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Thermodynamic Assessment (Suggestions) Of the Gold-Rubidium System

Achraf Benmechri[1], Ahmed Said Amer[1], Yassine Djaballah[1]
[1](*Laboratoire d'étude Physico-Chimique des Matériaux-Département de Physique, Université de Batna 1, Algeria)*

Abstract: Thermodynamic modellings of the Au–Rb system was carried out by means of the CALPHAD (calculation of phase diagrams) method. The liquid phase and the intermetallic compounds Au_5Rb, Au_2Rb, AuRb and Au_7Rb_3 and Au_3Rb_2 (new compounds) in addition to the compound $AuRb_2$ (suspected compound) are taken into consideration in this optimization. The substitutional solution model was used to describe the liquid phase. The six compounds are treated as stoichiometric phases. The enthalpies of formation used in these optimizations were calculated within ab-initio method in precedent work.

Keywords: CALPHAD, Au-Rb system,Thermodynamic assessment, Phase diagram.

I. INTRODUCTION

Many ambiguities and suspicions revolve around the phase diagram of the Au-Rb system. The first phase diagram established for this system was that of Kienast et al [1]. It contained three compounds Au_4Rb, Au_2Rb and AuRb, but Raub and Compton [2], in a subsequent work corrects the structure of the first compound which becomes Au_5Rb instead of Au_4Rb. In 1986, Pelton [3] publishes a phase diagram of the Au-Rb system based on the existence of the three Au_5Rb, Au_2Rb and AuRb compounds and this phase diagram is reported in the Massalski [4] compilation. A few years later, Zachwieja [5,6,7,8] tried to reproduce all the compounds present in the phase diagram. He was able to confirm the existence of the Au_5Rb [5] and AuRb [6] compounds, but he said that he had found no indication of the Au_2Rb compound and in his place discovered the Au_7Rb [7] and Au_3Rb_2 [8] compounds (upstream and downstream of the Au_2Rb composition). In 2014, Benmechri et al [9]. Published results in which they confirmed the stability of the Au_7Rb_3 and Au_3Rb_2 compounds and the high probability of the instability or even the lack of the Au_2Rb compound. In the same work [9], Benmechri et al. predict the existence of the $AuRb_2$ composition for which they calculated the elasticity constants and the bulk modulus. This compound ($AuRb_2$) was mechanically stable at 0K and therefore could well be a composition in the phase diagram of the system studied.

II. LITARATURE INFORMATION

Only two phase diagrams exist for the Au-Rb system. The first is that of Kienast et al. [1] which is shown in figure 1. The second is that of Pelton [3] which is shown in figure 2, and in which the three compounds are formed by peritectic reaction. Taking into account the work of Zachwieja [5,6,7,8] and Benmechri et al [9], the Pelton phase diagram has become doubtful and for this reason we have decided in this work to propose restitutions for this phase diagram Based on the Calphad method using the results provided by the ab-initio method.

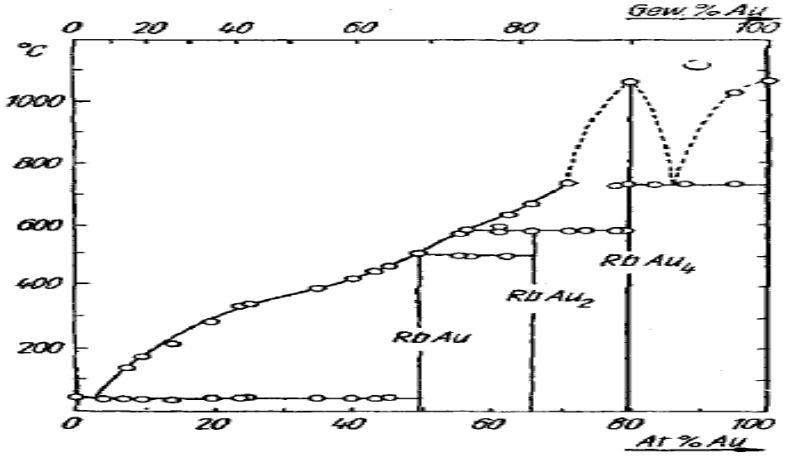

Fig. 1 Phase diagram of the Au-Rb system according to Kienast et al. [1]

