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Abstract

A thermodynamic analysis of the Fe-Ti-S ternary system was performed by incorporating first-principles calculations into the calculation of phase diagrams (CALPHAD) method. To evaluate the Gibbs energy, the Debye-Grüneisen model was applied for some sulfides of the Ti-S binary system. In addition, the cluster expansion and cluster variation methods were used for the solid solution phases in the Ti-S binary and (Fe,Ti)S phases. The calculated Ti-S binary phase diagram showed good agreement with the experimental results. The very low solubility of the Ti solid solution in the Ti-S system, as reported by Murray, agreed well with our calculated results. A binodal phase decomposition of the liquid phase was expected in the S-rich region. The Gibbs energy curve of (Fe,Ti)S between FeS and TiS was found to be convex downward. This is characteristic of an isomorphic solid solution, attributed to the attractive interaction between Fe and Ti in (Fe,Ti)S. The vertical phase diagram between FeS and TiS, obtained using the thermodynamic database, was in good agreement with the experimental results of Mitsui *et al*. The solubility products of (Fe,Ti)S have been experimentally estimated previously. The calculated solubility product agreed with the experimental value of TiS.

Key words

thermodynamic assessment, phase diagram, first-principles calculations, CALPHAD, iron sulfide, titanium sulfide

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1. Introduction

The formation mechanism and precipitation behavior of sulfide in steel have been investigated for a long time because of the importance of sulfide in the mechanical properties of steel. For example, titanium is added to enhance the mechanical properties of steel by removing the interstitial elements from the solid solution and forming very fine precipitates. These titanium-containing ultra-low-carbon steels have been used in the outer panels of automobiles as interstitial-free (IF) steels since they have good formability and drawability [1-7]. In this research field, knowledge about the phase stability of sulfides is an important factor in manufacturing, and basic information regarding the same is often obtained from phase diagrams. The calculation of phase diagrams (CALPHAD) approach [8] is very useful for calculating phase diagrams in multi-component and multi-phase systems. However, it is difficult to collect systematic experimental data about phase equilibria that include sulfur. Therefore, even for a simple Fe–Ti–S ternary system, there are some unsolved issues.

For the Ti–S binary system, experimental phase equilibria of the Ti-rich side have been reported by Eremenko *et al.* [9] Some experimental investigations on the crystal structures of several sulfides have been reported [10]. By using these experimental data, Murray constructed an experimental Ti–S binary phase diagram, which is shown in Fig. 1[10]. According to this phase diagram, the Ti–S binary system is composed of the liquid (L), BCC, HCP, NiAs-type hexagonal TiS, Ti_6S, Ti_3S, Ti_2S, Ti_8S_9, Ti_8S_{10}, $Ti_{16}S_{21}$, TiS_2, and TiS_3. The S-rich portion (S > 50 atm%) is undetermined because of the lack of experimental data. Murray suggested that the phase denoted as "polytypes" at approximately 60 mol% S content consists of several metastable sulfides. The experimental formation enthalpies of several sulfides, Ti_2S [11], TiS [12], [13,14], TiS_2 [15,16], and TiS_3 [15] have also been reported. For the Fe–Ti–S ternary system, the partial phase equilibria of the FeS–TiS system were investigated by Mitsui *et al.* [17], Kaneko *et al.* [18], and Vogel *et al.* [19] The miscibility gap between FeS and TiS was suggested by Kaneko *et al.* [18] and Vogel *et al.* [19] On the other hand, Mitsui *et al.* [17] pointed out that the NiAs structure in the FeS–TiS binary system forms a complete solid solution over the temperature range of 1173–1473 K. In this ternary system, the solubility products of TiS have been estimated experimentally by many researchers with respect to the equilibrium between TiS and FCC. The experimental values vary widely depending on the influence of impurities, difference in the heat-treatment conditions and measurement of the deviation of the composition analysis. Subramanian *et al.*[20] obtained the solubility product of TiS by quenching the sample after equilibrium heat treatment at several temperatures. Although Mitsui *et al.* [21] performed similar heat treatments as Subramanian *et al.*, they used diffusion couples as samples. Other researchers [5,22] have dealt with several samples that are cooled after hot rolling.

Recently, first-principles calculations have been often used for thermodynamic assessments using the CALPHAD approach when the phase under consideration is metastable and/or an experimentally unobtainable phase. Although first-principles calculations describe the physical properties of the stoichiometric compounds at the ground state, several calculation techniques have been developed to estimate the Gibbs energy at finite temperatures. To include the contribution of atomic vibrations, the direct method [23] and the Debye–Grüneisen [24-26] model have been examined, although the former is a somewhat time-consuming technique. On the other hand, the Gibbs energy of a solid solution can be calculated using the cluster expansion method (CEM) [27] and the cluster variation method (CVM) [27-29]. The resulting calculated phase diagrams are in good agreement with the experimental results [30]. In this study, we attempted to calculate the thermodynamic properties of various sulfides using first-principles calculations, CEM, CVM, and the Debye–Grüneisen model. The objective of this study was to clarify the phase equilibria of the Fe–Ti–S ternary system over the entire composition range by incorporating the abovementioned techniques into the CALPHAD method.

2. Computational procedure

2.1 First-principles calculations, Debye–Grüneisen model, and CVM

The total energy calculations were performed using the VASP code [31,32], which is based on density functional theory. The exchange and correlation functions were given by the generalized gradient approximation, as proposed by Perdew *et al.* [33]. We employed Blochl's projector-augmented wave (PAW) method as implemented by Kresse and Joubert. [34,35]. For the Ti-S binary compounds, the details of the first-principles calculations are as follows. The plane wave energy cutoff was chosen to be 364 eV to ensure lattice relaxations. The Methfessel-Paxton order 1 smearing was used with a sigma value as small as 0.1 eV. The convergence criterion was set to 10^{-5} eV in energy during the electronic iterations. The size of the k mesh depends on the crystal structure. We used $9\times9\times2$, $2\times2\times9$, $10\times10\times4$, $10\times10\times5$, and $6\times9\times4$ mesh sizes for Ti_8S_3, Ti_2S, TiS, TiS_2, and TiS_3, respectively.

The formation energy obtained by first-principles calculations is only useful for the evaluation of the thermodynamic parameters at 0 K. In this study, to determine the thermodynamic parameters of a stoichiometric compound at finite temperatures, the specific heat capacity is calculated using the Debye–Grüneisen model. First, the formation energies of the compounds were calculated within a band 30% to either side of the equilibrium volume by first-principles calculations. The relationship

between the total energy and volume during structure optimization was approximated by the Morse function (eq. 1).

$$E_{tot}(r) = A + D \cdot \exp[-2\lambda \cdot (r - r_0)] - 2D \cdot \exp[-\lambda \cdot (r - r_0)], \tag{1}$$

where the distance between the atoms, r, the equilibrium atomic distance, r_0, and the constants A, D, and λ were estimated as fitting parameters. These parameters determined the bulk modulus $B(r_0)$, as given in eq. 2.

$$B(r_0) = -\frac{D\lambda^3}{6\pi \ln(\exp(-\lambda \cdot r_0))} \tag{2}$$

This equation was applied to the Debye temperature at equilibrium volume.

$$\Theta_{D0} = \frac{h\omega_{D0}}{2\pi k_B} = (6\pi^2)^{1/3} \frac{\hbar}{k_B} \left(\frac{4\pi}{3}\right)^{1/6} \times k(v) \left(\frac{B(r_0)}{m_{A_xB_y}}\right)^{1/2} \tag{3}$$

The mass, m, is an effective atomic mass defined as the logarithmic average of all the masses. For several sulfides A_xB_y, m is calculated by

$$\ln(m_{A_xB_y}) = \frac{x}{x+y}\ln(m_A) + \frac{y}{x+y}\ln(m_B) \tag{4}.$$

where h is Planck's constant, $\hbar$ is Dirac's constant, k_B is Boltzmann's constant, ω_D is the Debye frequency, and $k(v)$ is the derived Poisson's ratio, as given in eq. 5.

$$k(v) = \left\{ \frac{2}{3}\left[\frac{2(1+v)}{3(1-2v)}\right]^{3/2} + \frac{1}{3}\left[\frac{1+v}{3(1-v)}\right]^{3/2} \right\}^{-1/3} \tag{5}$$

We calculated $k(v)$ as $v = 0.2$ for sulfides because most solids have a Poisson's ratio of 0.2–0.3. The relationship between the Debye temperature and volume is explained using the Grüneisen constant γ as follows:

$$\Theta_{\mathrm{D}}/\Theta_{\mathrm{D0}} = \left(V_0/V\right)^{\gamma} = \left(r_0/r\right)^{3\gamma} \qquad (6)$$

where

$$\gamma = \frac{\lambda r_0}{2}. \qquad (7)$$

γ is described by the Slater approximation [36] and the Dugdale-MacDonald approximation [37]. We used the Dugdale-MacDonald approximation for γ because it is suitable over a wide range of temperatures [25]. The Debye temperatures outside the equilibrium volume were estimated using eq. (6), and the temperature dependence of the Helmholtz energies at several volumes were determined using eq. (8).

$$F(T,V) = E_{tot}(V) - N_A k_B T \left[f_{\mathrm{D}}\left(\frac{\Theta_{\mathrm{D}}}{T}\right) - 3\ln\left(1 - \exp\left(-\frac{\Theta_{\mathrm{D}}}{T}\right)\right) \right] + \frac{9}{8} N_A k_B \Theta_D \qquad (8)$$

where f_{D} is the Debye function. In this work, the relationships between energy and volume at finite temperatures were approximated by the Birch–Murnaghan state equation [38] (eq. 9).

$$F(V) = \frac{9}{16}\left[B_0 V_0 \left[\left(\frac{V_0}{V}\right)^{\frac{2}{3}} - 1\right]^3 B_0' + \left[\left(\frac{V_0}{V}\right)^{\frac{2}{3}} - 1\right]^2 \left(6 - 4\times\left(\frac{V_0}{V}\right)^{\frac{2}{3}}\right)\right] + E_{tot}(V_0) \qquad (9)$$

At several temperatures, the equilibrium volumes V_0 and bulk modulus B_0 were obtained by the fitting eq. (9) to the calculated $F(T, V)$. These were necessary to obtain the isobaric specific heat. The thermal expansion coefficients were obtained using eq. (10).

$$\alpha(T) = \frac{1}{r_0}\frac{dr_0}{dT} \qquad (10)$$

The specific heat at constant volume was calculated with the following equation by using the Debye temperature:

$$C_{v0}(T, \Theta_{D0}) = 3Rf_{D}\left(\frac{\Theta_{D0}}{T}\right) = 9N_{A}k_{B}\left(\frac{T}{\Theta_{D0}}\right)^{3}\int_{0}^{\Theta_{D0}/T}\frac{e^{x}x^{4}}{\left(e^{x}-1\right)^{2}}dx \qquad (11)$$

where N_A is Avogadro's number and R is the gas constant.

