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Thermodynamic Assessment of the Ni-Ga System

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Phase diagram and thermodynamic properties of the Ni-Ga system are assessed based on the CALPHAD approach, using all available experimental data and applying appropriate thermodynamic models. The liquid phase and the Ni-based solid solution (Ni) are treated as disordered solutions. The thermodynamic behavior of the ordered intermetallic compounds with appreciable ranges of homogeneity, Ni_3Ga and NiGa, are described by a two-sublattice model, and the order-disorder transformation between Ni_3Ga and fcc-(Ni) is also explicitly considered in this work. The other five intermetallic compounds are treated as stoichiometric line compounds. The phase diagram and the thermodynamic properties calculated from the optimized model parameters are in good agreement with most of the experimental data.

1. Introduction

High melting intermetallic compounds, like Ni_3Al etc., are interesting materials, mostly for their superior high-temperature properties. Recently, considerable research activity has centered on their mechanical, electrical, corrosive, and other specific properties.[1-3] Ni_3Ga, an intermetallic phase with the same L12 crystal structure as Ni_3Al, may have similar interesting properties. According to the phase diagram evaluated by Lee and Nash,[4] which was mainly based on the study of Feschotte and Eggimann,[5] Ni_3Ga has a maximum homogeneity range between 22.5 and 30.0 at.% Ga. Based on x-ray diffraction (XRD) and a diffusion couple technique Micke et al.[6] actually found it to be narrower, with the Ga-rich limit in the vicinity of 27.5 at.% Ga. Ikeda et al.[7] examined the homogeneity range of Ni_3Ga by electron probe microanalysis, which also showed its composition range to be narrower than that reported in the earlier literature, especially on the Ga-rich side.

Early research work on the disorder in Ni_3Ga was presented by Chang and Hsiao,[8] who applied a statistical thermodynamic model to experimental Ga activities measured by Katayama et al.[9] and by Pratt and Bird.[10] They assumed only substitutional disorder in the Ni_3Ga phase and neglected vacancies altogether. Moreover, the number of experimental data points on which the statistical evaluation was based was rather limited.

To understand the physical properties important for any technological application of the intermetallic compound Ni_3Ga, it is necessary to obtain a better knowledge of its thermodynamic properties and the defect mechanism leading to nonstoichiometry in Ni_3Ga. An electromotive force (emf) method with solid oxygen-conducting electrolytes was used to measure the thermodynamic activity of Ga between 1073 and 1273 K within the homogeneity range of Ni_3Ga, and the variation of the lattice parameter with composition was determined by XRD over the entire homogeneity range.[11] A statistical-thermodynamic model developed by Krachler et al.[12] for nonstoichiometric phases with the L12 superstructure, considering anti-structure atoms (substitutional point defects) and vacancies as point defects, was used to evaluate the corresponding activity data, and there were hints that the nonstoichiometry of Ni_3Ga resulted mainly from anti-structure atoms (see the details in Ref 11). These findings were confirmed later on by ab initio calculations by Schweiger et al.[13]

One recent simplified thermodynamic modeling of the Ni-Ga system using the CALPHAD approach was reported by Gröbner et al.[14] Its main purpose was aimed at the development of isothermal sections of different ternary systems M-Ga-N (M = Ni, Co, Pd, Cr); therefore the modeling focused on the solid state equilibria, and the Ni_3Ga phase was simply treated as being stoichiometric.

The present work attempts a critical thermodynamic assessment of the Ni-Ga system by means of a CALPHAD approach based on all available experimental data, including our recent experimental information on the Ni_3Ga phase.[11] Appropriate thermodynamic models are used to describe the Gibbs energy of individual phases. The two phases Ni_3Ga and NiGa are treated as nonstoichiometric compounds with an ordered structure; they are thermodynamically described by a two-sublattice model.

2. Experimental Information

2.1 Phase Diagram Data

The Ni-Ga phase diagram has been studied by several groups of investigators.[5,15,16] Using XRD, thermal analysis and microscopic methods, Hellner[15] determined the liquidus over the entire composition range. Pearson and Rimek[16] revised the Ni-Ga system in the composition range between 10 and 33 at.% Ga. Feschotte and Eggimann[5] re-examined the Ni-Ga binary system in detail by differential thermal analysis (DTA), XRD, and x-ray microprobe analysis. Basing their work on these studies, Lee and Nash[4] presented an assessed version of the Ni-Ga phase

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diagram. Ipser et al.[17] determined lattice parameter and melting behavior of the ternary B2-phase in the Co-Ga-Ni system, and the results of the DTA measurements in the Ni-Ga binary system indicated a somewhat wider range of homogeneity on the gallium-rich side as compared with the literature data. Later on, the nickel-rich part of the phase diagram was again revised in the work of Micke et al.[6] by means of DTA and a diffusion couple technique.

The solubility of Ga in the (Ni) solid solution was measured by Hellner,[15] and the maximum solubility was found to be about 28 at.% Ga at 1211 °C. However, detailed studies by Pearson and Rimek[16] showed the maximum solubility to be 24.3 at.% Ga at 1212 °C. Feschotte and Eggimann[5] performed microprobe analyses on well annealed samples and confirmed the results of Pearson and Rimek.[16] Therefore, the data of Ref 5 and 16 are preferred in the present work since they are considered more reliable.

Because no data are available on the solubility of Ni in (Ga), solid Ga is treated as a pure phase in this study. As a consequence, the reaction between $NiGa_4$, liquid, and Ga must be treated as a eutectic in our calculations, in contrast to the diagram in Ref 4 in which it is shown as a peritectic reaction although the difference between the peritectic temperature, and the melting point of pure Ga is less than 0.5°.

