Phase stability and thermoelectric properties of semiconductor-like tetragonal FeAl$_2$

Kazuki Tobita$^{a}$, Koichi Kitahara$^{a,b}$, Yukari Katsura$^c$, Naoki Sato$^c$, Daisuke Nishio-Hamane$^d$, Hirotada Gotou$^d$ and Kaoru Kimura$^{a,b}$

$^a$Department of Advanced Materials Science, The University of Tokyo, Chiba, Japan; $^b$OPERANDO-OIL, National Institute of Advanced Industrial Science and Technology (AIST), Chiba, Japan; $^c$International Center for Materials Nanoarchitectonics (MANA), National Institute for Materials Science (NIMS), Tsukuba, Ibaraki, Japan; $^d$The Institute for Solid State Physics, The University of Tokyo, Chiba, Japan

ABSTRACT

Tetragonal FeAl$_2$ is a high-pressure phase and is predicted to exhibit semiconductor-like behavior. We investigated the pressure and temperature synthesizing conditions of tetragonal FeAl$_2$, supported by in situ X-ray diffractions, using synchrotron radiation during heating the sample under a pressure of 20 GPa. Based on the determined optimal conditions, we synthesized the bulk polycrystalline samples of tetragonal FeAl$_2$ at 7.5 GPa and 873 K, using a multi-anvil press and measured its thermoelectric properties. The Seebeck coefficient of tetragonal FeAl$_2$ showed a large negative value of $-105$ $\mu$V/K at 155 K and rapidly changed to a positive value of 75 $\mu$V/K at 400 K. Although these values are the largest among those of Fe–Al alloys, the maximum power factor remained at 0.41 mW/mK$^2$ because the carrier concentration was not tuned. A comparison of the Gibbs free energy of tetragonal FeAl$_2$, triclinic FeAl$_2$ and FeAl$+\text{Fe}_2\text{Al}_3$ revealed that tetragonal FeAl$_2$ became unstable as the temperature increased, because of its smaller contribution of vibrational entropy.

1. Introduction

Thermoelectric materials are functional materials that can directly convert heat into electricity. In recent years, thermoelectric materials have received a great amount of attention because they can contribute to the global energy demand by waste-heat energy harvesting. The conversion efficiency of thermoelectric materials is characterized by the dimensionless figure of merit $ZT = S^2\sigma T/(\kappa_{el} + \kappa_{ph})$, where $S$, $\sigma$, $\kappa_{el}$, $\kappa_{ph}$ and $T$ are the Seebeck coefficient, electrical conductivity, electron thermal conductivity, phonon thermal conductivity and temperature, respectively. To date, most of the state-of-the-art materials like Bi$_2$Te$_3$ [1] and PbTe [2], which exhibit a high $ZT$ of more than unity, contain toxic and/or expensive elements. For large-scale applications of thermoelectric materials, low-cost nontoxic materials with high performance are desirable. Iron aluminides are thus favorable as thermoelectric materials because of their abundance and environmentally benign constituent elements. We previously investigated the thermoelectric properties of triclinic FeAl$_2$ (α-FeAl$_2$, space group $P\overline{1}$), Fe$_2$Al$_3$ and Fe$_4$Al$_13$ in the Al-rich part of Fe–Al binary systems, and found that these materials have a low $\kappa_{ph}$ of 0.82 W/mK (for Fe$_4$Al$_13$) because of their complex and disordered crystal structures [3]. However, the maximum $ZT$ remained at 0.03 (for Fe$_4$Al$_13$) because of its low $S$ of $\sim$30 $\mu$V/K. To improve the thermoelectric properties in this binary system, semiconductors with a large magnitude of $S$ and a metallic $\sigma$ are...
required. However, none of the experimentally observed Fe–Al intermetallic compounds behave as semiconductors.

We previously reported that novel MoSi$_2$-type tetragonal FeAl$_2$ (t-FeAl$_2$, space group I4/mmm) can be synthesized through the laser-heated diamond-anvil cell (LHDAC) technique at 10 GPa and 1873 K [4]. This t-FeAl$_2$ was theoretically predicted to be stable (or at least metastable) [5,6], but could not be synthesized at ambient pressure [7]. Theoretical studies also predicted that t-FeAl$_2$ exhibits a bandgap near the Fermi level, which was explained by the 14 electrons rule or 18 electrons rule, which was explained by the 14 electrons rule [8]. Indeed, analog compounds RuAl$_2$ and RuGa$_2$ have been reported as narrow bandgap semiconductors [5,6,8–12].

