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STRUCTURAL STABILITY OF TERNARY ANTIMONIDES $T_{10}Sb_5T'$ (T=Ti, Zr, Hf, T'=V, Cr, Mn, Fe, Co, Ni, Cu, Pd, Pt, Rh)

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Abstract

The crystal and thermodynamic properties of $T_{10}Sb_5T'$ ternary compounds where T=Ti, Zr, Hf and T'= V, Cr, Mn, Fe, Co, Ni, Cu, Pd, Pt, Rh have been investigated by means of first principle calculations. The structure of these compounds is considered as a ternary variant of the W_5Si_3 type. Three possible ordered structures have been investigated in the present work. The two structures in which the Sb and T' atoms alternate along chains parallel to the c axis are the most stable ones. The calculated structural parameters are in good agreement with the experimental data. Both electronic and size effects allow to explain the stability of the ternary $T_{10}Sb_5T'$ compounds.
Keywords: DFT calculations; Enthalpies of formation; W_5Si_3 ternary variant; Nb_5Sn_2Si-type.

ESTABILIDADE ESTRUTURAL DE COMPOSTOS TERNÁRIOS DE ANTIMONIO $T_{10}Sb_5T'$ (T=Ti, Zr, Hf, T'=V, Cr, Mn, Fe, Co, Ni, Cu, Pd, Pt, Rh)

Resumo

As propriedades termodinâmicas e estruturas cristalinas dos compostos ternários do tipo $T_{10}Sb_5T'$ onde T=Ti, Zr, Hf and T'= V, Cr, Mn, Fe, Co, Ni, Cu, Pd, Pt, Rh foram investigadas através de cálculos de primeiros princípios. A estrutura destes compostos é considerada uma variante ternária da estrutura do tipo W_5Si_3. Tres possibilidades de ordenamento da estrutura foram investigadas neste trabalho. As duas estruturas nas quais os átomos de Sb e T' se alternam ao longo de cadeias paralelas ao eixo c da estrutura são as mais estáveis. Os parâmetros estruturais calculados estão em acordo com os valores experimentais. Tanto efeitos eletrônicos como de tamanho permitem explicar a estabilidade dos compostos ternários do tipo $T_{10}Sb_5T'$.
Palavras-chave: Cálculos DFT; Entalpias de formação; Variante ternária da estrutura W_5Si_3; Estrutura tipo Nb_5Sn_2Si.

1 INTRODUCTION

The existence of ternary compounds T_5X_2X' possessing the ternary $D8_m$ structure (Nb_5Sn_2Si-type, tI32, I4/mcm, N°140) [1] has been often reported in systems where T in an early transition metal (Ti, Zr, Hf, Nb, Ta), X a p element (Sn, Sb) and X' another p element (Al, Ga, Si, Ge). The Wyckoff positions of the atoms in the compound $D8_m$-T_5X_2X' are the following: the T atoms occupy the 4b and 16k positions, the X atoms occupy the 8h while the X' atoms occupy the 4a positions. This ternary $D8_m$ structure was found in several systems of the type T–X–X' [1-17]. Tanaka et al. [10], Kleinke [13], Voznyak et al. [16] emphasized the arrangement of the p elements in the $D8_m$ structure is controlled by size differences between X and X' elements.

In previous works [18-21], we performed *ab initio* calculations in order to determine the lattice parameters and the enthalpies of formation of $D8_m$-Ti_5Sn_2Si [18], $D8_m$-Ti_5Sn_2Ga [21], $D8_m$-Nb_5Sn_2Ga [19] and of several $D8_m$-Ti_5Sb_2X (X=Al, Ga, In, Si, Ge, Sn) [20] compounds. In these studies, we also concluded that the stability of these ternary $D8_m$ compounds is due to the size difference between X and X' elements ($V_{Sn} > V_{Si}$, $V_{Sn} > V_{Ga}$) or $V_{Sb} > V$(Al, Ga, In, Si, Ge, Sn). As a consequence, the distances X-X and T-T along the c axis are very short. Furthermore the stability of

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the compounds is favoured by an electronic factor due to a sufficient number of s and p electrons having the Fermi level near the bottom of the pseudo gap of the electronic density of states.

The aim of the present paper is to investigate the structural, thermodynamic, and electronic properties of another series of ternary compounds which possess a structure which is a variant-type of the W_5Si_3 structure. These compounds have the formula $T_{10}Sb_5T'$ where T is an early transition metal (T= Ti, Zr, and Hf) and T' a transition metal of the 3d, 4d, or 5d rows, T'= V, Cr, Mn, Fe, Co, Ni, Cu, Rh, Pd, Pt. Several of them have been sinthetized and characterized [22-44]. Table I gathers the systems in which this structure has been found and characterized.

The more recent investigations concern the compounds $Hf_5Sb_{3-x}Ru_X$ and $Zr_5Sb_{3-x}Ru_X$ [39,44] which have be found to be superconductors. Table S1 of the *Supplement* to this paper[1] gathers the lattice parameters of these compounds. Several ternary phase diagrams where the $T_{10}Sb_5T'$ compound is stable have been investigated experimentally and isothermal sections at relatively low temperature have been drawn [22,28-30,32,34-36,39,41,43]. These systems are indicated by a star in Table 1. In most cases, a small deviation with respect to the stoichiometry $T_{10}Sb_5T'$ is observed. The structure of these $T_{10}Sb_5T'$compounds is considered to be a substitution variant of the W_5Si_3-type structure. While in the stoichiometric $D8_m$-$T_{10}Sb_4T'_2$ compound, the 4a sites are occupied solely by the T' atoms, these sites are occupied by T' and Sb atoms in the $T_{10}Sb_5T'$ compound. Note that in both structures, the 8h sites are occupied by Sb atoms while the 4b and 16k sites are occupied by the T atoms. At high temperature, a random distribution of Sb and T' atoms on the 4a sites is expected. It could be possible to calculate the enthalpy of formation of a partially random structure by using either supercells or special quasi-random structures. However, these calculations are long and sometimes difficult. Therefore, we have considered in the present work three possible ordered structures which have been proposed by Kleinke et al. [42]. The lattice parameters, enthalpies of formation, electronic densities of states of several $T_{10}Sb_5T'$ compounds in these three structures have been computed. The results are also compared with those obtained for the $D8_m$-$T_{10}Sb_4T'_2$ compound.