Six intermetallic compounds were reported by Hellner[15] in the Ni-Ga system: β-NiGa, δ-Ni_5Ga_3, γ-Ni_3Ga_2, γ′-$Ni_{13}Ga_9$, β′-Ni_2Ga_3, and ε-$NiGa_4$. Pearson and Rimek[16] discovered the phase Ni_3Ga forming peritectically at 1210 °C and crystallizing in the L12 ordered superlattice. Ikeda et al.[7] determined the homogeneity range of Ni_3Ga. All relevant information on the intermetallic compounds in the Ni-Ga system is summarized in Table 1.

2.2 Thermodynamic Data

The enthalpies of formation of the solid phases in the Ni-Ga system were measured by Martosudirjo and Pratt,[18] Jacobi et al.,[19]and Predel et al.,[20] using tin solution calorimetry. In addition, Predel et al.[20] also determined gallium activities and Gibbs energies of formation of the solid phases by emf measurements. Using an emf method, partial and integral Gibbs energies of formation of Ni-Ga alloys were deduced by Katayama et al.[9] Pratt and Bird[10] reported activities, partial and integral Gibbs energies, entropies, and enthalpies for the fcc-(Ni) solid solution and the intermetallic phases Ni_3Ga, Ni_5Ga_3, Ni_3Ga_2, $Ni_{13}Ga_9$, NiGa, and Ni_2Ga_3. Partial Gibbs energies and enthalpies of Ga in the NiGa phase at 1173 K were obtained by Seybolt[21] and Mikula et al.[22] Recently, Meschel and Kleppa[23] reported standard enthalpies of formation of some 3*d* transition metal gallides by high temperature direct synthesis calorimetry, and both Yuan et al.[11] and Kushida et al.[24] measured independently the thermodynamic activities of Ga in the L12-Ni_3Ga phase by means of an emf method.

3. Thermodynamic Modeling

3.1 Unary Phases

The Gibbs energy function $G_i^{\Phi}(T) = {}^0G_i^{\Phi}(T) - H_i^{SER}$ (298.15 K) for the element i (i = Ni, Ga) in the phase Φ (Φ = liquid, fcc, ortho) is described by an equation of the following form:

$$G_{\mathrm{i}}^{\Phi}(T) = a + bT + cT\ln T + dT^2 + eT^3 + fT^{-1} + gT^7 + hT^{-9} \qquad \text{(Eq 1)}$$

where in different temperature ranges different sets of coefficients (a through h) may be used; H_i^{SER}(298.15 K), the molar enthalpy of the pure solid element i at 298.15 K, is taken as standard element reference (SER) state; fcc for pure Ni, and ortho for pure Ga.

Table 1 Intermetallic Compounds in the Ni-Ga System

Compounds	Composition, x_{Ga}	Melting or Transition Type	Temperature, K	Reference
α′-Ni_3Ga	0.23-0.295 (873 K)	peritectic	1485	[5]
	0.23-0.275 (873 K)	peritectic	…	[16]
	0.231-0.281 (1273 K)	peritectic	…	[7]
δ-Ni_5Ga_3	0.37	peritectoid	958	[15]
	0.365-0.38 (873 K)	peritectoid	1014 ± 1	[5]
	0.36-0.375 (873 K)	peritectoid	1004	[15]
γ-Ni_3Ga_2	0.36-0.41 (973 K)	peritectoid	1213	[15]
	0.38-0.41 (1023 K)	peritectoid	1222 ± 2	[5]
γ′-$Ni_{13}Ga_9$	0.40-0.42 (873 K)	polymorphic	958	[15]
	0.40-0.42 (873 K)	polymorphic	1063 ± 3	[5]
β-NiGa	0.47-0.55 (873 K)	congruent	1493	[15]
	0.354-0.50 (1373 K)	congruent	1493 ± 3	[5]
Ni_3Ga_4	0.565-0.575 (673 K)	peritectoid	815 ± 1	[5]
β′-Ni_2Ga_3	0.60	peritectic	1168	[15]
	0.60	peritectic	1223 ± 2	[5]
ε-$NiGa_4$	0.80	peritectic	525	[15]
	0.80	peritectic	636 ± 2	[5]

In the present work, the Gibbs energy functions of Ni and Ga are taken from the SGTE data for pure elements compiled by Dinsdale.[25]

3.2 Substitutional Solutions

For substitutional solutions, like the liquid and the fcc-(Ni) solid solution, the molar Gibbs energy is equal to

$$^{0}G_m^{\Phi} - H^{\mathrm{SER}} = {}^{\mathrm{ref}}G_m^{\Phi} + {}^{\mathrm{id}}G_m^{\Phi} + {}^{\mathrm{ex}}G_m^{\Phi} \qquad \text{(Eq 2)}$$

where H^{SER} is an abbreviation for $x_{\mathrm{Ni}}H_{\mathrm{Ni}}^{\mathrm{SER}}(298.15\ \mathrm{K}) + x_{\mathrm{Ga}}H_{\mathrm{Ga}}^{\mathrm{SER}}(298.15\ \mathrm{K})$ and

$$\begin{aligned} {}^{\mathrm{ref}}G_m^{\Phi} &= x_{\mathrm{Ni}}\,[{}^{0}G_{\mathrm{Ni}}^{\Phi}(T) - H_{\mathrm{Ni}}^{\mathrm{SER}}(298.15\ \mathrm{K})] + x_{\mathrm{Ga}}\,[{}^{0}G_{\mathrm{Ga}}^{\Phi}(T) \\ &\quad - H_{\mathrm{Ga}}^{\mathrm{SER}}(298.15\ \mathrm{K})], \\ {}^{\mathrm{id}}G_m^{\Phi} &= \mathrm{R}T\,(x_{\mathrm{Ni}}\ln x_{\mathrm{Ni}} + x_{Ga}\ln x_{\mathrm{Ga}}). \end{aligned}$$

