Thermodynamic Description of the Gd-Sb and Gd-Bi-Sb Systems

Jinming Liu1,2*, Xiaoyang Chen2, Yinghui Zhang1, Ming Zhang1, Lan Zhang1, Tao Zhong1, Juan Lin1 and Caifang Cao3

1School of Material Science and Engineering, Jiangxi University of Science and Technology, Ganzhou, 341000, PR China
2Xingle Group Co. Ltd., Yueqing, Zhejiang, 325604, PR China
3School of Metallurgy and Chemical Engineering, Jiangxi University of Science and Technology, Ganzhou, 341000, PR China

*Corresponding author: Jinming Liu, School of Material Science and Engineering, Jiangxi University of Science and Technology, Ganzhou, 341000, PR China, Tel: +867978312191; E-mail: liujm2011@sina.com

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Abstract

The thermodynamic modeling and optimization of the Gd-Sb and Gd-Bi-Sb systems were critically carried out by means of the CALPHAD (CALculation of PHase Diagram) technique. The solution phases, liquid, bcc, rhomb and hcp(Gd) were described by the substitutional solution model. The compounds, β-Gd5(Bi, Sb)3, γ-Gd4(Bi, Sb)3, δ-Gd(Bi, Sb), δ'-Gd(Bi, Sb) and GdBi, were treated as the formulae (Gd)\textsubscript{m}/(Gd, Bi, Sb)\textsubscript{n} using two sublattice model in the Gd-Bi-Sb system. A self-consistent thermodynamic description of the Gd-Sb and Gd-Bi-Sb system were developed. The isothermal section at 300 K for the Gd-Bi-Sb system in the literature were reproduced in the present work.

Keywords: Gd-Bi-Sb system; Phase diagram; CALPHAD technique; Thermodynamic properties

Introduction

In past years, the advanced magnetic materials and its potential as an energy savings technology greatly stimulated the interest of researchers and promoted the rapid development of magnetic refrigeration. Magnetic refrigeration could be realized by utilizing the heat release or absorption caused by the magnetic entropy change DSM of a magnetic material due to a magnetic field change DH [1]. The recent discovery of the giant magnetocaloric effect in Gd5(Si2Ge2) [1], gave further impulse towards the development of new materials [2]. Gd4Sb3 was one of the candidates for magnetic refrigerant near room temperature (266 K). Substitution of Bi for Sb in Gd4Sb3 increased its Curie temperature T\textsubscript{c} up to 330 K [3]. The calculation of phase diagrams (CALPHAD) method, which was a powerful approach to save cost and short time during development of materials, effectively provided a clear guideline for material design. So in order to better understand the interactions of Gd and Sb with Bi and design high performance thermoelectric materials, it was important to study the thermochemical properties and the phase equilibria concerning the Gd-Bi-Sb system and to obtain the thermodynamic parameters of the system.

Binary Systems

To obtain a thermodynamic description of a ternary system, the thermodynamic description of each involved binary system was necessary.

Gd-Bi system

The partial phase diagram of the composition range 0–60 at % Bi of the Gd-Bi binary system was firstly measured by Gambino [4], and three intermetallics, GdBi, GdBi\textsubscript{2} and GdBi\textsubscript{3}, were reported in this system. In 1993, the phase diagram of the Gd-Bi system was re-determined and a new phase, GdBi\textsubscript{2}, was discovered [5]. The four intermetallics, GdBi, GdBi\textsubscript{2}, GdBi\textsubscript{3}, GdBi, and GdBi\textsubscript{4}, were reported in the Gd-Bi binary system. All of the information of the Gd-Bi binary system was accomplished by Wang et al. [6]. The Gd-Bi binary system was assessed by Wang et al. [6]. Figure 1 presented the calculated phase diagram of Gd-Bi system using the thermodynamic description of Wang et al. [6]. The thermodynamic parameters obtained by Wang et al. [6] were adopted in the present work.