2 POSSIBLE ORDERED STRUCTURES OF $T_{10}Sb_5T'$ COMPOUNDS

The unit cell of $D8_m$-T_5Sb_2T' contains 32 atoms that are situated in a layered arrangement along c axis. The layers z=1/4 and z=3/4 are occupied by T' (4a) and T (4b) atoms while the layers z=0 and z=1/2 are occupied by the T (16k) and Sb (8h) atoms. Figure 1a and 1e show the $D8_m$ structure in the case of the Ti_5Sb_3 and Ti_5Sb_2Co

Table 1. $T_{10}Sb_5T'$ ternary compounds with a structure which is a variant-type of the W_5Si_3 structure

System	Composition	Ref
Ti-Cu-Sb*	$Ti_5Cu_{0.45}Sb_{2.55}$	[22-25]
	Ti_5CuSb_2	[26]
	$Ti_5Cu_{1-x}Sb_{2+x}$	[27]
Ti-Ni-Sb*	$Ti_5Ni_{0.57}Sb_{2.43}$	[25]
	$Ti_5Ni_{0.45}Sb_{2.55}$	[28]
	$Ti_5Ni_{0.45}Sb_{2.55}$	[27]
	$Ti_5Ni_{0.45}Sb_{2.55}$	[27]
Ti-Co-Sb*	$Ti_5Co_{0.46}Sb_{2.54}$	[25]
	$Ti_5Co_{0.46}Sb_{2.54}$	[29]
	$Ti_5Co_{0.5}Sb_{2.5}$	[27]
Ti-Fe-Sb*	$Ti_5Fe_{0.45}Sb_{2.55}$	[30]
	Ti_5FeSb_2	[30]
	$Ti_5Fe_{0.5}Sb_{2.5}$	[27]
	$Ti_5Fe_{0.58}Sb_{2.42}$	[25]
Ti-Mn-Sb	$Ti_5Mn_{0.45}Sb_{2.55}$	[25]
Ti-Cr-Sb	Ti_5CrSb_2	[31]
	$Ti_5Cr_{0.5}Sb_{2.5}$	[25]
Ti-Pd-Sb	$Ti_5Pd_{0.5}Sb_{2.5}$	[27]
Ti-Rh-Sb	Ti_5RhSb_2	[27]
	Ti_5RhSb_2	[27]
Ti-Ru-Sb	$Ti_5Ru_{0.5}Sb_{2.5}$	[27]
Zr-Cu-Sb*	$Zr_5Cu_{0.45}Sb_{2.55}$	[32]
	$Zr_5Cu_{0.35}Sb_{2.5}$	[33]
Zr-Ni-Sb*	$Zr_5Ni_{0.5}Sb_{2.5}$	[34]
Zr-Co-Sb*	$Zr_5Co_{0.5}Sb_{2.5}$	[35]
Zr-Fe-Sb*	$Zr_5Ni_{0.4}Sb_{2.55}$	[33]
	$Zr_5Fe_{0.45}Sb_{2.55}$	[33]
	$Zr_5Fe_{0.44}Sb_{2.56}$	[36]
	$Zr_5Fe_{0.44}Sb_{2.56}$	[37]
Zr-Mn-Sb*	$Zr_5Mn_{1-x}Sb_{2+x}$	[38]
	$Zr_5Mn_{0.45}Sb_{2.55}$	[32]
	$Zr_5Mn_{0.5}Sb_{2.5}$	[39]
Zr-Cr-Sb	$Zr_5Cr_{0.49}Sb_{2.51}$	[38]
Zr-Pd-Sb	$Zr_5Pd_{0.5}Sb_{2.5}$	[27]
Zr-Rh-Sb	$Zr_5Rh_{0.55}Sb_{2.5}$	[33]
Zr-Ru-Sb	$Zr_5Ru_{0.6}Sb_{2.4}$	[40]
Zr-Pt-Sb*	Zr_5PtSb_2	[41]
Hf-Cu-Sb*	$Hf_{10}CuSb_5$	[42]
	$Hf_5Cu_{0.45}Sb_{2.55}$	[43]
	$Hf_5Cu_{0.5}Sb_{2.5}$	[27]
Hf-Ni-Sb	$Hf_{10}NiSb_5$	[42]
	$Hf_{10}Ni_{1.18}Sb_{4.82}$	[38]
	$Hf_5Ni_{0.5}Sb_{2.5}$	[27]
Hf-Co-Sb	$Hf_{10}CoSb_5$	[42]
	$Hf_5Co_{0.5}Sb_{2.5}$	[27]

*Systems for which isothermal sections have been drawn.

[1] *See DATA SUPPLEMENT to this paper in the same issue of this Journal.*

Table 1. Continued...

System	Composition	Ref
Hf-Fe-Sb	$Hf_{10}FeSb_5$	[42]
	$Hf_{10}Fe_{1.54}Sb_{4.46}$	[42]
	$Hf_{4.929}Fe_{0.67}Sb_{2.33}$	[27]
Hf-Mn-Sb	$Hf_{10}MnSb_5$	[42]
	$Hf_{10}Mn_{1.16}Sb_{4.84}$	[42]
Hf-Cr-Sb	$Hf_{10}CrSb_5$	[42]
Hf-V-Sb	$Hf_{10}VSb_5$	[42]
	$Hf_{10}V_{0.8}Sb_{5.2}$	[42]
	$Hf_{10}V_{0.88}Sb_{5.12}$	[42]
Hf-Pd-Sb	$Hf_5Pd_{0.5}Sb_{2.5}$	[27]
Hf-Rh-Sb	$Hf_5Rh_{0.5}Sb_{.5}$	[27]
Hf-Ru-Sb	$Hf_5Ru_{0.5}Sb_{2.5}$	[27]
	$Hf_5Ru_{0.6}Sb_{2.4}$	[44]

*Systems for which isothermal sections have been drawn.

compounds. The structure is build up of two different columns of atoms running parallel to the tetragonal c axis. In the case of D8m- Ti_5Sb_2Co, one column consists of Co (4a) centred square antiprisms ($CoTi_8$), which share square faces. The other column consists of Ti (4b) centred Sb tetrahedra ($TiSb_4$) which share edges. These two columns are interconnected by numerous Ti-Sb and Ti-Ti bonds. The Ti (4b) as well as the Co (4a) atoms form parallel linear chains with short interatomic distances c/2.

The possible ordered structures of $T_{10}Sb_5T'$ compound which have been suggested by Kleinke et al. [42] are presented in Figures 1b-d: These structures, designated in the following by their space groups, are:

(i) N°97 in which the T' and Sb atoms alternate along the chains. The T' and Sb atoms also alternate in the planes z=0 and z=1/2.

