

## THERMODYNAMIC MODELING OF THE Na–X (X = Si, Ag, Cu, Cr) SYSTEMS

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### Abstract

The Na–X (X = Si, Ag, Cu, Cr) systems have been critically reviewed and modeled by means of the CALPHAD approach. The two compounds, NaSi and Ag<sub>2</sub>Na, are treated as stoichiometric ones. By means of first-principles calculations, the enthalpies of formation at 0 K for the LT–NaSi (low temperature form of NaSi) and Ag<sub>2</sub>Na have been computed to be –5210 and –29821.8 Jmol<sup>–1</sup>, respectively, with the desire to assist thermodynamic modeling. One set of self-consistent thermodynamic parameters is obtained for each of these binary systems. Comparisons between calculated and measured phase diagrams show that most of the experimental information can be satisfactorily accounted for by the present thermodynamic descriptions.

*Keywords:* Na–X (X = Si, Ag, Cu, Cr); Phase diagram; CALPHAD; First-principles calculations

### 1. Introduction

Al alloys are widely used for commercial applications mainly due to the low density as well as the good mechanical and processing properties. Na, Si, Ag, Cu, and Cr are several elements that affect the mechanical

properties of Al alloys noticeably. Na is an effective alloying element to enhance the corrosion resistance of multi-component commercial Al alloys. Si can improve the casting and machining characteristics of Al alloys. The addition of Ag to Al alloys can significantly increase their hardening

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response. Cu is an important alloy element, and it has a certain solid solution strengthening effect. Cr can improve the toughness and reduce stress corrosion cracking sensitivity of Al alloys. The design and development of high quality commercial Al alloys need information about the phase equilibria and thermodynamic properties of the Na–X (X = Si, Ag, Cu, Cr) systems.

The thermodynamic descriptions for the Na–X (X = Si, Ag, Cu, Cr) binary systems are also a continuing effort of our previous attempts [1–5] to establish a thermodynamic database for multi-component Al alloys. However, to the best of our knowledge, so far there are no thermodynamic assessments for these binary systems. Thorough thermodynamic assessments of the Na–X (X = Si, Ag, Cu, Cr) systems are needed in order to provide a reliable basis for thermodynamic extrapolations and calculations in related ternary and higher-order systems. The purpose of the present work is devoted to providing a self-consistent set of thermodynamic parameters for each of these binary systems by means of a hybrid approach of CALPHAD method and first-principles calculations.

## 2. Literature Review

The Na–Si system was critically reviewed by Sangster and Pelton [6] who considered the previous experimental results. In the Na–Si system, NaSi [7, 8], NaSi<sub>2</sub> [9], and clathrate compound Na<sub>x</sub>Si<sub>136</sub> (x = 0–24) [10, 11] were reported in the literature. The Na–Si phase diagram was firstly determined by Morito et al. [12] using the differential thermal analysis (DTA) and X-ray diffraction

(XRD). The NaSi<sub>2</sub> was not found by Morito et al. [12]. The melting point of NaSi was determined to be 798 °C [12]. There is no report on the melting point of Na<sub>x</sub>Si<sub>136</sub> [10, 11]. The LT–NaSi transforms to HT–NaSi (high temperature form of NaSi) at 612 °C [12]. Up to now, no crystallographic data for HT–NaSi compound is available. The experimental measurement [12] shows that there is a miscibility gap for the liquid at 680 °C. The experimental phase diagram data [12] were accepted in the present modeling.

The assessed Na–Ag phase diagram was reported by Pelton [13]. Quercigh [14] and Mathewson [15] measured the liquidus of the Na–Ag system using thermal analysis. Kienast and Verma [16] confirmed the existence of an Fcc-type intermediate Ag<sub>2</sub>Na and its crystal structure using XRD. The experimental phase diagram data [14, 15] were used in the present modeling.

