td>
<td>1.87</td>
<td>0</td>
<td>2.97</td>
<td>0.03</td>
</tr>
</tbody>
</table>

Fig. 3 Contour plots for electronic charge densities of (110) plane containing Hf and Al atoms (The Hf and Al sites in the charge density maps correspond to those in the crystal structures)

atoms of Hf site. For D0$_{22}$ structure, the bonding charges primarily locate along the [111] direction caused by the Al-p and Hf-d hybridization. The clear directionality of the bonding also suggests its covalent character in these HfAl$_3$ compounds.

3.3 Phonon and thermodynamic properties

The phonon dispersion curve, which is related to the lattice dynamical properties of solids, determines the specific heat capacity, heat transportation and sound velocity. Figure 4 plots the calculated phonon dispersions and phonon densities of states (PHDOS) for HfAl$_3$ compounds. Obviously, no soft modes can be observed at any high-symmetry direction in the phonon dispersion curves. This confirms the stability of the L1$_2$, D0$_{22}$ and D0$_{23}$ structures. The phonon dispersions of L1$_2$, D0$_{22}$ and D0$_{23}$ structures are significantly different because of their different symmetry. The unit cells of L1$_2$, D0$_{22}$ and D0$_{23}$ structures have 4, 8 and 16 atoms, respectively. This suggests that the total numbers of phonon branches are 12, 24 and 48 for L1$_2$, D0$_{22}$ and D0$_{23}$ structures, respectively. The shapes of the phonon dispersion curves and PHDOS are determined by the atomic mass of Hf and Al. It is obvious that the shapes of phonon dispersion and PHDOS of L1$_2$ structure exhibit large difference from those of D0$_{22}$ and D0$_{23}$ structures. This shows that the large atomic mass difference between Hf and Al results in the obvious divergences in the phonon dispersion and PHDOS of L1$_2$ structure. The acoustic branches in the low frequency region are contributed from the Hf atom, while the optical branches come from the Al atom. The frequencies increase from L1$_2$, D0$_{22}$ to D0$_{23}$ structures due to the difference in lattice constants and bond lengths. It has been shown in Table 2 that D0$_{23}$ structure has the shorter Hf–Al bond length than D0$_{22}$ and L1$_2$ structures. It is known that a shorter bond length is related to a larger force constant and a higher vibrational frequency [31,32]. As a result, the phonon dispersions shift to the high frequency from L1$_2$, D0$_{22}$ to D0$_{23}$ structures in Fig. 4. The long-range Coulomb interactions result in the frequencies of longitudinal optical modes (LO) above those of transversal optical (TO) modes [33,34]. Due to insignificant LO/TO splitting in the high frequency, the influences of LO/TO splitting on the predicted thermodynamic properties are not considered in the present work.

Figure 5 plots the predicted thermodynamic properties of the L1$_2$, D0$_{22}$ and D0$_{23}$ HfAl$_3$ compounds. Their different thermodynamic properties curves with temperature confirm the fact of their different phonon dispersions. When the temperature increases, the enthalpy $H$ and entropy $S$ increase. The enthalpies of these HfAl$_3$ compounds increase almost linearly with temperature and tend to display $k_B T$ behavior, and this phenomenon can be observed in other Al-TM compounds [35]. The entropies of these compounds also increase rapidly with the increasing temperature when temperature is below 300 K, and the speed of increase...
Fig. 4 Phonon dispersions and phonon density of states of HfAl$_3$ in L1$_2$ (a), D0$_{22}$ (b) and D0$_{23}$ (c) structures.

Fig. 5 Thermodynamic properties: enthalpy $H$ (a), entropy $S$ (b), free energy $F$ (c) and specific heat capacity $C_V$ (d) for HfAl$_3$ in L1$_2$, D0$_{22}$ and D0$_{23}$ structures.

- The phonon dispersion and density of states of HfAl$_3$ in L1$_2$, D0$_{22}$ and D0$_{23}$ structures are shown in Fig. 4.
- The phonon density of states slows down when temperature is above 300 K. Moreover, the $H$, $S$ and $F$ of D0$_{23}$ structure change more quickly than those of the other two structures. It can be explained by the difference of phonon frequency. The free energy of D0$_{23}$ structure is always lower than those of L1$_2$ and D0$_{22}$ structures with the increase of temperature. In other words, in the range of temperature the order of free energy is D0$_{23}$<D0$_{22}$<L1$_2$, suggesting that the D0$_{23}$ structure is always more stable than D0$_{22}$.

- The thermodynamic properties, including enthalpy $H$, entropy $S$, free energy $F$ and specific heat capacity $C_V$, are shown in Fig. 5 for HfAl$_3$ in L1$_2$, D0$_{22}$ and D0$_{23}$ structures.
and L12, and L12 structure is the most unstable phase. For the specific heat capacity \( C_v \), it increases proportionally to \( T^3 \) at low temperature, and then gently at high temperature. When the temperature is higher than the Debye temperature, the specific heat capacity approaches to the Dulong–Petit limit: the specific heat capacities for the L12, D022 and D023 structures reach 100, 200 and 400 \( J/(\text{mol} \cdot \text{K}) \) due to 4, 8, 16 atoms in their unit cells, respectively. The specific heat capacity \( C_v \) in Fig. 5 shows that the \( C_v \) of D023 structure increases more quickly than that of the other structures. It is similar to the variations of enthalpy \( H \) and entropy \( S \). The reason is that the number of Hf atoms in D023 structure is four and the contribution from Hf atoms to the low phonon frequency is different from L12 and D022 structures. This leads to the diversity of phonon frequency in the Brillouin zone for the D023 structure.

