First-Principles Calculations and Thermodynamic Assessment of the Li-Rh and Ti-Tm Systems

Yassine Djaballah, Ahmed Said Amer, Şule Uğur, Gökay Uğur, and Aissa Belgacem-Bouzida

Abstract—Thermodynamic modeling of the Li-Rh and Ti-Tm systems was carried out via a hybrid approach of CALPHAD (CALculation of PHase Diagrams) and first-principles calculations. The enthalpies of formation of LiRh, LiRh₃, Ti₃Tm, TiTm and Ti₃Tm₅ are computed via first-principles calculations by using the VASP code. The CALPHAD assessment of Li-Rh and Ti-Tm systems was then performed by considering both the first-principles computed enthalpies of formation and the experimental phase equilibrium data. The liquid phase was modeled with Redlich-Kister polynomial and the five intermetallic compounds were described as stoichiometric compounds. A consistent thermodynamic data set and phase diagrams for the Li-Rh and Ti-Tm systems are obtained.

Index Terms—CALPHAD, first-principles calculations, Li-Rh system, Ti-Tm system, phase diagrams.

I. INTRODUCTION

The alloy systems or intermetallic compounds composed of transition or rare earth metals have attracted much attention for the theoretical study of the solid state and for many industrial purposes, particularly in the fields of magnetism, energy and high technology [1].

The CALPHAD method, which is a powerful tool to cut down on cost and time during development of materials [2], effectively provides a clear guideline for materials design. In order to design high-performance alloys with rare earth elements, it is important to develop a thermodynamic database including transition and rare earth elements alloys.

In this work, the available experimental data of the Li-Rh and Ti-Tm systems are critically assessed and used to evaluate the model parameters defining the Gibbs energies of the phases in the systems. To supplement the experimental information, first-principles calculations of the formation enthalpies of the intermetallics compounds in this binary system are also included.

II. EXPERIMENTAL DATA

A. Li-Rh System

The Li-Rh has been reviewed by Sangster and Pelton[3].

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The assessed Li-Rh phase diagram is based on very limited data and contains two compounds LiRh and LiRh₃. No liquidus data have been published for this system. The evaluated phase diagram in Massalski [4] is given in Fig. 1. Magee [5] and Wheat *et al.* [6] performed some thermal analyses but no experimental details were given. The LiRh compound is prepared by direct reaction of the elements. A melting temperature of this compound is observed consistently at 2163 K. This may be interpreted as a eutectic temperature. Donkersloot and Van Vucht [7] detected the compound LiRh₃, which they characterized by X-Ray diffraction. The tentative congruent melting point of this compound is 1943 K [3]. The crystallographic structure of the compounds LiRh₃ was determined by Donkersloot and Van Vucht [7], while that of the LiRh compounds is given by Sidhu *et al.* [8] (see Table I). The enthalpies of formation of the intermetallic compounds LiRh and LiRh₃ were predicted by using the semi-empirical model of Miedema [9].

Fig. 1. Phase diagram of the Li-Rh system from Ref [4].

B. Ti-Tm System

An experimentally determined phase diagram is not known for the Ti-Tm system. Assuming similarity to La-Ti, Ce-Ti and Pr-Ti systems, Moffatt [10] has sketched a tentative phase diagram, which has been redrawn by Massalski [4] (Fig. 2). The Ti-Tm system consists of three terminal solution phases α Ti, β Ti and Tm and three intermetallic compounds Ti₃Tm, TiTm and Ti₃Tm₅. There are three eutectic reactions of the $L \leftrightarrow (\beta\text{Ti}) + \text{Ti}_3\text{Tm}$ at about 573 K, $L \leftrightarrow \text{TiTm} + \text{Ti}_3\text{Tm}$ and $L \leftrightarrow \text{Ti}_3\text{Tm}_5 + \text{Tm}$, and a eutectoid reaction of the $\beta\text{Ti} \leftrightarrow \alpha\text{Ti} + \text{Ti}_3\text{Tm}$ at about 503 K, and a peritectic reaction of the $L + \text{Ti}_3\text{Tm}_5 \leftrightarrow \text{TiTm}$. The crystal structures of the Ti₃Tm, TiTm and Ti₃Tm₅ compounds are

determined by Franceschi and Palenzona[11] and Moriarty *et al.* [12] and are listed in Table I. No experimental data on the thermodynamic properties is reported for the Tl-Tm system.