The Na–Cu system was critically reviewed by Pelton [17]. No compound was found in this system. The solubility of Cu in liquid Na was measured via equilibration and sampling technique by Walker and Pratt [18], Singer et al. [19], and Singer and Weeks [20], and radioactive tracer technique by Humphreys [21]. Above the melting point of Cu, a miscibility gap for the liquid most likely exists, showing a monotectic temperature close to the melting point of Cu [17]. The solubility of Na in solid (Cu) has not been measured. It was probably very small due to the large difference between the atomic radii of Cu and Na. On the basis of the results mentioned above, Pelton [17] constructed the Na–Cu phase diagram, which was accepted by Moffatt [22]. The experimental phase diagram data [18–21]

were reliable and thus adopted in the present modeling.

The schematic Na–Cr phase diagram was given by Venkatraman and Neumann [23]. The solubility of Cr in liquid Na was determined by Eichelberger and McKisson [24] and Singer et al. [25]. This solubility was discussed by Awasthi and Borgstedt [26]. The experimental data [24, 25] were accepted in the present modeling.

### 3. Enthalpies of formation calculated via first-principles method

The enthalpy of formation is crucial in evaluating phase diagram through thermodynamic modeling. There are two intermetallic compounds in the Na–X (X = Si, Ag) systems, and their crystal structures have been determined [7, 16, 27–29]. Due to the low melting point of Na, it is extremely difficult to prepare Na–Si and Na–Ag alloys, which are suitable for experimental measurement of enthalpy of formation. Since the crystal structure of the high temperature phase HT–NaSi is still unknown [12], only enthalpies of formation of LT–NaSi phase and Ag<sub>2</sub>Na have been calculated via first-principles calculations. In the present work, the generalized gradient approximation (GGA) proposed by Perdew-Burke-Ernzerhof [30] for the exchange-correlation potential has been used for all the calculations, and the valence electrons are explicitly treated by projector augmented plane-wave (PAW) potentials [31], as implemented in the Vienna ab initio simulation package (VASP) [32, 33]. The integration in the Brillouin zone is done on the special k-points determined from the

Monkhorst-Pack scheme [34]. Convergence tests indicate that a cutoff of 350 eV is sufficient to insure that the total energy difference is less than 1 meV/atom. The convergence criteria for electronic self-consistency and ionic relaxation loop are 10<sup>-5</sup> eV and 10<sup>-4</sup> eV/Å, respectively. The system is fully relaxed in respect of atomic positions and cell shape in order to find their stable state.

The crystal structures of LT–NaSi and Ag<sub>2</sub>Na are reported as monoclinic (*C2/c*) [7] and cubic (*Fd-3m*) [16], respectively. The enthalpy of formation of the intermetallic compound Na<sub>m</sub>X<sub>n</sub> (X = Si, Ag) is defined as follows:

$$\Delta H_f(\text{Na}_m\text{X}_n) = E(\text{Na}_m\text{X}_n) - \frac{m}{m+n}E(\text{Na}) - \frac{n}{m+n}E(\text{X}) \quad (1)$$

where  $E(\text{Na}_m\text{X}_n)$ ,  $E(\text{Na})$ , and  $E(\text{X})$  are the equilibrium energies of the compound Na<sub>m</sub>X<sub>n</sub>, and the pure elements Na and X in their standard reference structures, respectively. Since the calculations are performed at 0 K and 0 Pa, the energy of formation is taken as the enthalpy of formation at 298 K. The enthalpies of formation of LT–NaSi and Ag<sub>2</sub>Na from first-principles calculations are used as the input for the thermodynamic modeling in the present work.

## 4. Thermodynamic Models

### 4.1 Unary Phase

The Gibbs energy function for  ${}^0G_i^\phi(T) = G_i^\phi - H_i^{\text{SER}}$  ( $i = \text{Si, Ag, Cu, Cr}$ ) in the phase  $\phi$  is expressed by the following equation [35]:

$${}^0G_i^\phi(T) = a + b \cdot T + c \cdot T \cdot \ln T + d \cdot T^2 + e \cdot T^{-1} + f \cdot T^3 + g \cdot T^7 + h \cdot T^{-9} \quad (2)$$

where  $H_i^{\text{SER}}$  is the mole enthalpy of the element  $i$  at 298.15 K and 1 bar in its standard element reference (SER) state, and  $T$  is the absolute temperature. The last two terms in Eq. 2 are used only outside the ranges of stability [36],  $g \cdot T^7$  for a liquid below the melting point and  $h \cdot T^{-9}$  for solid phases above the melting point.