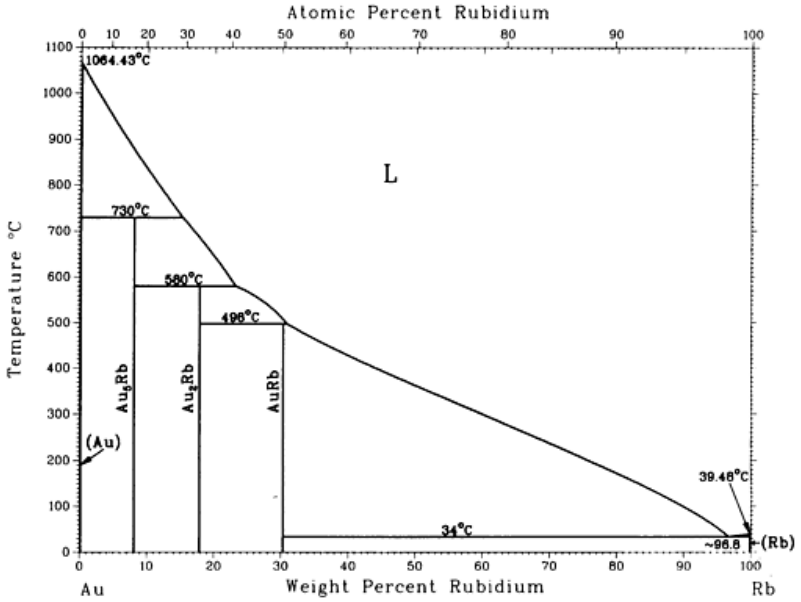

Fig. 2 Diagram of phases of the system Au-Rb according to Massalski [3].

III. THERMODYNAMIC MODELS

1. Pure elements

The Gibbs energies functions used in the present work are those collected in the database compiled dy Dinsdale [10]. We used the SGTE (Scientific Groupe Thermodata Europe) format for the Gibbs energy functions $G_i^{\Phi}(T)$ for the elements *i* (Au and Rb) in the phase ϕ (liquid, fcc and bcc).

$G_i^{\Phi} = {}^0G_i^{\Phi}(T) - H_i^{SER}(298.15\,K) = a + bT + cT\,Ln\,T + dT^2 + eT^3 + fT^{-1} + gT^7 + hT^{-9}$ where ${}^0G_i^{\Phi}(T)$ and G_i^{Φ} are the relative and absolute Gibbs energy of the element i in the ϕ state. $H_i^{SER}(298.15\,K)$ is the molar enthalpy of the element *i* at 298.15 K in its standard element reference (SER) state, fcc for Au and bcc for Rb.

2. Intermetallic compounds

All intermetallics are stoichiometric compounds. Their phases Gibbs energy per mol of atoms are given by the following expression : $G^{Au_pRb_q} = \frac{p}{p+q}H_{Au}^{SER} + \frac{p}{p+q}H_{Rb}^{SER} + \Delta H_f^{Au_pRb_q} - T\Delta S_f^{Au_pRb_q}$ with *p* and *q* : the number of Au and Rb in the intermetallic Au_pRb_q .

The enthalpy and entropy of formation were considered as independent of temperature.

3. Liquid solution phase

The solution phases were treated by the substitutional solution model with Redlich-Kister equation [11]. The sum of reference (*ref*), ideal (*id*) and excess (*exc*) terms gives the Gibbs energy for 1 mol of atoms.

$G^{Liq} = {}^{ref}G^{Liq} + {}^{id}G^{Liq} + {}^{exc}G^{Liq}$

With

${}^{ref}G^{Liq} = x_{Au}G_{Au}^{Liq} + x_{Rb}G_{Rb}^{Liq}$

${}^{id}G^{Liq} = RT[x_{Au}\,ln(x_{Au}) + x_{Rb}\,ln(x_{Rb})]$

${}^{exc}G^{Liq} = x_{Au}x_{Rb}\sum_{v=0}^{n} {}^vL_{Au,Rb}^{Liq}(x_{Au}-x_{Rb})^v$

Where ${}^vL_{Au,Rb}^{Liq}$ is the *v*th-order binary interaction parameter which can be expressed as $\alpha_v + \beta_v T$ with α_v and β_v are the parameters to be optimized.

IV. OPTIMIZATION METHODOLOGY:

Optimization methodology: The optimization of the parameters entering the previous models was carried out with the calculation code BATNABIN [12]. The latter allows the optimization of the thermodynamic functions of each phase existing in the system and the restoration of the corresponding phase diagram. The calculation is based on the collection of a set of experimental and theoretical data concerning the equilibrium points of the phase diagram and the thermodynamic quantities. These data will allow us to make a linear least square fit to obtain a mathematical description that reproduces as closely as possible all the experimental data while allowing favoring certain results which may appear more reliable than others.