${}^{\mathrm{ex}}G_m^{\Phi}$ is the excess Gibbs energy, expressed by the Redlich-Kister polynomial:

$${}^{\mathrm{ex}}G_m^{\Phi} = x_{\mathrm{Ni}}x_{\mathrm{Ga}}\sum_{i=0}^{n}{}^{i}L^{\Phi}\,(x_{\mathrm{Ni}} - x_{\mathrm{Ga}})^{i} \qquad \text{(Eq 3)}$$

where ${}^{i}L^{\Phi}$ stands for the interaction parameters between Ni and Ga, whose general form is

$${}^{\mathrm{i}}L^{\Phi} = a + bT + cT\ln T + dT^{2} + eT^{3} + fT^{-1} \qquad \text{(Eq 4)}$$

In the present work, the corresponding parameters of the ${}^{i}L^{\Phi}$ terms are evaluated.

3.3 Stoichiometric Intermetallic Compounds

The Gibbs energy of formation of a stoichiometric compound A_aB_b, referred to the pure elements as phases Aref and Bref, is expressed as follows:

$$\begin{aligned} \Delta_f G^{A_aB_b}(T) &= {}^{0}G^{A_aB_b}(T) - a\,{}^{0}G_{\mathrm{A}}^{A\mathrm{ref}}(T) - b\,{}^{0}G_{\mathrm{B}}^{B\mathrm{ref}}(T) \\ &= A + BT \end{aligned} \qquad \text{(Eq 5)}$$

In this paper δ-Ni_5Ga_3, Ni_3Ga_2, Ni_3Ga_4, β′-Ni_2Ga_3, and ε-$NiGa_4$ are treated as stoichiometric compounds, and their Gibbs energies can be obtained by

$$\begin{aligned} \Delta_f G^{\mathrm{Ni}_{(1-x)}\mathrm{Ga}_x}(T) &= {}^{0}G^{\mathrm{Ni}_{(1-x)}\mathrm{Ga}_x}(T) - (1-x)\,{}^{0}G_{\mathrm{Ni}}^{\mathrm{fcc}} - x\,{}^{0}G_{\mathrm{Ga}}^{\mathrm{orth}} \\ &= A_x + B_xT \end{aligned} \qquad \text{(Eq 6)}$$

where A_x and B_x are deduced by the optimization procedure.

3.4 Ordered Phases

3.4.1 The Ni_3Ga Phase With $L1_2$-Structure. The crystal lattice of the α′-Ni_3Ga phase with the cubic L12 crystal structure can be divided into two sublattices: the α-sublattice (face centered positions) and the β-sublattice (corner positions); in an ideally ordered crystal, all α-sites are occupied by A atoms and all β-sites by B atoms, which automatically yields the A_3B stoichiometry. The statistical thermodynamic study[11] of this phase which was later on confirmed by ab initio calculations[13] showed that the nonstoichiometry of Ni_3Ga is mainly due to substitutional point defects (anti-structure atoms), i.e., Ni or Ga atoms on "wrong" sublattice sites. Thus, a two-sublattice model $(\mathrm{Ni,Ga})_{0.75}(\mathrm{Ga,Ni})_{0.25}$ is used in this study to describe the Ni_3Ga ordered phase, where Ga and Ni atoms are the species in the two different sublattices.

To connect the ordered L12-compound Ni3Ga with the corresponding disordered fcc solid solution (Ni) in the calculation, and at the same time, to allow the disordered phase to be optimized independently, an approach is used that was successfully applied by Ansara et al.[26] in an investigation of the Ni-Al system. The compound Gibbs energy is split into three terms as follows:

$$G_m = G_m^{\mathrm{disord}}(x_i) + G_m^{\mathrm{ord}}(y_i',y_i'') - G_m^{\mathrm{ord}}(x_i,x_i) \qquad \text{(Eq 7)}$$

where $G_m^{\mathrm{disord}}(x_i)$ is the Gibbs energy of the disordered solution, which has the same mathematical expression as for a substitutional solution, and a Redlich-Kister equation is used to represent the excess Gibbs energy. $G_m^{\mathrm{ord}}(y_i',y_i'')$ is the Gibbs energy of the $L1_2$ ordered phase described by a two-sublattice model and contains implicitly a contribution of the disordered state. y_i',y_i'' are the site fractions of i on the two sublattices, respectively, and have the following relation with the mole fraction of component i:

$$x_i = 0.75y_i' + 0.25y_i''$$

$G_m^{\mathrm{ord}}(x_i,x_i)$ is the term that represents the energy contribution of the disordered state to the ordered phase. When the site fractions are equal, the last two terms in Eq 7 cancel each other, and G_m corresponds to the Gibbs energy of the disordered phase.