Bi-Sb system

The Bi-Sb system was very simple and only two phases, liquid and...
rhomb(Bi, Sb) in this system, which was calculated by Dinsdale et al. [7]. The calculated thermodynamic parameters [7] were accepted in the assessment of the Bi-Sb-Sn system [8] and the Ag-Bi-Sb system [9]. So the thermodynamic parameters obtained by Dinsdale et al. [7] were adopted in the present work. Figure 2 presented the calculated phase diagram of Bi-Sb system using the thermodynamic description of Dinsdale et al. [7]. Figure 2a presented the Bi-Sb system reproduced using the Thermo-Calc software [10] and Figure 2b presented the Bi-Sb system reproduced using the Pandat software [11].

Gd-Sb system

The Gd-Sb system was firstly determined in the concentration range 0-60 at% Sb by Gambino [4]. Later, Gerasimov [12] updated all the invariant equilibria temperatures. The whole composition and temperature ranges in the Gd-Sb phase diagram were established by Abdusalyamova et al. [13]. The four intermediate compounds, Gd$_5$Sb$_3$, Gd$_4$Sb$_3$, Gd$_{16}$Sb$_{39}$, and GdSb were reported in this system. Recently, the previously called "GdSb$_2$" phase was determined to be Gd$_{16}$Sb$_{39}$ [14], which was confirmed in the Gd-Bi-Sb ternary system [15]. So the Gd-Sb phase diagram was revised by Borzone et al. [14]. All of the information of the Gd-Sb system was compiled by Li et al. [16]. The updated phase diagram was assessed by Li et al. [16]. The thermodynamic parameters of the Gd-Sb system were well reproduced [16], but the parameters of Bcc(Gd) were difficult to reproduce the temperature of the Bcc(Gd). In the present work, to assess the Gd-Bi-Sb ternary system, the model of the five intermediate compounds, Gd$_5$Sb$_3$, Gd$_4$Sb$_3$, Gd$_{16}$Sb$_{39}$, α-GdSb (GdSb-low temperature as GdSb-LT) and β-GdSb(GdSb-high temperature as GdSb-HT), was re-built to consistent with other thermodynamic parameters of the relative compounds in the Gd-Bi system [6]. So the thermodynamic parameters of the five intermediate compounds were re-assessed in the present work. Figure 3 presented the calculated phase diagram of Gd-Sb system using the thermodynamic parameters of the five intermediate compounds calculated in this work and the thermodynamic parameters of the liquid assessed by Li et al. [16].

Experimental Information on the Gd-Bi-Sb System

The information about the Gd-Bi-Sb system was very scarce. Recently, the phase diagram of the Gd-Bi-Sb ternary system had been determined at room temperature using X-ray powder diffraction and differential scanning calorimetry analysis by Jian et al. [15]. There were composed of six single-phase regions, six two-phase regions and one three-phase region. No ternary compound was reported in the Gd-Bi-Sb ternary system. The compounds, Gd$_5$Sb$_3$, Gd$_4$Sb$_3$, and GdSb (α-GdSb and β-GdSb) in the Gd-Sb system and their relative compounds, Gd$_5$Bi$_3$, Gd$_4$Bi$_3$, and GdBi in the Gd-Bi system were formed the continuous solid solutions, respectively. So the six single-phase regions are (Gd, Bi, Sb) solid solution (α phase), Gd$_5$(Bi, Sb), solid solution (β phase), Gd$_4$(Bi, Sb), solid solution (γ phase), Gd$_4$(Bi, Sb) solid solution (δ and
δ phases), Gd₆Ga₂₈ (ε phase) phase and Gd (Hcp phase) phase in the Gd-Bi-Sb system. The maximum solid solubility of Gd in (Gd, Bi, Sb) at room temperature was determined to be 7.5 at %. The solid solubility of Gd in the other phases could not be detected. The above information was described in detail in the Ref. [15].

