

Ab-Initio Reinvestigation of the (Sr-In) Binary System

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Abstract: Sr-In intermetallics were studied by first-principles calculations within density functional theory (DFT) with the projector augmented-wave technique (PAW) and the generalized gradient approximations (GGA) as implemented in the ABINIT code. Six intermetallics: SrIn₅, SrIn₃, SrIn₂, SrIn, Sr₅In₃ and Sr₃In were investigated in their observed experimental structures. The lattice constants, enthalpies of formation and bulk modulus of the Sr-In intermetallics have been calculated. The calculated lattice constants and enthalpies of formation are in good agreement with experimental and other theoretical results.

Key words: Sr-In compounds, crystal structure, first principles, ABINIT.

1. Introduction

The experimental informations concerning the Sr-In system have been summarized by Wang *et al.* [1]. The experimental phase diagram was drawn by Bruzzone [2] using thermal analysis (TA), metallographic methods and X-ray diffraction (XRD). Eight intermetallic phases SrIn₅, SrIn₃, Sr₂In₅, SrIn₂, Sr₂In₃, SrIn, Sr₃In₂, and Sr₃In were reported (Fig. 1). The SrIn₂ and Sr₃In phases melt congruently at 930 °C and 558 °C respectively. The other compounds SrIn₅, SrIn₃, Sr₂In₅, Sr₂In₃, SrIn and Sr₃In₂ were formed via the peritectic reactions. Later Bruzzone *et al.* [3] reported a Sr₅In₃ phase instead of Sr₃In₂ and determined the crystal structure of Sr₅In₃ to be Cr₅B₃ type crystal by single crystal and powder techniques and in the work of Wang *et al.* [1] the Sr₅In₃ phase was considered instead of Sr₃In₂, which was consistent with the assessment of Okamoto [4].

The crystallographic structures of the pure elements Sr and In were determined by Hirst *et al.* [5] and Moshopoulou *et al.* [6]. Bruzzone [2] determined also the structure of the SrIn₅, SrIn₃ and Sr₃In, the first compound crystallize as hp6 type (P6/mmm, CaCu₅), the second hp8 (P63/mmc, Mg₃Cd), while the Sr₃In is cubic cF16 (Fm3m, BiF₃). The SrIn₂ compound was studied by Iandelli [7] (hp6 type, P63/mmm, CaIn₂) and the structure of the intermetallic SrIn was determined by Wendorff *et al.* [8] as oF64 type (Fdd2, SrIn). The structure the compounds Sr₂In₅ and Sr₃In were not determined until today.

The aim of the present work, based on first-principles calculations, is to investigate the relative stabilities of the different compounds involved in the Sr-In system. Having our calculations performed at 0 K, we will be mainly focusing on the determination of the ground state line of this system.

2. First-Principles Methodology

Our calculations were performed using the ABINIT code [9], [10] which is based on the plane wave

pseudo potential approach in the framework of the density functional theory (DFT) [11]. We used the projector augmented wave (PAW) method [12], [13] and the generalized gradient approximations (GGA) to treat the exchange interactions and correlation effects. The GGA is implemented according to the Perdew–Burke–Ernzerhof (PBE) functional [14]. The PAW atomic data sets for Strontium and Indium were generated with the Atom Paw code [15]. The atomic orbital's treated as valence states were 5s24p63d10 and 5s24d105p1 for Sr and In, respectively. The electron states were expanded in plane waves with kinetic energy cut-offs of 560 eV, and the Brillouin zone sampling was performed in such a way that the number of k-points multiplied by the number of atoms in the unit cell was greater than 104. A cold smearing [16] of 0.1 eV was used. The above parameters enabled us to obtain a total energy convergence of 1 meV per atom (0.1 kJ/mol-atom).