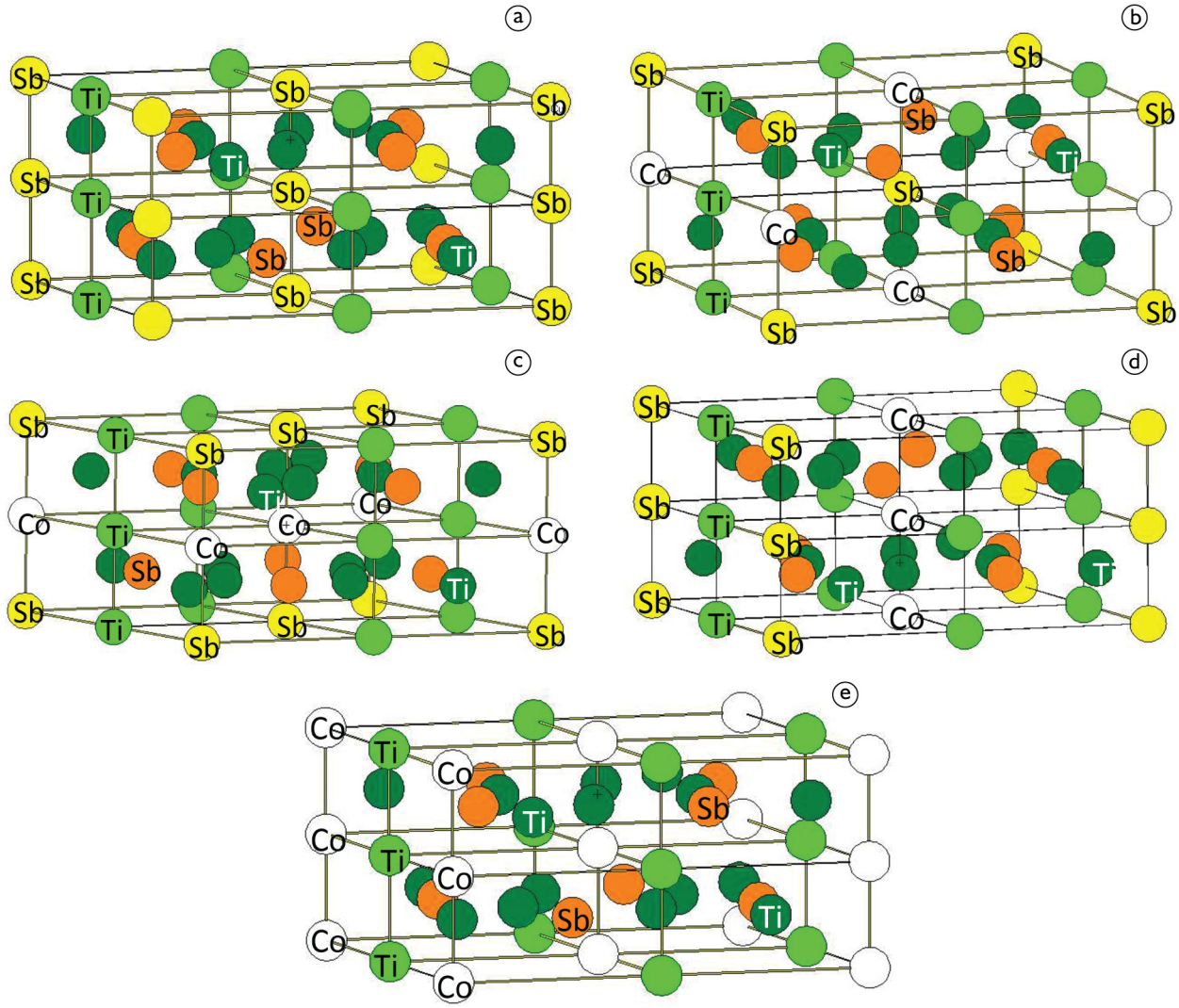

Figure 1. Structures of (a) $D8_m$-Sb_3Ti_5, (b) N°97-$Co_2Sb_{10}Ti_{20}$, (c) N°125- $Co_2Sb_{10}Ti_{20}$, (d) N°124- $Co_2Sb_{10}Ti_{20}$, (e) $D8_m$-$Co_4Sb_8Ti_{20}$. Green and dark green circles: Ti atoms (4b and 16k Wyckoff positions of the $D8_m$ structure), orange circles: Sb atoms (8h Wyckoff positions of the $D8_m$) yellow circles: Sb atoms (4a Wyckoff positions of the $D8_m$), white circles: Co atoms (4a Wyckoff positions of the $D8_m$).

(ii) N°125 in which again the T' and Sb atoms alternate along the chains but the T' atoms are in the z=0 plane while the Sb atoms in the z= 1/2 plane

(iii) N°124 in which there are alternate chains of T' atoms and Sb atoms parallel to the c axis.

The characteristics of these three ordered structures are given in Table 2 in the case of the $Ti_{10}Sb_5Co$ compound (the values of the lattice parameters and internal parameters have been calculated as indicated below) and in Table 3 in the case of $Hf_{10}Sb_5V$ compound.

Some remarks can already be done. In the three structures $Ti_{10}Sb_5Co$, the Ti atoms (4b in the $D8_m$ description) are in the middle of a tetrahedron formed by the Sb atoms (8h in the $D8_m$ description). On the other hand, the T' and Sb atoms (4a in the $D8_m$ des) form chains inside the antiprisms build with the Ti (16k in the $D8_m$ description) atoms. These chains are similar in the cases of the N°97 and N°125 structures. Figures S1 and S2 of the *Supplement* present the chains of Co and Sb atoms, and the chains of Ti atoms.

The aim of the present work is to perform first principles calculations of the enthalpies of formation of the N°97, N°125, and N°124 structures for several $Ti_{10}Sb_5T'$ compounds in order to obtain their relative stabilities.

3 COMPUTATIONAL METHOD

The density functional (DFT) calculations were performed with the Vienna ab initio simulation package (VASP) [45,46], making use of the projector augmented waves (PAW) technique [47,48]. The calculations include twelve valence electrons for Ti ($3s^2\ 3p^6\ 3d^3\ 4s^1$). A plane-wave cut-off energy of 350 eV for all the elements has been taken. For the generalized gradient approximation (GGA) exchange correlation functional, the Perdew-Berke-Erzenhof parameterization (PBE) [49] was used. For the Brillouin-zone integration, the Methfessel-Paxton [50] technique with a modest smearing of the one-electron levels (0.2 eV) was used. Care was taken so that a sufficient number of k points for the Brillouin-zone integration was chosen for each structure. A Gamma centred k-point grid was used for the hexagonal structures while a Monkhorst–Pack [51] grid was chosen for the other structures. The tetrahedron method is used in the case of the stable compounds and for the electronic density of states computations. In this later case, the number of k points has been slightly increased. Spin-polarized calculations have been performed in the case of compounds with Cr, Mn, Fe, and Co.

The energy of formation per atom, $\ddot{A}_fE$ ($T_{10/16}Sb_{5/16}T_{1/16}'$), of the $T_{10/16}Sb_{5/16}T_{1/16}'$ compound is obtained from Equation 1:

Table 2. Calculated lattice parameters and internal coordinates of the atoms of the $D8_m$, and ternary variants of the $D8_m$ structures in the Ti-Sb-Co system

Compound	Structure	Lattice parameters	Atomic positions
$Ti_{10}Sb_6$	$D8_m$, W_5Si3-type, tI32, I4/mmc, N°140	a= 10.5061 Å c= 5.4717 Å	Sb (4a) 0, 0, 1/4 Sb (8h) 0.16392, 0.66392, 0 Ti (4b) 0, 1/2, 1/4 Ti (16k) 0.07705, 0.22764, 0
$Ti_{10}Sb_5Co$	tI32, I422, N°97	a= 10.4907 Å c= 5.2147 Å	Co (2a) 0, 0, 0 Sb (2b) 0, 0, 1/2 Ti (4c) 0, 1/2, 0 Sb (8j) 0.16383, 0.66383, -0.25 Ti (16k) 0.07489, 0.21761, -0.24
$Ti_{10}Sb_5Co$	tP32, P4/nbm N°125	a= 10.4798 Å c= 5.2243 Å	Co (2a) 1/4, 1/4, 0 Sb (2b) 1/4, 1/4, 1/2 Ti (2c) 3/4, 1/4, 0 Ti (2d) 3/4, 1/4, ½ Sb (8m) 0.4139, 0.5861, 0.2532 Ti (16n) 0.6754, 0.5322, 0.2382
$Ti_{10}Sb_5Co$	tP32, P4/mcc, N°124	a= 10.4553 Å c= 5.3089 Å	Co (2a) 0, 0, 1/4 Sb (2c) 1/2, 1/2; 1/4 Ti (4f) 0, 1/2, 1/4 Sb (8m) 0.16141, 0.66672, 0 Ti (8m) 0.06969, 0.20045, 0.000 Ti (8m) 0.42301, 0.72846, 0.0000
$Ti_{10}Sb_4Co_2$	$D8_m$, Nb_5Sn_2Si-type tI32, I4/mmc, N°140	a= 10.4767 Å c= 5.0569 Å	Co (4a) 0, 0, 1/4 Sb (8h) 0.16413, 0.66413, 0 Ti (4b) 0, 1/2, 1/4 Ti (16k) 0.07052, 0.20120, 0

$$\Delta_f E\left(T_{10/16}Sb_{5/16}T_{1/16}'\right) = E^{min}_{T_{10/16}Sb_{5/16}T'_{1/16}} - \frac{5}{8}E^{min}_{A3-T} - \frac{5}{16}E^{min}_{A7-Sb} - \frac{1}{16}E^{min}_{T'} \quad (1)$$

The E^{min} are the minimum total energy of the compound (expressed per atom) and of the elements (hexagonal close-packed A3-T, rhomboedric A7-Sb and pure T' elements in their standard state at 298K. At T=0K and p=0 Pa, the formation enthalpy, $\Delta_f H\left(T_{10/16}Sb_{5/16}T_{1/16}'\right)$, equals the calculated formation energy, when the zero-vibration contribution is ignored, since it is much smaller than the formation energy.