In the present work, the parameters of both ordered and disordered phases are also connected and evaluated independently by using a recent version of the ChemSage software package (version 4.2.2).[27] There, $G_m^{\mathrm{ord}}(y_i',y_i'')$ is given by the form of a two-sublattice model as shown in Eq 8 as follows:

$$\begin{aligned} G_m^{\mathrm{ord}}(y_i',y_i'') &= y_{\mathrm{Ga}}'y_{\mathrm{Ga}}''\,{}^{0}G_{\mathrm{Ga:Ga}}^{\mathrm{ord}} + y_{\mathrm{Ga}}'y_{\mathrm{Ni}}''\,{}^{0}G_{\mathrm{Ga:Ni}}^{\mathrm{ord}} + y_{\mathrm{Ni}}'y_{\mathrm{Ga}}''\,{}^{0}G_{\mathrm{Ni:Ga}}^{\mathrm{ord}} \\ &\quad + y_{\mathrm{Ni}}'y_{\mathrm{Ni}}''\,{}^{0}G_{\mathrm{Ni:Ni}}^{\mathrm{ord}} + RT[0.75(y_{\mathrm{Ga}}'\ln y_{\mathrm{Ga}}' + y_{\mathrm{Ni}}'\ln y_{\mathrm{Ni}}') \\ &\quad + 0.25(y_{\mathrm{Ga}}''\ln y_{\mathrm{Ga}}'' + y_{\mathrm{Ni}}''\ln y_{\mathrm{Ni}}'')] \\ &\quad + y_{\mathrm{Ga}}'y_{\mathrm{Ni}}'(y_{\mathrm{Ga}}''L_{\mathrm{Ga,Ni:Ga}}^{\mathrm{ord}} + y_{\mathrm{Ni}}''L_{\mathrm{Ga,\,Ni:Ni}}^{\mathrm{ord}}) \\ &\quad + y_{\mathrm{Ga}}''y_{\mathrm{Ni}}''\,(y_{\mathrm{Ga}}'L_{\mathrm{Ga:Ga,Ni}}^{\mathrm{ord}} + y_{\mathrm{Ni}}'L_{\mathrm{Ni:Ga,Ni}}^{\mathrm{ord}}) \end{aligned} \qquad \text{(Eq 8)}$$

where ${}^{0}G_{\mathrm{Ga:Ni}}^{\mathrm{ord}} = {}^{0}G_{\mathrm{Ni:Ga}}^{\mathrm{ord}} = a_1 + b_1T$; ${}^{0}G_{\mathrm{Ni:Ni}}^{\mathrm{ord}} = {}^{0}\mathrm{G}_{\mathrm{Ni}}^{\mathrm{fcc}}$; ${}^{0}G_{\mathrm{Ga:Ga}}^{\mathrm{ord}} = {}^{0}G_{\mathrm{Ga}}^{\mathrm{fcc}}$. And the interaction parameters in Eq 8 have the following restraints:

$$\begin{aligned} {}^{0}L_{\mathrm{Ga,Ni:Ga}}^{\mathrm{ord}} &= {}^{0}L_{\mathrm{Ga,Ni:Ni}}^{\mathrm{ord}} = 2a_1 + 2b_1T \\ {}^{0}L_{\mathrm{Ga:Ga,Ni}}^{\mathrm{ord}} &= {}^{0}L_{\mathrm{Ni:Ga,Ni}}^{\mathrm{ord}} = 0 \\ {}^{1}L_{\mathrm{Ga,Ni:Ga}}^{\mathrm{ord}} &= {}^{1}L_{\mathrm{Ga,Ni:Ni}}^{\mathrm{ord}} = a_2 + b_2T \\ {}^{1}L_{\mathrm{Ga:Ga,Ni}}^{\mathrm{ord}} &= {}^{1}L_{\mathrm{Ni:Ga,Ni}}^{\mathrm{ord}} = \frac{1}{3}a_2 + \frac{1}{3}b_2T \end{aligned}$$

The four coefficients a_1, b_1, a_2, and b_2 are optimized in the present work.

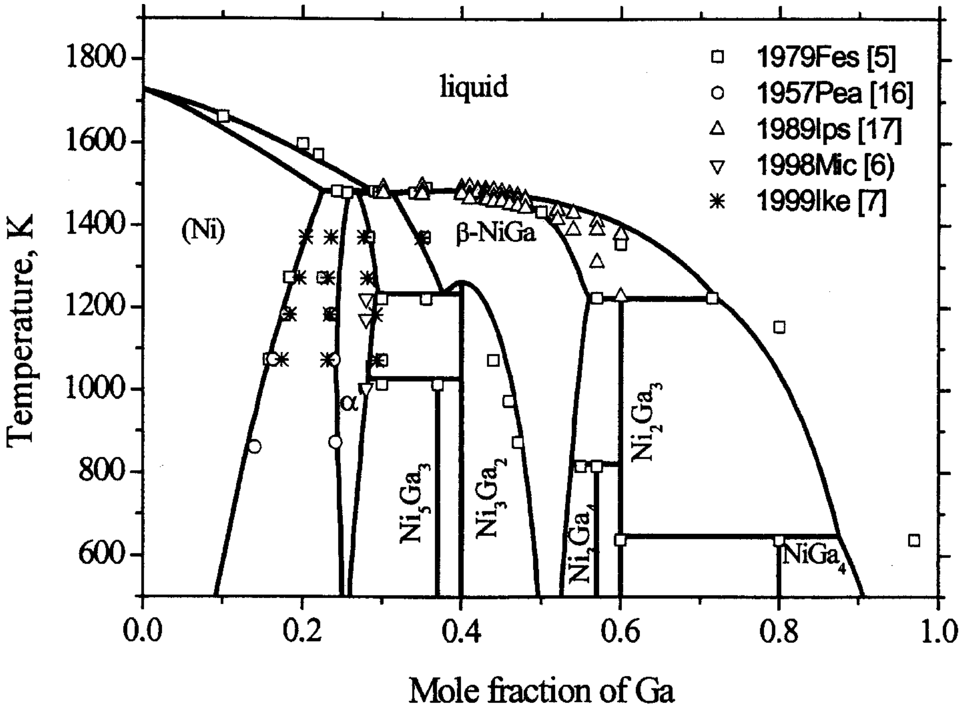

Fig. 1 The calculated Ni-Ga binary phase diagram compared with experimental data. The solid line stands for the calculated results, the individual symbols represent the experimental data of Ref 5, 6, 7, 16, 17 as defined in the insert.

