Available online at www.sciencedirect.com
ScienceDirect
Journal of Nuclear Materials 374 (2008) 79–86
journal of nuclear materials
www.elsevier.com/locate/jnucmat

# Thermodynamic modeling of the Al–U and Co–U systems

J. Wang, X.J. Liu, C.P. Wang *

*Department of Materials Science and Engineering, College of Chemistry and Chemical Engineering, and Research Center of Materials Design and Applications, Xiamen University, Xiamen 361005, PR China*

Received 9 February 2007; accepted 19 June 2007

**Abstract**

The thermodynamic assessments of the Al–U and Co–U systems have been carried out by using the CALPHAD (Calculation of Phase Diagrams) method on the basis of the experimental data including thermodynamic properties and phase equilibria. Gibbs free energies of the solution phases were described by the subregular solution models with the Redlich–Kister equation, and those of the intermetallic compounds described by the sublattice models. A consistent set of thermodynamic parameters has been derived for describing the Gibbs free energies of each solution phase and intermetallic compounds in the Al–U and Co–U binary systems. The calculated phase diagrams and thermodynamic properties in the Al–U and Co–U systems are in good agreement with experimental data.
Published by Elsevier B.V.

## 1. Introduction

The magnetic and superconducting properties for uranium based metallic glasses have been studied by various researchers [1,2]; the cobalt acts as an important element to improve the superconducting and magnetic properties of U-based glasses material [3]. Research reactors are being operated world wide with Al–U system plate type fueled with aluminum alloy clad [4–6]. Aluminum is chosen because of its low parasitic thermal neutron absorption cross-section, low-cost, easy availability, easy fabricability, adequate mechanical properties and corrosion resistance to coolant water up to 100 °C [4]. In order to design new U-based alloys, the thermodynamic assessment of the Al–Co–U system is necessary.

The purpose of this work is to carry out the thermodynamic assessments of the Al–U and Co–U systems by means of the CALPHAD (Calculation of Phase Diagrams) method, in which the Gibbs free energy of each phase is described by a thermodynamic model. The thermodynamic parameters of each phase in the Al–U and Co–U systems are optimized according to the available experimental data of the thermodynamic properties and phase equilibria.

## 2. Thermodynamic models

### 2.1. Solution phases

The Gibbs free energies of the solution phases in M (M: Al or Co)-U system are described by the following expression:

$$G_m^{\phi} = {}^0G_{\mathrm{M}}^{\phi}x_{\mathrm{M}} + {}^0G_{\mathrm{U}}^{\phi}x_{\mathrm{U}} + RT(x_{\mathrm{M}}\ln x_{\mathrm{M}} + x_{\mathrm{U}}\ln x_{\mathrm{U}}) + {}^{\mathrm{E}}G^{\phi} + {}^{\mathrm{mg}}G^{\phi}, \tag{1}$$

where $G_i^{\phi}$ is the molar Gibbs free energy of pure element $i$ with the structure $\phi$ in a nonmagnetic state, which is taken from the compilation by Dinsdale [7], and the term ${}^{E}G^{\phi}$ is the excess energy, which is expressed in the Redlich-Kister polynomials [8] as:

$${}^{\mathrm{E}}G^{\phi} = x_{\mathrm{M}}x_{\mathrm{U}}\sum_{m=0}^{n} {}^{m}L_{\mathrm{M,U}}^{\phi}(x_{\mathrm{M}} - x_{\mathrm{U}})^m, \tag{2}$$

where ${}^{m}L_{\mathrm{M,U}}^{\phi}$ is the interaction energy between M (M: Al or Co) and U atoms, and expressed as:

$${}^{m}L_{\mathrm{M,U}}^{\phi} = a + bT, \tag{3}$$

---

* Corresponding author.
*E-mail address:* wangcp@xmu.edu.cn (C.P. Wang).

0022-3115/$ - see front matter Published by Elsevier B.V.
doi:10.1016/j.jnucmat.2007.06.023

the parameters of *a* and *b* are evaluated based on the experimental data in the present work.

In the Co–U system, the magnetic contribution to the Gibbs free energies of the fcc phase is considered because magnetic transformation occurs in the fcc phase. The term ${}^{mg}G^{\mathrm{fcc}}$ is expressed as follows [9]:

$$ {}^{\mathrm{mg}}G^{\mathrm{fcc}} = RT\ln(\beta^{\mathrm{fcc}}+1)f(\tau^{\mathrm{fcc}}), \tag{4}$$

where $\beta^{\mathrm{fcc}}$ is a quantity related to the total magnetic entropy, which in most cases is set to the Bohr magnetic moment per mole of atoms; $\tau^{\mathrm{fcc}}$ is defined as $T/T_c^{\mathrm{fcc}}$, and $T_c^{\mathrm{fcc}}$ is the critical temperature for magnetic ordering, $T_c^{\mathrm{fcc}}$ and $\beta^{\mathrm{fcc}}$ are described by the following expression:

$$T_c^{\mathrm{fcc}} = {}^0T^{\mathrm{fcc}}_{c,\mathrm{Co}}x_{\mathrm{Co}} + {}^0T^{\mathrm{fcc}}_{c,\mathrm{U}}x_{\mathrm{U}} \tag{5}$$

and

$$\beta^{\mathrm{fcc}} = {}^0\beta^{\mathrm{fcc}}_{\mathrm{Co}}x_{\mathrm{Co}} + {}^0\beta^{\mathrm{fcc}}_{\mathrm{U}}x_{\mathrm{U}}, \tag{6}$$

where ${}^0T^{\mathrm{fcc}}_{c,\mathrm{Co}}$ and ${}^0T^{\mathrm{fcc}}_{c,\mathrm{U}}$ are the curie temperatures for pure Co and U, and ${}^0\beta^{\mathrm{fcc}}_{\mathrm{Co}}$ and ${}^0\beta^{\mathrm{fcc}}_{\mathrm{U}}$ are the Bohr magnetic moments for Co and U, respectively. The $f(\tau^{\mathrm{fcc}})$ represents the polynomials obtained by Hillert and Jarl [9] as follows:

$$f(\tau^{\mathrm{fcc}}) = 1 - \frac{1}{D}\left[\frac{79\tau^{-1}}{140P} + \frac{474}{497}\left(\frac{1}{P}-1\right)\left(\frac{\tau^3}{6}+\frac{\tau^9}{135}+\frac{\tau^{15}}{600}\right)\right] \quad \text{for} \quad \tau \leqslant 1 \tag{7}$$

and

$$f(\tau^{\mathrm{fcc}}) = -\frac{1}{D}\left(\frac{\tau^{-5}}{10}+\frac{\tau^{-15}}{315}+\frac{\tau^{-25}}{1500}\right) \qquad \text{for} \quad \tau > 1, \tag{8}$$

where $D = \frac{518}{1125} + \frac{11692}{15975}\left(\frac{1}{P}-1\right)$, and $P$ is 0.28 for the fcc structure.