4 RESULTS AND DISCUSSION

First of all, the ground state in the limiting binaries Ti-Sb, Zr-Sb, and Hf-Sb for the composition x_T=0.625 has been calculated. The results are reported in Table 4.

Table 3. Calculated lattice parameters and internal coordinates of the atoms of the $D8_m$, and ternary variants of the $D8_m$ structures in the Hf-Sb-V system

Compound	Structure	Lattice parameters	Atomic positions
$Hf_{10}Sb_6$	$D8_m$, W_5Si_3-type, tI32, I4/mmc, N°140	a= 11.0440 Å c= 5.7202 Å	Sb (4a) 0, 0, 1/4 Sb (8h) 0.16621, 0.66621, 0 Hf (4b) 0, ½, 1/4 Hf (16k) 0.07477, 0.22452, 0
$Hf_{10}Sb_5V$	tI32, I422, N°97	a= 11.0649 Å c= 5.5837 Å	V (2a) 0, 0, 0 Sb (2b) 1/2, 1/2, 0 Hf (4c) 0, 1/2, 0 Sb (8j) 0.66351, 0.16351, 0.25 Hf (16k) 0.07632, 0.21566, -0.23634
$Hf_{10}Sb_5V$	tP32, P4/nbm N°125	a= 11.0495 Å c= 5.6064 Å	V (2a) ¼, ¼, 0 Sb (2b) ¼, ¼, ½ Hf (2c) 3/4, 1/4, 0 Hf (2d) 3/4, 1/4, 1/2 Sb (8m) 0.33618, 0.83618, 0.25429 Hf (16n) 0.32543, 0.46597, 0.23645
$Hf_{10}Sb_5V$	tP32, P4/mcc, N°124	a= 11.0297 Å c= 5.6518 Å	V (2a) 0, 0, 1/4 Sb (2c) 1/2, 1/2; 1/4 Hf (4f) 0, 1/2, 1/4 Sb (8m) 0.16337, 0.664654, 0 Hf (8m) 0.07190, 0.20557, 0.000 HF (8m) 0.42244, 0.72416, 0.0000
$Hf_{10}Sb_4V_2$	$D8_m$, Nb_5Sn_2Si-type tI32, I4/mmc, N°140	a= 11.0506 Å c= 5.5640Å	V (4a) 0, 0, 1/4 Sb (8h) 0.16283, 0.66283, 0 Hf (4b) 0, ½, 1/4 Hf (16k) 0.07369, 0.20549, 0

Table 4. Enthalpies of formation of T_5Sb_3 (T=Ti, Zr, Hf) in the $D8_m$ (W_5Si_3-type), $D8_8$ (Mn_5Si_3-type), Yb_5Sb_3-type and Y_5Bi_3-type structures

System	Composition	Structure	$\Delta_f H$ (kJ/mol of atoms) Non magnetic
Ti-Sb	Ti_5Sb_3	$D8_m$	–44.15
		$D8_8$	–45.82
		oP32, Yb_5Sb_3-type	–48.37
		oP32, Y_5Bi_3-type	–47.82
Zr-Sb	Zr_5Sb_3	$D8_m$	–62.95
		$D8_8$	–64.92
		oP32, Yb_5Sb_3-type	–65.70
		oP32, Y_5Bi_3-type	–65.90
Hf-Sb	Hf_5Sb_3	$D8_m$	–41.19
		$D8_8$	–41.03
		oP32, Yb_5Sb_3-type	–44.88
		oP32, Y_5Bi_3-type	–44.93

The results are in agreement with the experimental information: the Yb_5Sb_3 structure type is the most stable in the case of the Ti_5Sb_3 compound while the Y_5Bi_3 structure type is the more stable in the cases of Hf_5Sb_3 compounds. In the case of the Zr_5Sb_3 compound, Garcia and Corbett [52] found that off stoichiometric $D8_8$-Zr_5Sb_{3+x} is stable and that the oP32-Y_5Bi_3-type is stable at high temperature. Our calculations indicate that the Zr_5Sb_3 in the Y_5Bi_3-type structure is 1kJ/mol of atoms more stable than the $D8_8$ structure. The calculated lattice parameters are in good agreement with the experimental data (Table 5).

For each investigated ternary system, the enthalpies of formation of the ordered compounds in structures $D8_m$, N°97, N°125, and N°124 are reported in Table 6. These results show that the N°97 and N°125 structures have very close enthalpies of formation, and that the enthalpy of formation of the N°124 structure is clearly less negative.

We have presented these results along sections in two cases: Ti_5Sb_3-Ti_5Co_3 (Figure 2) and Hf_5Sb_3-Hf_5V_3 (Figure 3).

The ground state in each limiting binary T-T' for x_T=0.625 molar fraction has been calculated and is indicated on the figures. These figures make possible getting some indication about the relative stability of the various compounds along the section. The ternary $D8_m$ structure T_5Sb_2T' appears stabilized with respect to the mechanical mixture of $D8_m$-T_5Sb_3 and $D8_m$-$T_5T'_3$. This is due to the fact that the T' atoms possess a size which is lower than the one of the T atoms (T=Ti, Zr, Hf). Considering now, the section $D8_m$-T_5Sb_3 to $D8_m$-T_5Sb_2T', one observes again that the structures N°97 and N°125 have very similar enthalpies of formation. There is an important stabilization of the N°97-$Ti_{10}Sb_5T'$ and N°125-$Ti_{10}Sb_5T'$ structure with respect to the mechanical mixture of $D8_m$-T_5Sb_3 and $D8_m$-T_5Sb_2T' (see Figure 2 and 3). This stabilization decreases from Cu to Mn in the 3d series (see Table 6). The enthalpy of formation of the N°124 structure is less negative or of the same order of magnitude than the mean value of the formation enthalpies of $D8_m$-T_5Sb_3 and $D8_m$-T_5Sb_2T'.