According to the above equations, C_{v0}, α, B_0, and V_0 were used to calculate the specific heat at a constant pressure, C_{p0}, according to eq. (12).

$$C_{p0} = C_{v0} + \alpha^2 B_0 V_0 T \qquad (12)$$

The Gibbs energies of solid solutions of the BCC, FCC, and HCP phases of the Ti–S system and (Fe,Ti)S were evaluated using CEM and CVM. First, the total energies of the ordered structures at several compositions, which were constructed on the lattice of each phase, were computed by first-principles calculations using the ATAT code [39]. The details of the first-principles calculations in CEM are as follows. The plane wave energy cutoff was chosen to be 400 eV to ensure lattice relaxations. The k-point meshes were created with k-points per reciprocal atom of 1000. The first-order Methfessel–Paxton method is used for the Fermi surface with a sigma value as small as 0.1 eV. The convergence criterion was set to 10^{-4} eV in energy during the electronic iterations. The cell volume, shape, and atomic positions were allowed to relax until stress was minimized, and the forces on any atom were below 0.02 eV/Å.

The formation enthalpies of sulfides are defined as in Eq. (13)

$$\Delta H = H(\text{Fe}_l\text{Ti}_m\text{S}_n) - l \cdot H_{\text{Fe}}^{\text{BCC}} - m \cdot H_{\text{Ti}}^{\text{HCP}} - n \cdot H_{\text{S}}^{\text{Orthorhombic}} \qquad (13)$$

The first term on the right-hand side is the total energy of the compounds that include l Fe, m Ti, and n S atoms; the second term is the total energy of BCC that consists of l Fe atoms; the third term is the total energy of HCP that consists of m Ti atoms; and the fourth term is the total energy of orthorhombic S that consists of n S atoms.

The obtained energies of formation are described using the effective cluster interaction (ECI) for cluster α, J_α, and the cluster correlation function, ξ_α, and are given by

$$E = \sum_\alpha J_a \xi_\alpha \qquad (14)$$

The cluster correlation function means the product of the occupation operator for site i in the cluster, and it is determined uniquely from the atomic configurations. The free energy of the phase under consideration at finite temperatures was calculated using J_α and adding a configurational entropy term, S_α, as follows:

$$F = \sum_\alpha J_a \xi_\alpha - T \sum_\alpha \gamma_\alpha S_\alpha \qquad (15)$$

where γ_α is the Kikuchi–Barker constant, which indicates the configuration entropy from cluster α. In CVM, the minimal Gibbs energy is evaluated by the configurational degree of freedom, which is calculated by variation in ξ_α. For cluster expansion and cluster variation, we used the CVM code developed by Sluiter $et\ al.$ [40,41].

2.2. Thermodynamic modeling of the solution phases

2.2.1. BCC, FCC, and HCP solid solutions

The regular solution approximation was applied to the solid-solution phase. For example, the molar Gibbs energy of the BCC phase, G^{BCC}, was calculated using the following equation:

$$
\begin{aligned}
G^{\mathrm{BCC}} = {} & x_{\mathrm{Fe}}\,{}^\circ G_{\mathrm{Fe}}^{\mathrm{BCC}} + x_{\mathrm{S}}\,{}^\circ G_{\mathrm{S}}^{\mathrm{BCC}} + x_{\mathrm{Ti}}\,{}^\circ G_{\mathrm{Ti}}^{\mathrm{BCC}} \\
& + RT(x_{\mathrm{Fe}} \ln x_{\mathrm{Fe}} + x_{\mathrm{S}} \ln x_{\mathrm{S}} + x_{\mathrm{Ti}} \ln x_{\mathrm{Ti}}) \\
& + x_{\mathrm{Fe}} x_{\mathrm{S}} L_{\mathrm{Fe,S}}^{\mathrm{BCC}} + x_{\mathrm{S}} x_{\mathrm{Ti}} L_{\mathrm{S,Ti}}^{\mathrm{BCC}} + x_{\mathrm{Fe}} x_{\mathrm{Ti}} L_{\mathrm{Fe,Ti}}^{\mathrm{BCC}} \\
& + x_{\mathrm{Fe}} x_{\mathrm{S}} x_{\mathrm{Ti}} L_{\mathrm{Fe,S,Ti}}^{\mathrm{BCC}}
\end{aligned}
\qquad (16)
$$

where ${}^\circ G_{\mathrm{i}}^{\mathrm{BCC}}$ denotes the molar Gibbs energy of element i in the solid state, R is the universal gas constant, and the term x_{i} is the mole fraction of element i in the ternary system.

This quantity is called the lattice stability parameter, and it is described by the formula

$${}^\circ G_i^{\mathrm{BCC}} - {}^\circ H_i^{\mathrm{BCC}} = a + bT + cT \ln T + dT^2 + eT^3 + fT^7 + iT^{-1} + jT^{-9} \qquad (17)$$

where $^\circ H_i^{\mathrm{BCC}}$ denotes the molar enthalpy of the pure element i in its stable state at $T = 25\ ^\circ\mathrm{C}$ and the symbols a–j are coefficients. The parameter $L_{i,j}^{\mathrm{BCC}}$ denotes the interaction energy between i and j in the BCC phase, and it shows a compositional dependency following the Redlich–Kister polynomial:

$$L_{i,j}^{\mathrm{BCC}} = {}^0L_{i,j}^{\mathrm{BCC}} + {}^1L_{i,j}^{\mathrm{BCC}}(x_i - x_j) + {}^2L_{i,j}^{\mathrm{BCC}}(x_i - x_j)^2 + \cdots + {}^nL_{i,j}^{\mathrm{BCC}}(x_i - x_j)^n \qquad (18)$$

where

$$^nL_{i,j}^{\mathrm{BCC}} = A + BT + CT\ln T + DT^2 + \cdots \qquad (19)$$

in which the symbols A–D are coefficients. The term $L_{\mathrm{Fe,S,Ti}}^{\mathrm{BCC}}$ is the ternary interaction parameter between elements Fe, S, and Ti. The compositional dependency of the interaction parameters is expressed as

$$L_{\mathrm{Fe,S,Ti}}^{\mathrm{BCC}} = x_{\mathrm{Fe}}\,{}^0L_{\mathrm{Fe,S,Ti}}^{\mathrm{BCC}} + x_{\mathrm{S}}\,{}^1L_{\mathrm{Fe,S,Ti}}^{\mathrm{BCC}} + x_{\mathrm{Ti}}\,{}^2L_{\mathrm{Fe,S,Ti}}^{\mathrm{BCC}} \qquad (20)$$

The BCC, FCC, and HCP solid solutions, which exhibit a range of non-stoichiometric alloys, were modeled using the same regular solution approximation. The contribution to the Gibbs free energy because of magnetic ordering was added to the non-magnetic part of the free energy [42,43]. It is noted that the solubility of Fe and Ti in orthorhombic S and monoclinic S was negligible, and hence not taken into account in this modeling.

2.2.2. Liquid phase

The associated solution approximation was applied to the liquid phase with an associate, FeS. The molar Gibbs energy of the liquid phase, G^{L}, was calculated using the following equation:

8

$$
\begin{aligned}
G^L = {}& x_{Fe}\,{}^\circ G_{Fe}^L + x_S\,{}^\circ G_S^L + x_{Ti}\,{}^\circ G_{Ti}^L + x_{FeS}\,{}^\circ G_{FeS}^L \\
& + RT(x_{Fe}\ln x_{Fe} + x_S\ln x_S + x_{Ti}\ln x_{Ti} + x_{FeS}\ln x_{FeS}) \\
& + x_{Fe}x_S\ L_{Fe,S}^L + x_{Ti}x_S\ L_{Ti,S}^L + x_{Ti}x_{FeS}\ L_{Ti,FeS}^L \\
& + x_{Fe}x_{FeS}\ L_{Fe,FeS}^L + x_{Fe}x_{Ti}\ L_{Fe,Ti}^L + x_{FeS}x_S\ L_{FeS,S}^L \\
& + x_{Fe}x_{FeS}x_S\ L_{Fe,FeS,S}^L + x_{Fe}x_{Ti}x_S\ L_{Fe,Ti,S}^L + x_{FeS}x_S x_{Ti}L_{FeS,S,Ti}^L \\
& + x_{Fe}x_{FeS}x_{Ti}L_{Fe,FeS,Ti}^L + x_{Fe}x_{FeS}x_S x_{Ti}L_{Fe,FeS,S,Ti}^L
\end{aligned}
\tag{21}
$$

where $^\circ G_i^L$ denotes the molar Gibbs energy of element i in the liquid state, R is the universal gas

constant, and the term x_i is the mole fraction of element i in the ternary system. $^n L_{i,j}^L$ (n = 0, 1, 2, 3

i, j = Fe, FeS, S, Ti) has a compositional dependency following the Redlich–Kister polynomial. The

temperature-dependent $^3 L_{Ti,S}^L$ parameter was used for the liquid phase of the Ti-S system in this

work because it was necessary to assess the liquidus of the Ti-rich region.