### 2.2. Stoichiometric intermetallic compounds

Intermetallic compounds of the $Al_2U$, $Al_3U$, $Co_{11}U_2$, $Co_4U$, $Co_3U$, CoU and $CoU_6$ in the Al–U and Co–U systems are treated as stoichiometric phases. The Gibbs free energy per mole of formula unit $(\mathrm{M})_m(\mathrm{U})_n$ (M: Al or Co) can be expressed by the two-sublatice model, as follows:

$$\Delta G_{\mathrm{f}}^{\mathrm{M}_m\mathrm{U}_n} = {}^0G_f^{\mathrm{M}_m\mathrm{U}_n} - m{}^0G_{\mathrm{A}}^{\mathrm{ref}} - n{}^0G_{\mathrm{B}}^{\mathrm{ref}} = a' + b'T, \tag{9}$$

where the $\Delta G_{\mathrm{f}}^{\mathrm{M}_m\mathrm{U}_n}$ denotes the standard Gibbs free energy of formation of the stoichiometric compound from the pure elements. The term ${}^0G_i^{\mathrm{ref}}$ is the molar Gibbs free energy of pure element *i* with its defined reference structure in a nonmagnetic state. The parameters $a'$ and $b'$ are evaluated in the present work.

### 2.3. Intermetallic compound with solubility

#### 2.3.1. Intermetallic compound $Co_2U$

The $Co_2U$ compound as a solubility phase which has fcc structure ($Cu_2Mg$ type), which was summarized by Pearson [10]. In the stoichiometric composition, Co and U atoms occupy the sites face center and cube corner sites respectively. With this information, the $Co_2U$ compound is modeled with the two-sublattice model $(\mathrm{Co,U})_{0.667}(\mathrm{Co,U})_{0.333}$, and the Gibbs free energy for the $Co_2U$ compound can be expressed by:

$$\begin{aligned} G^{\mathrm{Co_2U}} = {} & y^{\mathrm{I}}_{\mathrm{Co}}y^{\mathrm{II}}_{\mathrm{U}}{}^0G^{\mathrm{Co_2U}}_{\mathrm{Co:U}} + y^{\mathrm{I}}_{\mathrm{Co}}y^{\mathrm{II}}_{\mathrm{Co}}{}^0G^{\mathrm{Co_2U}}_{\mathrm{Co:Co}} + y^{\mathrm{I}}_{\mathrm{U}}y^{\mathrm{II}}_{\mathrm{Co}}{}^0G^{\mathrm{Co_2U}}_{\mathrm{U:Co}} \\ & + y^{\mathrm{I}}_{\mathrm{U}}y^{\mathrm{II}}_{\mathrm{U}}{}^0G^{\mathrm{Co_2U}}_{\mathrm{U:U}} + 0.667RT(y^{\mathrm{I}}_{\mathrm{Co}}\ln y^{\mathrm{I}}_{\mathrm{Co}} + y^{\mathrm{I}}_{\mathrm{U}}\ln y^{\mathrm{I}}_{\mathrm{U}}) \\ & + 0.333RT(y^{\mathrm{II}}_{\mathrm{Co}}\ln y^{\mathrm{II}}_{\mathrm{Co}} + y^{\mathrm{II}}_{\mathrm{U}}\ln y^{\mathrm{II}}_{\mathrm{U}}) \\ & + 0.667(y^{\mathrm{I}}_{\mathrm{Co}}y^{\mathrm{I}}_{\mathrm{U}}y^{\mathrm{II}}_{\mathrm{U}}L_{\mathrm{Co,U:U}} + y^{\mathrm{I}}_{\mathrm{Co}}y^{\mathrm{I}}_{\mathrm{U}}y^{\mathrm{II}}{}_{\mathrm{Co}}L_{\mathrm{Co,U:Co}}) \\ & + 0.333(y^{\mathrm{I}}_{\mathrm{U}}y^{\mathrm{II}}_{\mathrm{Co}}y^{\mathrm{II}}_{\mathrm{U}}L_{\mathrm{U:Co,U}} + y^{\mathrm{I}}_{\mathrm{Co}}y^{\mathrm{II}}_{\mathrm{Co}}y^{\mathrm{II}}_{\mathrm{U}}L_{\mathrm{Co:Co,U}}), \end{aligned} \tag{10}$$

where $y^{\mathrm{I}}_{*}$ and $y^{\mathrm{II}}_{*}$ are the site fractions of elements Co or U on the first and second sublattices, respectively. The ${}^0G^{\mathrm{Co_2U}}_{*:*}$ represent the Gibbs free energies of the $Co_2U$ compound when the first and second sublattices are occupied by element Co or U, respectively. The $L^{\phi}_{\mathrm{Co,U:*}}$ and $L^{\phi}_{\mathrm{*:Co,U}}$ are the interaction energy between Co and U atoms when the first and second sublattices are occupied by element Co or U respectively, and expressed as:

$$L^{\phi}_{\mathrm{Co,U:*}} = a'' + b''T \tag{11}$$

and

$$L^{\phi}_{\mathrm{*:Co,U}} = a''' + b'''T \tag{12}$$

The parameters $a''$, $b''$, $a'''$ and $b'''$ are evaluated in the present work.