In this study, to obtain the optimal conditions for synthesizing high-quality samples of t-FeAl$_2$ under high pressure, we investigated the pressure and temperature (P-T) synthesizing conditions of t-FeAl$_2$ using the multi-anvil type apparatus and in situ X-ray diffraction (XRD) experiments supported by synchrotron radiation. Based on the determined optimal conditions, we synthesized single-phase samples of t-FeAl$_2$ through the high-pressure and high-temperature (HPHT) process and characterized its thermoelectric properties. Furthermore, we present a study of the stability of t-FeAl$_2$ and neighboring phases using first-principles total energy calculations supplemented by a phonon-based calculation of vibrational entropy, which yields the Gibbs free energy under a quasi-harmonic approximation.

2. Experimental details

2.1 In situ x-ray diffraction experiments

The starting material powdered α-FeAl$_2$ was prepared by arc-melting and annealing, as has been described previously [4,19]. High-pressure and high-temperature in situ XRD experiments were performed using multi-anvil type apparatus MAX-III installed at the AR-NE7A beamline of Photon Factory (a Synchrotron radiation facility) in the High Energy Accelerator Research Organization (KEK). The MAX-III was used as 6–8 Kawai-type multi-anvil, consisting of first-stage cubic-anvil apparatus and eight second-stage tungsten carbide cubes truncated at one corner, to accommodate an octahedral cell containing the sample and heater. The sample container and heater were made of MgO and a thin rhenum film with a thickness of 0.025 mm, respectively. Detailed cell assembly was like that described elsewhere [20]. The energy-dispersive X-ray diffraction method was adopted with a fixed Bragg angle of 2θ = 6° in the horizontal direction. Pressure and temperature were determined by the lattice constant of a MgO internal pressure marker (following the third-order Birch–Murnaghan equation of states [21] of MgO from Ref [22]), and thermocouples installed near the sample and heater, respectively. The in situ XRD patterns were recorded during heating from 300 K to 1773 K at a constant pressure of 20 GPa.

2.2 Synthesis and characterization

Using the same starting material α-FeAl$_2$ as used in the in situ XRD experiments, bulk polycrystalline samples were synthesized with two types of multi-anvil apparatus depending on the pressure range of interest: a single-stage multi-anvil was used at 4 GPa and 7.5 GPa, and a double-stage Kawai-type multi-anvil was used at 20 GPa. The heating temperatures for synthesis at 4 GPa, 7.5 GPa and 20 GPa were 873–1173 K, 723–1173 K and 1173–2073 K, respectively. The heating time was 3 h for all experiments. Phase identification was accomplished by powder XRD with Cu Ka radiation and scanning electron microscopy (SEM; JSM-6010LA, JEOL). Lattice parameters were determined with the program package RIETAN-FP [23] using silicon (NIST 640d) as an internal standard. Refinement of the atomic positions and isotropic atomic displacements was also performed with RIETAN-FP [23]. Differential scanning calorimetry (DSC; EXSTAR DSC-7020, SII Co.) was performed to investigate the thermal stability of t-FeAl$_2$ at ambient pressure. Thermoelectric properties were characterized in the temperature range 10–600 K: S, σ, κ and Hall coefficient (R$_{H}$) at 10–300 K were measured with a physical properties measurement system (PPMS; Quantum design) using the thermal transport option for thermoelectric properties and the AC transport option for five-wire $R_{H}$; S at 300–600 K was measured with a ZEM-1 (ULVAC RIKO); σ and $R_{H}$ at 300–600 K were measured with a Resistest 8300 (Toyo Technica Co.).