**Thermodynamic Models**

**Unary phases**

The Gibbs energy function for the element \( i = \text{Gd, Bi, Sb} \) in the phase \( \varphi \) (\( \varphi = \text{liquid, hcp, rhomb} \)) was described as follows,

\[
G_i^\varphi(T) = \varphi_iG_i^\varphi(T) - H_i^\varphi^\text{SER}(298.15 K) = a + bT + cT \ln T + dT^2 + e T^3 + f T^{-1} + g T^{-2} + h T^{-3} \quad \text{(1)}
\]

Where \( H_i^\varphi^\text{SER} \) (298.15 K) was the molar enthalpy of the element \( i \) at 298.15 K in its standard element reference (SER) state, hcp for Gd, rhomb for Bi and Sb. The Gibbs energy of the element \( \varphi = \text{Gd, Bi, Sb} \), \( G_i^\varphi(T) \), in its SER state, was denoted by GHSER, i.e.,

\[
\text{GHSER}_i = \varphi_iG_i^\varphi(T) - H_i^\varphi^\text{SER}(298.15 K) \quad \text{(2)}
\]

In the present work, the Gibbs energy functions were taken from the SGTE(Scientific Group of Thermodata Europe) pure elements database compiled by Dinsdale [17] and listed in Table 1.

**Solution phases**

In the Gd-Bi-Sb system, there are three solution phases, liquid, hcp, and rhomb. Their molar Gibbs energies are described by the following expression:

\[
G^\varphi(T) = \varphi_iG_i^\varphi(T) + \varphi_{Gd,Bi,Sb}G_{Gd,Bi,Sb} + RT(\varphi_i\ln \varphi_i + \varphi_{Gd,Bi,Sb}\ln \varphi_{Gd,Bi,Sb}) + \left(\varphi_iG_i^\varphi(T) - H_i^\varphi^\text{SER}(298.15 K)\right) + \left(\varphi_{Gd,Bi,Sb}G_{Gd,Bi,Sb} - H_{Gd,Bi,Sb}^\text{SER}(298.15 K)\right)
\]

where \( R \) is the gas constant; \( \varphi_i \), \( \varphi_{Gd,Bi,Sb} \) and \( \varphi_{Gd:Bi,Sb} \) were the mole fractions of the pure elements Gd, Bi and Sb, respectively; \( \varphi_iG_i^\varphi(T) \) was the excess Gibbs energy, expressed by the Redlich–Kister polynomial [18].

\[
\varphi_iG_i^\varphi(T) = \sum_{j=1}^{N} \varphi_i \varphi_j G_{i,j}L_{i,j}(\varphi_j-\varphi_i)^{j-1}
\]

(3)

\[
G_{Gd,Bi,Sb} = \sum_{j=1}^{N} \varphi_{Gd,Bi,Sb} \varphi_j G_{Gd,Bi,Sb,j}L_{Gd,Bi,Sb,j}(\varphi_j-\varphi_{Gd,Bi,Sb})^{j-1}
\]

(4)

where \( L_{i,j} \), \( L_{Gd,Bi,Sb} \), and \( L_{Gd:Bi,Sb} \) were the binary interaction parameters between elements Gd and Bi, Gd and Sb, and Bi and Sb, respectively. Its general form was

\[
L_{i,j} = a_{ij} + b_{ij} T + c_{ij} T \ln T + d_{ij} T^2 + e_{ij} T^{-1}
\]

(5)

but in most case only the first one or two terms were used according to the temperature dependence of the experimental data. \( L_{Gd,Bi,Sb} \) was the ternary interaction parameter expressed as:

\[
L_{Gd,Bi,Sb} = x_{Gd}L_{Gd,Bi} + x_{Bi}L_{Bi,Sb} + x_{Sb}L_{Sb,Bi}
\]

(6)

where \( L_{Gd,Bi} \) and \( L_{Bi,Sb} \) were the parameters to be optimized in this work.