Table 2 Optimized Parameters for the Phases in the Ni-Ga System

Phase	Parameter	Function, J/mol atoms
Liquid	${}^{0}L^{\mathrm{liq}}_{\mathrm{Ga,Ni}}$	$-122\,488.59 + 35.72T$
	${}^{1}L^{\mathrm{liq}}_{\mathrm{Ga,Ni}}$	$-29\,685.00 + 14.00T$
	${}^{2}L^{\mathrm{liq}}_{\mathrm{Ga,Ni}}$	$-30\,751.90 + 22.10T$
fcc-(Ni)	${}^{0}L^{\mathrm{fcc}}_{\mathrm{Ga:Ni}}$	$-130\,526.00 + 40.00T$
$\mathrm{Ll_2}$-$\mathrm{Ni_3Ga}$	${}^{0}G^{\mathrm{L1_2}}_{\mathrm{Ga:Ni}} - 0.25{}^{0}\mathrm{G}^{\mathrm{fcc}}_{\mathrm{Ni}} - 0.75{}^{0}G^{\mathrm{fcc}}_{\mathrm{Ga}}$	$-27\,789.00 + 1.64T$
	${}^{0}G^{\mathrm{L1_2}}_{\mathrm{Ni:Ga}} - 0.75{}^{0}G^{\mathrm{fcc}}_{\mathrm{Ni}} - 0.25{}^{0}G^{\mathrm{fcc}}_{\mathrm{Ga}}$	$-27\,789.00 + 1.64T$
	${}^{0}G^{\mathrm{L1_2}}_{\mathrm{Ni:Ni}} - {}^{0}G^{\mathrm{fcc}}_{\mathrm{Ni}}$	0
	${}^{0}G^{\mathrm{L1_2}}_{\mathrm{Ga:Ga}} - {}^{0}G^{\mathrm{fcc}}_{\mathrm{Ga}}$	0
	${}^{0}L^{\mathrm{L1_2}}_{\mathrm{Ni,Ga:Ga}}$	$-55\,578.00 + 3.28T$
	${}^{0}L^{\mathrm{L1_2}}_{\mathrm{Ni,Ga:Ni}}$	$-55\,578.00 + 3.28T$
	${}^{1}L^{\mathrm{L1_2}}_{\mathrm{Ni,Ga:Ga}}$	$14\,040.00 - 8.01T$
	${}^{1}L^{\mathrm{L1_2}}_{\mathrm{Ni,Ga:Ni}}$	$14\,040.00 - 8.01T$
	${}^{0}L^{\mathrm{L1_2}}_{\mathrm{Ni:Ga,Ni}}$	0
	${}^{0}L^{\mathrm{L1_2}}_{\mathrm{Ga:Ga,Ni}}$	0
	${}^{1}L^{\mathrm{L1_2}}_{\mathrm{Ni:Ga,Ni}}$	$4680.00 - 2.67T$
	${}^{1}L^{\mathrm{L1_2}}_{\mathrm{Ga:Ga,Ni}}$	$4680.00 - 2.67T$
B2-NiGa	${}^{0}G^{\mathrm{B2}}_{\mathrm{Ga:Ni}} - 0.5{}^{0}G^{\mathrm{bcc}}_{\mathrm{Ga}} - 0.5{}^{0}G^{\mathrm{bcc}}_{\mathrm{Ni}}$	$-54\,030.75 + 16.50T$
	${}^{0}G^{\mathrm{B2}}_{\mathrm{Ni:Ni}} = {}^{0}G^{\mathrm{bcc}}_{\mathrm{Ni}}$	0
	${}^{0}L^{\mathrm{B2}}_{\mathrm{Ga,Ni:Ni}}$	$-8724.00 - 2.38T$
	${}^{0}L^{\mathrm{B2}}_{\mathrm{Ga,Ni:Va}}$	$-8724.00 - 2.38T$
	${}^{0}L^{\mathrm{B2}}_{\mathrm{Ga:Ni,Va}}$	$-35\,016.42 + 20.31T$
	${}^{0}L^{\mathrm{B2}}_{\mathrm{Ni:Ni,Va}}$	$-35\,016.42 + 20.31T$
$\mathrm{Ni_5Ga_3}$	${}^{0}G^{\mathrm{Ni_{0.63}Ga_{0.37}}} - 0.37{}^{0}G^{\mathrm{orth}}_{\mathrm{Ga}} - 0.63{}^{0}G^{\mathrm{fcc}}_{\mathrm{Ni}}$	$-37\,658.61 + 5.34T$
$\mathrm{Ni_3Ga_2}$	${}^{0}G^{\mathrm{Ni_{0.6}Ga_{0.4}}} - 0.4{}^{0}G^{\mathrm{orth}}_{\mathrm{Ga}} - 0.6{}^{0}G^{\mathrm{fcc}}_{\mathrm{Ni}}$	$-39\,753.31 + 5.55T$
$\mathrm{Ni_3Ga_4}$	${}^{0}G^{\mathrm{Ni_{0.43}Ga_{0.57}}} - 0.57{}^{0}G^{\mathrm{orth}}_{\mathrm{Ga}} - 0.43{}^{0}G^{\mathrm{fcc}}_{\mathrm{Ni}}$	$-47\,790.80 + 9.04T$
$\mathrm{Ni_2Ga_3}$	${}^{0}G^{\mathrm{Ni_{0.4}Ga_{0.6}}} - 0.6{}^{0}G^{\mathrm{orth}}_{\mathrm{Ga}} - 0.4{}^{0}G^{\mathrm{fcc}}_{\mathrm{Ni}}$	$-47\,426.09 + 8.94T$
$\mathrm{NiGa_4}$	${}^{0}G^{\mathrm{Ni_{0.2}Ga_{0.8}}} - 0.8{}^{0}G^{\mathrm{orth}}_{\mathrm{Ga}} - 0.2{}^{0}G^{\mathrm{fcc}}_{\mathrm{Ni}}$	$-24\,367.51 - 2.71T$