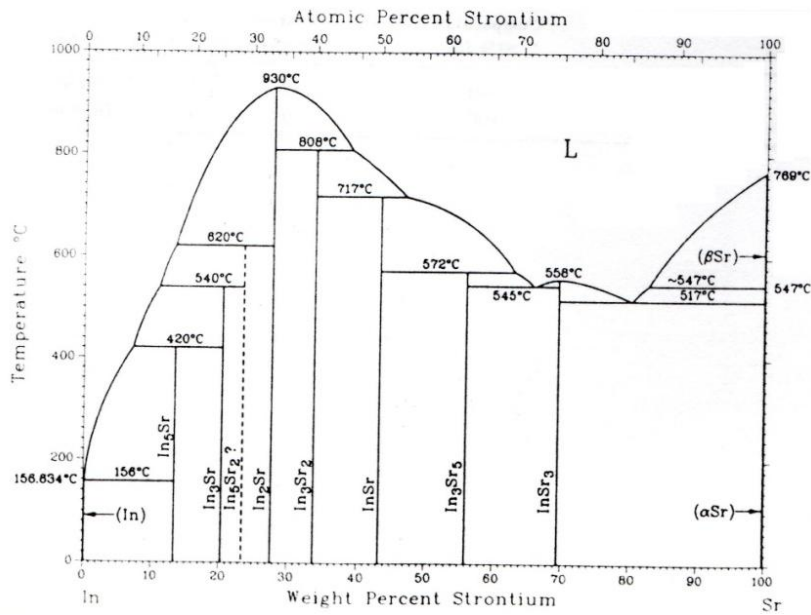


Fig. 1. Experimental phase diagram [2].

We carried out structure optimizations with respect to atom positions, cell shape and dimensions. After each full relaxation, self-consistent calculations were performed.

From the computed total energies of the equilibrium structures of all the phases considered we derived the corresponding enthalpies of formation at 0 K, for the Sr-In system with general formula by applying the following equation:

$$\Delta H_f (Sr_x In_y) = E_{tot} (Sr_x In_y) - \left[\frac{x}{x+y} E_{tot}^{bcc} (Sr) + \frac{y}{x+y} E_{tot}^{dia} (In) \right]. \quad (1)$$

where $E_{tot} (Sr_x In_y)$, $E_{tot}^{bcc} (Sr)$ and $E_{tot}^{dia} (In)$ are the computed total energies (per atom) of the compound $Sr_x In_y$ and constituents, Sr and In, respectively, each one was relaxed to its equilibrium (zero pressure and forces) geometry.

3. Results

3.1. Pure Elements

We started the present investigation by computing the equilibrium lattice constants of pure elements Sr

and In. In order to check the reliability of our generated atomic data sets, we compared them with experimental data and theoretical results. The results are shown in Table 1. The calculated lattice parameters show a good agreement with experiments and previous calculations from literature[1], [5], [6], [17], [18]. Thus, we can rely on our atomic data set in what follows for the present work.

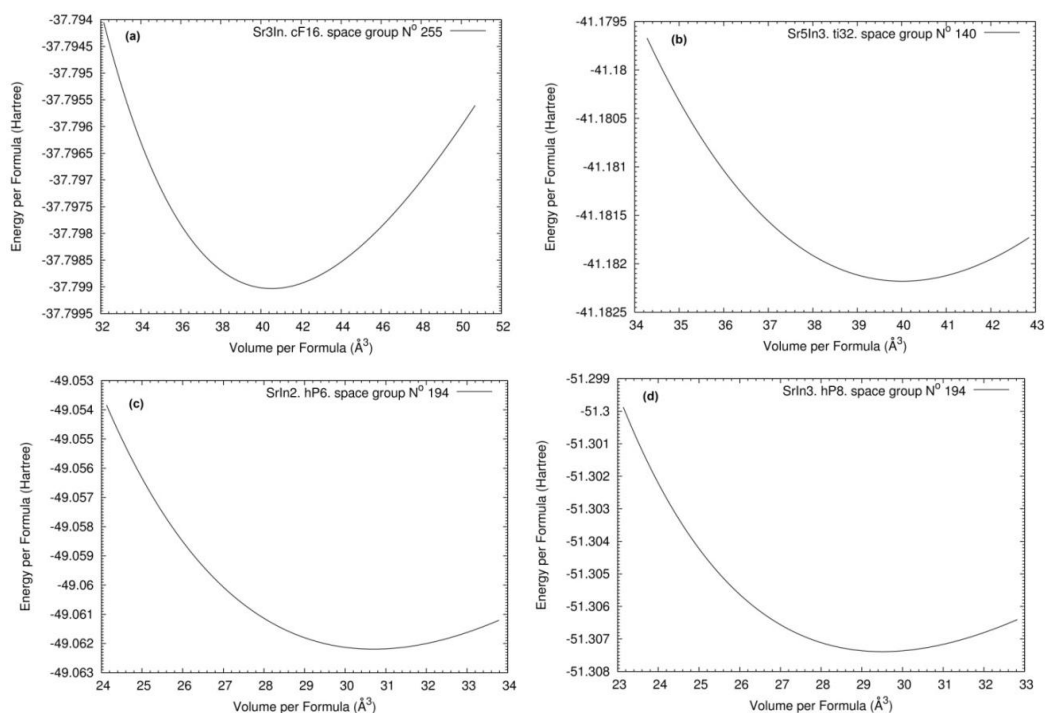
Table 1. Calculated and Experimental Lattice Parameters of Sr-In Elements