#### 2.3.2. Intermetallic compound $Al_4U$

The $Al_4U$ compound as a solubility phase which has an orthorhombic structure [10]. In this assessment, the compound is modeled with the two-sublattice model $(\mathrm{Al})_{0.8}(\mathrm{Al,U})_{0.2}$. The molar Gibbs free energy of this compound is presented by the following equation:

$$\begin{aligned} G^{\mathrm{Al_4U}} = {} & y^{\mathrm{II}}_{\mathrm{U}}{}^0G^{\mathrm{Al_4U}}_{\mathrm{Al:U}} + y^{\mathrm{II}}_{\mathrm{Al}}{}^0G^{\mathrm{Al_4U}}_{\mathrm{Al:Al}} + 0.2RT(y^{\mathrm{II}}_{\mathrm{Al}}\ln y^{\mathrm{II}}_{\mathrm{Al}} \\ & + y^{\mathrm{II}}_{\mathrm{U}}\ln y^{\mathrm{II}}_{\mathrm{U}}) + 0.2y^{\mathrm{II}}_{\mathrm{Al}}y^{\mathrm{II}}_{\mathrm{U}}L_{\mathrm{AL:Al,U}}, \end{aligned} \tag{13}$$

where $y^{\mathrm{II}}_{\mathrm{Al}}$ and $y^{\mathrm{II}}_{\mathrm{U}}$ are respectively the site fractions of elements Al and U on the second sublattice. The ${}^0G^{\mathrm{Al_4U}}_{\mathrm{Al:*}}$ represents the Gibbs free energies of the $Al_4U$ compound when the first sublattice occupied by element Al and the second sublattice are occupied by element Al or U, respectively. The $L_{\mathrm{Al:Al,U}}$ is the interaction energies between Al and U atoms when the first sublattice is occupied by Al, and is expressed as:

$$L^{\phi}_{\mathrm{Al:Al,U}} = a'''' + b''''T \tag{14}$$

The pazrameters $a''''$ and $b''''$ are evaluated in this work.

## 3. Evaluation of the experimental data

### 3.1. The Al–U system

The phase diagram of the Al–U system was investigated by various researchers [11–18] by thermal analysis, X-ray diffraction, resistance, and metallographic methods. The phase equilibria in the U-rich portion was investigated by Gordon and Kaufamann [11], Cabane et al. [12], Straatman and Neumann [13]. Straatman and Neumann [13] estimated that the solubility of Al in the γ (U) phase is 4.7 at.% Al by extrapolating from the experimental data, and suggested a maximum solubility is between 3 and 6 at.% Al by extrapolating the boundary between the γ (U) and the γ (U) + $Al_2U$ phase fields.

The maximum solubility of Al in β (U) phase was estimated to be between 0.4 and 0.6 at.% Al at 758 °C, where the invariant reaction (γ (U) → β(U) + $Al_2U$) occurs [14,15]. Roy [16] reported that the maximum solid solubility of U in fcc (Al) is 0.007 at.% at 646 °C and less than 0.005 at.% at 350 °C.

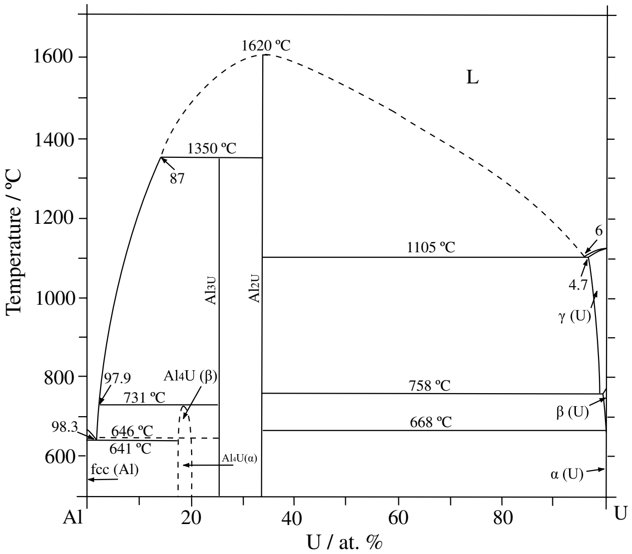

Fig. 1. The phase diagram of the Al–U system reviewed by Kassner et al. [19].

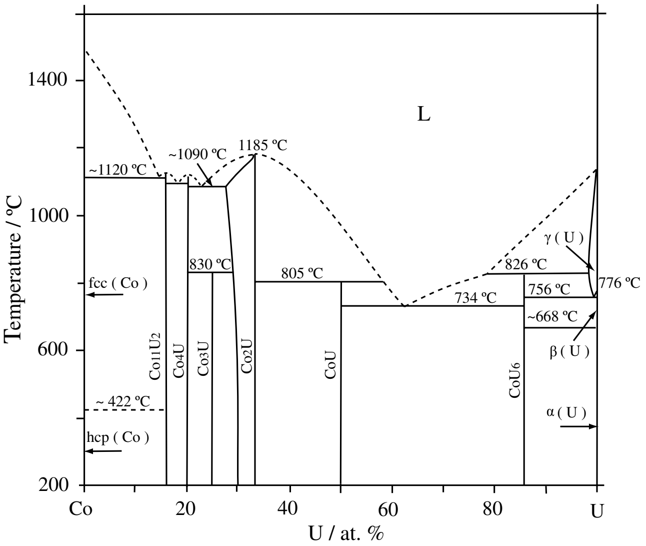

Fig. 2. The phase diagram of the Co–U system reviewed by Ishida and Nishizawa [21].

Gordon and Kaufman [11] and Bellot et al. [17] determined the eutectoid reaction (β (U) → α (U) + $Al_2U$) occurs between 645 °C and 675 °C by metallographic techniqued, and the average temperature 665 °C of was adopted in the reviewed diagram by Kassner et al. [19].

Petzow et al. [18] reported that the melting point of stoichiometric phase $Al_2U$ is 1620 °C, and Gordon and Kaufman [11] identified the stoichiometric $Al_3U$ phase, which forms by a peritectic reaction at 1350 °C. The homogeneity range for the compound $Al_4U$ is sbout from 80.0 to 82.8 at.% Al. Roy [16] determined that the maximum solid soubility of U in fcc (Al) is 0.007 at.% at 646 °C and less than 0.005 at 350 °C by metallographic technique.

The thermodynamic data was reviewed by Chiotti et al. [14] and Kassner et al. [19]. Lebedev et al. [20] measured the enthalpies and entropies of formation of the compounds at 627 °C by EMF measurements.

Based on the previous work, the phase diagram of the Al–U system was assessed by Kassner et al. [19], and the compiled diagram is shown in Fig. 1.