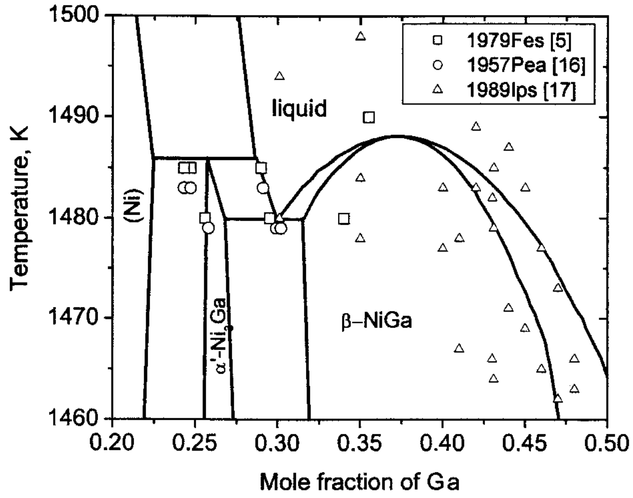

Fig. 2 Enlarged section of a part of the calculated Ni-Ga binary phase diagram between 20 and 50 at% Ga and between 1460 and 1500 K

3.4.2 The β-NiGa Phase With B2-structure.

Experimental evidence had shown that the nonstoichiometry of certain B2 phases was due to so-called triple-defects, i.e., anti-structure defects on one side and vacancies on the other.[28-30] In this paper, a vacancy is treated as a component, and the NiGa phase is modeled as $\mathrm{(Ga,Ni)_{0.5}(Ni,Va)_{0.5}}$, where Va represents a vacancy.

Following the approach by Ansara et al.[26], the Gibbs energy of the β-NiGa phase is represented by:

$$\begin{aligned} {}^0G_m^{\mathrm{B2}} - H^{\mathrm{SER}} = {} & y'_{\mathrm{Ga}} y''_{\mathrm{Ni}}\, {}^0G^{\mathrm{B2}}_{\mathrm{Ga:Ni}} + y'_{\mathrm{Ga}} y''_{\mathrm{Va}}\, {}^0G^{\mathrm{B2}}_{\mathrm{Ga:Va}} \\ & + y'_{\mathrm{Ni}} y''_{\mathrm{Ni}}\, {}^0G^{\mathrm{B2}}_{\mathrm{Ni:Ni}} + y'_{\mathrm{Ni}} y''_{\mathrm{Va}}\, {}^0G^{\mathrm{B2}}_{\mathrm{Ni:Va}} \\ & + \mathrm{R}T[0.5(y'_{\mathrm{Ga}} \ln y'_{\mathrm{Ga}} + y'_{\mathrm{Ni}} \ln y'_{\mathrm{Ni}}) \\ & + 0.5(y''_{\mathrm{Ni}} \ln y''_{\mathrm{Ni}} + y''_{\mathrm{Va}} \ln y''_{\mathrm{Va}})] \\ & + y'_{\mathrm{Ga}} y'_{\mathrm{Ni}}(\mathrm{y}''_{\mathrm{Ni}} L^{\mathrm{B2}}_{\mathrm{Ga,Ni:Ni}} + y''_{\mathrm{Va}} L^{\mathrm{B2}}_{\mathrm{Ga,Ni:Va}}) \\ & + y''_{\mathrm{Ni}} y''_{\mathrm{Va}}\,(y'_{\mathrm{Ga}} L^{\mathrm{B2}}_{\mathrm{Ga:Ni,Va}} + y'_{\mathrm{Ni}} L^{\mathrm{B2}}_{\mathrm{Ni:Ni,Va}}) \end{aligned} \qquad \text{(Eq 9)}$$

The following assumptions are used (in J/mol) for the four compound energies ${}^0G^{\mathrm{B2}}_{i:j}(i, j = \mathrm{Ga, Ni, Va})$ in Eq 9:

$$\begin{aligned} {}^0G^{\mathrm{B2}}_{\mathrm{Ni:Ni}} &= {}^0G^{\mathrm{bcc}}_{\mathrm{Ni}} \\ {}^0G^{\mathrm{B2}}_{\mathrm{Ga:Va}} &= 0.5\,{}^0G^{\mathrm{bcc}}_{\mathrm{Ga}} + 5000.0 - 0.5T \\ {}^0G^{\mathrm{B2}}_{\mathrm{Ni:Va}} &= -{}^0G^{\mathrm{B2}}_{\mathrm{Ga:Ni}} + {}^0G^{\mathrm{B2}}_{\mathrm{Ni:Ni}} + {}^0G^{\mathrm{B2}}_{\mathrm{Ga:Va}} \end{aligned} \qquad \text{(Eq 10)}$$

where ${}^0G^{\mathrm{bcc}}_{\mathrm{Ni}}$ and ${}^0G^{\mathrm{bcc}}_{\mathrm{Ga}}$ can be obtained from the SGTE data compilation.[25] Since simple cubic Ga, as represented by (Ga:Va), is a hypothetical compound and ${}^0G^{\mathrm{B2}}_{\mathrm{Ga:Va}}$ should therefore be more positive, an approximate term, 5000.0-0.5T, is added in Eq 10. Thus, only ${}^0G^{\mathrm{B2}}_{\mathrm{Ga:Ni}}$ needs to be optimized in the assessment.