Compound	Prototype	Pearson symbol	Space group	Lattice parameters (Å°)			
				GGA (This work)	GGA (VASP)	EXP.	
Sr	Cu	cF4	Im $\bar{3}$ m	a =	4.357	4.870 ^d	4.138 ^a
				a =	3,747	3.279 ^c	3.251 ^e
In	In	Tl2	I4mmm	b =	4,004	5.033 ^c	4.947 ^e

^a Ref [17], ^b Ref [5], ^c Ref [1], ^d Ref [18], ^e Ref [6].

3.2. Intermetallic Compounds

We calculated the equations of state of the six known SrIn structures: the three hexagonal structures hp6 (P6/mmm), hp8(P6₃/mmc) and hp6 (P6₃/mmc) and the two cubic oF64(Fdd2) and cF16(Fm3m) and finally the two tetragonal structures tl32(I4mcm) and Tl2(I4mmm). The EOS were obtained by calculating twenty first principles data points for a given structure in a range of ±10 % of the equilibrium volume and sometimes more points were added in compression. For each point both of external and internal degrees of freedom of the structure are fully relaxed at constant volume. The obtained set of points was then fitted to a Birch-Murnaghan 4th-order EOS. The fitting of these energy-volume data is made using the EOS utility implemented in the ELK code [19]. Fig. 2 shows State equations (Energy vs volume) of the compounds Sr₃In and Sr₅In₃, SrIn₂, SrIn₃ and SrIn₅.



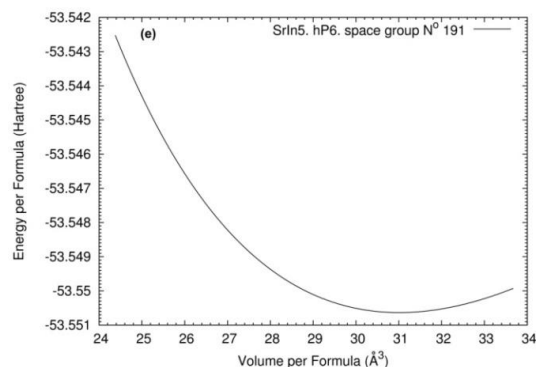


Fig. 2. Calculated total energies as a function of volume (a) Sr₃In, (b) Sr₅In₃, (c) SrIn₂, (d) SrIn₃, (e) SrIn₅.

The currently accepted Sr-In phase diagram contains eight intermetallics. But the crystallographic structures of two compounds are not known (Sr₂In₅ and Sr₂In₃), so we have study the six compounds which there structure are determined. Their structural information and optimized lattice constants are summarized in Table 2 along with theoretical results [1] and experimental data [2], [7], [8], [20]. As expected, Our results which are in agreement with experiments show the usual trends of GGA in underestimating the bonding and resulting in smaller cohesive energies and larger lattice parameters which are closer to experimental data with a mean of error between 0.3% and 8.9%, all calculations of errors were performed by making the comparison with the last column of experimental data of Table 2. Calculated enthalpies of formation are presented in Table 3 and Fig. 3 with experimental and other calculated values from literature for comparison. One can note that the current results may be taken as a starting point for further experimental or computational investigations.