V. RESULTS AND DISCUSSION

The Au-Rb system's phase diagram developed by Pelton [3] shows the existence of only three compounds: Au_5Rb, Au_2Rb and AuRb, all three formed by peritectic reaction (FIG.2.). But considering the great suspicions surrounding the Au_2Rb compound, we decided to propose three phase diagrams: the first one containing just the three compounds mentioned in the Pelton diagram. In the second, in addition to Au_5Rb and AuRb, the existence of the compounds Au_7Rb_3, Au_3Rb_2, which must normally replace Au_2Rb. The third encompasses all compounds that have been shown to be stable at 0K (Au_5Rb, Au_7Rb_3, Au_3Rb_2, AuRb and $AuRb_2$).

1. First optimization :

In this first optimization, we took into consideration the experimental phase diagram of Pelton [3] with the three compounds existing in this diagram. We have used as data some equilibrium points of the experimental diagram as well as the enthalpies of formation of the three compounds that have already been calculated by the ab initio method by Benmechri et al.[9]. The best optimization is obtained for a development of the free enthalpy of excess of the liquid phase to order 0. The calculated thermodynamic quantities of all the phases are summarized in Table 1. The calculated diagram is presented in Figure 3.

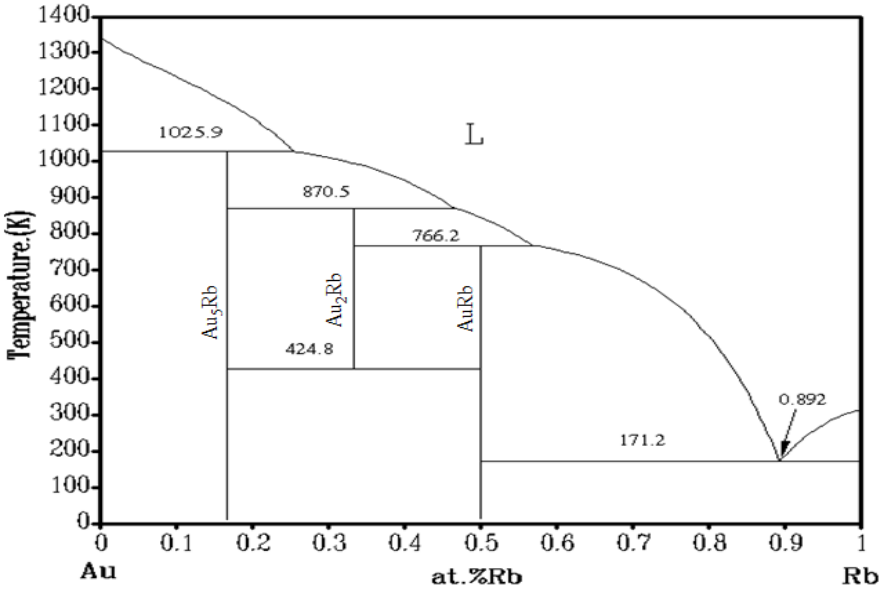

Fig. 3. First phase diagram computed by the CALPHAD modeling

Table 1. Parameters of the thermodynamic modeling of the phase diagram shown in Figure 3.

Phase	**Parameters**
Liquid	$L_0^{liquid} = -84345 + 75.851T$
Au_5Rb	$G^{Au_5Rb} = -19700 + 15.900\,T + 0.833\,H_{Au}^{SER} + 0.167\,H_{Rb}^{SER}$
Au_2Rb	$G^{Au_2Rb} = -23265 + 17.976\,T + 0.6661\,H_{Au}^{SER} + 0.3331\,H_{Rb}^{SER}$
AuRb	$G^{AuRb} = -28660 + 24.291\,T + 0.5\,H_{Au}^{SER} + 0.5\,H_{Rb}^{SER}$

Table 2. Temperatures and compositions of the invariant reactions of the phase diagram shown in Figure.3.