2.3 First-principles calculations

The phonon frequencies and corresponding thermodynamic properties at 0–20 GPa and 0–2000 K were calculated under the harmonic approximation by the finite displacement method [24,25] and supercell as implemented in the PHONOPY code [26]. To calculate the total energy of the supercells including displacements, we employed the plane-wave projector-augmented wave (PAW)
method [27] in the framework of DFT within the generalized gradient approximation (GGA) functional in the Perdew–Burke–Ernzerhof (PBE) parameterization [28], as implemented in the Quantum ESPRESSO code [29]. We examined the initial structure of FeAl [30], t-FeAl [8], a-FeAl [31] and Fe₂Al₅ [32]. Since a-FeAl [31] and Fe₂Al₅ [33] contain mixed or partially occupied sites in their unit cells, we examined the following unit cells: for the two equivalent mixing sites in a-FeAl₂, we examined ‘Al and Fe’ and ‘Fe and Fe’ arrangements labeled as a-FeAl₂(AF) and a-FeAl₂(FF), respectively (for more details, see elsewhere [4,6]); for the chains of partially occupied aluminum sites along the c-axis in Fe₂Al₅, we examined the experimental low-temperature tripled superlattice structure Fe₂Al₅ · mC44 reported by Okamoto et al. [32], and theoretical tripled superlattice structure Fe₂Al₅ · oP44 reported by Mihalkovic and Widom [6]. A 0.13 eV smearing width of the Methfessel–Paxton scheme [34] was used for all crystal structures except for t-FeAl₂. Force constants were obtained from the cells whose sizes corresponded to the 3 × 3 × 3, 2 × 1 × 1, 3 × 3 × 2, 2 × 1 × 1 and 1 × 2 × 1 supercells of the primitive FeAl, a-FeAl₂, t-FeAl₃, Fe₂Al₅ · mC44 and Fe₂Al₅ · oP44 unit cells, respectively. An atomic displacement of 0.01 Å was used for all supercells. The phonon band paths were determined by using SeeK-path [35]. We used the quasi-harmonic approximation that transforms thermodynamic parameters from the function of volume (V) to the function of pressure (P) [36]. The Gibbs free energy (G) at the finite P and T was obtained as \( G(P,T) = \min_V [U_{el} + U_{ph} + PV - TS_{vib}] \), where \( U_{el}, U_{ph} \) and \( S_{vib} \) are the electronic internal energy at 0 K, the phonon energy, and vibrational entropy, respectively. To compare the stabilities of a-FeAl₂, t-FeAl₂ and FeAl + Fe₂Al₅ at the stoichiometric composition of t-FeAl₂, we used \( 1/3 \times G(FeAl₂(FF)) + 2/3 \times G(a-FeAl₂(AF)) \) and \( 4/15 \times G(FeAl) + 11/15 \times G(Fe₂Al₅) \) as \( G(a-FeAl₂) \) and \( G(FeAl + Fe₂Al₅) \), respectively, for normalization. This normalization of composition is graphically explained in Fig. S1.

3. Results and discussion

3.1 Sample preparation and P-T synthesizing conditions of fea₁₂

Figure 1 shows in situ XRD patterns (log scale) of FeAl₂ at 20 GPa and 300–1773 K. The Bragg peaks of MgO (sample container) and characteristic X-ray peaks of rhenium (sample heater) were observed at all temperatures. The peaks represented by triangle symbols did not shift even when temperature increased, suggesting these peaks were derived from something outside sample container. Although the weak and broad peaks of the starting material a-FeAl₂ were observed at 300–1023 K, we observed the peaks of t-FeAl₂, where the intensity increased, and the peak sharpened as the temperature increased at 1023 K – 1523 K. However, the peaks of t-FeAl₂ disappeared at 1773 K, which indicated t-FeAl₂ was unstable. Instead of the peaks of t-FeAl₂, weak peaks similar to those of the neighboring phases FeAl, Fe₂Al₅ (high-temperature phase) and Fe₂Al₅ were observed. Unfortunately, the strong peaks of FeAl, Fe₂Al₅ and Fe₂Al₅ were so close to those of MgO that it was difficult to determine which phases appeared at 1773 K.