Table 2. Calculated and Experimental Lattice Parameters of Sr-In Intermetallics

Compound	Prototype	Pearson symbol	Lattice parameters (Å°)			
			Space group	GGA (This work)	GGA (VASP)	EXP.
SrIn ₅	CaCu ₅	hp6	P6/mmm	a = 6.392(7.6%)	6.301 ^a	5.937 ^b
				c = 5.259(8.9%)	5.270 ^a	4.827 ^b
SrIn ₃	Mg ₃ Cd	hP8	P6 ₃ /mmc	a = 7.182(6.1%)	7.141 ^a	6.769 ^b
				c = 5.272(3.8%)	5.249 ^a	5.481 ^b
SrIn ₂	CaIn ₂	hP6	P6 ₃ /mmc	a = 5.099	5.080 ^a	
				c = 8.170	8.116 ^a	8.021 ^c
SrIn	SrIn	oF64	Fdd2	a = 10,10(1.2%)	10.222 ^a	10.230 ^d
				b = 25,77(1.4%)	26.040 ^a	26.140 ^d
				c = 8,827(5.1%)	8.365 ^a	8.400 ^d
Sr ₅ In ₃	Cr ₅ B ₃	tI32	I4mcm	a = 8,811(0.8%)	8.788 ^a	8.744 ^e
				c = 16,48(0.3%)	16.496 ^a	16.429 ^e
Sr ₃ In	BiF ₃	cF16	Fm $\bar{3}$ m	a = 9.032(8.0%)	8.639 ^a	8.360 ^f

^a Ref [1], ^b Ref [2], ^c Ref [7], ^d Ref [8], ^e Ref [20], ^f Ref [2]

Table 3. Calculated and Experimental Enthalpies of Formation of Sr-Ge Intermetallics (kJ/mol)

Compound	GGA (This work) Abinit	GGA (VASP) [1]	CALPHAD [1]
Sr ₃ In	-11.30	-13.54	-22.00
Sr ₅ In ₃	-35.14	-33.86	-34.00
SrIn	-43.76	-42.62	-42.84
SrIn ₂	-46.74	-45.45	-45.00
SrIn ₃	-33.69	-32.58	-37.70
SrIn ₅	-15.57	-14.97	-26.00

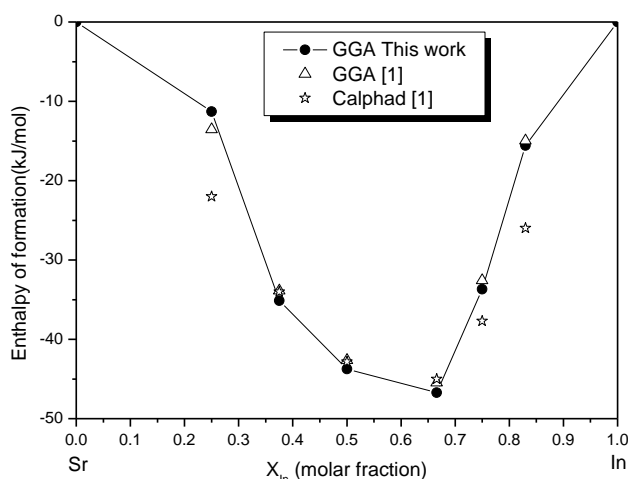


Fig. 3. Calculated enthalpies of formation for the Sr-In system compared with the first-principles calculations and the experimental data.

We have also calculated the equilibrium volume and the Bulk-modulus with its first and second pressure derivatives of the six compounds by fitting the calculated energies versus volume to the fourth-order Birch-Murnaghan equation of state. The results are shown in Table 4. We have not found any values for these parameters in the literatures to compare with our results.

Table 4. Calculated Atomic Volume (V_0 , Å³/atom), Bulk Modulus (B_0 , GPa), with Its First and Second Pressure Derivatives (B'), (B'' , GPa⁻¹) for SrIn Compounds

	Sr3In.cf16	Sr5In3.ti32	SrIn2.hp6	SrIn3.hp8	SrIn5.hp6
V_0	46.050	39.998	30.665	29.436	30.015
B_0	17.687	21.214	32.469	27.777	31.295
B'_0	3.94	3.21	4.36	5.04	4.51
$B'' \cdot 10^{-3}$	-0.044	0.061	-0.0046	0.056	-0.103

4. Conclusion

Through first-principles local density functional calculations, we have investigated the ground state line of the system Sr-In. We have calculated the enthalpies of formation of six compounds reported in the phase diagram (SrIn₅, SrIn₃, SrIn₂, SrIn, Sr₅In₃ and Sr₃In). The established ground state shows that, the two compounds SrIn₅ and Sr₃In are not in the ground state line and therefore not stable at 0 K. It is recommended to perform another study by introducing the effect of temperature on the stability of the two compounds mentioned above.

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The Inorganic Material Database (<http://crystdb.nims.go.jp/crystdb>) was used to obtain some crystallographic data of some structures.

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