Structures and crystal chemistry of MT$_6$X$_6$ phases, filled derivatives of the CoSn-B35 structure

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M atoms can be inserted into the host CoSn-type TX structure to give MT$_6$X$_6$ structures (M = Li, Mg, Ca, IIIA, IVA, lanthanides, U; T = Cr-Ni, X = Si, Ge, X' = Ga, In). The crystal structures of known MT$_6$X$_6$ compounds are reviewed and sorted into orthorhombic, monoclinic and hexagonal series. The diffraction results for ternary and pseudo-ternary compounds are summarized and discussed on the basis of preponderant M-X, T-X and M-T bonding. The structural evolutions in the pseudo-ternary compounds MT$_6$X$_{6-x}$X'_x as a function of X' are analyzed, underlining the role of the size and electronic structure of X'.

Crystal chemistry / Crystal structure / Host structure / Intermetallics

1. Introduction

The MT$_6$X$_6$ compounds and MT$_6$X$_{6-x}$X'_x pseudo-ternary compounds (M = Li, Mg, Ca, IIIA, IVA, lanthanides, U; T = Cr-Ni, X = Si, Ge, X' = Ga, In) have been studied by many research groups for their interesting and various physical properties [1-22]. Most of the studied compounds are isotypic to hexagonal HfFe$_6$Ge$_6$, but others crystallize in different orthorhombic superstructures. From a crystallographic point of view, all of them derive from the binary CoSn host structure through different filling schemes.

2. Crystal structures

2.1. The CoSn host structure and the filling process

The hexagonal CoSn structure [23] is a stacking of hexagonal Sn$_2$ planes and Co Kagomé planes with the hexagons centered by Sn$_1$ atoms. The Sn$_2$ atoms are located in cobalt trigonal prisms sharing edges in the (001) planes and faces along the [001] direction, building hexagonal channels occupied by the Sn$_1$ atoms (Fig. 1). The cobalt atoms are situated in tin octahedrons sharing faces in the (001) plane and edges along the [001] direction. This arrangement yields the formation of large empty hexagonal bi-pyramids. Taking into account a small deviation of the atoms at the apex of the bi-pyramids, this hole is suitable to guest large metallic atoms M, giving rise to the formula MT$_6$X$_6$. The relative height of the atoms M in the hexagonal channels leads to the different superstructures that will be described below. Typical diffraction patterns are shown in Fig. 2, which displays the diffracted intensities of some pseudo-ternary LuFe$_6$Ge$_6$Ga$_x$ compounds.

2.2. The HfFe$_6$Ge$_6$ and ScFe$_6$Ga$_6$-type structures

There exist two relatively simple structures corresponding to the formula MT$_6$X$_6$: the hexagonal HfFe$_6$Ge$_6$ type [24] (also called MgFe$_6$Ge$_6$ or (Fe,Mn)-Ge$_6$ [25,26]) and the orthorhombic ScFe$_6$Ga$_6$ type [27], which should be regarded as a ternary derivative of the tetragonal ThMn$_{12}$ type [28]. In the HfFe$_6$Ge$_6$ type, the M atoms are all located in the same (001) planes and there is an alternate stacking of filled and empty planes (Fig. 3), while in the ScFe$_6$Ga$_6$ type, the planes (110) are alternately filled and empty. These arrangements lead to different capping of the trigonal prisms: mono- or bi-capped for the ScFe$_6$Ga$_6$ type and uncapped or tri-capped for the HfFe$_6$Ge$_6$ type. It will be shown later that all the superstructures
Fig. 1 The CoSn structure: trigonal prisms around the Sn\textsubscript{2} atoms (a); octahedrons around the Co atoms (b); hexagonal rings of octahedrons (c); empty hexagonal bi-pyramid (d).

Fig. 2 Typical X-ray patterns of the LuFe\textsubscript{6}Ge\textsubscript{6-x}Ga\textsubscript{x} series: hexagonal HfFe\textsubscript{6}Ge\textsubscript{6} type (x = 0.5); orthorhombic superstructure (x = 1.05); monoclinic superstructure (x = 4.0); orthorhombic ScFe\textsubscript{6}Ga\textsubscript{6} type (x = 4.5).
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Fig. 3 Projections of the HfFe₆Ge₆- (a) and ScFe₆Ga₆-type (b) structures.