For some of the investigated system, the experimental and calculated values of the lattice parameters are displayed on Figures 4 and 5. The lattice parameters calculated in the N°97 and N°125 ordered structures are in good agreement with the experimental values in the case of $Ti_{10}Sb_5Co$. In the case of $Hf_{10}Sb_5V$, the calculated values of the c parameter are in good agreement with the experimental ones, however the calculated values of the a parameter are clearly greater

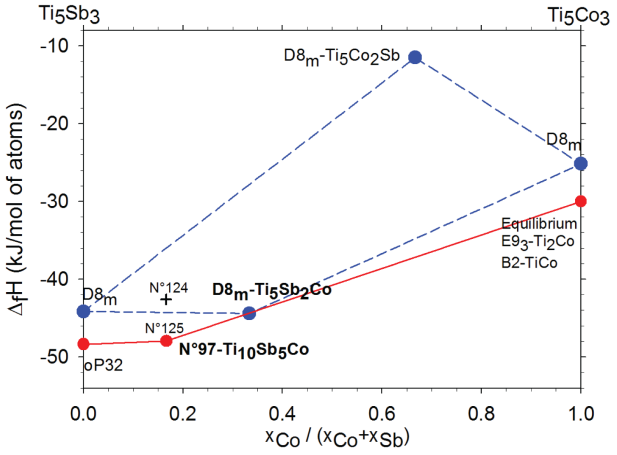

Figure 2. Calculated values of the enthalpies of formation of the compounds along the section Ti_5Sb_3-Ti_5Co_3.

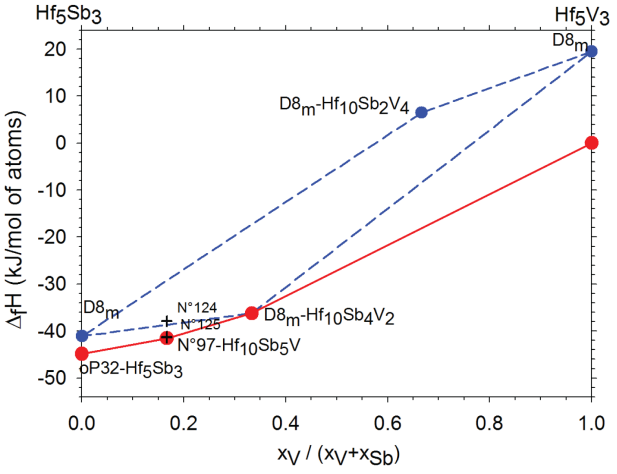

Figure 3. Calculated values of the enthalpies of formation of the compounds along the section Hf_5Sb_3-Hf_5V_3.

Table 5. Experimental and calculated lattice parameters of Ti_5Sb_3, Zr_5Sb_3, and Hf_5Sb_3

Compound	Structure		a [nm]	b [nm]	c [nm]	Reference
Ti_5Sb_3	Yb_5Sb_3, oP32	Exp.	1.02182	0.83432	0.71748	[30]
	Pnma, N°62	Exp.	1.02173	0.83281	0.71459	[53]
		Calc.	1.01777	0.83721	0.71983	This work
Zr_5Sb_3	Y_5Bi_3, oP32	Exp.	0.7465	0.8801	1.0865	[52]
	Pnma, N°62	Exp.	0.7465	0.8801	1.0865	[54]
		Calc.	0.7528	0.889	1.0966	This work
Zr_5Sb_3	Mn_5Si_3, hP16	Exp.	0.8422	0.8422	0.5696	[55,56]
	P63/mcm, N°193	Exp.	0.8488	0.8488	0.58	[57]
		Calc.	0.8515	0.8515	0.5797	This work
Hf_5Sb_3	Y_5Bi_3, oP32	Exp.	0.74075	0.8718	1.0736	[58]
	Pnma, N°62	Calc.	0.7443	0.8841	1.0786	This work

Table 6. Calculated values of the formation enthalpies of $D8_m$-$T_{10}T'_2Sb_4$ and $T_{10}T'Sb_5$ in the N°97, N°125, and N°124 structures

System	Composition	Structure	$\Delta_f H$ (kJ/mol of atoms) Non magnetic	$\Delta_f H$ (kJ/mol of atoms) Spin pol.
Ti-Cu-Sb	$Ti_{10}CuSb_5$	N°97	–47.03	
		N°125	–47.00	
		N°124	–40.43	
	$Ti_{10}Cu_2Sb_4$	$D8_m$	–38.16	
Ti-Ni-Sb	$Ti_{10}NiSb_5$	N°97	–49.71	
		N°125	–49.72	
		N°124	–42.98	
	$Ti_{10}Ni_2Sb_4$	$D8_m$	–44.60	
Ti-Co-Sb	$Ti_{10}CoSb_5$	N°97	–48.09	–48.10
		N°125	–47.87	–47.91
		N°124	–42.59	–42.60
	$Ti_{10}Co_2Sb_4$	$D8_m$	–44.41	–44.46
Ti-Fe-Sb	$Ti_{10}FeSb_5$	N°97	–46.30	–46.57
		N°125	–45.98	–46.38
		N°124	–41.77	–41.78
	$Ti_{10}Fe_2Sb_4$	$D8_m$	–42.20	–42.09
Ti-Mn-Sb	$Ti_{10}MnSb_5$	N°97	–45.32	–45.22
		N°125	–44.90	–44.97
		N°124	–40.76	–40.89
	$Ti_{10}Mn_2Sb_4$	$D8_m$	–40.45	–40.58
Ti-Cr-Sb	$Ti_{10}CrSb_5$	N°97	–42.93	
		N°125	–42.64	
		N°124	–38.46	
	$Ti_{10}Cr_2Sb_4$	$D8_m$	–35.71	
Ti-Pt-Sb	$Ti_{10}PtSb_5$	N°97	–55.24	
		N°125	–55.19	
		N°124	–50.84	
	$Ti_{10}Pt_2Sb_4$	$D8_m$	–58.34	
Ti-Rh-Sb	$Ti_{10}RhSb_5$	N°97	–52.08	
		N°125	–52.22	
		N°124	–46.19	
	$Ti_{10}Rh_2Sb_4$	$D8_m$	–50.51	
Zr-Cu-Sb	$Zr_{10}CuSb_5$	N°97	–62.05	
		N°125	–62.00	
		N°124	–57.01	
	$Zr_{10}Cu_2Sb_4$	$D8_m$	–50.91	
Zr-Ni-Sb	$Zr_{10}NiSb_5$	N°97	–63.48	
		N°125	–63.65	
		N°124	–58.83	
	$Zr_{10}Ni_2Sb_4$	$D8_m$	–55.32	
Zr-Co-Sb	$Zr_{10}CoSb_5$	N°97	–61.46	
		N°125	–61.29	
		N°124	–57.70	
	$Zr_{10}Co_2Sb_4$	$D8_m$	–53.52	

Table 6. Continued...