Based on the results of the in situ observation, HPHT synthesis was performed at 20 GPa. Figure 2 shows the XRD patterns with Cu Kα of the samples synthesized at 20 GPa. We successfully synthesized t-FeAl₂ at 1173 K, whereas the sample recovered from the run at 2073 K mainly decomposed to FeAl and Fe₂Al₅. The presence of t-FeAl₂ at 1173 K and mostly its absence at 2073 K were in good agreement with the in situ XRD observation. The backscattered electron composition image (BECI) of the sample synthesized at 20 GPa and 2073 K showed three kinds of regions: FeAl (light contrast), t-FeAl₂ (gray) and Fe₂Al₅ (dark) as shown in Figure 3. We observed a lamellar matrix of FeAl and t-FeAl₃ and t-FeAl₅ at the phase boundaries between the lamellar matrix and Fe₂Al₅. X. Li et al. observed the same microstructure in a levitation melted Fe₃₃₂Al₆₆₈ at ambient pressure, and explained the microstructure by the eutectic reaction of the high-temperature phase Fe₂Al₅ into FeAl and a-FeAl₂ [19]. Assuming the same situation at high pressure except for replacing a-FeAl₂ with t-FeAl₂, the microstructure in Figure 3 is well explained as follows: the sample formed Fe₂Al₅ and Fe₂Al₅ at 2073 K, and then t-FeAl₂ grew peritectoidally between Fe₂Al₅ and Fe₂Al₅ during cooling process; in a later stage of cooling, Fe₂Al₅ decomposed into FeAl and t-FeAl₂ by eutectoid reaction. Therefore, t-FeAl₂ was suggested to be unstable and decomposed at 2073 K. To obtain the large bulk samples, we attempted to synthesize the samples at lower pressure. Figures 4(a) and 5 show XRD patterns of the sample synthesized at 4 GPa and 7.5 GPa, respectively. We successfully synthesized single-phase t-FeAl₂ at 7.5 GPa and 873 K, but we observed small impurities in the BECI shown in Figure 4(b)–(c). The composition of these small impurities, Fe₁₄Al₆₄ (light contrast) and Fe₁₉Al₆₈ (dark), was slightly different from FeAl₂. Since we did not observe any peaks derived from these impurities, the amount of the impurities should be low. With the increasing temperature at 7.5 GPa, the peak of t-FeAl₂ faded, and those of FeAl and Fe₂Al₅ were observed. When we synthesized the samples at 4 GPa, t-FeAl₂ was not observed at all in the temperature range and direct decomposition from a-FeAl₂ to FeAl and Fe₂Al₅ was observed at 873 K.
We summarized the series of experiments as a $P$-$T$ synthesizing conditions (not an equilibrium phase diagram, but merely shows the phases observed after HPHT synthesis) of FeAl$_2$ using $\alpha$-FeAl$_2$ as a starting material, as is shown in Figure 6. We have to note that these results may change with starting materials and heating time. According to the phase diagram at ambient pressure, $\alpha$-FeAl$_2$ was stable until the temperature...
reached 1418 K [19]. However, the decomposition or phase transition of \( a \)-FeAl\(_2\) was observed at a lower temperature when subjected to a higher pressure. This trend was in good agreement with the enthalpy calculation where \( a \)-FeAl\(_2\) became less stable than \( t\)-FeAl\(_2\) and FeAl + Fe\(_5\)Al\(_5\) at high pressure [4]. One can see that as the pressure increased from 7.5 GPa to 20 GPa, the temperature range where \( t\)-FeAl\(_2\) was stable expanded monotonically. However, with a further increase in temperature, \( t\)-FeAl\(_2\) decomposed into FeAl and Fe\(_2\)Al\(_5\) over the entire pressure range. When we synthesized \( t\)-FeAl\(_2\) by LHDAC technique, the temperatures (1873 K at 10 GPa and 2123 K at 20 GPa) were higher than our present study [4]. One possible explanation for this discrepancy may be the inhomogeneity during the heating process in our previous LHDAC samples. Since the diameter of heating laser (10 \( \mu \)m) was much smaller than sample diameter (100 \( \mu \)m), the temperature outside the laser lower may be lower than the measured temperature, resulting in we observed \( t\)-FeAl\(_2\) at such high temperatures. Therefore, we did not include the results of LHDAC samples in Figure 6.