Reaction	Composition	Temperature (K)	Type of reaction	Reference
$Au + L \leftrightarrow Au_5Rb$	0.297	1003	Peritectic	[3]
	0.167	1025.9		This work
$Au_5Rb + L \leftrightarrow Au_2Rb$	0.410	853	Peritectic	[3]
	0.464	870.5		This work
$Au_2Rb + L \leftrightarrow AuRb$	0.506	796	Peritectic	[3]
	0.566	766.2		This work
$Au_2Rb \leftrightarrow AuRb + Au_5Rb$	0.592	424.8	Decomposition	This work
$L \leftrightarrow Rb + AuRb$	0.986	307	Eutectic	[3]
	0.891	171.8		This work

2. Second optimization :

In this second optimization, the compounds Au_5Rb and AuRb have been taken into consideration in addition to the two compounds Au_7Rb_3 and Au_3Rb_2 which we have already found to be stable at 0K. We have used as data some equilibrium points of the experimental diagram as well as the enthalpies of formation of the three compounds that have already been calculated by the ab initio method. The best optimization is obtained for a development of the free enthalpy of excess of the liquid phase to order 0. The calculated thermodynamic quantities of all phases are summarized in Table 3. The calculated diagram is shown in Figure 4.

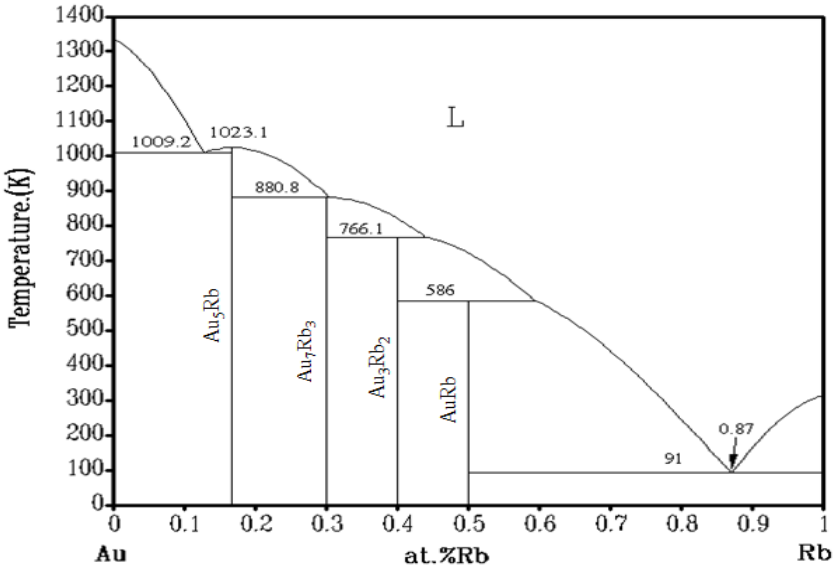

Fig. 4. Second phase diagram computed by the CALPHAD modelling

Table 3. Parameters of the thermodynamic modeling of the phase diagram shown in figure 4.

Phase	Parameters
Liquid	$L_0^{liquid} = -84345 - 35.851\ T$
Au_5Rb	$G^{Au_5Rb} = -19051 + 4.981\ T + 0.833\ H_{Au}^{SER} + 0.167\ H_{Rb}^{SER}$
Au_7Rb_3	$G^{Au_7Rb_3} = -27012 + 5.650\ T + 0.7\ H_{Au}^{SER} + 0.3\ H_{Rb}^{SER}$
Au_3Rb_2	$G^{Au_3Rb_2} = -29374 + 10.875\ T + 0.6\ H_{Au}^{SER} + 0.4\ H_{Rb}^{SER}$
AuRb	$G^{AuRb} = -28132 + 9.789\ T + 0.5\ H_{Au}^{SER} + 0.5\ H_{Rb}^{SER}$

Table 4. Temperatures and compositions of the invariant reactions of the phase diagram shown in Figure 4.

Reaction	Composition	Temperature (K)	Type of reaction	Reference
$L \leftrightarrow Au + Au_5Rb$	0.167	1006.23	Eutectic	This work
$L + Au_5Rb \leftrightarrow Au_7Rb_3$	0.303	880.8	Peritectic	This work
$L + Au_7Rb_3 \leftrightarrow Au_3Rb_2$	0.439	766.1	Peritectic	This work
$L + Au_3Rb_2 \leftrightarrow AuRb$	0.592	585.5	Peritectic	This work
$L \leftrightarrow Rb + AuRb$	0.986	307	Eutectic	[3]
	0.870	90.9		This work

3. Third optimization :

In this third optimization, we considered the Au_5Rb, AuRb, Au_7Rb_3 and Au_3Rb_2 compounds and also the suspected $AuRb_2$ compound that our calculations have asserted is mechanically stable at 0K. We have used as data some equilibrium points of the experimental diagram as well as the enthalpies of formation of the three compounds that have already been calculated by the ab initio method. The best optimization is obtained for a development of the free enthalpy of excess of the liquid phase to order 0. The calculated thermodynamic quantities of all phases are summarized in Table 5. The calculated diagram is presented in Figure 5.