Fig. 2. phase diagram of the Tl-Tm system from Ref.[4].

III. MODELING

A. First Principles Calculation

In order to enhance the reliability of thermodynamic assessment, first-principles calculations based on density functional theory (DFT) [13] are carried out using Vienna Ab-initio Simulation Package (VASP) [14] to get formation energy of compounds involved.

The energy of formation at 0 K of the compounds LiRh, LiRh₃, Tl₃Tm, TlTm and Tl₃Tm₅ compounds is obtained by the following equations:

$$\Delta E(A_x B_y) = E(A_x B_y) - xE(A) - yE(B). \quad (1)$$

where $E(A_x B_y)$, $E(A)$ and $E(B)$ are the total energy for $A_x B_y$, pure element A and B ($A = \text{Li or Tl}$ and $B = \text{Rh or Tm}$) at 0 K respectively. At 0 K, energy formation corresponds also to the enthalpy of formation.

The calculations are performed using the projected augmented wave (PAW) pseudo-potentials [15] with the Perdew-Burke-Ernzerhof [16] GGA for the exchange correlation potential. A plane wave cutoff energy of 300 eV is used, a value that is more than 1.3 times greater than the highest plane wave energy cutoff of the elements in the both systems. An energy convergence criterion of 10^{-5} eV for electronic structure self-consistency was used in the calculations. Brillouin zone integrations were performed using the Monkhorst-Pack k-point mesh scheme [17], and the total energy differences were converged to within 10^{-4} J/mol.

B. Thermodynamic Models

Pure elements: The Gibbs energy functions ${}^0G_i^\phi = G_i^\phi - H_i^{\text{SER}}(298.15\text{ K})$ or the elements i ($i = \text{Li, Rh, Tl or Tm}$) in the phase ϕ is expressed by the following equation:

$${}^0G_i^\phi = a + bT + cT \ln T + dT^2 + eT^3 + fT^{-1} + gT^7 + hT^{-9} \quad (2)$$

where $H_i^{\text{SER}}(298.15\text{ K})$ is the molar enthalpy of the element i

at 298.15 K in its standard element reference (SER) state. ${}^0G_i^\phi$ and G_i^ϕ are the absolute and the relative Gibbs energy of the element i in the ϕ state, and T is the absolute temperature. In the present modeling, the Gibbs energies for pure elements were taken from the compilation by Dinsdale [18].

Intermetallic compounds: The intermetallic compounds in the Li-Rh and Tl-Tm systems present no solubility range according to the available experimental data. Thus, they have been treated as stoichiometric compounds:

The Gibbs energy of the $A_p B_q$ ($A = \text{Li, Tl}$ and $B = \text{Rh, Tm}$) intermediate phases, can be expressed as:

$$G^{A_p B_q} = \Delta H_f^{A_p B_q} - T \Delta S_f^{A_p B_q} \quad (3)$$

The enthalpy and entropy of formation ($\Delta H_f^{A_p B_q}$ and $\Delta S_f^{A_p B_q}$) of the $A_p B_q$ phase were considered as temperature independent optimizing parameters.

Solution phase: The liquid phases in the two systems were modeled as substitutional solutions and the Gibbs energy is described by the following formalism:

$$G^\phi = \sum_i x_i {}^0G_i^\phi + G^{\text{ide}} + G^{\text{exc}} \quad (4)$$

where x_i is the molar fraction of the component i in the ϕ phase ($i = \text{Li, Rh, Tl or Tm}$), ${}^0G_i^\phi$ is the molar Gibbs energy of pure component in the ϕ phase, which are taken from the compilation of Dinsdale [18]. The terms G^{ide} and G^{exc} stand for the molar Gibbs energy of ideal and excess mixing. The excess Gibbs energy G^{exc} can be expressed as an empirical Redlich Kister polynomial [19]:

$$G^{\text{exc}} = x_A x_B \sum_{\nu=0}^n {}^\nu L_{A;B}^{\text{Liq}} (x_A - x_B)^\nu \quad (5)$$

whereas G^{ide} can be calculated according the theoretical relationship

$$G^{\text{ide}} = RT[x_A \ln(x_A) + x_B \ln(x_B)] \quad (6)$$

where R is the gas constant, x_A and x_B are the mole fraction of elements Li or Tl and Rh or Tm respectively. ${}^\nu L_{A;B}^{\text{Liq}}$ is the ν interaction parameters expressed as ${}^\nu L_{A;B}^{\text{Liq}} = A_\nu + TB_\nu$ and A_ν and B_ν are model parameters to be evaluated.

C. Assessment Procedure

Most of the experimental data mentioned above were used in the thermodynamic evaluation. The optimization was carried out by using our computer program [20], [21]. Each piece of the selected information was given a certain weight by personal judgment, and changed by trial and error during the assessment, until most of the selected experimental information was reproduced within the expected uncertainty limits. All the parameters were evaluated together to give the best description of the system.

IV. RESULTS AND DISCUSSION

Lattice parameters and enthalpies of formation for Li-Rh and Tl-Tm compounds, obtained from first principles

calculations, are reported in Table I. The calculated lattice parameters are in good agreement with experimental data, with a maximum difference of about 1.5 %. Table II lists the optimized thermodynamic parameters of each phase in the Li-Rh and Ti-Tm systems.

TABLE I: CRYSTAL STRUCTURES DATA AND ENTHALPIES OF FORMATION OF THE LI-RH AND TI-TM SYSTEMS

Phase	Pearson symbol and Space group	Lattice parameters (nm)			Ref.
LiRh	<i>hP2</i> (<i>P-6m2</i>)	0.2649	0.2649	0.4359	[8]
		0.2658	2.6578	0.4360	This work
LiRh ₃	<i>oI8</i> (<i>Imm2</i>)	0.2658	0.8602	0.4657	[7]
		0.2670	0.8641	0.4667	This work
Ti ₃ Tm	<i>cP4</i> (<i>Pm-3m</i>)	0.4655	0.4655	0.4655	[12]
		0.4760	0.4761	0.4760	This work
TiTm	<i>cP2</i> (<i>Pm-3m</i>)	0.3670	0.3670	0.367	[12]
		0.3768	0.3768	0.3768	This work
Ti ₃ Tm ₅	<i>hP16</i> (<i>P6₃/mcm</i>)	0.8798	0.8798	0.6495	[11]
		0.8936	0.8936	0.6547	This work

TABLE II: THE OPTIMIZED PARAMETERS OF LI-RH AND TI-TM SYSTEMS

System	Phases	Thermodynamic parameters
Li-Rh	Liquid	${}^0L_{Li,Rh}^{Li} = -34966 + 5.266 * T$
	LiRh	$\Delta G^{LiRh} = -17481 - 2.737 * T$
	LiRh ₃	$\Delta G^{LiRh3} = 12009 - 0.695 * T$
Ti-Tm	Liquid	${}^0L_{Ti,Tm}^{Li} = -49408 + 25.079 * T$
	Ti ₃ Tm	$\Delta G^{Ti3Tm} = -13340 - 2.131 * T$
	TiTm	$\Delta G^{TiTm} = -22434 + 2.359 * T$
	Ti ₃ Tm ₅	$\Delta G^{Ti3Tm5} = -22771 + 5.045 * T$

Fig. 3 shows the calculated Li-Rh phase diagram. Comparison of the calculated invariant reactions with the experimental and predicted ones in this system is listed in Table III. All reactions are reproduced with experiment uncertainties. Table IV and Fig. 4 shows the evaluated enthalpies of formation of the LiRh and LiRh₃ intermetallics by Calphad method together with the predicted data obtained by the Miedema model [9], as well as the calculated values determined by first principles calculations. Our calculations are acceptable in comparison with the predicted ones, if we take into account the large uncertainties of the Miedema model.