## 3.2. The Co–U system

The Co–U phase diagram was reviewed by Ishida and Nishizawa [21] as shown in Fig. 2, which is based primarily on the work of Waldron and Brown [22] and the reviewed data of Dreizler et al. [23]. However, the phase diagram of

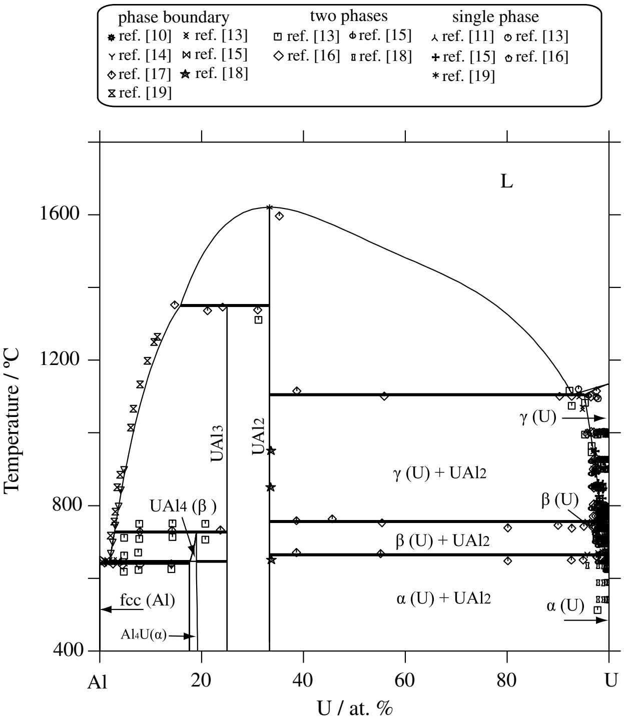

Fig. 3(a). Calculated phase diagram of Al–U system with experimental data [10,11,13–19].

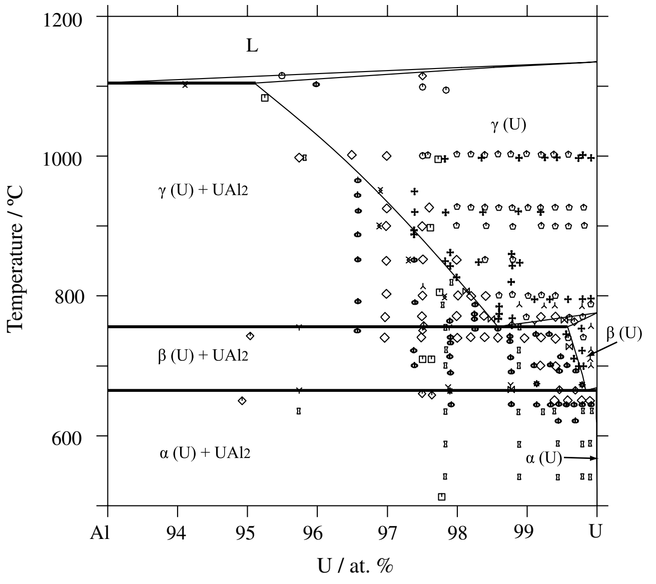

Fig. 3(b). Calculated phase diagram of Al–U system in the U-rich portion with experimental data [10,11,13–19].

the Co–U system is not well established, particularly for the liquidus line and phase equilibria in the Co-rich side. The liquidus line in the reviewed phase diagram is shown in dashed line due to a lack of experimental data. The congruent melting temperatures of the intermediate phases $Co_{11}U_2$ and $Co_4U$ were undetermined, which were respectively estimated to be 1130 °C and 1120 °C by Ishida and Nishizawa [21]. The compound $Co_3U$ is stable up to the peritectoid temperature of 830 °C, and the $Co_2U$ compound, with a homogeneity range from 27 to 33 at.% U is stable up to the congruent temperature of 1185 °C [23]. The solubility of U in the fcc (Co) and hcp (Co) phases can be neglected. The maximum solid solubility of Co in the $\gamma$ (U) phase is 1.6 at.%, and the solid solubility of Co in the $\beta$ (U) and $\alpha$ (U) phases can be neglected [21].

The magnetic properties of the $Co_2U$ compound were studied by Pletyushkin et al. [24] and Meskhishvili et al. [25]. The $Co_2U$ compound is paramagnetic, and the susceptibility is independent of temperature [25]. The $Co_{11}U_2$ compound is ferromagnetic, and the Curie temperature was reported to be 87 °C by Deryagin and Andreev [26] and 116 °C by Yermolenko et al. [27], respectively. The $CoU_6$ compound shows superconductivity below the transition temperature of about −271.6 °C [28,29]. The values of the $T_c$ and $\beta$ of these compounds are very small, so the magnetic contributions to their Gibbs free energies are ignored in this work.

Lebedev et al. [30] measured the enthalpies, entropies and Gibbs free energies of formation of the compounds $Co_{11}U_2$, $Co_4U$, $Co_3U$, $Co_2U$ and $CoU_6$ in the temperature range from 700 to 1000 °C by EMF measurements. Chiotti et al. [14] estimated the value of enthalpies, entropies and Gibbs free energies of formation of the CoU compound.

## 4. Optimized results and discussion

The optimization was carried out by using the PARROT [31] module in the Themo-Calc software [32]. The procedure involves a weighted least-square optimization of the model parameters based on the experimental information on thermodynamic properties and phase diagram.

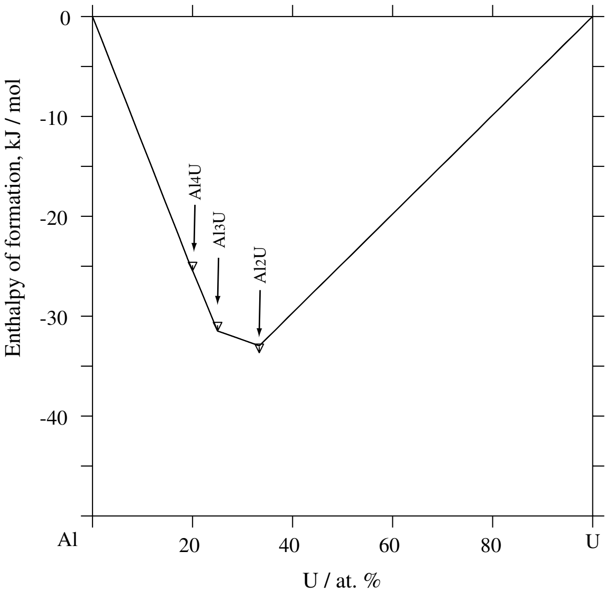

Fig. 4. Calculated enthalpy of formation of intermetallic compounds at 627 °C in the Al–U system compared with the experimental data [20]. (The reference states: $\gamma$ (U) phase and fcc (Al) phase.)