#### 4.2 Solution Phase

The liquid, (Ag), (Cu), (Na), and (Cr) phases are modeled as completely disordered solutions. The Gibbs energy of the phase is described by a Redlich-Kister (R-K) polynomial [37]:

$$G_m^\phi - H^{\text{SER}} = x_{\text{Na}} \cdot {}^0G_{\text{Na}}^\phi + x_i \cdot {}^0G_i^\phi + R \cdot T \cdot [x_{\text{Na}} \cdot \ln(x_{\text{Na}}) + x_i \cdot \ln(x_i)] + x_{\text{Na}} \cdot x_i \cdot \sum_{j=0}^n L_{\text{Na},i}^{j,\phi} (x_{\text{Na}} - x_i)^j \quad (3)$$

where  $H^{\text{SER}}$  is the abbreviation of  $x_{\text{Na}} \cdot H_{\text{Na}}^{\text{SER}} + x_i \cdot H_i^{\text{SER}}$ ,  $R$  is the gas constant,  $x_{\text{Na}}$  and  $x_i$  are the mole fractions of Na and  $i$  ( $i = \text{Si}, \text{Ag}, \text{Cu}$ ), respectively.  $x_{\text{Na}} \cdot {}^0G_{\text{Na}}^\phi + x_i \cdot {}^0G_i^\phi$  denotes the mechanical mixing to the Gibbs energy.

$x_{\text{Na}} \cdot x_i \cdot \sum_{j=0}^n L_{\text{Na},i}^{j,\phi} (x_{\text{Na}} - x_i)^j$  is the excess Gibbs energy.  $L_{\text{Na},i}^{j,\phi}$  is the  $j$ th R-K parameter of solution phase  $\phi$  and it is expressed as  $L_{\text{Na},i}^{j,\phi} = a_j + b_j \cdot T$ . The coefficients  $a_j$  and  $b_j$  ( $j = 0, 1, 2$ ) are the parameters to be optimized.

#### 4.3 Intermetallic Compound

NaSi and  $\text{Ag}_2\text{Na}$  were treated as stoichiometric compounds  $A_mB_n$ . The Gibbs

energy of  $A_mB_n$  per mole formula is expressed as follows:

$${}^0G_m^{A_mB_n} - m \cdot H_A^{\text{SER}} - n \cdot H_B^{\text{SER}} = a + b \cdot T + m \cdot {}^0G_A^{\text{SER}} + n \cdot {}^0G_B^{\text{SER}} \quad (4)$$

where  $a$  and  $b$  are the parameters to be optimized.

#### 4.4 Gas Phase

The gas phase is described as an ideal gas mixture of the species Na,  $\text{Na}_2$  with Si,  $\text{Si}_2$ ,  $\text{Si}_3$ , Ag,  $\text{Ag}_2$ , Cu,  $\text{Cu}_2$ , Cr,  $\text{Cr}_2$ . Its Gibbs energy per mol of species is given by the following expression [38]:

$$G^{\text{Gas}} - H^{\text{Gas}} = \sum y_i \left[ G_i^{\text{Gas}} - H_i^{\text{SER}} + R \cdot T \cdot \ln(y_i) \right] + R \cdot T \cdot \ln(0.98692 \cdot P / \text{bar}) \quad (5a)$$

$$(n_{\text{Na}}^0 + n_j^0) / n = y_{\text{Na}} + 2 \cdot y_{\text{Na}_2} + y_i + 2 \cdot y_{j_2} \quad (5b)$$

where  $n$  is the number of moles of the species in the gas in internal equilibrium,  $(n_{\text{Na}}^0 + n_j^0)$  is the number of moles of atoms in the gas,  $y_i = (n_i/n)$  is the mole fraction of the species  $i$ ,  $G^{\text{Gas}} - H^{\text{Gas}}$  is the Gibbs energy of the species  $i$ , and  $P$  is the pressure. The Gibbs energy functions of the individual gas species are taken from the SGTE substances database [39].