**Intermetallic compounds**

The compounds, Gd₆Bi₂₉, Gd₆Sb₂₉, and Gd₆Sb₁₈ (Gd₆Sb-high temperature named as Gd₆Sb-HT and Gd₆Sb-low temperature named as Gd₆Sb-LT) in the Gd-Sb system and their relative compounds, Gd₆Bi, Gd₆Bi₂₉, and Gd₆Sb in the Gd-Bi system were formed the continuous solid solutions, respectively. So the three continuous solid solutions single-phase (named as Gd₆(Bi, Sb)₂₉), β-Gd₆(Bi, Sb)₂₉, γ-Gd₆(Bi, Sb)₂₉, δ-Gd(Bi, Sb) and δ’-Gd(Bi, Sb) in the Gd-Bi-Sb system were treated as two-sublattice model (Gd₆(Bi, Sb)₂₉) and Gd₆(Sb)₂₉. In the Gd-Bi-Sb system, δ-Gd(Bi, Sb) and δ’-Gd(Bi, Sb) were the relative compounds, Gd₆Sb-high temperature (as Gd₆Sb-HT) and Gd₆Sb-low temperature (as Gd₆Sb-LT) in the Gd-Sb system. The Gibbs energy per mole of formula unit Gd₆(Bi, Sb)₂₉ was given by the following expression:

\[
G_{Gd,Bi,Sb}^\text{GdSb}(\varphi_i, \varphi_{Gd,Bi,Sb}) = \varphi_iG_{Gd,Bi,Sb}^\varphi(T) + \varphi_{Gd,Bi,Sb}G_{Gd,Bi,Sb}^\varphi(T) + \left(\varphi_iG_i^\varphi(T) - H_i^\varphi^\text{SER}(298.15 K)\right) + \left(\varphi_{Gd,Bi,Sb}G_{Gd,Bi,Sb} - H_{Gd,Bi,Sb}^\text{SER}(298.15 K)\right)
\]

(7)

The parameter \( \varphi_i \) was the site fractions of Bi or Sb (\( i = \text{Bi or Sb} \)) on the second sublattice; the parameter \( G_{Gd,Bi,Sb}^\text{GdSb}(\varphi_i, \varphi_{Gd,Bi,Sb}) \) represented the Gibbs energies of the compound Gd₆(Bi, Sb)₂₉ when the second sublattice was occupied by only one element Bi or Sb, respectively, which were relative to the enthalpies of pure rhomb for Bi and Sb in their SER state. \( L_{Gd,Bi,Sb} \) represented the jth interaction parameters \( j = 0 \) between the elements Bi or Sb on the second sublattice. The other binary intermetallic compounds, GdBi, Gd₆Bi₂₉ in the Gd-Bi and Gd-Sb system were treated as stoichiometric compounds, and were used as the two-sublattice model, which was consisted with the relative binary system [6, 16].