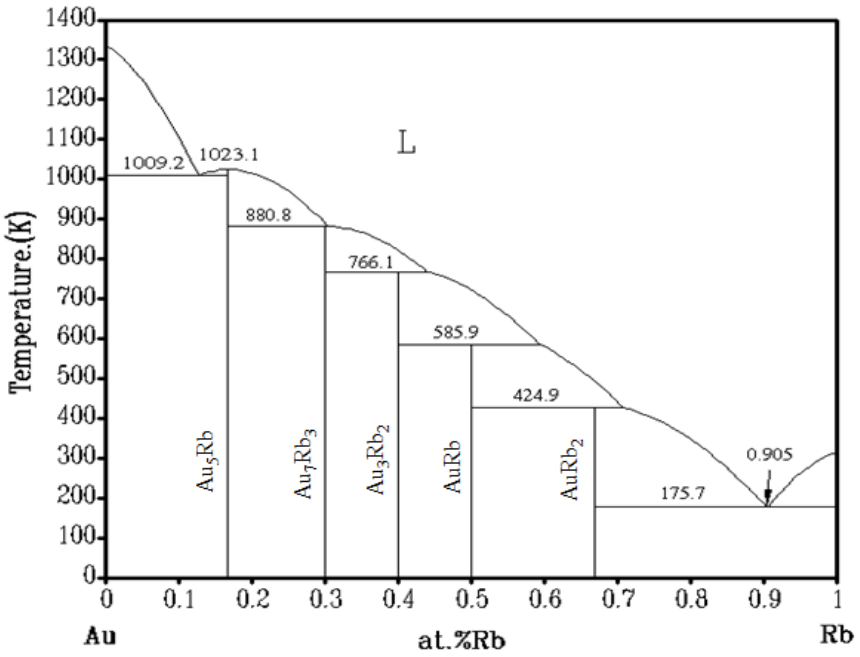

Fig. 5 Third phase diagram computed by the CALPHAD modelling

Table 5. Parameters of the thermodynamic modeling of the phase diagram shown in figure 5.

Phase	Parameters
Liquid	$L_0^{liquid} = -84345 - 35.851\ T$
Au_5Rb	$G^{Au_5Rb} = -19051 + 4.981\ T + 0.833\ H_{Au}^{SER} + 0.167\ H_{Rb}^{SER}$
Au_7Rb_3	$G^{Au_7Rb_3} = -27012 + 5.650\ T + 0.7\ H_{Au}^{SER} + 0.3\ H_{Rb}^{SER}$
Au_3Rb_2	$G^{Au_3Rb_2} = -29374 + 10.875\ T + 0.6\ H_{Au}^{SER} + 0.4\ H_{Rb}^{SER}$
AuRb	$G^{AuRb} = -28132 + 9.789\ T + 0.5\ H_{Au}^{SER} + 0.5\ H_{Rb}^{SER}$
$AuRb_2$	$G^{AuRb_2} = -22232 + 8.789\ T + 0.333\ H_{Au}^{SER} + 0.667\ H_{Rb}^{SER}$

Table 6. Temperatures and compositions of the invariant reactions of the phase diagram shown in Figure 5.

Reaction	Composition	Temperature (K)	Type of reaction	Reference
$L \leftrightarrow Au + Au_5Rb$	0.167	1009.23	Eutectic	This work
$L + Au_5Rb \leftrightarrow Au_7Rb_3$	0.320	880.8	Peritectic	This work
$L + Au_7Rb_3 \leftrightarrow Au_3Rb_2$	0.440	766.1	Peritectic	This work
$L + Au_3Rb_2 \leftrightarrow AuRb$	0.592	585.9	Peritectic	This work
$L + AuRb \leftrightarrow AuRb_2$	0.708	424.9	Peritectic	This work
$L \leftrightarrow Rb + AuRb_2$	0.904	175.7	Eutectic	This work

4. Discussion

The first restitution, which only takes into account the Au_5Rb, Au_2Rb and AuRb stoichiometries, shows that the Au_2Rb compound is metastable at 0K, while the other two compounds are perfectly stable.