Projections of the known structures are given in Fig. 4. They may be described as infinite HfFe₆Ge₆ (H) and ScFe₆Ga₆ (S) slabs of different thickness, stacked along the propagating direction. The sequence of the slabs is also formulated in Table 1. It may be calculated that the concentration in ScFe₆Ga₆ slabs (S) is given by the value of the propagating vector component \( q_y \) \[ S/(S+H) = q_y = n/p \].

2.4. The monoclinic series
In this series, the indexing of the diffraction patterns is done considering a two-component propagating vector \( Q = (q_x, q_y, 0) \). In this case, the \( z \) coordinates of the M atoms are related to the sign of the expression \( C = \cos(2\pi(q_x^* x_M + q_y^* y_M)) \), where \( x_M \) and \( y_M \) are the coordinates of the M atoms in the (001) plane [31,32]. Two space groups deduced from the atomic positions have been recognized so far: \( C2/m \) and \( P2/m \), where the pseudo-hexagonal axis becomes the unique axis. The concentration of ScFe₆Ga₆-units is also related to the components of the propagating vector through the relation \( S/(S+H) = q_x + q_y \). Six sets of propagating vector components have been clearly established (Table 2). Four of them reasonably account for a commensurate model and the corresponding structures are gathered in Fig. 5. They display HfFe₆Ge₆-columns constituted of 2, 4 and 6 units, elongated along the unique axis and separated

| Table 1 Summary of crystallographic data of the orthorhombic series. |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| M               | \( q_x \)       | \( n/p \)       | Space group     | Sequence        |
| ErFe₆Sn₆        | 0.25            | 1/4             | Cmcm            | \( H^1 S^1 \)   |
| ScFe₆Ge₂Ga₃₃₅   | 0.268           | 3/11            | Immm            | \( 2(H^2 S^1)H^1 S^1 \) |
| HoFe₆Sn₆        | 0.333           | 1/3             | Immm            | \( H^1 S^1 \)   |
| YFe₆Sn₆         | 0.375           | 3/8             | Cmcm            | \( 2(H^2 S^1)H^1 S^1 \) |
| DyFe₆Sn₆        | 0.400           | 2/5             | Cmcm            | \( H^1 S^1 \)   |
| TbFe₆Sn₆        | 0.500           | 1/2             | Cmcm            | \( H^1 S^1 \)   |
| TbFe₆Ge₂Ga₂₅    | 0.667           | 2/3             | Cmcm            | \( 2(H^2 S^1)H^1 S^1 \) |
| TbFe₆Ge₃Ga₃     | 0.706           | 12/17           | Cmcm            | \( 2(H^2 S^1)H^1 S^1 \) |
Fig. 4 Projections along the pseudo-hexagonal axis of the structures belonging to the orthorhombic series.
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Fig. 5 Projections along [001] of the structures belonging to the monoclinic series: LuFe$_6$Ge$_2$Ga$_4$ (a), ScFe$_6$GeGa$_5$ (b), TbFe$_6$Ge$_2$Ga$_2$ (c), TbFe$_6$Ge$_{4.25}$Ga$_{1.75}$ (d).

Table 2 Summary of the crystallographic data of the monoclinic series.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$q_x$</th>
<th>$q_y$</th>
<th>$n_x/p_x$</th>
<th>$n_y/p_y$</th>
<th>$\Sigma q_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ScFe$<em>6$Ge$</em>{1.5}$Ga$_{4.5}$</td>
<td>0.232</td>
<td>0.403</td>
<td>3/13</td>
<td>2/5</td>
<td>0.635</td>
</tr>
<tr>
<td>TbFe$<em>6$Ge$</em>{4.25}$Ga$_{1.75}$</td>
<td>0.241</td>
<td>0.400</td>
<td>6/25</td>
<td>2/5</td>
<td>0.641</td>
</tr>
<tr>
<td>LuFe$_6$Ge$<em>2$Ga$</em>{3.5}$</td>
<td>0.244</td>
<td>0.420</td>
<td>11/45</td>
<td>21/50</td>
<td>0.664</td>
</tr>
<tr>
<td>TbFe$_6$Ge$_2$Ge$_2$</td>
<td>0.247</td>
<td>0.422</td>
<td>1/4</td>
<td>5/12</td>
<td>0.669</td>
</tr>
<tr>
<td>LuFe$_6$Ge$_2$Ga$_4$</td>
<td>0.249</td>
<td>0.500</td>
<td>1/4</td>
<td>1/2</td>
<td>0.749</td>
</tr>
<tr>
<td>ScFe$_6$Ge$_3$Ga$_3$</td>
<td>0.334</td>
<td>0.496</td>
<td>1/3</td>
<td>1/2</td>
<td>0.830</td>
</tr>
</tbody>
</table>