2.2.3.Fe$_2$Ti Laves phase

The C14 Laves phase, Fe$_2$Ti, appears over a wide compositional range. To account for the
homogeneity range, Kumar *et al.* [44] used a three-sublattice model. This thermodynamic description
was used in our study.

2.2.4. Stoichiometric compounds

The binary compound phases with zero homogeneity ranges (i.e., FeTi, FeS$_2$, Ti$_3$S, Ti$_8$S$_9$, Ti$_8$S$_{10}$,
Ti$_8$S$_3$) were treated as stoichiometric compounds.

2.2.5. Ternary compounds

  In this study, three ternary phases are considered. First, the solubility of Fe in the TiS phase has
been reported from experiments [17-19]. This phase was denoted as (Fe,Ti)S in this work. The Gibbs
energy of this phase was expressed using a two-sublattice model, in which the Fe atoms were
substituted with Ti. Furthermore, the solubility of this phase has been experimentally observed [45]
on the S-rich side in Fe–S systems and on the S-poor side in Ti–S systems. Therefore, vacancies are
considered for the two sublattices, and the Gibbs energy was modeled using the formula

$(Fe_{y_{Fe}^{(1)}}, Ti_{y_{Ti}^{(1)}}, Va_{y_{Va}^{(1)}})(S_{y_S^{(2)}}, Va_{y_{Va}^{(2)}})$ in the present study. The molar Gibbs energy of (Fe,Ti)S was described using the following equation:

$$
\begin{aligned}
G_m^{(Fe,Ti)S} =\ & y_{Fe}^{(1)}(y_S^{(2)} {}^\circ G_{Fe:S}^{(Fe,Ti)S} + y_{Fe}^{(1)} {}^\circ G_{Fe:Va}^{(Fe,Ti)S}) + y_{Ti}^{(1)}(y_S^{(2)} {}^\circ G_{Ti:S}^{(Fe,Ti)S} + y_{Va}^{(2)} {}^\circ G_{Ti:Va}^{(Fe,Ti)S}) \\
& + y_{Va}^{(1)}(y_S^{(2)} {}^\circ G_{Va:S}^{(Fe,Ti)S} + y_{Va}^{(2)} {}^\circ G_{Va:Va}^{(Fe,Ti)S}) \\
& + RT\left(y_{Fe}^{(1)} \ln y_{Fe}^{(1)} + y_{Ti}^{(1)} \ln y_{Ti}^{(1)} + y_{Va}^{(1)} \ln y_{Va}^{(1)} + y_S^{(2)} \ln y_S^{(2)} + y_{Va}^{(2)} \ln y_{Va}^{(2)}\right) \\
& + y_{Fe}^{(1)} y_{Ti}^{(1)}(y_S^{(2)} L_{Fe,Ti:S}^{(Fe,Ti)S} + y_{Va}^{(2)} L_{Fe,Ti:Va}^{(Fe,Ti)S}) + y_{Fe}^{(1)} y_{Va}^{(1)}(y_{Va}^{(2)} L_{Fe,Va:Va}^{(Fe,Ti)S} + y_S^{(2)} L_{Fe,Va:S}^{(Fe,Ti)S}) \\
& + y_{Ti}^{(1)} y_{Va}^{(1)}(y_S^{(2)} L_{Ti,Va:S}^{(Fe,Ti)S} + y_{Va}^{(2)} L_{Ti,Va:Va}^{(Fe,Ti)S}) \\
& + y_{Fe}^{(1)} y_{Ti}^{(1)} y_{Va}^{(1)}(y_S^{(2)} L_{Fe,Ti,Va:S}^{(Fe,Ti)S} + y_{Va}^{(2)} L_{Fe,Ti,Va:Va}^{(Fe,Ti)S}) + y_S^{(2)} y_{Va}^{(2)}(y_{Fe}^{(1)} L_{Fe:S,Va}^{(Fe,Ti)S} + y_{Ti}^{(1)} L_{Ti:S,Va}^{(Fe,Ti)S} + y_{Va}^{(1)} L_{Va:S,Va}^{(Fe,Ti)S}) \\
& + y_{Fe}^{(1)} y_{Ti}^{(1)} y_{Va}^{(1)} y_S^{(2)} y_{Va}^{(2)} L_{Fe,Ti,Va:S,Va}^{(Fe,Ti)S}
\end{aligned}
$$

(22)

The terms $y_i^{(1)}$ and $y_i^{(2)}$ are the site fractions of element i on the first and second sublattice, respectively. For example, the parameter $L_{i,j:k}^{(Fe,Ti)S}$ denotes the interaction energy between dissimilar atoms in the first sublattice. The interaction parameters vary with the composition as a polynominal expansion. For example, $L_{Fe,Ti:S}^{(Fe,Ti)S}$ is expressed as

$$
L_{Fe,Ti:S}^{(Fe,Ti)S} = {}^0 L_{Fe,Ti:S}^{(Fe,Ti)S} + (y_{Fe}^{(1)} - y_{Ti}^{(1)})\, {}^1 L_{Fe,Ti:S}^{(Fe,Ti)S}
$$

(23)

A similar compositional dependency was introduced in $L_{Fe,Va:S}^{(Fe,Ti)S}$ and $L_{Va:S,Va}^{(Fe,Ti)S}$. $L_{Fe:S,Va}^{(Fe,Ti)S}$, $L_{Fe,Va:Va}^{(Fe,Ti)S}$, $L_{Ti,Va:S}^{(Fe,Ti)S}$, and $L_{Ti:Va,S}^{(Fe,Ti)S}$ were assumed to be independent of composition.

In this system, other ternary compounds, $Fe_{0.5}TiS_2$ [46], $FeTi_2S_4$ [47], and $FeTi_4S_8$ [48], have been reported. For example, the crystal structures of $Fe_{0.5}TiS_2$ are compared to the crystal structures of (Fe,Ti)S in Figs. 2(a) and (b). We can see the similarity in the crystal structure between the two materials. The structure parameters of $Fe_{0.5}TiS_2$, TiS_2 [49] and TiS [50] are shown in Table 1. In $Fe_{0.5}TiS_2$, Fe and Ti occupy one site of the metallic sites of (Fe,Ti)S. The vacancies were introduced on Fe sites with a site occupation of 0.5. Therefore, the $Fe_{0.5}TiS_2$ structure can be considered as the ordered structure of the (Fe,Ti)S structure, where Fe and Ti occupy random metal sites. $FeTi_2S_4$ and

FeTi$_4$S$_8$ are also ordered structures of the (Fe,Ti)S structure. These phases were treated as individual (Fe,Ti)S$_2$ phases in this work. In addition, Fig. 2(c) shows that the crystal structure of TiS$_2$ is almost identical to the Fe$_{0.5}$TiS$_2$ structure as if the site occupation of Fe is 0. Therefore, the binary compound TiS$_2$ is also described as the same (Fe,Ti)S$_2$ phase. As a result, the three-sublattice model denoted by $(\text{Fe}_{y_{\text{Fe}}^{(1)}}, \text{Va}_{y_{\text{Va}}^{(1)}})(\text{S}_{y_{\text{S}}^{(2)}}, \text{Va}_{y_{\text{Va}}^{(2)}})_2(\text{Ti}_{y_{\text{Ti}}^{(3)}}, \text{Va}_{y_{\text{Va}}^{(3)}})$ was applied to this phase.

Another FeTi$_3$S$_6$ has been reported as a stoichiometric compound [51], but the substitution between Fe and Ti was considered, and the four-sublattice model denoted by

$(\text{Fe}_{y_{\text{Fe}}^{(1)}}, \text{Ti}_{y_{\text{Ti}}^{(1)}})_2 \text{S}_{12} (\text{Fe}_{y_{\text{Fe}}^{(3)}}, \text{Ti}_{y_{\text{Ti}}^{(3)}})_4 (\text{Fe}_{y_{\text{Fe}}^{(4)}}, \text{Ti}_{y_{\text{Ti}}^{(4)}})_2$ was applied to this phase. The ratio between metal and sulfur is 2:3 with respect to this thermodynamic model and this phase was described as (Fe,Ti)$_2$S$_3$ in this work.

3. Results and discussion

3.1. Fe–Ti and Fe–S binary systems

Most of the descriptions of the lattice stability parameters for each pure element were obtained from the Scientific Group Thermodata Europe (SGTE) data [52] and are shown in Table 2. The lattice stability of HCP-sulfur is not present in the SGTE data. Wang *et al.* have calculated the lattice stability of HCP-sulfur, which was referenced to FCC-sulfur by first-principles calculation [53]. Therefore, the formation energy was used to add the lattice stability of FCC-sulfur in this work.

The Fe–Ti binary system is composed of the liquid (L), BCC, FCC, Fe_2Ti, FeTi, and HCP phases. A thermodynamic analysis of this binary system has been performed by Kumar *et al.* [44], and these results were used in our study. The adopted thermodynamic description is shown in Table 3, and the calculated Fe–Ti binary phase diagram is shown in Fig. 3(a). The Fe–S binary system is composed of the liquid (L), BCC, FCC, FeS, FeS_2, and orthorhombic and monoclinic S phases. In this study, the thermodynamic parameters assessed by Lee [54] were adopted and are listed in Table 3. The calculated Fe–S binary phase diagram is shown in Fig. 3(b).