**Assessment procedure**

A general rule for selection of the adjustable parameters was that only those coefficients determined by the experimental values should be adjusted [19]. The assessment was carried out by means of the optimization module PARROT of the thermodynamic software Thermo-Calc [10], which could deal with various kinds of experimental information. A careful examination of thermodynamic descriptions of the Gd-Bi [6] and the Bi-Sb [7] systems were made. The thermodynamic optimization of the Gd-Bi and Gd-Bi-Sb system were carefully performed in this work. The thermodynamic parameters for the Gd-Bi-Sb system were optimized on the basis of the experimental information available in the experimental data. The thermodynamic parameters of liquid were taken from the assessed data [16]. The compounds, Gd₆Bi₂₉, Gd₆Sb₂₉, Gd₆Sb₁₈, a-GdSb and β-GdSb in the Gd-Sb system were assessed in the present work. The experimental results of Jian et al. [15] were given more weight during the process of optimization. The thermodynamic parameters for the Gd-Bi-Sb system were optimized on the basis of the experimental information available in the experimental data [15]. The experimental results of Jian et al. [15] were given more weight during the process of optimization. The thermodynamic parameters of liquid, bcc, rhomb and hcp in the Gd-Bi-Sb system, are obtained by a combination of the corresponding Gibbs energy functions from the assessments of the binary systems using Muggianu interpolation of binary terms [20]. The interaction parameters of the Gd-Bi and Bi-Sb system and the liquid of the Gd-Sb system were taken from the calculated data assessed by Wang et al. [6], Dinsdale et al. [7] and Li et al. [16]. The binary parameters of the compounds of the Gd-Bi-Sb system and the ternary parameters in the Gd-Bi-Sb system were optimized according to the experimental data [15].
| Phase      | Thermodynamic parameters                                                                 | Reference |
|------------|------------------------------------------------------------------------------------------|-----------|
| **Temperature (K)** | **GHSER**<sub>liq</sub>                                                                 | [17]      |
| 200–1300   | −11600.525 +151.1119487–32.501371ln(7)+0.028216257<sup>e</sup>                           |           |
|            | −1.081237×10<sup>−7</sup>T<sup>e</sup>+4213637<sup>e</sup>−1                                |           |
| 1300–1535  | −8106.163+115.9536057–27.459 7ln(7)                                                       |           |
|            | −2.761235×10<sup>−7</sup>T<sup>e</sup>–7.37325×10<sup>−7</sup>T<sup>e</sup>               |           |
| 1535–3600  | −125618.511+711.9941977–103.403757ln(7)                                                   |           |
|            | +0.0158179497–6.72548×10<sup>−7</sup>T<sup>e</sup>−30183452<sup>e</sup>−1                |           |
|            | **GHSER**<sub>bcc</sub>                                                                  | [17]      |
| 298.15–544.54 | −7817.776+128.4189257–28.40965297ln(7)+0.012338887<sup>e</sup>                      |           |
|            | −8.381598×10<sup>−7</sup>T<sup>e</sup>                                                   |           |
| 544.54–800  | +30208.022–393.6503517+51.85565927ln(7)−0.0753111637<sup>e</sup>                       |           |
|            | +1.3499885×10<sup>−7</sup>T<sup>e</sup>–3616168T<sup>e</sup>−1.66145×10<sup>−12</sup>T<sup>e</sup> |           |
| 800–1200   | −11045.664+182.5489717–35.982477ln(7)+0.00742667<sup>e</sup>                            |           |
|            | −1.048×10<sup>−7</sup>T+1.66145×10<sup>−12</sup>T<sup>e</sup>                           |           |
| 1200–3000  | −7581.312+124.7714477–27.19677ln(7)+1.66145×10<sup>−12</sup>T<sup>e</sup>             |           |
|            | **GHSER**<sub>SB</sub>                                                                  | [17]      |
| 298.15–903.78 | −9242.858+156.1546897–30.5130527ln(7)                                                   |           |
|            | +7.748768×10<sup>−7</sup>T–3.003415×10<sup>−7</sup>T+100625<sup>e</sup>−1               |           |
| 903.78–2000 | −11738.83+169.4858727−31.3877ln(7)+1616.8491024<sup>e</sup>                            |           |
| **liquid** | model: (Gd, Bi, Sb)<sub>i</sub>                                                           |           |
|            | **G**(liquid, Gd)<sup>e</sup>                                                             | [17]      |
| 200–1000   | +13557.615–8.6127277×GHSER<sub>liq</sub>                                                |           |
| 1000–1535  | +80721.646–609.7648757+74.8351133 7ln(7)−0.061538127<sup>e</sup>                         |           |
|            | +6.061728×10<sup>−7</sup>T–10325075T<sup>e</sup>−1                                       |           |
| 1535–3600  | −3485.133×182.1162587–37.1539 7ln(7)                                                    |           |
| **bcc**    | model: (Gd, Bi, Sb)<sub>i</sub>                                                           |           |
| 298.14–3000 | **G**(bcc, Gd)<sup>e</sup>                                                                 | [17]      |
| 200–1000   | +3572.065–2.3049977×GHSER<sub>liq</sub>                                                |           |
| 1000–1535  | +86079.486–747.9605077+95.1961984 7ln(7)−0.072542756T<sup>e</sup>                      |           |
\[
\begin{align*}
+7.116157 \times 10^{-7} T^7 - 12664161 T^6 \\
-14097.626 \times 10^{2} T^5 - 37.656 T^4 \\
+9.53751 \times 10^{-6} T^3 - 4.1967 \times 10^{-7} T^2 + 1107440 T^{-1}
\end{align*}
\]

\[
G_{\text{bcc, Bi}} = 298.14 - 3000 + 11297 - 13.9 T + G_{\text{HSER}}^{\text{Bi}}
\]

\[
G_{\text{bcc, Sb}} = 298.14 - 2000 + 19874 - 15.1 T + G_{\text{HSER}}^{\text{Sb}}
\]