#### 5. Results and Discussion

The optimization of the thermodynamic parameters in the Na-X ( $X = \text{Si}, \text{Ag}, \text{Cu}, \text{Cr}$ ) systems was performed with the PARROT module of the Thermo-calc software [40]. The step-by-step optimization procedure described by Du et al. [38] was adopted in the present assessment. Table 1 shows the crystal structures of the two compounds and the pure elements. As shown in the table,

Table 1. Enthalpy of formation for the NaSi and Ag<sub>2</sub>Na compounds and the crystal structures of the Na–X (X = Si, Ag) systems

Compound/Element	Pearson symbol	Space group	Lattice parameter (Å)			$\Delta H_f$ (J/mol)	Ref.
			a	b	c		
Na	cI2	<i>Im-3m</i>	4.235	-	-	-	[27]
			4.203	-	-	-	TW <sup>a</sup>
Si	cF8	<i>Fd-3m</i>	5.431	-	-	-	[28]
			5.467	-	-	-	TW
LT–NaSi	mS32	<i>C2/c</i>	12.19	6.55	11.18	-	[7]
			12.083	6.553	11.03	-5210	TW
Ag	cF4	<i>Fm-3m</i>	4.085	-	-	-	[29]
			4.149	-	-	-	TW
Ag <sub>2</sub> Na	cF24	<i>Fd-3m</i>	7.923	-	-	-	[16]
			8.019	-	-	-29821.8	TW

<sup>a</sup> TW = This work, first-principles calculation.

the presently computed lattice parameters agree well with the literature data [7, 16, 27–29].

Taking the Na–Si system as an example, the optimization began with the LT–NaSi phase. First, the coefficient  $a$  for LT–NaSi phase in Eq. 4 was set to be the enthalpy of formation calculated by the first-principles method. Second, the liquid phase was considered in the optimization.  $a_0$ ,  $b_0$ ,  $a_1$ , and  $b_1$  were introduced in order to give an adequate description of the liquid phase. Third, HT–NaSi was included in the optimization. The Gibbs energy of the HT–NaSi phase is equal to that of the LT–NaSi phase at the transition temperature of 612 °C. Finally, the thermodynamic parameters for all the phases were optimized simultaneously. The optimized thermodynamic parameters are listed in Table 2. The optimization procedure for the remaining Na–X (X = Ag, Cu, Cr) binary

system is analogy with that for the Na–Si system. The calculated invariant equilibria in the Na–X (X = Si, Ag, Cu, Cr,) systems along with the literature data are listed in Table 3.

Fig. 1 shows the calculated Na–Si phase diagram using the present set of thermodynamic parameters. It can be seen that the present calculation can well describe the experimental data. According to the calculation, a miscibility gap for the liquid phase appears at 679 °C.

The calculated Na–Ag phase diagram along with the experimental data [14, 15] is presented in Fig. 2. The enthalpy of formation of intermetallic compound Ag<sub>2</sub>Na is calculated to be -29821.8 J/mol via first-principles method. The coefficient  $a$  in Eq. 4 was set to be equal to this value in the optimization. As shown in Fig. 2, the present calculation agrees well with the experimental data [14, 15].

Table 2. Summary of the thermodynamic parameters in the Na-X (X = Si, Ag, Cu, Cr) systems