by ScFe$_6$Ga$_6$-units. Two of them, LuFe$_6$Ge$_2$Ga$_4$ and ScFe$_6$GeGa$_5$, display the same type of column, more or less diluted into the ScFe$_6$Ga$_6$ matrix.

Attempts have been made to analyze one of the compounds in the superspace model using the JANA program [33]. The refined components are $q_x = 0.2440(3)$ and $q_y = 0.4198(4)$. The structure, presented in Fig. 6, is mainly constituted of isolated columns of four HfFe$_6$Ge$_6$-units and therefore close to the TbFe$_6$Ge$_2$Ga$_2$ structure.

2.5. The hexagonal series

Hexagonal superstructures of the CoSn type have been known for a long time (Fig. 7). The LiFe$_6$Ge$_6$-type ($P6_3/mmc; a = \sqrt{3} a_h; c = 2c_h$) [34], like the ScFe$_6$Ga$_6$ type, does not display HfFe$_6$Ga$_6$ units.
The ScNi₆Ge₆-type (P6/mmm; a = 2a₀; c = 2c₀) [35] displays hexagonal rings of HfFe₆Ge₆ units (S/[H+S] = 0.75). Both types, together with the HfFe₆Ge₆ type, may be considered as the first terms of a hypothetical hexagonal series, whose next terms might be characterized by an increasing parameter: a = \sqrt{3} a₀, a = 3a₀ and of course by an increasing number of combinations of the structural units.

2.6. The disordered YCo₆Ge₆-type structure and deviations from the idealized structures

The YCo₆Ge₆ type has been described as a filled derivative of the CoSn type, without any indication of long range ordering [36]. It is worth noting that some iron stannide and germanide superstructures have been observed later [29,30]. Some deviations from the idealized HfFe₆Ge₆ structure, or from the idealized orthorhombic structures, have been reported. According to Zaharko et al. [37], complete ordering of the M atoms is not observed in germanides. Mazet [38] reported a not fully occupied M site in the HfFe₆Ge₆-type compounds and related this to filling of anti-bonding states.

Interesting works have been devoted to the existence and shape of the satellites in the orthorhombic series [39,40]. In particular, an anisotropic broadening of the superstructure lines has been observed and the half-width of the peaks was found to be dependent on the annealing temperature.

3. Crystal chemistry

3.1. Results of the structure refinements

3.1.1. Single crystal refinement of ternary MMn₆X₆ (X = Ge, Sn)

The atomic coordinates in hexagonal MMn₆X₆ (M = Sc, Tb, Er, Tm; X = Ge, Sn) compounds have been refined from single crystal diffraction for various M sizes [41,42]. The variation of the atomic coordinates as a function of the size of the M atom is summarized in Fig. 8. It was found that zₘ is smaller in stannides than in germanides. This feature should account for a displacement of the Mn planes towards the M planes, thus suggesting bonding between the
two species. The $z_X$ coordinate acts on the relative lengths of the M-X and X-X distances in the M-X-X-M chain running along the six-fold axes. For increasing X size, the variation of $z_X$ indicatethat the $d_{X,X}$ distance increases to a larger extent than the $d_{M,X}$ distance. The variation of $z_X$ with the M size leads to an unusual variation of the X-X distance: it was found that $d_{X,X}$ increases with decreasing cell volume ($d_{Sc,Sn} = 2.98 \text{ Å}$ and $d_{Sn,Sn} = 2.93 \text{ Å}$ for $\mathbf{V} = 233.6 \text{ Å}^3$ and $238.9 \text{ Å}^3$ in ScMn$_x$Sn$_6$ and TbMn$_x$Sn$_6$, respectively). This suggests that the X-X distances are too compressed when the M-X distance increases and that a smaller M atom enables a relaxation of the X-X distance. This feature should be a limiting factor concerning the stability of these phases for the largest M atoms.