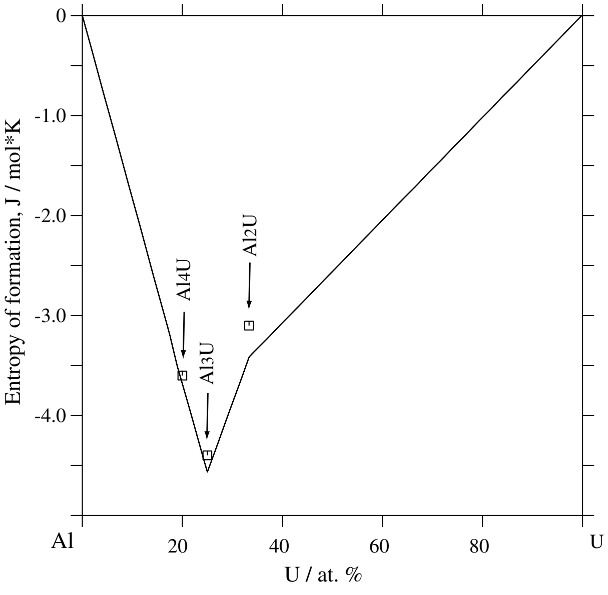

Fig. 5. Calculated entropy of formation of intermetallic compounds at 627 °C in the Al–U system compared with the experimental data [20]. (The reference states: $\gamma$ (U) phase and fcc (Al) phase.)

Each piece of selected information was given a certain weight according to the importance of data, and changed by trial and error during the assessment, until most of the selected experimental information is reproduced within the expected uncertainty limits. No experimental thermodynamic data for the liquid phase, and the optimized parameters of liquid phase were based on the liquid line and the experimental thermodynamic data of intermediate phases.

Table 1
Thermodynamic parameters in the Al–U and Co–U systems in this work

| System | Parameters in each phase (J/mol) |
|---|---|
| Al–U | Liquid phase, format (Al, U)<br>${}^{0}L^{\mathrm{Liq}}_{\mathrm{Al,U}} = -42\,716 + 12.376 * T$<br>${}^{1}L^{\mathrm{Liq}}_{\mathrm{Al,U}} = -66\,098 + 20.347 * T$<br>${}^{2}L^{\mathrm{Liq}}_{\mathrm{Al,U}} = -5000 - 8.656 * T$<br>γ (U) phase, format (Al, U)<br>${}^{0}L^{\gamma(\mathrm{U})}_{\mathrm{Al,U}} = -19\,247 + 6.023 * T$<br>β (U) phase, format (Al, U)<br>$G^{\beta(\mathrm{U})}_{\mathrm{Al}} = G^{\mathrm{fcc}}_{\mathrm{Al}} + 15\,000$<br>${}^{0}L^{\beta(\mathrm{U})}_{\mathrm{Al,U}} = 12\,438 - 23.626 * T$<br>α (U) phase, format (Al, U)<br>$G^{\alpha(\mathrm{U})}_{\mathrm{Al}} = G^{\mathrm{fcc}}_{\mathrm{Al}} + 15\,000$<br>$Al_2U$ phase, format $(\mathrm{Al})_{0.667}(\mathrm{U})_{0.333}$<br>$\Delta G^{\mathrm{Al_2U}}_{\mathrm{Al:U}} = -32966.7 + 3.4167 * T$<br>$Al_3U$ phase, format $(\mathrm{Al})_{0.75}(\mathrm{U})_{0.25}$<br>$\Delta G^{\mathrm{Al_3U}}_{\mathrm{Al:U}} = -31475.0 + 4.5663 * T$<br>$Al_4U$ ( β) phase, format $(\mathrm{Al})_{0.8}(\mathrm{Al,U})_{0.2}$<br>$G^{\mathrm{Al_4U}(\beta)}_{\mathrm{Al:U}} = 0.8 * G^{\mathrm{fcc}}_{\mathrm{Al}} + 0.2 * G^{\alpha(\mathrm{U})}_{\mathrm{U}} - 25200.0 + 3.5022 * T$<br>$G^{\mathrm{Al_4U}(\beta)}_{\mathrm{Al:Al}} = G^{\mathrm{fcc}}_{\mathrm{Al}} + 10\,000$<br>$L^{\mathrm{Al_4U}(\beta)}_{\mathrm{Al:Al,U}} = -2500 + 4.4574 * T$<br>$Al_4U$ ( α) phase, format $(\mathrm{Al})_{0.8}(\mathrm{Al,U})_{0.2}$<br>$G^{\mathrm{Al_4U}(\alpha)}_{\mathrm{Al:U}} = 0.8 * G^{\mathrm{fcc}}_{\mathrm{Al}} + 0.2 * G^{\alpha(\mathrm{U})}_{\mathrm{U}} - 25480.4 + 3.8072 * T$<br>$G^{\mathrm{Al_4U}(\alpha)}_{\mathrm{Al:Al}} = G^{\mathrm{fcc}}_{\mathrm{Al}} + 10\,000$<br>$L^{\mathrm{Al_4U}(\alpha)}_{\mathrm{Al:Al,U}} = -2500 + 4.4574 * T$ |
| U–Co | Liquid phase, format (Co, U)<br>${}^{0}L^{\mathrm{Liq}}_{\mathrm{Co,U}} = -16\,3347 + 39.880 * T$<br>${}^{1}L^{\mathrm{Liq}}_{\mathrm{Co,U}} = -79\,798 + 41.399 * T$<br>${}^{2}L^{\mathrm{Liq}}_{\mathrm{Co,U}} = 48\,002 - 21.715 * T$<br>γ (U) phase, format (Co, U)<br>${}^{0}L^{\gamma(\mathrm{U})}_{\mathrm{Co,U}} = -153882 + 88.309 * T$<br>β (U) phase, format (Co, U)<br>$G^{\beta(\mathrm{U})}_{\mathrm{Co}} = G^{\mathrm{hcp}}_{\mathrm{Co}} + 15\,000$<br>α (U) phase, format (Co, U)<br>$G^{\alpha(\mathrm{U})}_{\mathrm{Co}} = G^{\mathrm{hcp}}_{\mathrm{Co}} + 15\,000$<br>$CoU_6$ phase, format $(\mathrm{Co})_{0.143}(\mathrm{U})_{0.857}$<br>$\Delta G^{\mathrm{CoU_6}}_{\mathrm{Co:U}} = -46\,040 + 30.529 * T$<br>CoU phase, format $(\mathrm{Co})_{0.5}(\mathrm{U})_{0.5}$<br>$\Delta G^{\mathrm{CoU}}_{\mathrm{Co:U}} = -67\,772 + 31.744 * T$<br>$Co_2U$ phase, format $(\mathrm{Co,\ U})_{0.667}(\mathrm{Co,\ U})_{0.333}$<br>$G^{\mathrm{Co_2U}}_{\mathrm{Co:Co}} = G^{\mathrm{hcp}}_{\mathrm{Co}} + 30\,000$<br>$G^{\mathrm{Co_2U}}_{\mathrm{U:U}} = G^{\alpha}_{\mathrm{U}} + 30\,000$<br>$G^{\mathrm{Co_2U}}_{\mathrm{Co:U}} = 0.667 * G^{\mathrm{hcp}}_{\mathrm{Co}} + 0.333 * G^{\alpha(\mathrm{U})}_{\mathrm{U}} - 61\,256 + 20.404 * T$<br>$G^{\mathrm{Co_2U}}_{\mathrm{U:Co}} = 0.333 * G^{\mathrm{hcp}}_{\mathrm{Co}} + 0.667 * G^{\alpha(\mathrm{U})}_{\mathrm{U}} + 61\,256 - 20.404 * T$<br>$L^{\mathrm{Co_2U}}_{\mathrm{Co:Co,U}} = -66\,950 + 24.561 * T$<br>$Co_3U$ phase, format $(\mathrm{Co})_{0.75}(\mathrm{U})_{0.25}$<br>$\Delta G^{\mathrm{Co_3U}}_{\mathrm{Co:U}} = -53\,122 + 19.443 * T$<br>$Co_4U$ phase, format $(\mathrm{Co})_{0.80}(\mathrm{U})_{0.20}$<br>$\Delta G^{\mathrm{Co_4U}}_{\mathrm{Co:U}} = -43\,950 + 15.503 * T$<br>$Co_{11}U_2$ phase, format $(\mathrm{Co})_{0.846}(\mathrm{U})_{0.154}$<br>$\Delta G^{\mathrm{Co_{11}U_2}}_{\mathrm{Co:U}} = -35\,408 + 12.425 * T$ |