System	Phase	Sublattice model	Evaluated parameters
Na-Si	Liquid	(Na,Si) <sub>1</sub>	${}^0L^{\text{Liquid}} = -58420 + 16.938 \cdot T$
			${}^1L^{\text{Liquid}} = 47005 - 9.994 \cdot T$
	HT-NaSi	(Na) <sub>1</sub> (Si) <sub>1</sub>	${}^0G^{\text{HT-NaSi}} = -1463 - 16.339 \cdot T + {}^0G_{\text{Si}}^{\text{Diamond}} + {}^0G_{\text{Na}}^{\text{Bcc\_A2}}$
	LT-NaSi	(Na) <sub>1</sub> (Si) <sub>1</sub>	${}^0G^{\text{LT-NaSi}} = -5210 - 12.105 \cdot T + {}^0G_{\text{Si}}^{\text{Diamond}} + {}^0G_{\text{Na}}^{\text{Bcc\_A2}}$
Na-Ag	Liquid	(Na,Ag) <sub>1</sub>	${}^0L^{\text{Liquid}}_{\text{Ag,Na}} = 20096 - 3.448 \cdot T$
			${}^1L^{\text{Liquid}}_{\text{Ag,Na}} = -1615$
	Bcc_A2	(Ag,Na) <sub>1</sub> Va <sub>3</sub>	${}^0L^{\text{Bcc\_A2}}_{\text{Ag,Na:Va}} = 18287$
	Fcc_A1	(Ag,Na) <sub>1</sub> Va <sub>1</sub>	${}^0L^{\text{Fcc\_A1}}_{\text{Ag,Na:Va}} = 27340$
	Ag <sub>2</sub> Na	(Ag) <sub>2</sub> (Na) <sub>1</sub>	${}^0L^{\text{Liquid}}_{\text{Cu,Na}} = 56137 + 16.484 \cdot T$
Na-Cu	Liquid	(Cu,Na) <sub>1</sub>	${}^0G^{\text{Ag}_2\text{Na}}_{\text{Ag,Na}} = -29821.8 + 47.364 \cdot T + 2 \cdot G_{\text{Ag}}^{\text{Fcc\_A1}} + G_{\text{Na}}^{\text{Bcc\_A2}}$
			${}^1L^{\text{Liquid}}_{\text{Cu,Na}} = -2953$
	Bcc_A2	(Cu,Na) <sub>1</sub> (Va) <sub>3</sub>	${}^0L^{\text{Bcc\_A2}}_{\text{Cu,Na:Va}} = 63711$
	Fcc_A1	(Cu,Na) <sub>1</sub> (Va) <sub>1</sub>	${}^0L^{\text{Fcc\_A1}}_{\text{Cu,Na:Va}} = 73861$
Na-Cr	Liquid	(Na,Cr) <sub>1</sub>	${}^0L^{\text{Liquid}}_{\text{Cr,Na}} = 56433$
	Bcc_A2	(Na,Cr) <sub>1</sub> Va <sub>3</sub>	${}^0L^{\text{Bcc\_A2}}_{\text{Na,Cr:Va}} = 49609$

\* In J/(mol-formula); Temperature (T) in Kelvin.

Table 3. Calculated invariant equilibria in the Na-X (X = Si, Ag, Cu, Cr) systems compared with the literature data

Systems	Reactions	T, °C	Comment	Reference
Na-Si	Liquid#2 ↔ (Si) + HT-NaSi	750	Measured	[12]
		750.85	Calculated	TW <sup>a</sup>
	Liquid#2 ↔ Liquid#1 + HT-NaSi	680	Measured	[12]
		679	Calculated	TW
	HT-NaSi ↔ LT-NaSi	612	Measured	[12]
		612	Calculated	TW
Liquid#1 → Bcc_A2(Na)	95	Measured	[12]	
	95.7	Calculated	TW	
Na-Ag	Fcc_A1(Ag) + Liquid ↔ Ag <sub>2</sub> Na	322	Measured	[16]
		322	Calculated	TW
	Liquid → Bcc_A2(Na)	97.7	Assessed	[13]
		98	Calculated	TW
Na-Cu	Liquid#2 ↔ Liquid#1 + Fcc_A1(Cu)	1084	Assessed	[17]
		1084.3	Calculated	TW
	Liquid#1 ↔ Bcc_A2(Na) + Fcc_A1(Cu)	97.6	Assessed	[17]
		97.2	Calculated	TW
Na-Cr	Liquid(Cr) ↔ Gas + Bcc_A2(Cr)	1906.6	Calculated	TW
	Gas + Bcc_A2(Cr) ↔ Liquid	884	Assessed	[23]
		886	Calculated	TW
	Liquid ↔ Bcc_A2(Na) + Bcc_A2(Cr)	98	Assessed	[23]
		97.9	Calculated	TW

<sup>a</sup> TW = This work, calculation.