3.1.2. Single crystal refinement of DyFe$_6$Sn$_6$ and powder refinement of ErFe$_6$Sn$_6$

An interesting single crystal refinement of the DyFe$_6$Sn$_6$ stannide has been undertaken by Oleksyn and Bohm [43]. This unique study, devoted to the orthorhombic compounds, provides information on the atomic coordinates in this series. Particularly, displacements of the Dy atoms are observed, yielding an increase of the thickness of the HfFe$_6$Ge$_6$ slabs with respect to the ScFe$_6$Ga$_6$ ones (Fig. 9). This leads to an increase of the Dy-Sn distances within the HfFe$_6$Ge$_6$ slab, thus suggesting that the stabilization of the orthorhombic phases might be an alternative to too short contacts between the M atom in 1(α) and the X atom in 2(c) in the hexagonal HfFe$_6$Ge$_6$-type compounds. The observation of orthorhombic compounds only for the largest M elements in manganese stannides should be related to a dilated Mn-Sn sublattice. A refinement of a powder sample of ErFe$_6$Sn$_6$ using the JANA software [33] led to the same conclusions.

3.1.3. Pseudo-ternary compounds

The distribution of the X and X’ atoms has been checked for various pseudo-ternary compounds, using different experimental procedures. Neutron diffraction studies have been used for the (Ge,Ga) and (Sn,In) couples [44,45]. The contrast of the Fermi lengths is rather good for the (Sn,In) couple ($L_{Sn}/L_{In} = 1.53$), but less suitable for the (Ge,Ga) one ($L_{Ge}/L_{Ga} = 1.12$). The Mn$_x$Sn$_{6-x}$Ge$_x$ compounds have been studied by single crystal X-ray diffraction and the Mn$_x$Sn$_{6-x}$Ga$_x$ compounds by powder X-ray diffraction [42,46,47]. Whatever X and X’, it is observed that, when X’ is larger than X, X is mainly located in the 2(d) site and there is mainly an increase of the $a$ parameter, whereas when X’ is smaller than X, X’ is mainly located in the 2(c) site, close to the 1(a) site of M, and both cell parameters decrease. In all cases, a decrease of the $z_T$ coordinate is observed.

This leads to the following conclusions concerning the evolution of the interatomic distances. The HfFe$_6$Ge$_6$ type uses all its free variables (cell parameters and atomic coordinates) to adjust the M-X(X’) and T-X(X’) distances to the size of the X and X’ atoms. Moreover, whatever the size of X’, the M-T distance remains constant or decreases. This suggests that the site preference is driven by an optimization of this contact. This conclusion should be related to electronic structure calculations, which indicate hybridization between the 3dT and ndM states [48].

3.2. Structural evolution in pseudo-ternary compounds

3.2.1. MT$_6$Sn$_{6-x}$Ge$_x$ (M = RE element; T = Fe, Mn)

From the conclusions of section 3.1.3, it was expected that in the isoelectronic pseudo-ternary compounds MT$_6$Sn$_{6-x}$Ge$_x$, the small germanium atoms will occupy the 2(c) site to minimize the T-M distances. On the other hand, in section 3.1.2, it has been concluded that the occurrence of orthorhombic ternary stannides might be driven by a relaxation of the M-X(2c) contacts. These observations suggest that a transition from orthorhombic structures towards the hexagonal HfFe$_6$Ge$_6$ type might take place in Ge-doped stannides. This assumption has been checked and confirmed for the orthorhombic stannides REM$_x$Sn$_{6-x}$Ge$_x$ (RE = Gd-Er) and REM$_x$Sn$_{6-x}$ (RE = Nd, Sm) [46,49]. The minimum concentration giving rise to a transition was checked for the GdFe$_6$Sn$_{6-x}$Ge$_x$ and the value $x = 0.15$ was found. This should enable comparative studies of the effect of crystallographic order on the magnetic properties.

3.2.2. MF$_6$Ge$_{6-x}$Ga$_x$ (M = Sc, Tb, Lu) and ErFe$_6$Sn$_{6-x}$In$_x$.

The MF$_6$Ga$_6$ compounds (M = lanthanide) crystallize in the ThMn$_{12}$ structure, or in its ternary ordered derivative, the ScFe$_6$Ga$_6$ type. On the other hand, the MF$_6$Ge$_6$ compounds crystallize either in the hexagonal HfFe$_6$Ge$_6$ type, or in orthorhombic types characterized by a large concentration of HfFe$_6$Ge$_6$ slabs. It seemed of interest to examine the
Fig. 9 Projections of the refined DyFe$_6$Sn$_6$ (a) and ErFe$_6$Sn$_6$ (b) structures showing the thickness of the HfFe$_6$Ge$_6$ (H) and ScFe$_6$Ga$_6$ (S) slabs.