3.2. Ti–S binary system

According to Fig. 1, the Ti–S binary system is composed of the liquid (L), BCC, and HCP phases, NiAs-type hexagonal TiS, Ti_6S, Ti_3S, Ti_2S, Ti_8S_9, Ti_8S_{10}, $Ti_{16}S_{21}$, TiS_2, and TiS_3. Murray suggested that the phase denoted as "polytypes" at around 60 mol% S consists of several metastable sulfides. The polytypes, $Ti_{16}S_{21}$, Ti_6S, and Ti_3S were excluded from consideration in this thermodynamic analysis because details of the constituent phase, space groups of these sulfides, and melting points have not been confirmed. Ti_8S_3 has a composition close to that of Ti_3S and the crystal structure of this sulfide has been determined [55]. Therefore, Ti_8S_3, instead of Ti_3S is considered in this work.

The formation enthalpies of these sulfides were assessed by using first-principles calculations. The enthalpies of formation and the lattice parameters of the sulfides in this binary system were evaluated using the first-principles calculations listed in Table 4. For the enthalpies of formation, the HCP and gas phases were used as the reference state of Ti and S [56], respectively. The experimental values of several sulfides are also described in Table 4. For Ti_2S, the enthalpy of formation was predicted by the other enthalpies of sulfides [11]. For TiS, several experimental values were reported by the sulfur activity measurement [12], a development of Pauling's electronegativity rules [13] and mass spectrometry studies [14]. For TiS_2, the experimental formation enthalpies have been estimated by combustion calorimetry [15] and partial pressure measurement of S_2 [16]. For TiS_3, the combustion calorimetric value reported by [15]. Our calculated enthalpies lie within reasonable agreement with the experimental values.

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Furthermore, to obtain the Gibbs energies, including the contribution of the lattice vibration, the isobaric specific heat of sulfides was calculated by the Debye–Grüneisen model. Fig. 4 shows the isobaric specific heat of sulfides in the Ti–S system obtained by the Debye–Grüneisen model and the thermodynamic analysis. The results of the thermodynamic analysis are in good agreement with the results of the Debye–Grüneisen model.

For the Ti–S system, it is important to determine the Gibbs energy of solid solutions in order to examine the solubility more precisely. According to Murray's review, the maximum solubility of BCC and HCP is 0.01 mol% and 0.02 mol%, respectively. However, experimental values for the phase boundaries are not available; therefore, the experimental maximum solubility is insufficient for thermodynamic assessment. The Gibbs energies of solid solutions in HCP, BCC, and FCC were calculated using CEM and CVM.

The number of crystal structures based on HCP, BCC, and FCC, which were calculated by first principles calculations, was 151, 92, and 91, respectively. Fig. 5 shows the structure of (a) HCP, (b) BCC, and (c) FCC and the number of points for each cluster listed in Table 5. As shown in the table, clusters of an optimal set are composed of point, pair triangle, and four points for this binary system. To extract the values for ECIs, the enthalpies of formation were utilized to express the free energy of this binary system as given in Table 5.

The metastable FCC was included in this analysis because it is considered to have an effect on the phase equilibria between FCC and the sulfides in the Fe–Ti–S ternary system. Fig. 6 shows the energies of the (a) HCP, (b) BCC, and (c) FCC phases calculated by CVM and thermodynamic analysis. The results of the thermodynamic analysis are in good agreement with the CVM results. The Gibbs energies of the solid solutions at finite temperatures were obtained.

Fig. 7 shows the calculated phase diagram as compared to the experimental data of Eremenko *et al.* [8], which is the basis of Murray's phase diagram. The calculated phase diagram is in good agreement with the experimental results for the Ti-rich side. The phase equilibria in the S-rich side have not been determined experimentally because of the difficulty in performing the experiments. Phase decomposition of the liquid was found in the calculated Ti–S phase diagram. In metals and sulfur systems such as Fe–S, Cu–S, and Mn–S, binodal phase decomposition in liquid is often observed to result from short-range ordering. Hence, short-range ordering of the liquid phase is predicted although it has not been reported.

The solubility of the solid-solution phases was confirmed to be very small (Fig. 8), which shows the enlarged Ti-rich portion of the calculated Ti–S phase diagram. The solvus of BCC and HCP is smaller than that in Murray's report. The low solubility of the metal solid solutions has been observed in other metal and sulfur binary systems. In the Ti–S system, the low solubility is a result of the high stability of metal sulfides, i.e., Ti_8S_3. A compatible calculated phase diagram comparable

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to similar alloy systems can be constructed by evaluating the Gibbs energy based on theoretical calculations in an undetermined alloy system that has little experimental data on phase equilibria.

3.3. Fe–Ti–S ternary system

Formation energies of superstructures based on (Fe,Ti)S over the composition range FeS to TiS were calculated by first-principles calculations and their phase stabilities were assessed at finite temperatures by using CEM and CVM. To extract the values for the 15 ECIs shown in Table 6, 75 enthalpies of formation for the ordered structures were calculated. Fig. 9 shows the structure of (Fe,Ti)S and the number of points for each cluster listed in Table 6. As shown in the table, clusters of an optimal set are composed of point, pair triangle, and four points for this system.

Fig. 10 shows the free energies of (Fe,Ti)S at finite temperatures calculated by CVM; ECIs obtained by CEM were used in this calculation. For this system, isomorphic and phase-separating behavior around Fe and Ti, respectively, has been reported [17-19]. The calculated free energy curve is convex downward, which indicates the behavior of an isomorphic solid solution because of the attractive interaction between Fe and Ti in (Fe,Ti)S.

For the (Fe,Ti)S_2 phase, vacancies were introduced in both the Fe and Ti sites, and

$$(Fe_{y_{Fe}^{(1)}}, Va_{y_{Va}^{(1)}})(S_{y_S^{(2)}}, Va_{y_{Va}^{(2)}})_2(Ti_{y_{Ti}^{(3)}}, Va_{y_{Va}^{(3)}})$$ was used as a thermodynamic model. In order to assess

the formation enthalpy curve of this phase, the formation energies of superstructures of various compositions were calculated by first-principles calculations by changing the site occupation of Fe and Ti. The composition ranges in this ground-state analysis were between FeS$_2$ and FeTiS$_2$ and between FeTiS$_2$ and TiS$_2$. Table 7 shows the results of the ground-state analysis over these composition ranges. The results of the first-principles calculations and thermodynamic analysis are shown in Figs. 11(a) and (b), which show the composition ranges between FeS$_2$ and FeTiS$_2$ and between FeTiS$_2$ and TiS$_2$, respectively. The stability of this phase increases drastically from FeS$_2$ to TiS$_2$. $P\bar{3}m1$-FeS$_2$ is unstable compared to $Pa\bar{3}$-FeS$_2$, which is the equilibrium phase, and it is in good agreement with a previous thermodynamic analysis by Lee *et al*. [54] According to this calculation, both FeTi$_2$S$_4$ and FeTi$_4$S$_8$ belong to the $C2/m$ space groups, as stable phases. This result shows good agreement with the experimental observations that FeTi$_2$S$_4$ and FeTi$_4$S$_8$ have been reported to have $C2/m$ space groups [47,48].

For FeTi$_3$S$_6$, which has a $P6_322$ space group, ground-state analysis was performed by considering the substitution between Fe and Ti as the (Fe,Ti)$_2$S$_3$ phase. Figure 12 shows the assessed enthalpy of formation for the (Fe,Ti)$_2$S$_3$ phase as a solid line between Fe$_2$S$_3$ and Ti$_2$S$_3$. The white circles indicate the results of the ground-state analysis. Similar to (Fe,Ti)S$_2$, the formation enthalpy of this phase drastically decreases from Fe$_2$S$_3$ to Ti$_2$S$_3$. $P6_322$-Fe$_2$S$_3$ and $P6_322$-Ti$_2$S$_3$ behave as metastable phases

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in the calculated Fe–S and Ti–S binary phase diagrams, and good agreement with the experimental phase diagram is obtained.

The Fe–Ti–S ternary phase diagrams were calculated by using the above free energies of those phases. Fig. 13 (a) and (b) show the calculated isothermal section diagram of the Fe–Ti–S ternary system at 1273 K and the portion of this phase diagram near the composition of 50 mol% S, respectively. In Fig. 13 (b), the single phase of (Fe,Ti)S is the gray region. Experimental results by Mitsui *et al.* [17] show that the mono-sulfide in this system is a complete substitution between FeS and TiS. In the figure, (Fe,Ti)S is an isomorphic solid solution, and this thermodynamic analysis confirms the results by Mitsui *et al.* Mitsui *et al.* pointed out the effect of microsegregation during the solidification of samples in the experimental results by Kaneko *et al.* [18] and Vogel *et al.* [19] On the other hand, the good agreement with our calculated results indicates that the powder-synthesis method performed by Mitsui *et al.* is supposed to cause the system to be under equilibrium. The calculated results were compared in a vertical phase diagram of FeS and TiS, which is shown in Fig. 14. Experiments confirmed that (Fe,Ti)S is observed over a wide range of concentrations, and this is consistent with our calculated phase diagram, although the appearance of a small portion of secondary phases is also predicted. Around the TiS side, the calculated phase diagram shows the two-phase region of (Fe,Ti)S and Ti_8S_9. This is roughly consistent with the experimental results, denoted by the open circles. It should be noted that the solvus of the Ti-rich side of (FeTi)S is expanded by addition of Ti, which can be confirmed from the bottom line of the single (Fe,Ti)S in Fig. 13(b). That is why there is large single phase of (Fe,Ti)S at about 20–40 mol% Ti in Fig. 14.