This work

\[
0 \ fcc \ Gd,Sb = 267618.599 L = -
\]

This work

\[
G_{\text{hcp$_A$3}} \ model: (Gd, Bi, Sb)
\]

This work

\[
200 - 3600 G_{\text{hcp$_A$3, Gd}} = +G_{\text{HSER}}^{\text{Gd}}
\]

This work

\[
298.14 - 3000 G_{\text{hcp$_A$3, Bi}} = +9900 - 11.8 T + G_{\text{HSER}}^{\text{Bi}}
\]

This work

\[
298.14 - 2000 G_{\text{hcp$_A$3, Sb}} = +19874 - 13 T + G_{\text{HSER}}^{\text{Sb}}
\]

This work

\[
0 \ hcp_A3 \ Gd,Sb = 10150.0 \times 6.3000 T
\]

This work

\[
1 \ hcp_A3 \ Gd,Sb = 150
\]

This work

\[
0 \ hcp_A3 \ Gd,Bi,Sb = +
\]

This work

\[
1 \ hcp_A3 \ Gd,Bi,Sb = -2202320.0 - 20.03232 T
\]

This work

\[
2 \ hcp_A3 \ Gd,Bi,Sb = -2202320.0 - 20.03232 T
\]

This work

\[
B-Gd$_{(Bi, Sb)}$ \ model: (Gd)
\]

This work

\[
G_{Gd,Bi}^{\text{calc}} = +0.625 G_{\text{HSER}}^{\text{Gd}} + 0.375 G_{\text{HSER}}^{\text{Bi}}
\]

This work

\[
-75332.61 + 4.1 T
\]

This work

\[
G_{Gd,Sb}^{\text{calc}} = +0.625 G_{\text{HSER}}^{\text{Gd}} + 0.375 G_{\text{HSER}}^{\text{Sb}}
\]

This work

\[
-104159.14 + 3.1036 T
\]

This work

\[
0 \ Gd$_{(Bi, Sb)}$ = -100200.0
\]

This work

\[
G_{Gd$_{(Bi, Sb)}$} = +0.5714 \times G_{\text{HSER}}^{\text{Gd}} + 0.4286 \times G_{\text{HSER}}^{\text{Sb}}
\]

This work

\[
-383701.2 + 5.1 T
\]

This work

\[
G_{Gd$_{(Bi, Sb)}$} = +0.5714 \times G_{\text{HSER}}^{\text{Gd}} + 0.4286 \times G_{\text{HSER}}^{\text{Sb}}
\]

This work

\[
-118710.41 + 5.8351 T
\]

This work

\[
0 \ Gd$_{(Bi, Sb)}$ = -100200.0
\]

This work

\[
G_{\delta(GdBs-HT)} \ model: (Gd)_{\delta(GdBs-HT)}
\]

This work
**Table 1: Thermodynamic parameters of the Gd–Bi–Sb system (in J mole⁻¹ of the formula units).**

| Compound            | Temperature, K | ΔH    | References |
|---------------------|----------------|-------|------------|
| Gd₂Sb₂              | 300            | -110  | [16]       |
| Gd₂Sb₂              | 673            | -141.9| [23]       |
| Gd₂Sb₂              | 300            | -103.664| This work |
| Gd₂Sb₂              | 673            | -93.623| This work  |
| Gd₂Sb₂              | 300            | -116  | [16]       |
| Gd₂Sb₂              | 673            | -145.1| [23]       |
| Gd₂Sb₂              | 300            | -118.254| This work |
| Gd₂Sb₂              | 673            | -108.228| This work |
| Gd₂Sb₂              | 693            | -120  | [16]       |
| Gd₂Sb₂              | 300            | -131  | [25]       |
| Gd₂Sb₂              | 693            | -102.5| [21]       |
| Gd₂Sb₂-LT            | 300            | -118.994| This work |
| Gd₂Sb₂-LT            | 753            | -106.672| This work |
| Gd₂Sb₂-LT            | 693            | -108.429| This work |
| Gd₁₁₂Sb₂₃₄₀       | ≈753           | -137.1| [22]       |
| Gd₁₁₂Sb₂₃₄₀       | 300            | -78   | [16]       |
| Gd₁₁₂Sb₂₃₄₀       | 300            | -87.697| This work  |
| Gd₁₁₂Sb₂₃₄₀       | 803            | -73.972| This work  |
| Gd₁₁₂Sb₂₃₄₀       | 803            | -96   | [24]       |

