Two-sublattice intermetallics

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Abstract Some magnetic and structural properties of two sublattice Laves phase, pure or pseudobinary compounds, are reviewed. New experimental results are briefly presented together with some theoretical developments.

1. Introduction

Among the existing two-sublattice intermetallics, we may quote the Laves phases[1], Heusler alloys[2], the magnets with hexagonal structure like R Cu$_5$ [3] (see fig. **1** for some examples) and many others. Here we restrict ourselves to Laves phase pure intermetallics or pseudobinaries. Situations which are specific to these particular cases are explicitly mentioned.

One of the important characteristics of Laves compounds is the possibility of selective impurity dissolution in a specific sublattice (see fig. **2**). The general chemical formula for these magnetic pseudobinaries is

$$A_{1-x}A'_y(B_{1-x}B'_x)_z$$
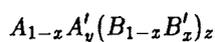
where B is usually Fe or Co and B' may belong to the transition metal group 4 or the sp atom **group**[5,6]. On the other **hand** *A* and *A'* are usually **4d** or **5d** transition metals, or as in one **class** of important cases, rare earthes. In the last case we may also include as *A'* atoms the trivalent Y atoms, with the idea of studying percolation effects. Such percolation effects enable rich studies to be performed on the magnetic properties associated to the **A** sublattice[7]. Combining **localized** spins in the *A* sublattice with almost non-magnetic impurities in the same sublattice, the combination of geometric and magnetic properties may induce rich behaviours such **as** random anisotropies, spin **glass** behaviour etc. The **following** cases will be explicitly mentioned:

i) **isoelectronic** intermetallics like: $TiFe_2$, $ZrFe_2$, $HfFe_2$

ii) intermetallics differing in one electron per formula unit like: YFe_2, $ZrFe_2$, $NbFe_2$

iii) intermetallics with spherical, non spherical, anomalous or non-magnetic rare earthes like: $GdFe_2$, $DyFe_2$, CeF_2, $LuFe_2$

iv) intermetallics of actinides in the beginning of the series: UFe_2, UCo_2, UNi_2

1 - The electronic structure: some examples of the literature

Among the methods of great **applicability** to the materials **discussed** here, we quote the recursion method within the tight binding formalism. The first results obtained within the recursion method for the Laves phase compounds belong to the Japanese roup (see for instance[8]). Nevertheless, most of those results were obtained using five d-orbitals only and the parameters were fitted to the **avail**-able experimental data. Recently, it has been recognized the **importance** of a first **principles** determination of the hopping and hybridization parameters, in the description of these materials[g].

To illustrate, in the simplest way, the **dependence** of the band strucure on the crystal lattice , we show in fig. 3a the results obtained for $ZrFe_2$ in the cubic C15 and hexagonal **C14 phases**[8]. The **existence** of two different local densities of states (DOS), associated to the two crystallographycally distinct Fe sites in these **C14**
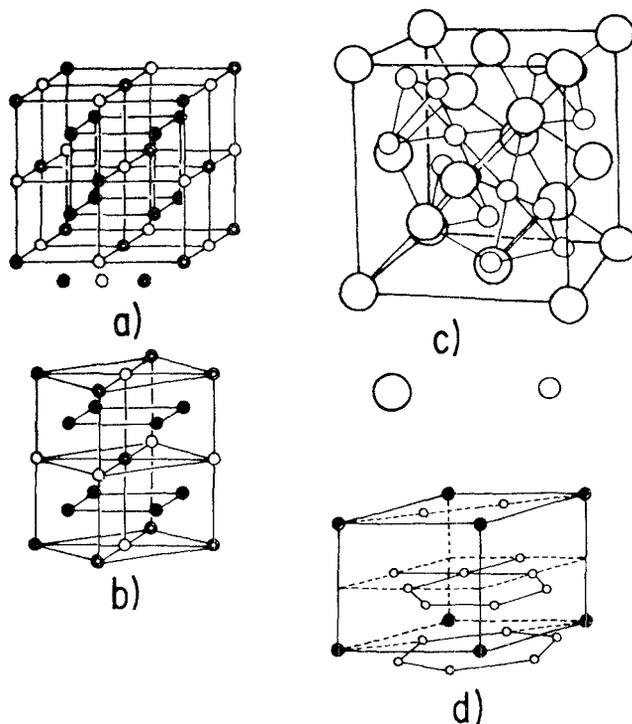
J. E. Schmidt, S. Zamora, C. *M*. da Silva, *A. A.* Gomes

Fig. 1 - Examples of two sublattice intermetallics: a) Heusler alloys (cubic); b) Heusler alloys (tetragonal); c) Cubic C15 Laves phase; d) $CaCu_5$ structure.

intermetallics is shown in this figure, as compared to the case of the cubic C15. We expect that in this simplified description of d-like only orbitals, the geometric effects do persist. On the contrary the difference (see fig. 3b), between the cases of $ZrFe_2$ and $NbFe_2$ is more subtle and may require a complete calculation including spd hybridization effects.