Structural evolution among the pseudo-ternary MFe$_6$Ge$_{6-x}$Ga$_x$ compounds.

Investigations of various series (M = Sc, Tb, Lu) [31,32] clearly indicate a continuous structural evolution, displayed in Fig. 10. This study has evidenced a new monoclinic series, characterized by structures displaying a concentration of ScFe$_6$Ga$_6$ slabs greater than 1/2 and up to 5/6.

Recent investigations in the system ErFe$_6$Sn$_{6-x}$In$_x$ (x < 1.5) have shown the same tendency with a transition from the ErFe$_6$Sn$_6$ type (S/[H+S] = 1/4) towards the HoFe$_6$Sn$_6$ type (S/[H+S] = 1/3).

Although the role of the decreasing valence electron concentration (VEC) might be invoked, such an explanation disagrees with the occurrence of HfFe$_6$Ge$_6$-type MCr$_6$Ge$_6$ compounds [50], characterized by even smaller VEC. An alternative way to explain this phenomenon may be that the Ga or In atoms prefer the mono- and di-capped coordination of the ScFe$_6$Ga$_6$ slab. In this case, the new ErFe$_6$Sn$_{6-x}$In$_x$ compounds might be appropriate to check the site occupation, either by using the large contrast in Fermi lengths of tin and indium, or by using $^{119}$Sn as local probe.

3.2.3. MFe$_6$Sn$_{6-x}$Ga$_x$ (M = Tb, Ho, Er)

Investigations in these series are interesting because gallium differs both by its smaller size and its different electronic structure.

The erbium series is characterized by a large concentration range (0.25 < x$_{Ga}$ < 2.5) where the hexagonal HfFe$_6$Ge$_6$ structure is stabilized; powder refinements indicate that the gallium atoms are mainly located in the 2(c) site [47]. An increase of the atomic size of the M element leads to a different behavior. For the holmium series, the stability range is narrower (1.0 < x$_{Ga}$ < 1.5) and there is no more stabilization of the hexagonal structure for the terbium series. This evolution suggests that in

![Fig. 10](chart.png) Evolution of the concentration of ScFe$_6$Ga$_6$-slabs as a function of the gallium content in the compounds MFe$_6$Ge$_{6-x}$Ga$_x$ (M = Sc, Tb, Lu).
MFe$_2$Sn$_6$Ga$_6$ compounds there is effectively a competition between the size effect and the electronic effect and that this competition is tuned by the M size.

Preliminary powder refinements of the TbFe$_2$Sn$_6$ type TbFe$_2$Sn$_6$Ga$_6$ compounds ($0.5 < x < 1.5$) suggest that the gallium atoms are mainly located in the two Sn sites belonging to the ScFe$_2$Ga$_6$ slab and in the pseudo-2(c) site of the HfFe$_2$Ge$_6$ slab.

4. Conclusions

The MT$_x$X$_6$ compounds display a rich crystal chemistry characterized by three structural series: the hexagonal, orthorhombic and monoclinic series. They account for different relative locations of the M atoms in the hexagonal channels of the CoSn host structure.

The various structure refinements undertaken on ternary and pseudo-ternary compounds emphasize the three preponderant hetero-atomic contacts T-X, M-X and M-T. In particular, it has been observed that the X’ atoms are not randomly distributed on the three X sites of the HfFe$_2$Ge$_6$ structure, a feature which seems to be related to the M-T bonding and to the relative size of the X and X’ atoms.

Besides this size effect, structural evolutions in systems MFe$_6$Ge$_6$Ga$_6$ and MFe$_6$Sn$_6$In$_6$ have also been observed, which can be related to the electronic structure of the X’ element. This phenomenon is still not well understood and will need further investigations.

Finally, it seems that optimized substitutions should enable the stabilization of “taylor-cut” samples, in order to check the variation of the physical properties as a function of the crystallographic order.

References