*The nominal composition of Gd₂Sb₂ was determined by Borzone et al. [14] to be Gd₁₁₂Sb₂₃₄₀ (70.91% at %Sb). (under 300 K), the rhomb was broken down into two component parts rhomb1 and rhomb2, as shown in Figure 2b. So there was some different at the rhomb phase side from the experiment data [15].

**Conclusions**

The thermodynamic parameters in the Gd-Sb and Gd-Bi-Sb ternary system were critically evaluated from the experimental information available in the literature. A set of self-consistent thermodynamic...
| Reaction | T (K) | x(Sb) | Reference |
|----------|-------|-------|-----------|
| Liq. + bcc(Gd) → hcp(Gd) | 1505 | 0.065 | 0.025 | 0.02 | [13] |
| | 1501 | 0.058 | 0.0191 | 0.0183 | [16] |
| Liq. + hcp(Gd) → Gd₅Sb₁₃ | 1393 | 0.135 | 0.025 | 0.375 | [13] |
| | 1390 | 0.1018 | 0.4042 | 0.375 | [16] |
| Liq. + Gd₅Sb₁₃ → Gd₄Sb₃ | 1913 | 0.35 | 0.375 | 0.4286 | [13] |
| | 1917 | 0.3029 | 0.375 | 0.4286 | [16] |
| Liq. + Gd₄Sb₃ → βGdSb | 2043 | 0.389 | 0.4286 | 0.50 | [13] |
| | 2048 | 0.3517 | 0.4286 | 0.50 | [16] |
| Liq. → GdSb-HT | 2403 | 0.50 | 0.50 | - | [13] |
| | 2401 | 0.50 | 0.50 | - | [16] |
| GdSb-HT → GdSb-LT | 2113 | 0.50 | 0.50 | - | [13] |
| | 2113 | 0.50 | 0.50 | - | [16] |
| Liq. + GdSb-LT → Gd₁₆Sb₃₉ | 1053 | 0.958 | 0.7091 | 0.50 | [13] |
| | 1054 | 0.9665 | 0.709 | 0.50 | [16] |
| Liq. + GdₓSbₓ → rhomb | 897 | >0.99 | 0.7091 | 1.0 | [13] |
| | 903 | >0.99 | 0.709 | 1.0 | [16] |
| | 903 | 0.9984 | 0.709 | 1.0 | This work |

*The nominal composition of GdSb₂ was determined by Borzone et al. [14] to be GdₓSbₓ (70.91% at% Sb).

Table 3: Invariant reactions of the Gd–Sb system.

Figure 3: Calculated Gd-Sb phase diagram in the present work and using the parameters of liquid by Li et al. [16], and comparison with the experimental data [13].

Figure 4: Calculated enthalpies of formation at 300 K in the Gd-Sb system and comparison with the experimental data [14] and the calculated data [16]. The reference states for the elements were hcp for Gd and rhomb for Sb.

Figure 5: Calculated enthalpies of mixing of liquid at 6000 K in the Gd-Sb system. The reference states were liquid for Gd and Sb.

parameters describing the Gibbs energy of each individual phase as a function of composition and temperature was derived.

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Figure 6: Calculated isothermal section of the Gd-Bi-Sb system at 300 K by the present thermodynamic description and comparison with the experimental data [15].

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