Table 2
Invariant reactions in the Al–U system

| Reaction type | Reaction | Al/at.% | | | T (°C) | Reference |
|---|---|---|---|---|---|---|
| Eutectic | L → fcc (Al) + $Al_4U$ (α) | 98.3 | 0.007 | 82.8 | 641 | [19] |
| | | 98.2 | 0 | 82.4 | 641 | [This work] |
| Eutectic | L → γ (U) + $Al_2U$ | 5–7 | 4.7 | 66.7 | 1105 | [13] |
| | | 6 | 4.7 | 66.7 | 1105 | [19] |
| | | 7.13 | 4.88 | 66.7 | 1105 | [This work] |
| Eutectoid | γ (U) → β (U) + $Al_2U$ | 1.4 | 0.54 | 66.7 | 750 | [13,15,16] |
| | | | | | 760 | |
| | | 1–1.6 | 0.4 | 66.7 | 758 | [19] |
| | | | 0.6 | | | |
| | | 1.41 | 0.40 | 66.7 | 756 | [This work] |
| Peritectic | L + $Al_3U$ → $Al_4U$ (β) | – | – | – | 732 | [12] |
| | | 97.7 | 75 | 81.8 | 731 | [19] |
| | | 97.2 | 75 | 81.4 | 731 | [This work] |
| Peritectic | L + $Al_2U$ → $Al_3U$ | 83.2 | 66.7 | 75 | 1350 | [12,13] |
| | | 87 | 66.7 | 75 | 1350 | [19] |
| | | 84.5 | 66.7 | 75 | 1351 | [This work] |
| Polymorphic | $Al_4U$ (α) → $Al_4U$ (β) | 80 | | | 646 | [19] |
| | | 82.8 | | | | |
| | | 80.9 | | | 646 | [This work] |
| | | 82.4 | | | | |
| Congruent | L → $Al_2U$ | 66.7 | | | 1590 | [12] |
| | | 66.7 | | | 1620 | [19] |
| | | 66.7 | | | 1620 | [This work] |

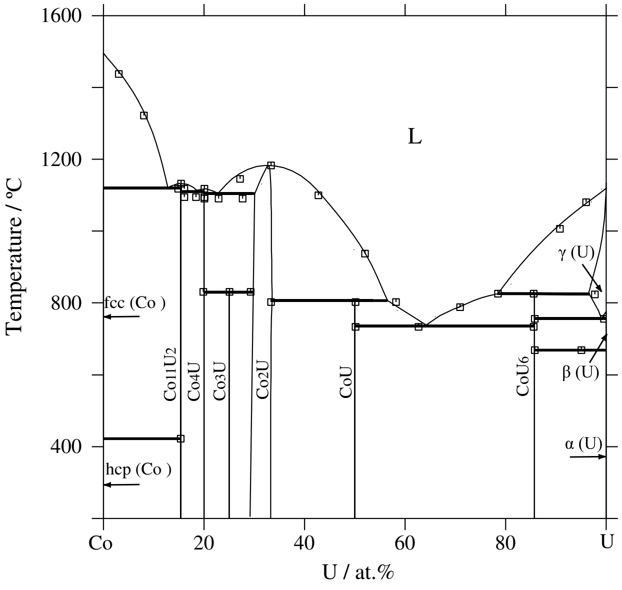

Fig. 6. Calculated phase diagram of Co–U binary system with experimental data [21].

### 4.1. The Al–U system

The calculated phase diagram in the Al–U system with all experimental data used in the present optimization is shown in Fig. 3(a), and the calculated result in the U-rich portion is shown in Fig. 3(b). In order to describe the polymorphic reaction of the $UAl_4$ (α) → $UAl_4$ (β), the same two-sublattice model, $(Al)_{0.8}(Al,U)_{0.2}$, was adopted to describe the compounds $UAl_4$ (α) and $UAl_4$ (β), respectively. The calculated transition temperature in this work is 646 °C, which is the same with the experimental data [19]. The calculated enthalpies and entropies of formation of the compounds with the experimental data at 627 °C are plotted in Figs. 4 and 5. All thermodynamic parameters optimized in the present work are listed in Table 1. All invariant equilibria in the Al–U system are summarized in Table 2. It is seen that the calculated results are in good agreement with the experimental data.

### 4.2. The Co–U system

The calculated phase diagram in the Co–U system is shown in Fig. 6, comparing with all experimental data used in the present optimization. It is seen from Fig. 6 that the calculated results are in agreement with the experimental data of phase diagram [21]. The calculated melting temperatures of the $Co_{11}U_2$and $Co_4U$ are respectively at 1125 °C and 1114 °C, which are closed to those estimated by Ishida and Nishizawa [21]. The thermodynamic parameters optimized in the present work are listed in Table 1, and all calculated invariant equilibria in the Co–U system are summarized in Table 2, in which the experimental data is also listed for comparison [21].