Calculated Ti-Tm phase diagram is shown in Fig. 5. Comparison of the calculated invariant equilibria temperatures and compositions with experimental and calculated ones is listed in Table V. A satisfactory agreement is noted between our result and the experimental. The enthalpies of formation of the Ti-Tm intermetallic compounds calculated in this work are presented in Fig. 6 and

Table IV. As we can see that the convex hull for compounds is stable.

Fig. 3. Calculated phase diagram of the Li-Rh system.

TABLE III: THE INVARIANT REACTIONS IN THE LI-RH SYSTEM

Reaction	Type of reaction	This work		Ref. [3]	
		X _{Rh} (Liq)	T(K)	X _{Rh} (Liq)	T(K)
L ↔ (Li) + LiRh	Eutectic	0.0073	451.3	≈ 0	453.0
L ↔ LiRh	Congruent	0.5	2147.4	0.5	2163.0
L ↔ LiRh + LiRh ₃	Eutectic	0.705	1913.3	≈ 0.7	1893.0
L ↔ LiRh ₃	Congruent	0.75	1924.7	0.75	1933.0
L ↔ Rh + LiRh ₃	Eutectic	0.819	1896.0	≈ 0.8	1843.0

TABLE IV: ENTHALPIES OF FORMATION OF INTERMETALLIC COMPOUNDS IN THE LI-RH AND TI-TM SYSTEMS IN KJ/MOLQ

Phase	first principles calculations this Work	Calphad This Work	Miedema Model [9]
LiRh	-17.3319	-17.481	-20.0
LiRh ₃	-12.7246	-12.009	-13.0
Ti ₃ Tm	-13.1193	-13.340	
TiTm	-22.8245	-22.434	
Ti ₃ Tm ₅	-22.7717	-22.771

Fig. 4. Enthalpies of formation of intermetallic phases in the Li-Rh system.

Fig. 5. Calculated phase diagram of the Tl-Tm system.

TABLE V: THE INVARIANT REACTIONS IN THE Tl-Tm SYSTEM

Reaction	Type of reaction	This work		Ref. [4]	
		X_{Rh} (Liq)	T (K)	X_{Rh} (Liq)	T (K)
$(\beta Tl) \leftrightarrow (\alpha Tl) + Tl_3Tm$	Eutectoid	0.00	507.0	≈ 0.0	503.0
$L \leftrightarrow (\alpha Tl) + Tl_3Tm$	Eutectic	0.0044	576.3	≈ 0.0	573.0
$L \leftrightarrow Tl_3Tm$	Congruent	0.25	1892.3	0.25	1893.0
$L \leftrightarrow Tl_3Tm + TlTm$	Eutectic	0.32	1826.4	≈ 0.35	1723.0
$L \leftrightarrow TlTm$	Congruent	0.5	1978.5	0.5	1983.0
$L + TlTm \leftrightarrow Tl_3Tm_5$	Peritectic	0.75	1651.5	≈ 0.79	1663.0
$L \leftrightarrow Tl_3Tm_5 + Tm$	Eutectic	0.85	1552.7	≈ 0.87	1563.0

Fig. 6. Enthalpies of formation of intermetallic phases in the Tl-Tm system.

V. CONCLUSION

The Tl-Tm and Li-Rh systems have been assessed for the first time. The enthalpies of formation of intermetallic phases in the two systems are determined via first principles calculations and used in the assessment of these systems. A consistent set of thermodynamic parameters from various thermodynamic models has been obtained, for each solution phase and intermetallic compounds in the Tl-Tm and Li-Rh binary systems. Due to the scarcity of the experimental data, further experimental investigations are desirable.