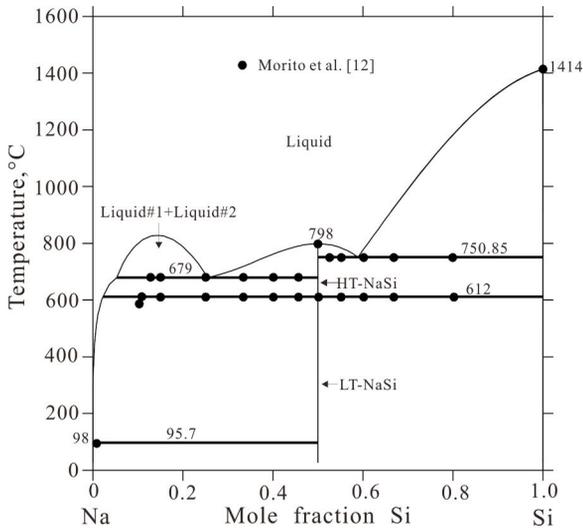


Fig. 1. Calculated Na-Si phase diagram along with the experimental data [12]

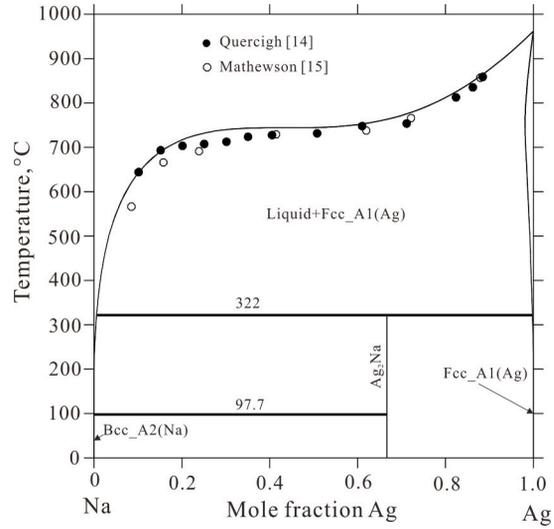


Fig. 2. Calculated Na-Ag phase diagram along with the experimental data [14, 15]

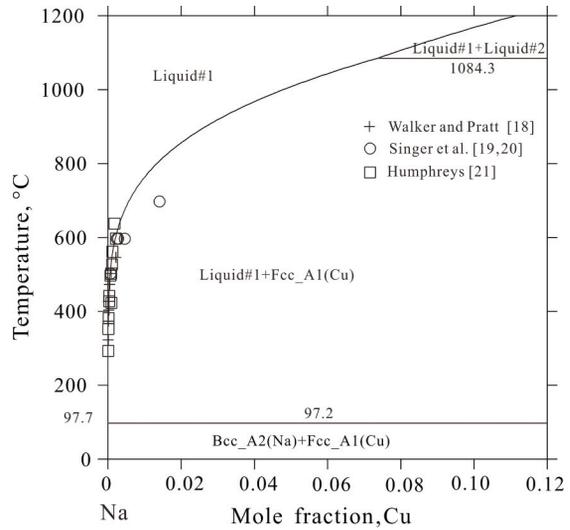
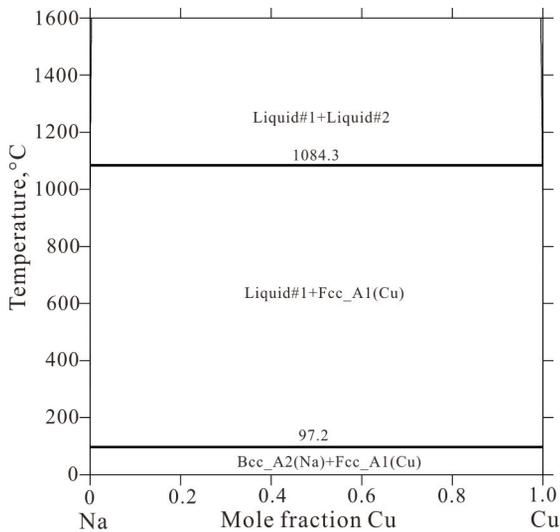


Fig. 3. (a) Calculated Na-Cu phase diagram. (b) Na-rich side along with the experimental data [18-21]

The calculated Na-Cu phase diagram with the experimental data [18-21] is presented in Fig. 3(a). The Na-rich side of the Na-Cu phase diagram is shown in Fig. 3(b). The experimental information about the monotectic reaction of Liquid#2 = Liquid#1 + Fcc\_A1(Cu) can be well reproduced by the present calculation. The calculated

temperature for the monotectic reaction is located at 1084 °C. The temperature of eutectic reaction Liquid#1 ↔ Bcc\_A2(Na) + Fcc\_A1(Cu) is calculated to be 97.2 °C according to this work. A good agreement is obtained between the calculated results and the experimental data.