Figure 15 shows the solubility products of TiS calculated using our thermodynamic database and experimental values. The experimental values vary widely depending on the influence of impurities, difference in the heat-treatment conditions and measurement of the deviation of the composition analysis. Our calculated result shows very a close gradient of the solubility product, in agreement with the reports of Yang *et al.* and Mitsui *et al.* To the best of our knowledge, the experimental solubility products of TiS have never been reproduced by calculation using the current thermodynamic database. The solubility product of TiS is described as $-\alpha_1/T + \alpha_2$, where $\alpha_1 \sim$

$$L_{\text{Fe,Ti}}^{\text{FCC}} + L_{\text{Fe,S}}^{\text{FCC}} - \Delta G_{\text{TiS}}^{f} \text{ and } \alpha_2 \sim \log(w_{\text{Ti}}w_{\text{S}}/w_{\text{Fe}}^2) + 2.$$ The term $\Delta G_{\text{TiS}}^{f}$ is the formation energy and w_i

is the atomic weight of the elements Fe, Ti, and S. Therefore, the thermodynamic parameters determined in this study only affect α_1, which is the gradient of the solubility product. Although the calculated solubility product against 10 000/T is slightly larger than the experimental values, the gradient of the solubility product seems to be consistent with the experimental results. We think the reason for the finite difference between the experimental and calculated value is the unavoidable experimental deviation of the atomic concentration, because even a very small difference of 0.01 mass% can cause the observed deviation. We can conclude that the thermodynamic parameters of

this study can reproduce the experimental solubility products of TiS reported by Yang *et al.* and Mitsui *et al.*

4. Conclusion

A thermodynamic analysis of the Fe-Ti-S ternary system was performed by incorporating first-principles calculations into the CALPHAD approach, yielding the following results.

(1) For the Ti-S binary system, CEM and CVM were performed on the BCC, FCC, and HCP solid solution. The calculated phase diagram is in good agreement with the experimental results for the Ti-rich side. Phase decomposition of the liquid was found in the calculated Ti–S phase diagram. The low solubility of the solid-solution phases was also revealed from this calculation.

(2) For the Fe-Ti-S ternary system, CEM and CVM were performed on the (Fe,Ti)S phase. The calculated free energy curve is convex downward, which indicates the behavior of an isomorphic solid solution due to the attractive interaction between Fe and Ti in (Fe,Ti)S. The thermodynamic analysis is consistent with the results reported by Mitsui *et al*., where the mono-sulfide forms complete substitution between FeS and TiS.

(3) The solubility products of TiS are calculated using our thermodynamic database. Although the calculated value is slightly larger than the experimental values, our result, especially its gradient against 10 000/T, seems to be consistent with the experimental results. The thermodynamic parameters of this study can reproduce the gradient of the experimental solubility products of TiS.

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Figure captions

Fig. 1. The experimental Ti–S binary phase diagram by Murray [10].

Fig. 2. The crystal structure of (a) $Fe_{0.5}Ti\,S_2$, (b) (Fe,Ti)S, and (c) TiS_2. Black and gray spheres indicate the sites of Ti and Fe, respectively.

Fig. 3. The calculated binary phase diagrams of the (a) Fe–Ti and (b) Fe–S systems.

Fig. 4. The isobaric specific heat of the sulfides (a) Ti_8S_3, (b) Ti_2S, (c) TiS, (d) TiS_2, and (e) TiS_3 in the Ti–S binary system obtained by the Debye–Grüneisen model and thermodynamic analysis.

Fig. 5. The crystal structures of (a) HCP, (b) BCC, and (c) FCC. The numbers denote atomic sites and correspond to the third column of Table 1. The gray spheres indicate the sites of Ti and S.

Fig. 6. The Gibbs energies of (a) HCP, (b) BCC, and (c) FCC phases at 1500 K obtained by CVM and thermodynamic analysis.

Fig. 7. The calculated Ti–S binary phase diagram with experimental data by Eremenko *et al.* [8]

Fig. 8. The Ti-rich portion of the calculated Ti–S binary phase diagram.

Fig. 9. The crystal structures of (Fe,Ti)S. The numbers denote atomic sites and correspond to Table 6. The black spheres indicate the Fe and Ti sites. The gray spheres show the S sites.

Fig. 10. The calculated free energy of the (Fe,Ti)S phase between FeS and TiS at several temperatures.

Fig. 11. The assessed enthalpy of formation for the $(Fe,Ti)S_2$ phase as a result of thermodynamic analysis.

Fig. 12. The enthalpy of formation for the $(Fe,Ti)_2S_3$ phase between Fe_2S_3 and Ti_2S_3.

Fig. 13. (a)The calculated isothermal section diagram of the Fe–Ti–S ternary system at 1273 K.
(b) The portion of the calculated Fe-Ti-S ternary phase diagram near the composition of 50 mol% S.

Fig. 14. The calculated vertical phase diagram between FeS and TiS with experimental results.

Fig. 15. The solubility products of the TiS phase with experimental results.

Table captions

Table 1. The lattice and structure parameters of $Fe_{0.5}TiS_2$, TiS_2, and TiS.

Table 2. The lattice stability parameters for Fe, Ti, and S.

Table 3. The thermodynamic parameters for the binary and ternary systems.

Table 4 The calculated thermodynamic and physical parameters of sulfide. The enthalpy of formation, HCP, and gas phase were dealt as the reference state of Ti and S [56].

Table 5. Effective cluster interaction for the multibody cluster with respect to HCP, BCC, and FCC in the Ti-S binary system. The site numbers correspond to the number denoted in Fig. 5.

Table 6. Effective cluster interaction for the multibody cluster with respect to $(Fe,Ti)S$. The site numbers correspond to the number denoted in Fig. 11.

Table 7. The results of ground state analysis of $(Fe,Ti)S_2$.

Table 1. The lattice and structure parameters of $Fe_{0.5}TiS_2$, TiS_2 and TiS.

Compound	Space group	Lattice parameters	Wyckoff position	x	y	z	Occ.
$Fe_{0.5}TiS_2$	$P\bar{3}m1$	$a = b = 0.3423$ nm	S(2d)	0.33333	0.66667	0.245	1
		$c = 0.5711$ nm	Fe(1b)	0	0	0.5	0.5
			Ti(1a)	0	0	0	1
TiS_2	$P\bar{3}m1$	$a = 0.341$ nm	S(2d)	0.33333	0.66667	0.25	1
		$c = 0.5705$ nm	Ti(1a)	0	0	0	1
TiS	$P6_3/mmc$	$a = 0.3305$ nm	S(2c)	0.33333	0.66667	0.25	1
		$c = 0.6360$ nm	Ti(2a)	0	0	0	1

Table 2. The lattice stability parameters for Fe,Ti, and S.

Species	Phase		Lattice stability parameters, J/mol	Temperature, K	Ref.
Fe					[52]
	L	$^\circ G_{Fe}^{L} - ^\circ G_{Fe:Va}^{BCC}$	$= 12040.17 - 6.55843T$ $-3.6751551 \times 10^{-21} T^7$	$298.15 < T < 1811$	
			$= -10839.7 + 291.302T - 46T \ln T$	$1811 < T < 6000$	
	BCC	$^\circ G_{Fe:Va}^{BCC} - ^\circ H_{Fe:Va}^{BCC}$	$= 1225.7 + 124.134T - 23.5143T \ln T$ $-4.39752 \times 10^{-3} T^2 - 5.8927 \times 10^{-8} T^3$ $+77359 T^{-1}$	$298.15 < T < 1811$	
			$= -25383.581 + 299.31255T$ $-46T \ln T + 2.29603 \times 10^{31} T^{-9}$	$1811 < T < 6000$	
			$T_c^{BCC} = 1043$, $\beta^{BCC} = 2.22$	$298.15 < T < 6000$	
	FCC	$^\circ G_{Fe:Va}^{FCC} - ^\circ G_{Fe:Va}^{BCC}$	$= -1462.4 + 8.282T$ $-1.15T \ln T + 6.4 \times 10^{-4} T^2$	$298.15 < T < 1811$	
			$= -27097.3963 + 300.252559T$ $-46T \ln T + 2.78854 \times 10^{31} T^{-9}$	$1811 < T < 6000$	
			$T_c^{FCC} = -201$, $\beta^{FCC} = -2.1$	$298.15 < T < 6000$	
	HCP	$^\circ G_{Fe:Va}^{HCP} - ^\circ G_{Fe:Va}^{BCC}$	$= -3705.78 + 12.591T - 1.15T \ln T$ $+6.4 \times 10^{-4} T^2$	$298.15 < T < 1811$	
			$= -3957.199 + 5.24951T$ $+4.9251 \times 10^{30} T^{-9}$	$1811 < T < 6000$	
Ti					[52]
	HCP	$^\circ G_{Ti}^{HCP} - ^\circ H_{Ti}^{HCP}$	$= -8059.921 + 133.615208T$ $-23.9933T \ln T + 4.777975 \times 10^{-3} T^2$ $-1.06716 \times 10^{-7} T^3 + 72636 T^{-1}$	$298.15 < T < 900$	
			$= -7811.815 + 132.988068T$ $-23.9887T \ln T + 4.2033 \times 10^{-3} T^2$ $-9.0876 \times 10^{-8} T^3 + 42680 T^{-1}$	$900 < T < 1155$	
			$= 908.837 + 66.976538T$ $-14.9466T \ln T - 8.1465 \times 10^{-3} T^2$ $+2.02715 \times 10^{-7} T^3 - 1477660 T^{-1}$	$1155 < T < 1941$	
			$= -124526.786 + 638.806871 \times T$ $-87.2182461T \ln T + 8.204849 \times 10^{-3} T^2$ $-3.04747 \times 10^{-7} T^3 + 36699805 T^{-1}$	$1941 < T < 4000$	