Table 1 shows the lattice parameters obtained with an internal silicon standard, and the atomic positions and isotropic atomic displacements of \( t\)-FeAl\(_2\) synthesized at 7.5 GPa and 873 K. The lattice parameters \( a = 3.0307(1) \, \text{Å}^3 \) and \( c = 8.4959(3) \, \text{Å}^3 \) were in good agreement with those calculated in previous reports within 1.5% [4,8]. The corresponding atomic volume of 13.8 \( \text{Å}^3 \)/atom was denser than the 13.8 \( \text{Å}^3 \)/atom of \( a\)-FeAl\(_2\) [31], which indicated that \( t\)-FeAl\(_2\) became more stable than \( a\)-FeAl\(_2\) as the pressure increased. In the assigned space group \( I4/mmm\), only the \( z \) position of Al atoms was refined to be \( z = 0.3429(3) \).

When \( t\)-FeAl\(_2\) was heated at ambient pressure, \( t\)-FeAl\(_2\) decomposed into FeAl and Fe\(_2\)Al\(_5\), as

Figure 3. (a) SEM-BECI image of the sample synthesized at 20 GPa and 2073 K. (b) Magnified image shows the growth of \( t\)-FeAl\(_2\) at phase boundaries between a lamellar matrix of FeAl + \( t\)-FeAl\(_2\) and Fe\(_2\)Al\(_5\).
observed from the strong endothermic signal in the DSC measurement at around 787 K during heating (see Figure 7(a)). Integration of the endothermic peak shows that \( t\text{-FeAl}_2 \) is more stable than \( \text{FeAl} + \text{Fe}_2\text{Al}_5 \) by 11 meV/atom in terms of the formation enthalpy. However, in this study, we did not observe the phase transition during cooling process, suggesting the transition temperature during cooling process may be lower than the temperature during heating process, and/or atomic diffusion may be so slow that we cannot observe it. The powdered XRD patterns observed from the strong endothermic signal in the DSC measurement at around 787 K during heating (see Figure 7(a)). Integration of the endothermic peak shows that \( t\text{-FeAl}_2 \) is more stable than \( \text{FeAl} + \text{Fe}_2\text{Al}_5 \) by 11 meV/atom in terms of the formation enthalpy. However, in this study, we did not observe the phase transition during cooling process, suggesting the transition temperature during cooling process may be lower than the temperature during heating process, and/or atomic diffusion may be so slow that we cannot observe it. The powdered XRD patterns
Figure 6. Pressure and temperature synthesizing conditions of FeAl2 determined by the in situ XRD and quenching experiments using α-FeAl2 as a starting material. As the pressure increases, the temperature range at which t-FeAl2 is stable expands monotonically. However, further increase of temperature results in the decomposition to FeAl and Fe2Al5. Note that the results at low temperature may change if heating time is extended because heating time was as short as 3 h.

Table 1. Results of structure refinement for t-FeAl2

| Crystal data       | Tetragonal |
|--------------------|------------|
| Space group, Pearson symbol | 4/mmm, tI6 |
| a(Å)               | 3.030(1)   |
| c(Å)               | 8.4959(3)  |
| Atomic parameters  |            |
| Wyckoff notation   |            |
| Fe                  | 2a         |
| Al                  | 4e         |
| α                  |            |
| x                  | 0          |
| y                  | 0          |
| z                  | 0          |
| Uiso (Å²)          | 0.0071(8)  |
| Reliability factors|            |
| Rwp                | 4.63%      |
| Rp                 | 3.59%      |
| Rb                 | 6.77%      |
| Rv                 | 6.15%      |
| S                  | 1.79       |

showed the complete absence of t-FeAl2 after DSC measurements (see Figure 7(b)). This decomposition seemed to be strange since a-FeAl2 is stable below 1418 K from the phase diagram [19], but it could be explained by the fact that the nucleation and/or growth of a-FeAl2 was much slower than that of Fe2Al5 at 823–913 K [37].