The Debye temperatures of L12, D022 and D023 structures obtained from \( C_v \) are 399, 407 and 416 K, respectively. The theoretical Debye temperatures of HfAl1 in the L12, D022 and D023 structures by ab initio calculations are 331, 335 and 334 K, respectively [15] which are obtained from the expression as \( \Theta_D = K r_{WS} B/M^{1/2} \), where \( M \) is the atomic mass of the compound, \( r_{WS} \) is the Wigner-Seitz radius, \( B \) is the bulk modulus and \( K \) is a constant. In the ab initio calculations, the same \( K \) as obtained for pure aluminum is used in the HfAl1 compounds, which results in lower Debye temperatures than our results. However, our Debye temperatures are close to each other, which is similar to the reported literature [15]. Such similar values of Debye temperatures lead to negligible differences in formation enthalpies at \( T=0 \) K. The Debye temperature is the temperature of a crystal’s highest normal mode of vibration [36]. The similar values of Debye temperatures also suggest that the differences in the free energies even at high temperature \( T<\Theta_D \) are small, which can be observed in Fig. 5.

Although the difference in Debye temperatures is small, the correlation between the calculated Debye temperatures (\( \Theta_D \)) and the formation enthalpies (\( \Delta H \)) of the HfAl1 compounds has also been investigated. Interestingly, for these HfAl1 compounds the Debye temperature is larger if the compound has a more negative formation enthalpy. Generally, a more negative formation enthalpy derives from stronger bonding. It is to be expected that a larger Debye temperature is an indicator of a stronger interatomic bonding. In the considered HfAl1 compounds, the D023 structure has the largest Debye temperature (416 K) than the other structures, and it implies that the D023 structure has the most negative formation enthalpy (−39.224 kJ/mol). The experimental data are not available for the Debye temperatures of HfAl1 compounds. However, our calculated results can provide support for future works on these HfAl1 compounds.

Figure 6 shows the volume thermal expansion coefficients of HfAl1 in L12, D022 and D023 structures. From Fig. 6 it can be seen that at much less than the Debye temperature, the thermal expansion coefficients increase exponentially. This behavior is determined by thermal energy of lattice vibrations [37]. For example, when the temperature is lower than 200 K, the thermal energy of the lattice vibrations is increased rapidly due to the phonon excitations. The anharmonic effect is greatly enhanced in this temperature range. As a result, the volume thermal expansion coefficients increase quickly with respect to temperature. When the temperature is above 300 K, as shown in Fig. 6, the volume thermal expansion coefficients increase linearly versus temperature. Additionally, it should also be noted that the calculations of the thermal expansion coefficient are performed for the perfect crystal. The anharmonic effect is importantly influenced by the various defects (vacancies and impurities) in the real crystal. The total thermal energy of the lattice vibrations for a defective crystal is higher than that of perfect crystal. Thus, the thermal expansion coefficient for a real crystal is larger than the calculated value for a perfect crystal. This means that the true volume thermal expansion coefficients of these HfAl1 compounds may be slightly larger than our calculated values. Meanwhile, in the Debye–Grüneisen model, bulk modulus \( B \) and Grüneisen parameter \( \gamma \) are theoretical ground-state values at the temperature lower than the Debye temperature. The ground-state values for \( B \) and \( \gamma \) suggest that the calculated thermal expansion coefficients are more accurate at the low temperature. In fact, the thermal expansion coefficients calculated by Debye–Grüneisen model at \( T=300 \) K are in good agreement with the experiment data [38].

![Fig. 6 Volume thermal expansion coefficients as function of temperature for HfAl1 in L12, D022 and D023 structures](Image)
4 Conclusions

1) The calculated formation enthalpy shows that the structural stability of these three structures for HfAl$_3$ is in the order of D0$_{22}$+D0$_{22}$→L1$_2$.

2) The total densities of states for all structures have a similar shape characterized by the presence of pseudogap near the Fermi level ($E_F$). The $E_F$ of D0$_{22}$ structure is exactly located at the pseudogap, suggesting that the D0$_{22}$ structure is the most stable.

3) No soft modes at any high-symmetry direction in the phonon dispersion curves are observed in the whole BZ, indicating that the current structures are thermodynamically stable.

4) The specific heat capacity $C_V$ increases proportionally to $T^3$ at low temperature and approaches to the Dulong–Petit limit at the high temperature. The similar Debye temperatures of L1$_2$, D0$_{22}$ and D0$_{23}$ structures obtained from $C_V$ are 399, 407 and 416 K, respectively.

5) The volume thermal expansions for HfAl$_3$ increase exponentially at the low temperature, whereas the thermal expansion coefficients increase linearly at the high temperature.

References


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L12、D022和D023结构HfAl3的电子结构与热力学性质

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摘要：为了更好地理解L12、D022和D023结构HfAl3的相对稳定性和键合特征，采用第一性原理计算了L12、D022和D023结构HfAl3的形成焓、电子结构和热力学性质。结果表明：平衡晶格参数与形成焓的计算结果与实验结果一致，不同结构的HfAl3稳定性大小为D023＞D022＞L12；状态密度、电荷与键布局分析结果表明D023为最稳定结构；声子计算得到的热力学性质与温度的关系表明，D023结构的熵和自由能随温度变化比L12和D022结构要快得多；L12、D022和D023结构HfAl3的德拜温度分别为399、407和416K；HfAl3的体积热膨胀系数在低温时成倍增加，而在高温时线性增加。

关键词：第一性原理；HfAl3；电子结构；热力学性质

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