		- -	
		$= -1272.064 + 134.78618T$ $- 25.5768T \ln T - 6.63845 \times 10^{-4}T^2$ $- 2.788803 \times 10^{-7}T^3 + 7208T^{-1}$	$298.15 < T < 1155$
BCC	$^\circ G_{Ti,Va}^{BCC} - ^\circ H_{Ti}^{HCP}$	$= 6667.385 + 105.438379T$ $- 22.377T \ln T - 1.21707 \times 10^{-3}T^2$ $- 8.4534 \times 10^{-7}T^3 - 2002750T^{-1}$	$1155 < T < 1941$
		$= 26483.26 - 182.354471T$ $+ 19.0900905T \ln T - 2.200832 \times 10^{-2}T^2$ $+ 1.228863 \times 10^{-6}T^3 + 1400501T^{-1}$	$1941 < T < 4000$
FCC	$^\circ G_{Ti,Va}^{FCC} - ^\circ G_{Ti}^{HCP}$	$= 6000 - 0.1T$	$298.15 < T < 4000$

S			[52]
		$= -4196.575 + 85.63027T$ $- 17.413T \ln T - 0.000993935T^2$ $- 7.0062 \times 10^{-8}T^3 + 1250T^{-1}$	$298.15 < T < 335$
		$= 1790361.98 - 44195.4514T$ $+ 7511.61943T \ln T - 13.9855175T^2$ $+ 0.0048387386T^3 - 79880891T^{-1}$	$335 < T < 388.36$
		$= -876313.954 + 23366.873T$ $- 4028.756T \ln T + 7.954595T^2$ $- 0.002908851333T^3 + 33980035T^{-1}$	$338.36 < T < 432.25$
L	$^\circ G_S^L - ^\circ H_S^{Orthorhombic}$	$= 454088.687 - 7814.67023T$ $+ 1237.001T \ln T - 1.5607295T^2$ $+ 3.59883667 \times 10^{-4}T^3 - 31765395T^{-1}$	$432.25 < T < 500$
		$= 18554.561 - 144.895285T$ $+ 16.535T \ln T - 0.0454119T^2$ $+ 8.327402 \times 10^{-6}T^3 - 2705030T^{-1}$	$500 < T < 700$
		$= 21243.126 - 113.298877T$ $+ 9.944T \ln T - 0.0288384T^2$ $+ 3.791365 \times 10^{-6}T^3 - 3507570T^{-1}$	$700 < T < 900$
		$= 16117.849 - 32.79523T$ $- 2.425T \ln T - 0.01712545T^2$ $+ 1.84974 \times 10^{-6}T^3 - 3215170T^{-1}$	$900 < T < 1300$
		$= -6461.814 + 175.590536T - 32T \ln T$	$1300 < T < 1301$
Orthorhombic	$^\circ G_S^{Orthorhombic} - ^\circ H_S^{Orthorhombic}$	$= -5198.294 + 53.913855T$ $- 10.726T \ln T - 0.0273801T^2$ $+ 8.179537 \times 10^{-6}T^3$	$298.15 < T < 368.3$

		$= -6475.706 + 94.182332T$ $-17.8693298T \ln T$ $-0.010936877T^2$ $+1.406467 \times 10^{-6}T^3$ $+36871T^{-1}$	$368.3 < T < 1300$	
		$= -12485.546 + 188.304687T$ $-32T \ln T$	$1300 < T < 1301$	
BCC	$^\circ G_{\text{S:Va}}^{\text{BCC}} - {}^\circ H_{\text{S}}^{\text{Orthorhombic}}$	$= 99801.706 + 53.913855T$ $-10.726T \ln T - 0.0273801T^2$ $+8.179537 \times 10^{-6}T^3 + 105000$	$298.15 < T < 368.3$	
		$= 98524.294 + 94.182332T$ $-17.8693298T \ln T - 0.010936877T^2$ $+1.406467 \times 10^{-6}T^3 + 36871T^{-1}$ $+105000$	$368.3 < T < 1300$	
		$= +92514.454 + 188.304687T$ $-32T \ln T + 105000$	$1300 < T < 1301$	
FCC	$^\circ G_{\text{S:Va}}^{\text{FCC}} - {}^\circ H_{\text{S}}^{\text{Orthorhombic}}$	$= +99801.706 + 53.913855T$ $-10.726T \ln T - 0.0273801T^2$ $+8.179537 \times 10^{-6}T^3 + 105000$	$298.15 < T < 368.3$	
		$= +98524.294 + 94.182332T$ $-17.8693298T \ln T - 0.010936877T^2$ $+1.406467 \times 10^{-6}T^3$ $+36871T^{-1} + 105000$	$368.3 < T < 1300$	
		$= +92514.454 + 188.304687T$ $-32T \ln T + 105000$	$1300 < T < 1301$	
HCP	$^\circ G_{\text{S:Va}}^{\text{HCP}} - {}^\circ H_{\text{S}}^{\text{Orthorhombic}}$	$^\circ G_{\text{S:Va}}^{\gamma} - 43630$	$298.15 < T < 6000$	This work

Table 3. The thermodynamic parameters for the binary and ternary systems.

System	Phase and model	Thermodynamic parameters, J/mol of model	Temperature, K	Ref.
Fe-S	L:(Fe,FeS,S)	$^\circ G_{FeS}^L - {}^\circ G_{Fe}^L - {}^\circ G_S^L = -104225 - 1.479T$ $^0 L_{Fe,FeS}^L = 53879 - 23.1867T$ $^0 L_{FeS,S}^L = 48313 - 21.807T$ $^1 L_{FeS,S}^L = -72983 + 24.7145T$	$298.15 < T < 6000$	
	BCC:(Fe,S)	$^0 L_{Fe,S}^{BCC} = -119675 - 18.7201T$	$298.15 < T < 6000$	
	FCC:(Fe,S)	$^0 L_{Fe,S}^{FCC} = -108733 - 18T$	$298.15 < T < 6000$	
	(Fe,Ti)S: (Fe,Va)(S,Va)	$^\circ G_{Fe:S}^{(Fe,Ti)S} - {}^\circ G_{Fe:Va}^{BCC} - {}^\circ G_S^{Orthorhombic}$ $= -107518 - 18.19T + 1.78T \ln T$ $^\circ G_{Fe:Va}^{(Fe,Ti)S} - {}^\circ G_{Fe:Va}^{BCC} = 65000$ $^\circ G_{Va:S}^{(Fe,Ti)S} - {}^\circ G_S^{Orthorhombic} = 258600$ $^\circ G_{Va:Va}^{(Fe,Ti)S} = 1000000$ $^0 L_{Fe,Va:S}^{(Fe,Ti)S} = -409000 + 10T$ $^1 L_{Fe,Va:S}^{(Fe,Ti)S} = 60000 + 20T$ $^0 L_{FeS,Va}^{(Fe,Ti)S} = 100000$ $^0 L_{Va:S,Va}^{(Fe,Ti)S} = -407000 + 10T$ $^1 L_{Va:S,Va}^{(Fe,Ti)S} = 60000 + 20T$ $^0 L_{Fe,Va:Va}^{(Fe,Ti)S} = 100000$	$298.15 < T < 6000$	[54]
	FeS$_2$: (Fe)(S)$_2$	$^\circ G_{FeS:Va}^{FeS_2} - {}^\circ G_{Fe:Va}^{BCC} - 2{}^\circ G_S^{Orthorhombic}$ $= -177763 + 48.567T$	$298.15 < T < 6000$	
Fe-Ti	L:(Fe,Ti)	$^0 L_{Fe:Ti}^L = -67589 + 9.809T$ $^1 L_{Fe:Ti}^L = -4731$	$298.15 < T < 6000$	
	HCP:(Fe,Ti)	$^0 L_{Fe,Ti}^{HCP} = 15132 - 8.668T$	$298.15 < T < 6000$	
	BCC:(Fe,Ti)	$^0 L_{Fe,Ti}^{BCC} = -57943 + 14.954T$ $^1 L_{Fe,Ti}^{BCC} = -6059$	$298.15 < T < 6000$	
	FCC:(Fe,Ti)	$^0 L_{Fe,Ti}^{FCC} = -50304 + 5.487T$	$298.15 < T < 6000$	[44]
	Fe$_2$Ti:(Fe,Va)$_2$(Fe,Ti)$_4$(Fe)$_6$	$^\circ G_{Fe:Fe:Fe}^{Fe_2Ti} - 8{}^\circ G_{Fe}^{FCC} - 4{}^\circ G_{Fe}^{BCC} = 69869$ $^\circ G_{Va:Fe:Fe}^{Fe_2Ti} - 6{}^\circ G_{Fe}^{FCC} - 4{}^\circ G_{Fe}^{BCC} = 60724$ $^\circ G_{Fe:Ti:Fe}^{Fe_2Ti} - 8{}^\circ G_{Fe}^{FCC} - 4{}^\circ G_{Ti}^{HCP} = -429782$ $^\circ G_{Va:Ti:Fe}^{Fe_2Ti} - 6{}^\circ G_{Fe}^{FCC} - 4{}^\circ G_{Ti}^{HCP} = -356573$	$298.15 < T < 6000$	
	FeTi:(Fe)(Ti)	$^\circ G_{Fe:Ti}^{FeTi} - {}^\circ G_{Fe}^{BCC} - {}^\circ G_{Ti}^{HCP} = -53650 + 7.5T$	$298.15 < T < 6000$	
Ti-S	L:(Ti,S)	$^0 L_{Ti,S}^L = -180000 - 65T$ $^1 L_{Ti,S}^L = 100000 + 48T$	$298.15 < T < 6000$	This work