3.2 Thermoelectric properties of FeAl2

Figure 8(a)–(d) shows the temperature dependence of S, σ, RHH and total thermal conductivity (κ), respectively. The standard uncertainty was calculated by considering the uncertainty in the sample dimensions and instruments. We observed a semiconductor-like large S, which rapidly changed from a negative value of −105 μV/K (at 155 K) to a positive value of 75 μV/K (at 400 K). Our previous calculation [4] showed that the density of states (DOS) at the conduction band minimum was higher than that at the valence band maximum, which was in good agreement with the larger S observed in the n-type. The S decreased above 400 K since the estimated bandgap of t-FeAl2 was as narrow as 0.035 eV [4]. The major carrier type change from negative to positive was well reproduced in the RHH. The σ was kept almost constant up to 250 K, which was approximately the sign change temperature of RHH and S, and began to decrease to ~1.3 × 105 S/m. The κel was estimated using the measured σ in conjunction with the Wiedemann–Franz law at 10–300 K, which showed that κel was less than 0.2 W/mK over the entire temperature range (See Figure 8(d)). The κph is written as follows by applying the phonon gas theory:

\[
\kappa_{ph} = \frac{1}{3} C_v \tau^2 \nu
\]

where \( C_v \), \( \tau \) and \( \nu \) are the heat capacity, phonon relaxation time and average phonon group velocity, respectively. The increase in κph with increasing \( T \) below 80 K mainly arose from the increase of \( C_v \), whereas the reduction in κph above 80 K resulted from a decrease in \( \tau \). As shown in the inset of Figure 8(d), the temperature dependence of κph from 150 K to 300 K was proportional to 1/\( T \), which suggested that Umklapp scattering played the main role in the decrease of κph. One can compare the thermoelectric properties of t-FeAl2 with those of other intermetallic thermoelectrics, Fe2VAI [38–42] and Al2Fe5Si3 [43–46]. The κph of t-FeAl2 was several times larger than that of Al2Fe5Si3. The maximum S of t-FeAl2 was comparable to those of Fe2VAI and Al2Fe5Si3, but σ of t-FeAl2 was approximately one order of magnitude smaller than Fe2VAI. Therefore, the maximum power factor \( S^2\sigma \) remained as low as ~0.41 mW/mK² (at 400 K). The poor \( S^2\sigma \) and large \( \kappa \)
Figure 7. (a) DSC measurement with the endothermic signal at 787 K, which indicates decomposition of $t$-FeAl$_2$. (b) X-ray diffraction patterns of $t$-FeAl$_2$ after DSC measurement, which results in the complete decomposition into FeAl and Fe$_2$Al$_5$.

Figure 8. Thermoelectric properties of pristine $t$-FeAl$_2$: (a) Seebeck coefficient, (b) electrical conductivity, (c) Hall coefficient and (d) thermal conductivity. The inset of (d) shows phonon thermal conductivity versus $1000/T$ plot.
led to a low maximum ZT of $2.3 \times 10^{-3}$ (at 180 K). However, we previously predicted that t-FeAl₂ will have a larger power factor if n-type doping is possible [4]. Thus, further research concerning carrier tuning will enhance the thermoelectric properties of t-FeAl₂.

### 3.3 Phonon calculations

We found the phonon band structure of Fe₃Al₆-oP44 shows imaginary phonon modes at gamma points (see Fig. S2(a)). However, the imaginary phonon modes were disappeared by shifting the atomic coordinates of Fe₃Al₆-oP44 in the direction of the eigenvector where the imaginary phonon modes appeared (see Fig. S2). Tables S1–S6 show the structural parameters of all structures obtained by the structural relaxation including the shifted Fe₃Al₆-oP44 as labeled Fe₃Al₆-oP44'. Since our total energy calculation revealed that the shifted structure labeled as Fe₃Al₆-oP44' is slightly more stable than Fe₃Al₆-mC44 by 2.2 meV/atoms, we used Fe₃Al₆-oP44' in the following Gibbs energy calculations. The phonon DOS of FeAl, a-FeAl₂, t-FeAl₂ and Fe₃Al₆-oP44' at 0–20 GPa are shown in Figure 9, respectively. All of the structures exhibited no imaginary phonon modes, which indicated these structures were dynamically stable even at high pressure. With increasing pressure, the phonon frequencies shifted to high energy, whereas the shape of the phonon DOS was retained. The phonon contributions for Helmholtz free energy, $F_{\text{vib}}$, is obtained from the following equation:

$$F_{\text{vib}} = \frac{1}{2} \sum_{q\nu} \hbar w(q\nu) - k_B T \sum_{q\nu} \ln \left( 1 - \exp \left(-\frac{\hbar w(q\nu)}{k_B T}\right) \right)^{-1}$$