In the second restitution, we assumed the existence of the Au_7Rb_3 and Au_3Rb_2 compounds that were discovered by Zachwieja [7,8] and we omitted the Au_2Rb compound that Zachwieja could not form and its attempts resulted in the two compounds Au_7Rb_3 and Au_3Rb_2. This second restitution shows that at 0K the Au_5Rb and AuRb compounds, as well as Au_7Rb_3 and Au_3Rb_2 are thermodynamically stable, like the results provided by the ab-initio method. The result obtained by the two methods (ab-initio and Calphad) supports the probability that the compound Au_2Rb is not a stable compound (at the limit of 0K) because this favors the questions posed and Zachwieja's suspicions about the existence of this compound.

The third restitution, which took into account in addition to the compounds of the second restitution the compound $AuRb_2$ of which we have predicted the existence, provided the information that the compounds Au_5Rb, AuRb, Au_7Rb_3, Au_3Rb_2 as well as $AuRb_2$ are all stable at 0K. This result provided by the Calphad method is consistent with ab-initio results which also resulted in both the high probability of existence and the stability of the Au_7Rb_3, Au_3Rb_2 and $AuRb_2$ compounds. A comparison based on the results of the third restitution and the results of the ab initio method shows a very high coherence and correspondence concerning the enthalpies of formation (Table 7 and figure 6) shows the training enthalpies obtained using the two methods used.

Table 7. Enthalpies of formations of the defined compounds (by the ab-initio and Calphad methods).

Compound	Enthalpies of formation (kJ/mol-atom)	
	Ab-initio method	Calphad method
Au_5Rb	-19.1	-19.0
Au_7Rb_3	-28.1	-27.0
Au_3Rb_2	-30.7	-29.4
AuRb	-28.3	-28.1
$AuRb_2$	-18.8	-22.2

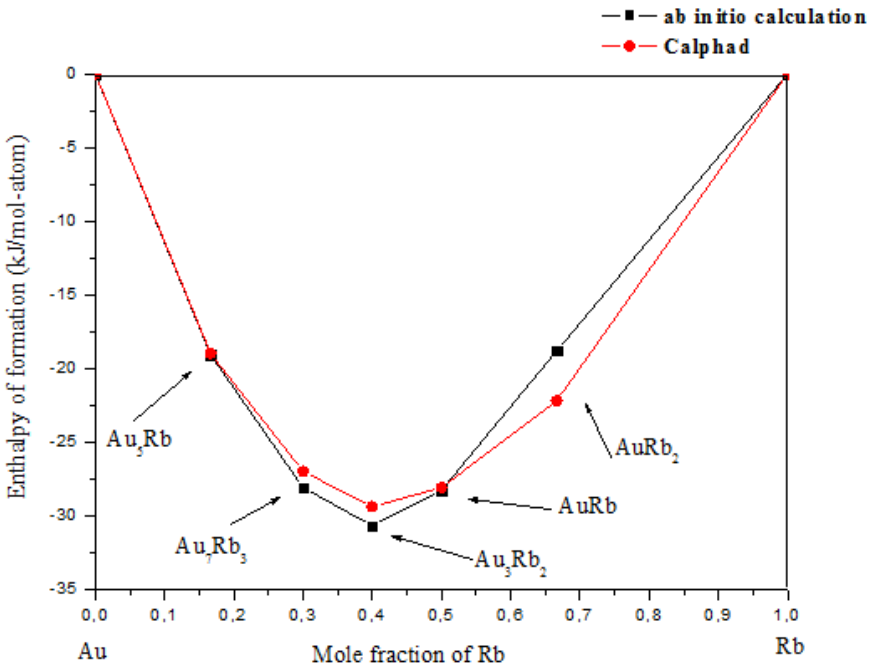

Fig. 6 Enthalpies of formation of Au–Rb intermetallics.

VI. CONCLUSION

- Using the results provided by the DFT, we have been able to reconstruct the phase diagram of the Au-Rb system according to three possibilities.
- The basic state of the system was obtained and shows that the compositions Au_5Rb, Au_7Rb_3, Au_3Rb_2, AuRb as well as $AuRb_2$ are all stable there is a great coherence between the results obtained by the calculation ab initio and those of the method Calphad.
- The enthalpies of formation calculated by the ab-initio method [9] and found at the end of the restoration of the phase diagram by the Calphad method show that the compound $AuRb_2$ can represent a new compound in this system
- The current results strongly suggest that the continuation of the experimental investigation is necessary for the Au-Rb system to confirm the inferences and conclusions that are obtained by our study.

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