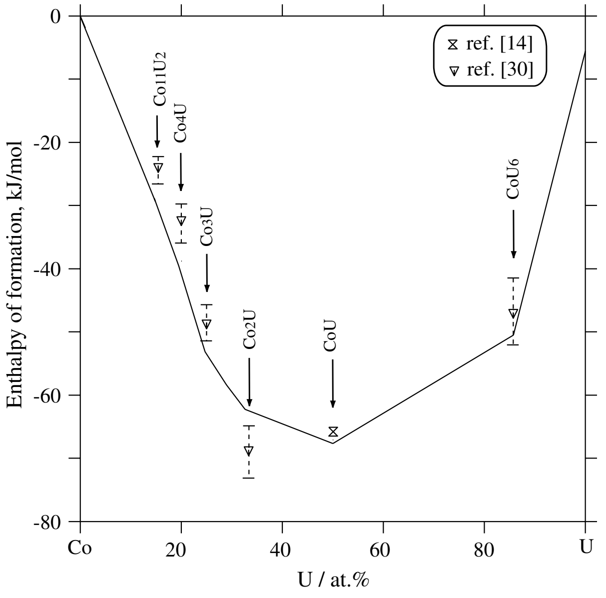

Fig. 7. Calculated enthalpies of formation of intermetallic compounds at 727 °C in the Co–U sysetm compared with the experimental data [14,30]. (The reference states: γ (U) phase and fcc (Co) phase).

The calculated enthalpies, entropies and Gibbs free energies of formation for the compounds are plotted in Figs. 7–9. It is a reasonable agreement between the calculated and experimental results [30]. Chiotti et al. [14] pointed out that the experimental data of the entropy reported by Lebedev et al. [30] are too negative, and in this work the calculated entropies of the $Co_2U$ and CoU compounds are more positive than those reported by Lebedev et al. [30] and Chiotti et al. [14]. Therefore, the calculated results are more reasonable (see Table 3).

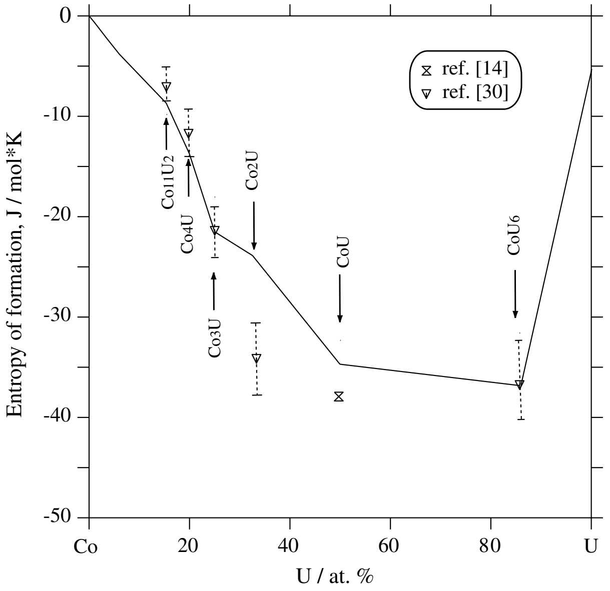

Fig. 8. Calculated entropies of formation of intermetallic compounds at 727 °C in the Co–U sysetm compared with the experimental data [14,30]. (The reference states: γ (U) phase and fcc (Co) phase).

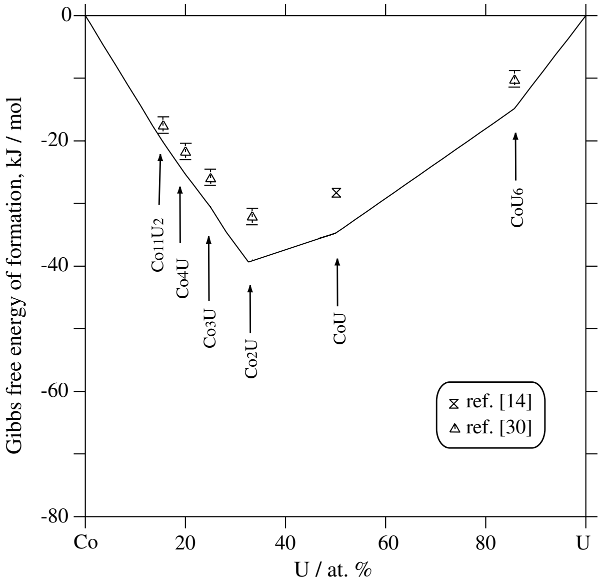

Fig. 9. Calculated Gibbs free energy of formation of intermetallic compounds at 727 in the Co–U system compared with the experimental data [14,30]. (The reference states: γ (U) phase and fcc (Co) phase).

Table 3
Invariant reactions in the Co–U system

| Reaction type | Reaction | Co/at.% | | | T (°C) | Reference |
|---|---|---|---|---|---|---|
| Peritectoid | $Co_4U + Co_2U \rightarrow Co_3U$ | 80 | 75 | 75 | ~830 | [21] |
| | | 80 | 75 | 75 | 830 | [This work] |
| Peritectoid | $CoU_6 + \gamma\,(U) \rightarrow \alpha\,(U)$ | 84.6 | 98.5 | 0.06 | 756 | [21] |
| | | 84.6 | 96.8 | 0.06 | 758 | [This work] |
| Eutectic | $L \rightarrow fcc\,(Co) + Co_{11}U_2$ | ~96 | 0.01 | 84.6 | ~1120 | [21] |
| | | 96.9 | 0 | 84.6 | 1120 | [This work] |
| Eutectic | $L \rightarrow Co_{11}U_2 + Co_4U$ | ~82 | 84.6 | 80 | ~1110 | [21] |
| | | 80.5 | 84.6 | 80 | 1114 | [This work] |
| Eutectic | $L \rightarrow Co_4U + Co_2U$ | ~77 | 80 | 66.7 | ~1090 | [21] |
| | | 77.9 | 80 | 66.7 | 1112 | [This work] |
| Eutectic | $L \rightarrow CoU + CoU_6$ | 34 | 50 | 14.3 | 734 | [21] |
| | | 35.3 | 50 | 14.3 | 737 | [This work] |
| Peritectic | $L + \gamma(U) \rightarrow CoU_6$ | 21.5 | 98.5 | 14.3 | 826 | [21] |
| | | 21.6 | 96.8 | 14.3 | 824 | [This work] |
| Peritectic | $L + Co_2U \rightarrow CoU$ | 42.7 | 66.7 | 50 | 805 | [21] |
| | | 43.7 | 66.7 | 50 | 804 | [This work] |
| Congruent | $L \rightarrow Co_2U$ | 66.7 | | | 1185 | [21] |
| | | 66.7 | | | 1183 | [This work] |
| Congruent | $L \rightarrow Co_{11}U_2$ | 84.6 | | | 1130 | [21] |
| | | 84.6 | | | 1125 | [This work] |
| Congruent | $L \rightarrow Co_4U$ | 80 | | | 1120 | [21] |
| | | 80 | | | 1114 | [This work] |