	$^2L^{\mathrm{L}}_{\mathrm{Ti,S}} = 445000 - 160T$	
	$^3L^{\mathrm{L}}_{\mathrm{Ti,S}} = 20000 - 15T$	
BCC:(Ti,S)	$^0L^{\mathrm{BCC}}_{\mathrm{Ti,S}} = -450000$ $^1L^{\mathrm{BCC}}_{\mathrm{Ti,S}} = -80000$ $^2L^{\mathrm{BCC}}_{\mathrm{Ti,S}} = 200000$	$298.15 < T < 6000$
HCP:(Ti,S)	$^0L^{\mathrm{HCP}}_{\mathrm{Ti,S}} = -370000$ $^0L^{\mathrm{HCP}}_{\mathrm{Ti,S}} = -115000$	$298.15 < T < 6000$
FCC:(Ti,S)	$^0L^{\mathrm{FCC}}_{\mathrm{Ti,S}} = -410000$ $^1L^{\mathrm{FCC}}_{\mathrm{Ti,S}} = -100000$ $^2L^{\mathrm{FCC}}_{\mathrm{Ti,S}} = 30000$	$298.15 < T < 6000$
$\mathrm{Ti_8S_3}$:$(\mathrm{Ti})_8(\mathrm{S})_3$	$^\circ G^{\mathrm{Ti_8S_3}}_{\mathrm{Ti:S}} - 8\,^\circ G^{\mathrm{HCP}}_{\mathrm{Ti:Va}} - 3\,^\circ G^{\mathrm{Orthorhombic}}_{\mathrm{S}}$ $= -960410 - 77T + 14.0591T\ln T$ $+ 3.68379\times10^{-2}T^2 - 1.78871\times10^{-6}T^3$	$298.15 < T < 6000$
$\mathrm{Ti_2S}$:$(\mathrm{Ti,Va})_2(\mathrm{S,Va})$	$^\circ G^{\mathrm{Ti_2S}}_{\mathrm{Ti:S}} - 2\,^\circ G^{\mathrm{HCP}}_{\mathrm{Ti:Va}} - ^\circ G^{\mathrm{Orthorhombic}}_{\mathrm{S}}$ $= -303980 + 4T + 1.0010T\ln T$ $+ 1.2143\times10^{-2}T^2 - 8.3354\times10^{-7}T^3$ $^\circ G^{\mathrm{Ti_2S}}_{\mathrm{Ti:Va}} - 2\,^\circ G^{\mathrm{HCP}}_{\mathrm{Ti:Va}} = 100000$ $^\circ G^{\mathrm{Ti_2S}}_{\mathrm{Va:S}} - ^\circ G^{\mathrm{Orthorhombic}}_{\mathrm{S}} = 170000 + 10T$ $^\circ G^{\mathrm{Ti_2S}}_{\mathrm{Va:Va}} = 300000$ $^0L^{\mathrm{Ti_2S}}_{\mathrm{Ti,Va:S}} = -450000 + 10T$ $^0L^{\mathrm{Ti_2S}}_{\mathrm{Ti:S,Va}} = -47000 - 60T$	$298.15 < T < 6000$
$(\mathrm{Fe,Ti})\mathrm{S}$:$(\mathrm{Ti,Va})(\mathrm{S,Va})$	$^\circ G^{\mathrm{(Fe,Ti)S}}_{\mathrm{Ti:S}} - ^\circ G^{\mathrm{HCP}}_{\mathrm{Ti:Va}} - ^\circ G^{\mathrm{Orthorhombic}}_{\mathrm{S}}$ $= -279121.17 + 14T + 0.8T\ln T$ $+ 6.6\times10^{-3}T^2 - 4.6\times10^{-7}T^3$ $^\circ G^{\mathrm{(Fe,Ti)S}}_{\mathrm{Ti:Va}} - ^\circ G^{\mathrm{HCP}}_{\mathrm{Ti:Va}} = 121418 + 30T$ $^\circ G^{\mathrm{(Fe,Ti)S}}_{\mathrm{Va:S}} - ^\circ G^{\mathrm{Orthorhombic}}_{\mathrm{S}} = 258600$ $^\circ G^{\mathrm{(Fe,Ti)S}}_{\mathrm{Va:Va}} = 1000000$ $^0L^{\mathrm{(Fe,Ti)S}}_{\mathrm{Ti,Va:S}} = -125000 - 45T$ $^0L^{\mathrm{(Fe,Ti)S}}_{\mathrm{Ti:Va,S}} = -125000 - 45T$ $^0L^{\mathrm{(Fe,Ti)S}}_{\mathrm{Va:S,Va}} = -409000 + 10T$ $^1L^{\mathrm{(Fe,Ti)S}}_{\mathrm{Va:S,Va}} = 60000 + 20T$	$298.15 < T < 6000$
$\mathrm{Ti_8S_9}$:$(\mathrm{Ti})_8(\mathrm{S})_9$	$^\circ G^{\mathrm{Ti_8S_9}}_{\mathrm{Ti:S}} - 8\,^\circ G^{\mathrm{HCP}}_{\mathrm{Ti:Va}} - 9\,^\circ G^{\mathrm{Orthorhombic}}_{\mathrm{S}}$ $= -2400000 + 272T$	$298.15 < T < 6000$
$\mathrm{Ti_8S_{10}}$:$(\mathrm{Ti})_8(\mathrm{S})_9$	$^\circ G^{\mathrm{Ti_8S_{10}}}_{\mathrm{Ti:S}} - 8\,^\circ G^{\mathrm{HCP}}_{\mathrm{Ti:Va}} - 10\,^\circ G^{\mathrm{Orthorhombic}}_{\mathrm{S}}$ $= -2490000 + 304.5T$	$298.15 < T < 6000$

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	(Fe,Ti)S$_2$: (Ti,Va)(S,Va)$_2$	$\circ G_{\text{Va:S:Ti}}^{(\text{Fe,Ti})\text{S}_2} - \circ G_{\text{Ti:Va}}^{\text{HCP}} - 2\circ G_{\text{S}}^{\text{Orthorhombic}}$ $= -340634.8 + 34T - 1.2376T\ln T$ $\quad + 12.836 \times 10^{-3} T^2 - 9.988 \times 10^{-7} T^3$ $\circ G_{\text{Va:Va:Ti}}^{(\text{Fe,Ti})\text{S}_2} - \circ G_{\text{Ti:Va}}^{\text{HCP}} = 400000 + 120T$ $\circ G_{\text{Va:S:Va}}^{(\text{Fe,Ti})\text{S}_2} - \circ G_{\text{S}}^{\text{Orthorhombic}} = 100000$ $^0 L_{\text{Va:S,Va:Ti}}^{(\text{Fe,Ti})\text{S}_2} = -800000$	$298.15 < T < 6000$
	TiS$_3$:(Ti)(S,Va)$_3$	$\circ G_{\text{Ti:S}}^{\text{TiS}_3} - \circ G_{\text{Ti:Va}}^{\text{HCP}} - 3\circ G_{\text{S}}^{\text{Orthorhombic}}$ $= -380204 + 84T - 3.2784T\ln T$ $\quad + 1.80908 \times 10^{-2} T^2 - 1.54316 \times 10^{-6} T^3$ $\circ G_{\text{Ti:Va}}^{\text{TiS}_3} - \circ G_{\text{Ti:Va}}^{\text{HCP}} = 40000$ $^0 L_{\text{Ti:S,Va}}^{\text{TiS}_3} = -80000$	$298.15 < T < 6000$
Fe-Ti-S	(Fe,Ti)S:(Fe,Ti,Va)(S,Va)	$^0 L_{\text{Fe,Ti:S}}^{(\text{Fe,Ti})\text{S}} = -45000 - 20T$ $^1 L_{\text{Fe,Ti:S}}^{(\text{Fe,Ti})\text{S}} = -20000$	$298.15 < T < 6000$
	(Fe,Ti)S$_2$:(Fe,Va)(S,Va)$_2$(Ti,Va)	$\circ G_{\text{Fe:S:Ti}}^{(\text{Fe,Ti})\text{S}_2} - \circ G_{\text{Fe:Va}}^{\text{BCC}} - \circ G_{\text{Ti:Va}}^{\text{HCP}} - 2\circ G_{\text{S}}^{\text{Orthorhombic}}$ $= -317783.784 + 60T$ $\circ G_{\text{Fe:S:Va}}^{(\text{Fe,Ti})\text{S}_2} - \circ G_{\text{Fe:Va}}^{\text{BCC}} - 2\circ G_{\text{S}}^{\text{Orthorhombic}}$ $= -68143.48 + 47.4T$ $\circ G_{\text{Fe:Va:Ti}}^{(\text{Fe,Ti})\text{S}_2} - \circ G_{\text{Fe:Va}}^{\text{BCC}} - 2\circ G_{\text{Ti:Va}}^{\text{HCP}} = 0$ $\circ G_{\text{Fe:Va:Va}}^{(\text{Fe,Ti})\text{S}_2} - \circ G_{\text{Fe:Va}}^{\text{BCC}} = 0$ $\circ G_{\text{Va:Va:Va}}^{(\text{Fe,Ti})\text{S}_2} = 100000$ $^0 L_{\text{Fe,Va:S:Ti}}^{(\text{Fe,Ti})_2\text{S}} = -33000$ $^0 L_{\text{Fe:S:Ti,Va}}^{(\text{Fe,Ti})_2\text{S}} = -31263.21$	$298.15 < T < 6000$
	(Fe,Ti)$_2$S$_3$:(Fe,Ti)(S)$_6$(Fe,Ti)$_2$(Fe,Ti)	$\circ G_{\text{Fe:S:Fe:Fe}}^{(\text{Fe,Ti})_2\text{S}_3} - 4\circ G_{\text{Fe:Va}}^{\text{BCC}} - 6\circ G_{\text{S}}^{\text{Orthorhombic}}$ $= -193319.05$ $\circ G_{\text{Ti:S:Fe:Fe}}^{(\text{Fe,Ti})_2\text{S}_3} - 3\circ G_{\text{Fe:Va}}^{\text{BCC}} - \circ G_{\text{Ti:Va}}^{\text{HCP}} - 6\circ G_{\text{S}}^{\text{Orthorhombic}} = 0$ $\circ G_{\text{Fe:S:Ti:Fe}}^{(\text{Fe,Ti})_2\text{S}_3} - \circ G_{\text{Fe:Va}}^{\text{BCC}} - \circ G_{\text{Ti:Va}}^{\text{HCP}} - 3\circ G_{\text{S}}^{\text{Orthorhombic}} = -157928 + 10T$ $\circ G_{\text{Ti:S:Ti:Fe}}^{(\text{Fe,Ti})_2\text{S}_3} - \circ G_{\text{Fe:Va}}^{\text{BCC}} - 3\circ G_{\text{Ti:Va}}^{\text{HCP}} - 6\circ G_{\text{S}}^{\text{Orthorhombic}} = 0$ $\circ G_{\text{Fe:S:Fe:Ti}}^{(\text{Fe,Ti})_2\text{S}_3} - 3\circ G_{\text{FeVa}}^{\text{BCC}} - \circ G_{\text{Ti:Va}}^{\text{HCP}} - 6\circ G_{\text{S}}^{\text{Orthorhombic}} = 0$ $\circ G_{\text{Ti:S:Fe:Ti}}^{(\text{Fe,Ti})_2\text{S}_3} - \circ G_{\text{Fe:Va}}^{\text{BCC}} - \circ G_{\text{Ti:Va}}^{\text{HCP}} - 3\circ G_{\text{S}}^{\text{Orthorhombic}} = 0$ $\circ G_{\text{Fe:S:Ti:Ti}}^{(\text{Fe,Ti})_2\text{S}_3} - \circ G_{\text{Fe:Va}}^{\text{BCC}} - 3\circ G_{\text{Ti:Va}}^{\text{HCP}} - 6\circ G_{\text{S}}^{\text{Orthorhombic}}$ $= -1105000 + 111T - 6.709T\ln T$ $\quad + 3.9812 \times 10^{-2} T^2 - 6.0360 \times 10^{-6} T^3$ $\circ G_{\text{Ti:S:Ti:Ti}}^{(\text{Fe,Ti})_2\text{S}_3} - 2\circ G_{\text{Ti:Va}}^{\text{HCP}} - 3\circ G_{\text{S}}^{\text{Orthorhombic}} = -626680 + 500T$	$298.15 < T < 6000$