Fig. 4(a) presents the Na-Cr phase

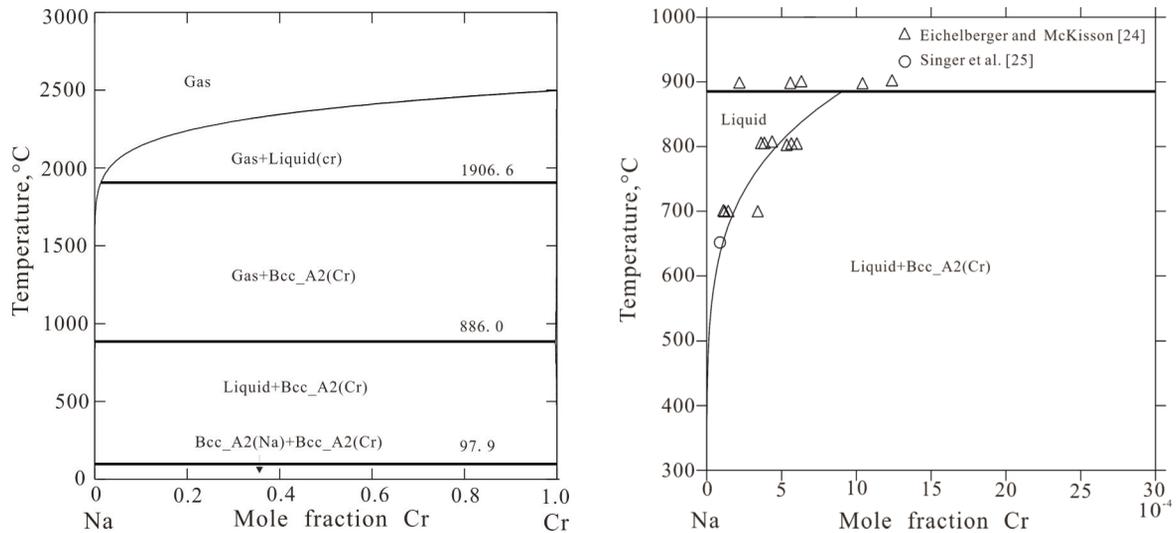


Fig. 4. (a) Calculated Na–Cr phase diagram. (b) Na–rich side along with the experimental data [24, 25]

diagram with gas phase. The Na–rich side of the Na–Cr system with the experimental data [24, 25] is shown in Fig. 4 (b). The temperatures of the three invariant reactions,  $\text{Liquid}(\text{Cr}) \leftrightarrow \text{Gas} + \text{Bcc\_A2}(\text{Cr})$ ,  $\text{Gas} + \text{Bcc\_A2}(\text{Cr}) \leftrightarrow \text{Liquid}$ , and  $\text{Liquid} \leftrightarrow \text{Bcc\_A2}(\text{Na}) + \text{Bcc\_A2}(\text{Cr})$ , are calculated to be 1906 °C, 886 °C, and 97.9 °C respectively.

## 6. Conclusion

The enthalpies of formation for the two LT–NaSi and Ag<sub>2</sub>Na compounds computed via first-principles calculations were used in the present thermodynamic modeling.

A critical literature review of the Na–X (X = Si, Ag, Cu, Cr) systems has been made, and the thermodynamic modeling for each of the binary systems was performed.

One set of self-consistent thermodynamic parameters for each binary side was obtained by means of the CALPHAD approach. The comprehensive comparison shows that the

calculated phase diagrams are in a good agreement with the experimental data.

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