## 5. Conclusions

The phase diagrams and thermodynamic properties in the Al–U and Co–U systems were evaluated by combining the thermodynamic models with the available experimental information. A consistent set of thermodynamic parameters has been derived from describing the Gibbs free energies of each solution phase and intermetallic compounds in the Al–U and Co–U binary systems, leading to a good agreement between the calculated results and most of the experimental data found in the literature. More experimental details in Co–U binary system still need to be determined, such as the liquidus line and the uncertain temperature of the eutectic reaction.

## Acknowledgements

This work was supported by the National Natural Science Foundation of China Nos. 50425101, 50771087 and Fujian province department of science and technology (2002I018, E0310023, 2001J028). One of the authors (X.J. Liu) acknowledges the Minjiang Chair Professorship by Fujian Province of PR China for financial support.

## References

[1] M. Kuznietz, H. Pinto, M. Meland, Physica B 234 (1996) 223.
[2] A.J. Drehman, K.M. Wong, J. Alloy. Compd. 183 (1992) 116.
[3] K.M. Wong, A.J. Drehman, Physica B+C 135 (1) (1985) 299.
[4] G.W. Gibson, Inaho Nuclear (USA) Report (1967) IN-1133.
[5] C. Ganguly, P.V. Hegde, T.R.G. Kutty, Proceedings of the 2nd International Conference on Aluminum: INCAL-91 2 (1991), Bangolore 765.
[6] S. Nazare, G. Ondracek, F. Thummler, Report KFK-585, Kernforschungszentrum, Karlsruhe, (1967).
[7] A.T. Dinsdale, CALPHAD 15 (1991) 317.
[8] O. Redlich, A.T. Kister, Ind. Eng. Chem. 40 (1948) 345.
[9] M. Hillert, M. Tsrl, CALPHAD 2 (1978) 227.
[10] W.B. Pearson, Handbook of Lattice Spacings and Structures of Metals and Alloys 1 (1958).
[11] P. Gordon, A.R. Kaufman, Trans. AIME 188 (1950) 182.
[12] G. Cabane, M. Englander, J. Lehmann, Proceedings of UN International Conference on Peaceful Uses of Atomic Energy 9 (1955) 120.
[13] J.A. Straatman, N.F. Neumann, U.S. Atomic Energy Comm. Report MCW-1488 (1964).
[14] P. Chiotti, V.V. Akhachinskji, I. Ansara, M.H. Rand, The Chemical Thermodynamics of Actinide Elements and Compounds, part 5, 1981.
[15] D.K. Khakimova, Yu.S. Virgilev, O.S. Ivanov, in: Stroenie i Svoistva Splavov Urana, Toriya i Tsirkoniya, O.S. Ivanov Ed., Gosatomizdat, Moscow, 5 (1963).
[16] P.R. Roy, J. Nucl. Mater. 11 (1) (1964) 59.
[17] J. Bellot, J.M. Hery, G. Cabane, Mem. Sci. Rev. Met. 56 (1959) 301.
[18] G. Petzow, S. Steeb, I. Ellinghaus, J. Nucl. Mater. 4 (1961) 316.
[19] M.E. Kassner, P.H. Adler, M.G. Adamson, J. Nucl. Mater. 167 (1989) 160.
[20] V.A. Lebedev, V.I. Sal'nikov, I.F. Nichkov, S.P. Raspopin, At. Energy 2 (1972) 32.
[21] K. Ishida, T. Nishizawa, Desk Handbook-Phase Diagrams for Binary Alloys, ASM International, 2000.
[22] M.B. Waldron, J.D. Brown, Atomic Energy Research Establishment, 1956.
[23] W. Dreizler, F. Aldinger, G. Petzow, Z. Metallkd. 70 (1979) 769.
[24] V.A. Pletyushkin, V.I. Chechernikov, V.V. Muzaleva, V.A. Semenov, R.N. Kuzmin, V.K. Slovyanskikh, Fiz. Met. Metalloved. 39 (1) (1975) 217–220 (in Russian);

V.A. Pletyushkin, V.I. Chechernikov, V.V. Muzaleva, V.A. Semenov, R.N. Kuzmin, V.K. Slovyanskikh, TR: Phys. Met. Metallogr. 39 (1) (1975) 200.

[25] A.I. Meskhishvili, V.A. Peltyushkin, V.K. Slovyanskikh, V.I. Chechernikov, T.M. Shaviskvili, Fiz. Met. Metalloved. 45 (5) (1978) 935 (in Russian);
A.I. Meskhishvili, V.A. Peltyushkin, V.K. Slovyanskikh, V.I. Chechernikov, T.M. Shaviskvili, TR: Phys. Met. Metallogr. 43 (2) (1978) 30.

[26] A.V. Deryagin, A.V. Andreev, Zh. Eksp. Teor. Fiz. 71 (1976) 1166 (in Russian);
A.V. Deryagin, A.V. Andreev, TR: Sov. Phys. JETP 44 (1976) 610.

[27] A.S. Yermolenko, A.V. Ivanov, V.Y. Komarov, L.M. Magat, G.M. Makarova, Y.S. Shur, Fiz. Met. Metalloved. 43 (2) (1977) 446 (in Russian);
A.S. Yermolenko, A.V. Ivanov, V.Y. Komarov, L.M. Magat, G.M. Makarova, Y.S. Shur, TR: Phys. Met. Metallogr. 43 (2) (1977) 195.

[28] H.H. Hill, B.T. Matthias, Phys. Rev. 168 (1968) 464.

[29] J.J. Engelhardt, J. Phys. Chem. Solids 36 (1975) 123.

[30] V.A. Lebedev, V.I. Sal'nikov, I.F. Nichkov, S.P. Raspopin, Russ. Metall. 6 (1972) 107.

[31] B. Jansson, PhD thesis, Division of physical Metallurgy, Royal Institute of Technology, Stockholm, Sweden.

[32] B. Sundman, B. Jansson, J.-O. Andersson, CALPHAD 9 (1985) 153.