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Table 4. The calculated thermodynamic and physical parameters of sulfide. About enthalpy of formation, the reference state of Ti and S were dealt with HCP and gas[56], respectively.

System	Compound	Space group	Optimized lattice parameter [Å]	Calculated enthalpy of formation [kJ/mol of atom]	Experimental enthalpy of formation [kJ/mol of atom]	Ref.
Ti-S	Ti_8S_3	*C 2 / m*	a=25.01 b=3.32 c=19.21 α=γ=90° β=122.8°	-91.43	-	-
	Ti_2S	*P n n m*	a=11.36 b=14.02 c=3.32 α=β=γ=90°	-110.9	-93.5±14.0	[11]
	TiS	*P 6 $_3$ / m m c*	a=b= 3.26 c=6.47 α=β=90° γ=120°	-146.3	-150.7±14.7 -165.3±20.9 -136.0±14.7	[12] [13] [14]
	TiS_2	*P$\bar{3}$m1*	a=b=3.41 c=6.24 α=β=90° γ=120°	-127.0	-142.3 -135.8±11.2	[15] [16]
	TiS_3	*P 2 $_1$ / m*	a=11.36 b=14.02 c=3.32 α=γ=90° β=97.1° α=β=90° γ=120°	-104.7	-107.5±8.4	[15]

Table5. Effective cluster interaction for the multibody cluster with respect to HCP, BCC and FCC in Ti-S binary system. The site numbers correspond to the number denoted in Fig. 5.

HCP			
N	type	site	ECI [meV/atom]
1	point	1	-4074.3
2	pair	1, 2	1269.3
3	pair	1, 3	1269.3
4	pair	2, 4	1087.5
5	pair	4, 5	1087.5
6	pair	1, 6	-219.9
7	pair	1, 7	-219.9
8	pair	4, 8	21.9
9	pair	1, 9	-147.1
10	pair	4, 10	-83.5
11	pair	4, 11	67.2
12	pair	4, 12	67.2
13	pair	4, 13	355.2
14	triangle	1, 2, 3	-796.8
15	triangle	1, 2, 6	289.6
16	triangle	1, 7, 14	289.6
17	triangle	1, 2, 15	-473.3
18	triangle	1, 6, 9	45.5
19	triangle	1, 7, 16	105.0
20	triangle	2, 4, 13	-302.1
21	triangle	1, 6, 11	28.6
22	triangle	1, 7, 17	28.6
23	triangle	2, 4, 8	78.3
24	triangle	1, 9, 15	452.6
25	triangle	1, 7, 18	520.9
26	triangle	4, 10, 12	218.5
27	four-point	1, 7, 18, 14	-660.0
28	four-point	1, 2, 3, 17	-142.8
29	four-point	1, 7, 16, 17	-133.8
BCC			
N	type	site	ECI [meV/atom]
1	point	1	-3232.4

N	type	site	ECI [meV/atom]
2	pair	1, 2	3417.9
3	pair	1, 3	-807.7
4	pair	1, 4	-204.5
5	pair	1, 5	-189.1
6	pair	1, 6	-38.3
7	triangle	1, 2, 3	-1086.7
8	triangle	1, 2, 4	1025.4
9	triangle	1, 2, 6	-838.6
10	triangle	1, 2, 5	1286.6
11	triangle	1, 4, 6	873.5
12	triangle	1, 5, 6	1342.7
13	triangle	1, 5, 7	402.9
14	triangle	1, 5, 8	-286.4
15	four-point	1, 2, 5, 6	-851.5
16	four-point	1, 3, 5, 7	-289.1
17	four-point	1, 3, 5, 6	-409.1
18	four-point	1, 5, 7, 9	-125.6

FCC

N	type	site	ECI [meV/atom]
1	point	1	-3726.7
2	pair	1, 2	4055.4
3	pair	1, 3	-1401.1
4	pair	1, 4	758.4
5	triangle	1, 2, 5	-427.4
6	triangle	1, 2, 3	1939.6
7	triangle	1, 2, 4	-1475.6
8	triangle	1, 3, 6	-397.5
9	triangle	1, 3, 7	717.8
10	triangle	1, 3, 8	314.2
11	triangle	1, 4, 9	414.9
12	triangle	1, 4, 10	335.2
13	four-point	1, 2, 5, 11	-317.1
14	four-point	1, 2, 5, 6	212.9
15	four-point	1, 2, 6, 12	79.6
16	four-point	1, 2, 3, 7	-96.4
17	four-point	1, 2, 4, 6	-365.6

18	four-point	1, 2, 3, 8	-415.5
19	four-point	1, 3, 5, 7	-504.1
20	four-point	1, 3, 6, 11	-151.0
21	four-point	1, 3, 4, 6	883.5
22	four-point	1, 3, 6, 7	-273.2
23	four-point	1, 2, 4, 9	-167.0
24	four-point	1, 3, 4, 11	464.9
25	four-point	1, 3, 4, 9	-275.9
26	four-point	1, 3, 4, 13	231.2
27	four-point	1, 3, 8, 13	77.2
28	four-point	1, 3, 4, 10	-277.1
29	four-point	1, 4, 6, 10	-195.4

Table6. Effective cluster interaction for the multibody cluster with respect to (Fe,Ti)S. The site numbers correspond to the number denoted in Fig. 11.

N	type	site	ECI [meV/atom]
1	point	1	-23.8
2	pair	1, 2	-330.2
3	pair	1, 3	-202.0
4	pair	1, 4	28.3
5	pair	1, 5	-27.3
6	triangle	1, 6, 7	7.8
7	triangle	1, 3, 4	1011.3
8	triangle	1, 2, 5	368.3
9	triangle	1, 7, 8	-497.5
10	triangle	1, 4, 9	35.9
11	four-point	1, 3, 4, 10	-170.0
12	four-point	1, 3, 6, 8	200.8
13	four-point	1, 6, 8, 11	20.8
14	four-point	1, 3, 4, 9	-874.7
15	four-point	1, 7, 8, 12	434.5

Table 7. The results of ground state analysis about $(Fe,Ti)S_2$.

Formula	Space group	Ti mol%	Energy (kJ/mol of atom)
FeS_2	$P\bar{3}m1$	0	-19.423
Fe_6TiS_{12}	$P\bar{1}$	5.2632	-38.183
Fe_2TiS_4	$C2/m$	14.286	-61.64
$Fe_6Ti_4S_{12}$	$R\bar{3}$	18.182	-68.811
$Fe_4Ti_3S_8$	$C2/m$	20	-71.242
$FeTiS_2$	$P\bar{3}m1$	25	-77.155
$Fe_8Ti_9S_{18}$	$R\bar{3}m$	25.714	-83.502
$Fe_6Ti_7S_{14}$	$P\bar{1}$	25.926	-84.632
$Fe_5Ti_6S_{12}$	$C2/m$	26.087	-86.554
$Fe_4Ti_5S_{10}$	$P\bar{1}$	26.316	-87.66
$Fe_6Ti_8S_{16}$	$P\bar{1}$	26.667	-89.97
$Fe_2Ti_3S_6$	$R\bar{3}$	27.273	-94.89
$Fe_4Ti_7S_{14}$	$P\bar{1}$	28	-98.315
$Fe_2Ti_4S_8$	$C2/m$	28.571	-102.52
$Fe_4Ti_9S_{18}$	$P\bar{1}$	29.032	-103.43
$FeTi_3S_6$	$R\bar{3}$	30	-108.23
$Fe_2Ti_7S_{14}$	$P\bar{1}$	30.435	-108.87
$FeTi_4S_8$	$C2/m$	30.769	-110.94
TiS_2	$P\bar{3}m1$	33.333	-113.52