System	Composition	Structure	$\Delta_f H$ (kJ/mol of atoms) Non magnetic	$\Delta_f H$ (kJ/mol of atoms) Spin pol.
Zr-Fe-Sb	$Zr_{10}FeSb_5$	N°97	–59.59	–60.27
		N°125	–58.91	–59.99
		N°124	–56.21	–56.21
	$Zr_{10}Fe_2Sb_4$	$D8_m$	–50.24	–49.47
Zr-Pt-Sb	$Zr_{10}PtSb_5$	N°97	–70.84	
		N°125	–70.78	
		N°124	–67.60	
	$Zr_{10}Pt_2Sb_4$	$D8_m$	–72.47	
Hf-Cu-Sb	$Hf_{10}CuSb_5$	N°97	–44.83	
		N°125	–44.80	
		N°124	–39.67	
	$Hf_{10}Cu_2Sb_4$	$D8_m$	–37.53	
Hf-Ni-Sb	$Hf_{10}NiSb_5$	N°97	–47.17	
		N°125	–47.23	
		N°124	–42.39	
	$Hf_{10}Ni_2Sb_4$	$D8_m$	–43.57	
Hf-V-Sb	$Hf_{10}VSb_5$	N°97	–41.40	
		N°125	–41.24	
		N°124	–37.91	
	$Hf_{10}V_2Sb_4$	$D8_m$	–36.22	

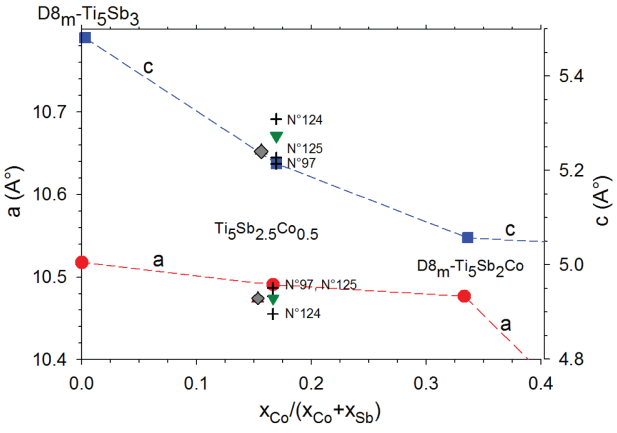

Figure 4. Calculated and experimental [25,27,29] values of the lattice parameters of the $D8_m$ compounds along the section Ti_5Sb_3-Ti_5Co_3.

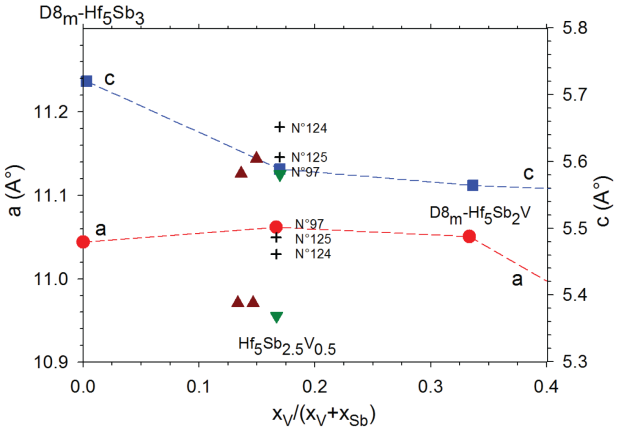

Figure 5. Calculated and experimental [41] values of the lattice parameters of the $D8_m$ compounds along the section Hf_5Sb_3-Hf_5V_3.

than the experimental ones. One explanation could be that the lattice parameters calculated in the GGA approximation are the more often greater than the experimental values. The values of the lattice parameters calculated for all compounds investigated in the present work are reported in the *Supplement* to this paper.

The distances between the atoms may be calculated and are reported in Table 7 in the case of the $D8_m$-$Ti_{10}Sb_4Co_2$ compound and in Tables 8-10 in the cases of the three possible ordered structures of $Ti_{10}Sb_5Co$.

One may observe that the interatomic distances are the same in the N°97 and N°125 structures. Indeed as indicated in section 2, the only difference between the two structures is the positions of the Co and Sb atoms in the planes z=0 and z=1/2 (see Figures S1 and S2 of the *Supplement*). In another hand, the lattice parameters and the interatomic distances are different in the N°124 structure. In fact, the N°124 structure may be considered as the weighted sum of the $D8_m$-Ti_5Sb_3 and $D8_m$-Ti_5Sb_2Co structures. This is true for the lattice parameters and for the atomic distances. As a

Table 7. Bond lengths in the ternary $D8_m$-Ti_5Sb_2Co compound

	Co (4a)		Sb (8h)		Ti (4b)		Ti (16k)	
Co (4a)	2	2.530 Å					8	2.568 Å
Sb (8h)					2	2.742 Å	8	2.808-3.058 Å
Ti (4b)			4	2.742 Å	2	2.530 Å	8	3.458 Å
Ti (16k)	2	2.568 Å	4	2.808-3.058 Å	2	3.458 Å	5	2.930-3.186 Å

Table 8. Bond lengths in the ternary N°97-Ti10Sb5Co compound

	Co (2a)		Sb (2b)		Sb (8j)		Ti (4c)		Ti (16k)	
Co (2a)			2	2.607 Å					8	2.719 Å
Sb (2b)	2	2.607 Å							8	2.769 Å
Sb (8j)							2	2.758 Å	8	2.797-3.081 Å
Ti (4c)					4	2.758 Å	2	2.607 Å	8	3.311-3.351 Å
Ti (16k)	1	2.719 Å	1	2.769 Å	4	2.797-3.081 Å	2	3.311-3.351 Å	7	2.955-3.414 Å

Table 9. Bond lengths in the ternary N°125-Ti10Sb5Co compound

	Co (2a)		Sb (2b)		Sb (8k)		Ti (2c), Ti (2d)		Ti (16l)	
Co (2a)			2	2.612 Å					8	2.715 Å
Sb (2b)	2	2.612 Å							8	2.773 Å
Sb (8k)							1	2.766 Å	8	2.799-3.078 Å
							1	2.750 Å		
Ti (2c)					4	2.766 Å	2	2.612 Å	8	3.302 Å
Ti (2d)					4	2.750 Å	2	2.612 Å	8	3.351 Å
Ti (16l)	1	2.715 Å	1	2.773 Å	4	2.799-3.078 Å	1	3.302 Å	7	2.939-3.462 Å
							1	3.351 Å		

Table 10. Bond lengths in the ternary N°124-Ti10Sb5Co compound

	Co (2a)		Sb (2c)		Sb (8m)		Ti (4f)		Ti (16l)	
Co (2a)	2	2.654 Å	2	2.654 Å					8	2.585 Å
Sb (2c)	2	2.654 Å							8	2.849 Å
Sb (8k)							2	2.765 Å	4	2.786-3.146 Å
Ti (4f)					4	2.765 Å	2	2.654 Å	8	3.236-3.479 Å
Ti (16l)	2	2.585 Å	2	2.849 Å	4	2.786-3.146 Å	2	3.236, 3.479 Å	6	3.028-3.473 Å

consequence, the enthalpy of formation of N°124-$Ti_{10}Sb_5Co$ is in the middle of the line joining the enthalpies of formation of $D8_m$-Ti_5Sb_3 and $D8_m$-Ti_5Sb_2Co structures. This observation can be made in all other systems we have studied in the present work.

The Bader charges for the series $D8_m$-Ti_5Sb_2T' and N°97- $Ti_5Sb_{2.5}T'_{0.5}$ (T'= Co, Ni) have been computed. The transfer from the Ti atoms to the late transition metal is in these cases of about 1.5 e^-, leading in these cases to a filled d band of Co and Ni.

At high temperature, one expects a random distribution of the Sb and T' atoms along the chains corresponding to the 4a sites of the $D8_m$ structure. As a consequence the formation enthalpy of the disordered phase will be less negative than the ones of N°97 and N°125 but the stability will be maintained by the mixing entropy of Sb and T'.

5 CONCLUSION

In the present work, we have investigated ternary compounds $T_{10}Sb_5T'$ where T=Ti, Zr, Hf, and T' a 3d, or 4d, or 5d transition metal of the end of the series. We have calculated the enthalpies of formation of $D8_m$-T_5Sb_2T' and of ordered structures of composition $T_{10}Sb_5T'$. We have shown that the structures where the T' and Sb atoms alternate along the chains formed by the 4a sites of the W_5Si_3 structure are the most stable structures (structures N°97 and N°125). These structures are very similar, the only difference is the positions of T' and Sb atoms in the plans z=0 and z=1/2. On the contrary, the structure where chains formed by T' atoms and Sb atoms solely is the less stable one (structure N°124).