(2)

where $w(q\nu)$ are phonon frequencies of band index $\nu$ at each $q$-point. The lower-frequency phonons make the second term of Eq. (2) larger, contributing to the stability at high temperature. Figure 9(f) shows a-FeAl₂ and Fe₃Al₆-oP44' exhibit the larger density of low-frequency phonons than other structures, suggesting these two structures will be more stabilized at high temperature. Figure 10 shows the temperature dependence of the relative Gibbs free energies of a-FeAl₂ and FeAl + Fe₂Al₃ with respect to t-FeAl₂. When the pressure increased, $PV$ shifted in the direction of the stabilization of t-FeAl₂ due to its denser structure, whereas $TS_{\text{vol}}$ was almost constant at various pressures. Owing to the small contribution of $TS_{\text{vol}}$ in t-FeAl₂, t-FeAl₂ became unstable with respect to FeAl + Fe₂Al₃ and a-FeAl₂ as the temperature increased. The most stable phase at 0GPa and low temperature was t-FeAl₂ in our calculations, which is in good agreement with the DSC measurement. Our calculations show the formation enthalpy difference between t-FeAl₂ and FeAl + Fe₂Al₃ is 22 meV/atoms, which is slightly larger than the DSC measurement. It was suggested that FeAl + Fe₂Al₃ was most stable at high temperatures and high pressures since the contribution of $TS_{\text{vol}}$ in FeAl + Fe₂Al₃ was slightly inferior to a-FeAl₂, but FeAl + Fe₂Al₃ was more stable than a-FeAl₂ in terms of $PV$. Comparing the $P$-$T$ synthesizing conditions obtained from the experiment with these calculations, unfortunately, the phase transition temperature was overestimated from those investigated in the experiment. The difficulty in reproducing the atomic disorders in a-FeAl₂ and Fe₂Al₃ in the primitive cells results in our calculations underestimated the Gibbs free energies of these structures. However, the trends that (i) the stable temperature range of t-FeAl₂ expanded as pressure increased, and (ii) FeAl + Fe₂Al₃

![Figure 9. Phonon density of states (DOS) of (a) FeAl, (b) a-FeAl₂(FF), (c) a-FeAl₂(AF), (d) t-FeAl₂, (e) Fe₃Al₆-oP44' and (f) all structures at 0 GPa. The phonon DOS of a-FeAl₂ and Fe₂Al₃ show enhanced low-frequency phonons, which can contribute to vibrational entropy.](image-url)
became more stable than $\alpha$-FeAl$_2$ and t-FeAl$_5$ at high temperature and high pressure, were well reproduced in the calculations.

4. Conclusions

In this study, using $\alpha$-FeAl$_2$ as the starting material, the $P$-$T$ synthesizing conditions of t-FeAl$_5$ were determined for the first time. Supported by in situ XRD measurements, we found t-FeAl$_5$ was synthesized at 7.5 and 20 GPa. However, by increasing the temperature to 1173 K (at 7.5 GPa) and 1773 K (at 20 GPa), t-FeAl$_5$ decomposed into the neighboring phases FeAl and Fe$_5$Al$_3$. The $S$ of t-FeAl$_5$ is $-105 \mu$V/K (at 150 K), which is the largest value in a Fe–Al binary system, however, the maximum power factor is retained as 0.41 mW/mK$^2$ because the carrier concentration is not tuned. The calculated phonon DOS for FeAl, $\alpha$-FeAl$_2$, t-FeAl$_2$ and Fe$_5$Al$_3$ shows no imaginary frequencies over the entire pressure range, which indicates these phases are dynamically stable. A comparison of the $G$ of FeAl, $\alpha$-FeAl$_2$, t-FeAl$_2$ and Fe$_5$Al$_3$ reveals that (i) although t-FeAl$_5$ is stable at high pressure owing to the $PV$, t-FeAl$_2$ becomes unstable as the temperature increases, and (ii) FeAl + Fe$_5$Al$_3$ is most stable at high pressure and high temperature. Although the phase transition and decomposition temperature were overestimated from those obtained from experiment, these results explain the trends we observe in the experiments.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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