The interaction parameters in Eq 9, which represent the interaction between Ga and Ni atoms or Ni atoms and vacancies in the same sublattice, are assumed to have the following relationships:

$$\begin{aligned} L^{\mathrm{B2}}_{\mathrm{Ga,Ni:Ni}} &= L^{\mathrm{B2}}_{\mathrm{Ga,Ni:Va}} \\ L^{\mathrm{B2}}_{\mathrm{Ga:Ni,Va}} &= L^{\mathrm{B2}}_{\mathrm{Ni:Ni,Va}} \end{aligned} \qquad \text{(Eq 11)}$$

4. Assessment Procedure

Most of the experimental thermodynamic data of the Ni-Ga system, i.e., enthalpies of formation of the solid phases and activities of Ga from emf measurements, are selected for the evaluation of the thermodynamic model parameters.

Phase equilibria data mostly come from the work of Feschotte and Eggimann.[5] As for the solid solubility of the L12-type Ni_3Ga phase, the data of Micke et al.[6] and Ikeda et al.[7] are chosen due to the consistency between their results and our previous work.[11]

The optimization is carried out by means of the ChemSage software package.[27] The program works by selecting the experimental data to be used and by entering initial estimates for the parameters that are to be optimized; an error sum is minimized where a certain weight is given for each of the selected data sets based on personal experience. A "trial and error" method is used during the optimization procedure until most of the selected experimental information is reproduced within the expected uncertainty limits.

Some starting values for the liquid phase, the fcc-(Ni) solid solution as well as for the stoichiometric compounds Ni_5Ga_3, Ni_3Ga_4 and $NiGa_4$ are obtained from the study by Gröbner et al.[14] who presented the parameters of a simplified approximation of the Ni-Ga system.

Assuming at the beginning that the Ni_3Ga phase is a stoichiometric compound, the corresponding parameters for the β-NiGa phase are optimized by a two-sublattice model as described in Section 3.4.2. In a next step, fixing the optimized parameters for the β-NiGa phase, a two-sublattice model is used to calculate the solid solubility of the Ni_3Ga phase, and the order-disorder transformation of this phase is accounted for in the optimization.

5. Results and Discussion

The optimized model parameters for all phases in the Ni-Ga system obtained in the present work are listed in Table 2. The calculated Ni-Ga phase diagram is given in

Table 3 The Calculated Invariant Equilibria in the Ni-Ga Binary System Compared With the Experimental Data[5,16]

Equibrium Phases	Data Resource	Composition, x_{Ga}			Temperature, K	Reaction Type
(Ni), Ni_3Ga, Liquid	This Work	0.225	0.257	0.287	1486	peritectic
	[5]	0.243	0.247	0.29	1485	
	[16]	0.243	0.247	0.291	1483	
Ni_3Ga, Liquid, NiGa	This Work	0.268	0.300	0.315	1480	eutectic
	[5]	0.257	0.295	0.304	1480	
	[16]	0.258	0.299	0.302	1479	
Ni_3Ga, NiGa, Ni_3Ga_2	This Work	0.29	0.38	0.40	1225	eutectoid
	[5]	0.30	0.355	0.35	1222 ± 2	peritectoid
Ni_3Ga, Ni_5Ga_3, Ni_3Ga_2	This Work	0.28	0.375	0.40	1017	peritectoid
	[5]	0.30	0.375	0.38	1014 ± 1	
NiGa, Ni_2Ga_3, Liquid	This Work	0.56	0.60	0.72	1222	peritectic
	[5]	0.57	0.60	0.715	1223 ± 3	
NiGa, Ni_3Ga_4, Ni_2Ga_3	This Work	0.55	0.57	0.60	815	peritectoid
	[5]	0.55	0.57	0.60	815 ± 1	
Ni_2Ga_3, $NiGa_4$, Liquid	This Work	0.60	0.80	0.88	638	peritectic
	[5]	0.60	0.80	0.96	636 ± 2	

Fig. 1 compared with experimental data measured in Ref 5, 6, 7, 16, and 17. Figure 2 shows an enlarged part of Fig. 1 between 20 and 50 at.% Ga and between 1460 and 1500 K. The calculated phase diagram agrees well with most experimental data, especially for the solid solubility of the Ni_3Ga phase and the NiGa phase. As shown in Fig. 2, the calculated congruent melting point of the NiGa phase is 1487 K at 37 at.% Ga, which is in good agreement with the results of Feschotte and Eggimann (35.5 at.% Ga, 1490 ± 3K).[5]

The invariant equilibria in the Ni-Ga system are listed in Table 3. Satisfactory agreement is obtained between the calculations and experiments, where the largest deviation in temperature is about 3 K. Considering the possible experimental errors, the majority of the experimental compositions of the invariant reactions are well reproduced.