The stability of the $T_{10}Sb_5T'$ compound is due to several factors. First, even if the $D8_m$-structure of Ti_5Sb_3,

Zr_5Sb_3, and Hf_5Sb_3 is not the ground state in the binaries Ti-Sb, Zr-Sb, and Hf-Sb, the energy difference between the $D8_m$ and the ground state structure is not very important (less than 4.2 kJ/mol of atoms). Secondly, the $D8_m$- T_5Sb_2T' compound in the Nb_5Sn_2Si-type is stabilized with respect the two $D8_m$-T_5Sb_3 and $D8_m$-T'_5Sb_3 compounds, due to the size of the T' atom which is smaller than the one of the T atoms. In previous publications, this fact was shown in the case of T_5Sb_2X compounds where X is a p element. Finally the composition $T_{10}Sb_5T'$ is favoured by an electronic factor, which is a complete or partial filling of the d band of the T' transition metal.

At high temperature, the Sb and T' atoms present a random distribution on the 4a chains of the W_5Si_3-type structure. The formation enthalpy is therefore less negative than the one of the N°97 or N°125. The corresponding increase of the Gibbs energy is compensated by a configurational entropy due to the random mixing of Sb and T' atoms along the chains.

This study is a first step in the investigation of isothermal sections in the T-Sb-T' systems. Such studies require the knowledge of the formation enthalpies of all compounds present in the system.

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Supplement. Structural stability of ternary antimonides $T_{10}Sb_5T'$ (T=Ti, Zr, Hf, T'=V, Cr, Mn, Fe, Co, Ni, Cu, Pd, Pt, Rh)

Suplemento. Estabilidade estrutural de compostos ternários de antimonio $T_{10}Sb_5T'$ (T=Ti, Zr, Hf, T'=V, Cr, Mn, Fe, Co, Ni, Cu, Pd, Pt, Rh)

Table S1a. Calculated values of the formation enthalpies of Ti based compounds

System	Composition	Structure	$\Delta_f H$ (kJ/mol of atoms) Non magnetic	$\Delta_f H$ (kJ/mol of atoms) Spin pol
Ti-Cu-Sb	$Ti_{10}CuSb_5$	N°97	–47.027	
		N°125	–47.002	
		N°124	–40.432	
	$Ti_{10}Cu_2Sb_4$	$D8_m$	–38.158	
	$Ti_{10}Cu_6$	$D8_m$	–0.708	
	GS C11b-Ti_2Cu	C11b-Ti_2Cu	–11.686	
	+B11-TiCu	B11-TiCu	–13.389	
Ti-Ni-Sb	$Ti_{10}NiSb_5$	N°97	–49.710	
		N°125	–49.721	
		N°124	–42.982	
	$Ti_{10}Ni_2Sb_4$	$D8_m$	–44.596	
	$Ti_{10}Ni_6$	$D8_m$	–26.323	
	GS $E9_3$-Ti_2Ni	$E9_3$-Ti_2Ni	–27.049	
	+B27-TiNi	B27-TiNi	–38.776	
Ti-Co-Sb	$Ti_{10}CoSb_5$	N°97	–48.086	
		N°125	–47.869	
		N°124	–42.590	–48.095
	$Ti_{10}Co_2Sb_4$	$D8_m$	–44.409	–47.911
	$Ti_{10}Co_6$	$D8_m$	–25.180	–42.602
	GS $E9_3$-Ti_2Co	$E9_3$-Ti_2Co	–27.683	–44.463
	+B2-TiCo	B2-TiCo	–36.571	
Ti-Fe-Sb	$Ti_{10}FeSb_5$	N°97	–46.298	
		N°125	–45.984	–46.574
		N°124	–41.768	–46.380
	$Ti_{10}Fe_2Sb_4$	$D8_m$	–42.200	–41.782
	$Ti_{10}Fe_6$	$D8_m$	–13.240	–42.089
	GS $E9_3$-Ti_2Fe	$E9_3$-Ti_2Fe	–21.316	–13.659
	+B2-Ti-Fe	B2-Ti-Fe	–40.316	
Ti-Mn-Sb	$Ti_{10}MnSb_5$	N°97	–45.3171	
		N°125	–44.9047	
		N°124	–40.7612	–45.2151
	$Ti_{10}Mn_2Sb_4$	$D8_m$	–40.451	–44.9660
	$Ti_{10}Mn_6$	$D8_m$	–1.9705	–40.8914
	GS A3-Ti	A3-Ti	0	–40.576
	+B2-TiMn	B2-TiMn	–23.702	
Ti-Pt-Sb	$Ti_{10}PtSb_5$	N°97	–55.244	
		N°125	–55.190	
		N°124	–50.840	
	$Ti_{10}Pt_2Sb_4$	$D8_m$	–58.339	
	$Ti_{10}Pt_6$	$D8_m$	–71.509	
	GS $D8_8$-Ti_5Pt_3	$D8_8$-Ti_5Pt_3	–75.673	

Table S1a. Continued...

System	Composition	Structure	$\Delta_f H$ (kJ/mol of atoms) Non magnetic	$\Delta_f H$ (kJ/mol of atoms) Spin pol
	$Ti_{10}RhSb_5$	N°97	–52.002	
		N°125	–52.616	
		N°124	–46.578	
Ti-Rh-Sb	$Ti_{10}Rh_2Sb_4$	$D8_m$	–50.463	
	$Ti_{10}Rh_6$	$D8_m$	–52.500	
	GS C11b-Ti_2Rh	C11b-Ti_2Rh	–63.131	
	+$L1_0$-TiRh	$L1_0$-TiRh	–75.847	

Table S1b. Calculated values of the formation enthalpies of Zr based compounds

System	Composition	Structure	$\Delta_f H$ (kJ/mol of atoms) Non magnetic	$\Delta_f H$ (kJ/mol of atoms) Spin pol
	$Zr_{10}CuSb_5$	N°97	–62.047	
		N°125	–62.004	
		N°124	–57.012	
Zr-Cu-Sb	$Zr_{10}Cu_2Sb_4$	$D8_m$	–50.910	
	$Zr_{10}Cu_6$	$D8_m$	–4.074	
	GS C11b-Zr_2Cu	C11b-Zr_2Cu	–13.2936	
	+Zr_7Cu_{10}	oS68-Zr_7Cu_{10}	–15.7476	
	$Zr_{10}NiSb_5$	N°97	–63.480	
		N°125	–63.654	
		N°124	–58.834	
Zr-Ni-Sb	$Zr_{10}Ni_2Sb_4$	$D8_m$	–55.321	
	$Zr_{10}Ni_6$	$D8_m$	–25.164	
	GS C16-Zr_2Ni	C16-Zr_2Ni	–31.299	
	+B33-ZrNi	B33-ZrNi	–44.028	
	$Zr_{10}CoSb_5$	N°97	–61.456	
		N°125	–61.294	
		N°124	–57.698	
Zr-Co-Sb	$Zr_{10}Co_2Sb_4$	$D8_m$	–53.521	
	$Zr_{10}Co_6$	$D8_m$	–19.930	
	GS C16-Zr_2Co	C16-Zr_2Co	–24.540	
	+B27-ZrCo	B27-ZrCo	–31.389	
	$Zr_{10}FeSb_5$	N°97	–59.587	–60.272
		N°125	–58.914	–59.992
		N°124	–56.213	–56.213
Zr-Fe-Sb	$Zr_{10}Fe_2Sb_4$	$D8_m$	–50.235	–49.472
	$Zr_{10}Fe_6$	$D8_m$	–5.864	–5.981
	GS $E9_3$-Zr_2Fe	$E9_3$-Zr_2Fe	–11.649	
	+C15-ZrFe2	C15-ZrFe2	–16.884	–26.980
	$Zr_{10}PtSb_5$	N°97	–70.840	
		N°125	–70.776	
Zr-Pt-Sb		N°124	–67.599	
	$Zr_{10}Pt_2Sb_4$	$D8_m$	–72.472	
	GS $D8_m$-$Zr_{10}Pt_6$	$D8_m$-$Zr_{10}Pt_6$	–79.127	