REFERENCES

- [1] Z. Xia, Z. Chen, Y. Shi, N. Mu, and N. Sun, "Effect of rare earth element additions on the microstructure and mechanical properties of tin-silver-bismuth solder," *Journal of Electronic Materials*, vol. 31, pp. 564-567, 2002.
- [2] N. Saunders and A. P. Miodownik, *CALPHAD, Calculation of Phase Diagrams, A Comprehensive Guide*, Pergamon, 1998, pp. 7-26.
- [3] J. Sangster and A. Pelton, "The Li-Rh (lithium-rhodium) system," *J. Phase Equilibria*, vol. 12, pp. 682-684, 1991.
- [4] T. B. Massalski and O. Okamoto, *Binary Alloy Phase Diagrams*, ASM International, Materials Park, Ohio, 1990, p. 2462, 3504.
- [5] C. Magee, "A study of the synthesis and properties of the transition-metal hydrides," Final Report to the Joint US/EURATOM Research and Development Program. Contract No. AT (II-I)-1185, Denver Research Institute, University of Denver, EURAEC 1251, 1964.
- [6] H. G. Wheat, C.-Y. Cheng, R. J. Bayuzick, R. W. Sullivan, and C. B. Magee, "Compounds and phase relationships in the Li-RhSystem," *J. Less-Common Met.*, vol. 58, pp. 13-29, 1978.
- [7] H. C. Donkersloot and J. H. N. Van Vucht, "The crystal structure of IrLi, Ir3Li and LiRh3," *J. Less-Common Met.*, vol. 50, pp. 279-282, 1976.
- [8] S. S. Sidhu, K. D. Anderson, and D. D. Zaubers, "Neutron and X-ray diffraction study of LiRh," *Acta Crystallogr.*, vol. 18, pp. 906-907, 1965.
- [9] F. R. de Boer, R. Boom, W. C. M. Mattens, A. R. Miedema, and A. K. Niessen, *Cohesion in Metals: Transition Metal Alloys*, North-Holland Physics Publishing, Amsterdam, 1988, pp. 463.
- [10] W. G. Moffatt, *The Handbook of Binary Phase Diagrams*, Genium Pub. Corp., Schenectady, N.Y. : General Electric, 1981, pp. 373.
- [11] E. A. Franceschi and A. Palenzona, "The crystal structure of RE5Ti3 and Y3Ti3 compounds," *J. Less-Common Met.*, vol. 18, pp. 93-98, 1969.
- [12] J. L. J. Moriarty, J. E. Humphreys, R. O. Gordon, and N. C. Baenziger, "X-ray examination of some rare-earth-containing binary alloy systems," *Acta Crystallographica*, vol. 21, pp. 840-841, 1966.
- [13] W. Kohn and L. J. Sham, "Self-consistent equations including exchange and correlation effects," *Phys. Rev.*, vol. 140, pp. 1133-1138, 1965.
- [14] G. Kresse and J. Furthmüller, "Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set," *Phys. Rev. B*, vol. 54, pp. 11169-11186, 1996.
- [15] G. Kresse and D. Joubert, "From ultrasoft pseudopotentials to the projector augmented-wave method," *Phys. Rev. B*, vol. 59, pp. 1758-1775, 1999.
- [16] J. P. Perdew, K. Burke, and M. Ernzerhof, "Generalized gradient approximation made simple," *Phys. Rev. Lett.*, vol. 77, pp. 3865-3868, 1996.
- [17] H. J. Monkhorst and J. D. Pack, "Special points for Brillouin-zone integrations," *Phys. Rev. B*, vol. 13, pp. 5188-5192, 1976.
- [18] A. T. Dinsdale, "SGTE data for pure elements," *Calphad*, vol. 15, pp. 317-425, 1991.
- [19] O. Redlich and A. T. Kister, "Thermodynamics of nonelectrolyte solutions in a binary system," *Ind. Eng. Chem.*, vol. 40, pp. 341-345, 1948.
- [20] Y. Djaballah, "Modeling liquids and solid solutions of non-stoichiometric binary and ternary alloys," PhD thesis, Physics Department, Batna University, Algeria, 2005.
- [21] A. Belgacem-Bouzida, Y. Djaballah, and M. Notin, "Calorimetric measurement of the intermetallic compounds Cr3Ga and CrGa4 and thermodynamic assessment of the (Cr-Ga) system," *J. Alloys Comp.*, vol. 397, pp. 155-160, 2005.

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