However, the calculated composition of the Ga-rich liquidus is considerably lower compared with the experimental data.[5] Actually, by using somewhat different interaction parameters for the liquid phase, the situation could be much improved, but then the decomposition temperature of $NiGa_4$ increases unreasonably and becomes more than 200 K higher than the experimental value. Considering the experimental difficulties in determining a rather steep liquidus line at low temperatures by thermo-analytical methods, the good fit of the peritectic temperature with the experimental value in Ref 5 is given priority in the current study, whereas the agreement between measured and calculated composition of the Ga-rich liquidus has to be sacrificed. As another result of this compromise, the reaction between the phases $NiGa_4$, liquid, and Ga is calculated to be eutectic with a eutectic temperature of 232 K. This is in contrast to the diagram in Ref 5.

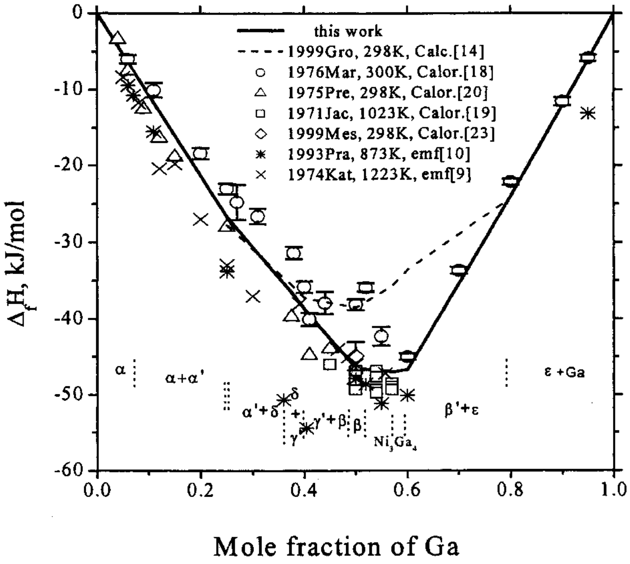

Fig. 3 The calculated enthalpy of formation for the solid phases in the Ni-Ga system at 298 K compared with experimental data; reference state: Ni(s), Ga(s). The solid line stands for the calculated results; the other symbols represent the experimental results of Ref 9, 10, 18, 19, 20, 23 and the calculated values of Ref 14.

It should also be noticed that the calculated reaction among the phases Ni_3Ga, Ni_3Ga_2, and NiGa in Fig. 1 is similar to the situation in the recent Ref 14, i.e., eutectoid rather than peritectoid as in the work of Ref 5. The reason for this latter discrepancy comes possibly from the treatment of Ni_3Ga_2 as a stoichiometric phase in the present work and from the omission of its transformation into $Ni_{13}Ga_9$ (below 1063 K).[5] This will be improved in a future study.

Figure 3 shows a comparison of the calculated enthalpy of formation of the solid phases at 298 K with experimental data from Refs. 9,10,18-20, and 23 and the calculated values from Ref 14. The calculated results in the present work fit well with the values of the calorimetric measurements in Ref 18-20, 23.

The activities of Ga and Ni (in the form of log *a*) were calculated as shown in Fig. 4 for 1100 K. Within the experimental uncertainty, good agreement is observed between the experimental data from Ref 9, 10, 11, 21, 22, 24 and the calculated values. There is one exception; i.e., the calculated activities in the composition range between 28 and 40 at% Ga which corresponds to the two-phase region Ni_3Ga + Ni_3Ga_2 in Fig. 1, are quite different from the experimental data in Ref 11. The reason might again arise from the treatment of Ni_3Ga_2 as a stoichiometric phase in the present work and from the neglect of its transformation into $Ni_{13}Ga_9$, as discussed before.

6. Conclusions

Phase relations and thermodynamic properties in the Ni-Ga system are presented in an optimized version based on all experimental information available in the literature. In the present work, the liquid phase and the fcc-(Ni) phase are treated as disordered solutions; the thermodynamic behavior of the ordered intermetallic compounds with appreciable

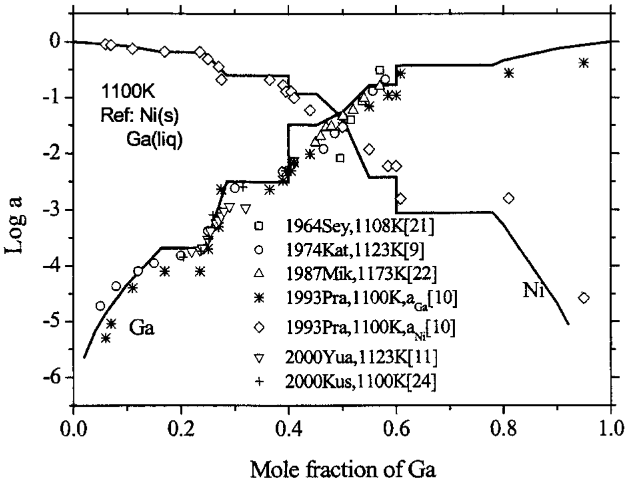

Fig. 4 The calculated Ga and Ni activity at 1100 K compared with experimental data; reference state: Ga(l) and Ni(s). The solid line stands for the calculated results; the other symbols represent experimental results from Ref 9, 10, 11, 21, 22, 24.

ranges of homogeneity, Ni_3Ga and NiGa, are described by a two-sublattice model, taking also into consideration the order-disorder transformation between the Ni_3Ga phase and the fcc-(Ni) phase. The other five compounds in the Ni-Ga system are treated as stoichiometric line compounds. Most of the experimental information on thermodynamic properties and phase equilibria are well reproduced by the present description.

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