Table S1c. Calculated values of the formation enthalpies of Hf based compounds

System	Composition	Structure	$\Delta_f H$ (kJ/mol of atoms) Non magnetic	$\Delta_f H$ (kJ/mol of atoms) Spin pol
	$Hf_{10}CuSb_5$	N°97	–44.832	
		N°125	–44.798	
		N°124	–39.670	
Hf-Cu-Sb	$Hf_{10}Cu_2Sb_4$	$D8_m$	–37.531	
	$Hf_{10}Cu_6$	$D8_m$	–1.827	
	GS C11b-Hf_2Cu	C11b-Hf_2Cu	–15.639	
	+Hf_7Cu_{10}	oS68-Hf_7Cu_{10}	–16.903	
	$Hf_{10}NiSb_5$	N°97	–47.169	
		N°125	–47.228	
		N°124	–42.387	
Hf-Ni-Sb	$Hf_{10}Ni_2Sb_4$	$D8_m$	–43.571	
	$Hf_{10}Ni_6$	$D8_m$	–27.959	
	GS C16-Hf_2Ni	C16-Hf_2Ni	–32.916	
	+B33-HfNi	B33-HfNi	–50.007	
	$Hf_{10}VSb_5$	N°97	–41.402	
		N°125	–41.240	
		N°124	–37.910	
Hf-V-Sb	$Hf_{10}V_2Sb_4$	$D8_m$	–36.217	
	$Hf_{10}V_6$	$D8_m$	19.502	
	GS		0	
	C14-	C14-HfV2	0.8829	

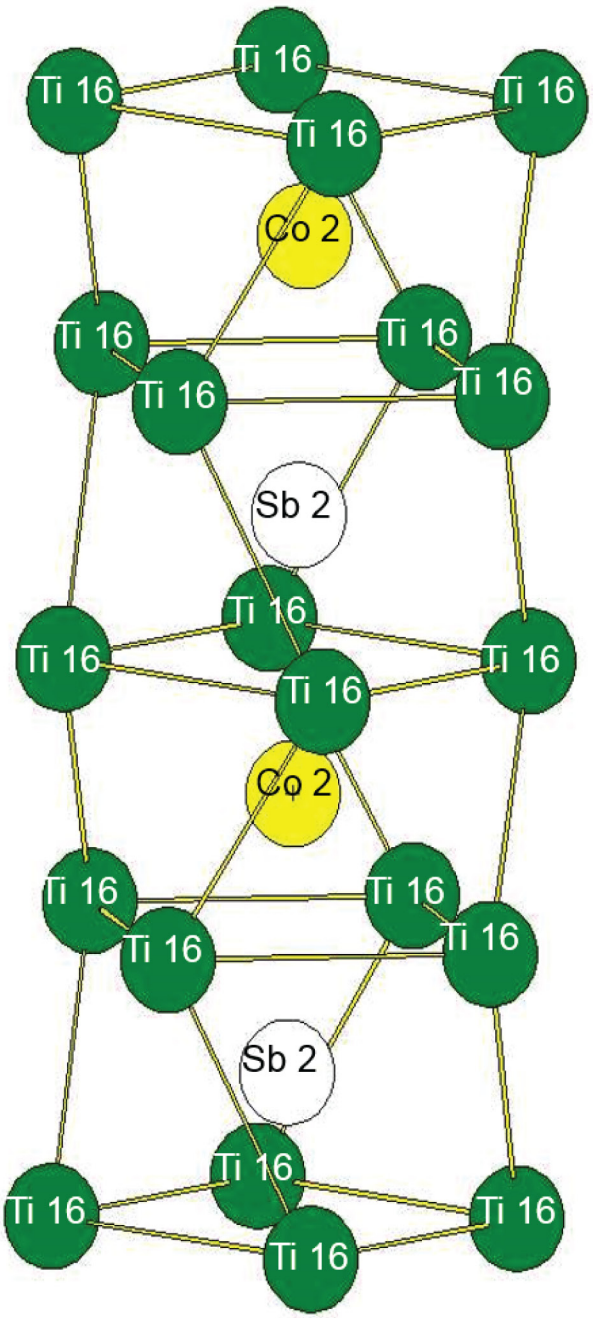

Figure S1. Chains of Sb and Co atoms in the cases of N°97 and N°125 structures of $Ti_{10}Sb_5Co$. The Ti atoms form antiprisms which share faces.

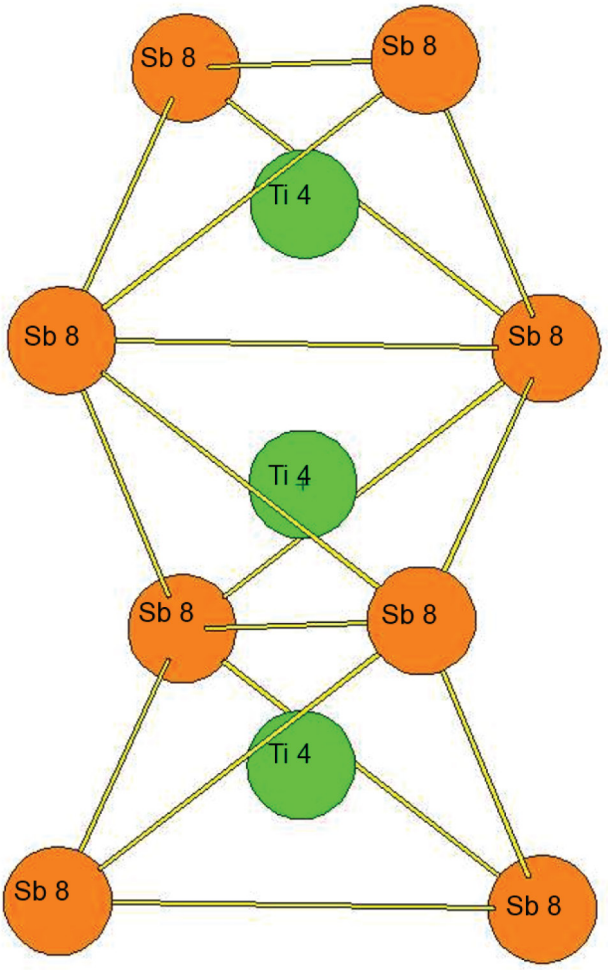

Figure S2. Ti 4 centred Sb tetrahedra which share edges. This figure is the same in the N°97, N°125 and N°124 structures.