The case of the rare earth, or actinide intermetallics with transition atoms, is characterized by the existence or not of *finite* width f bands, introducing the distinction between these two groups. In the case of the stable rare earth inter-metallics, besides the localized f-states, the electronic states are suitably described by minimum basis composed of s, p and d states. On the other hand we emphasize
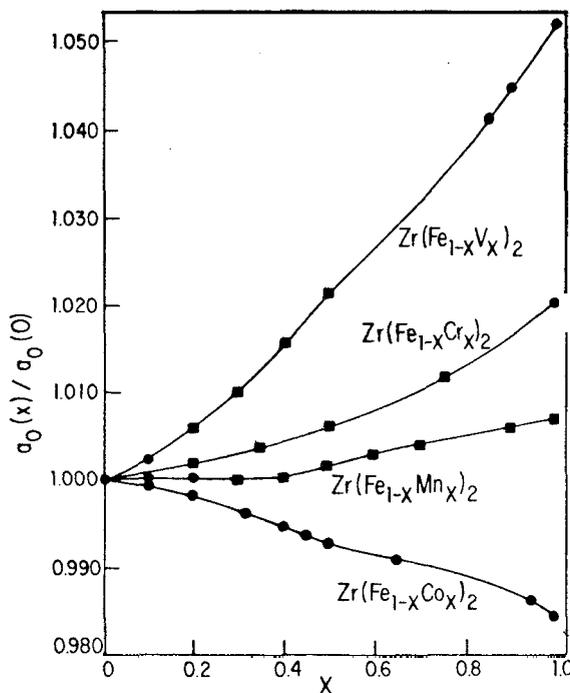
Fig. 2 – Transition **metal Laves phase intermetallics: lattice parameters versus concentration; filled circles: C15 phase, filled squares: C14 phase. Data from reference 4.**

that in the case of anomalous rare earthes and actinide compounds, this minimum basis is not adequate any more, since an f-band must be included[10].

2. Magnetic properties: dominant sublattices

i) Transition metal intermetallics with Fe

Classical examples are the compounds with Y, Zr, and Sc, where the B sublattice is responsible for the ferromagnetic order. Recently is was experimentally obtained[11] that a small antiparallel magnetization exists at the A sites. The *ferrimagnetism* of these transition metal intermetallics is associated to the higher energy region where the 4d or 5d states are located, as compared with the 3d ones. When magnetized (at $T = K$), the 3d up-spin states lie at lower energy than
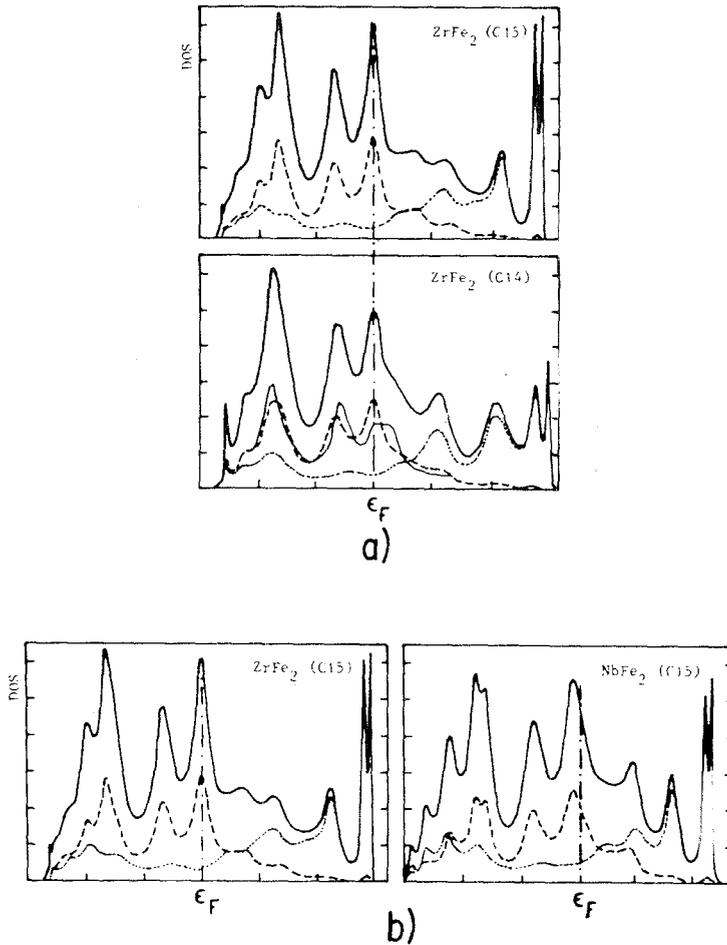
Fig. 3 – Densities of states for pure AB$_2$ compounds: a) ZrFe$_2$ in C15 and C4 crystal structures; for the C15 case, the dotted and dashed lines correspond to the local DOS at the A and B sites, respectively. For the C14 case, the two inequivalent B sites are indicated by dashed and thin continuous lines. b) ZrFe$_2$ and NbFe$_2$ in the C15 phase; the dotted and dashed lines correspond to the local DOS at the A and B sites, respectively. The Fermi level ϵ_f is shown in all figs.. Results from reference 8.

Two-sublattice intermetallics

the down-spin ones. Then the hybridization with 4d or 5d states is stronger for the down-spins, thus implying a larger amount of down spin than up-spin polarization at the A sites. Then "the 3d to 4d or 5d hopping hybridization" is the responsible for the occurrence of ferrimagnetism in these intermetallics[12].

ii) Intermetallics RB_2 with stable rare earthes

Two classes of compounds should be considered separately: the first one considers intermetallics with transition metals M, such as LuM_2, which like $LuCo_2$ are paramagnetic in the absence of magnetic rare earths. The other considers a ferromagnetic B sublattice, as observed in $LuFe_2$.

In the first case the rare earth spin moment is the responsible for the magnetic ordering, through the indirect RKKY interaction. This interaction is proportional to the square of the exchange interaction J_{df} between the localized f-electrons and the itinerant d states, times the real space susceptibility $X(R-R')$. The latter quantity can be calculated if a k-space band calculation for the material is available[13] and if itinerant-electron exchange enhancement effects is estimated. Given the so described RKKY exchange couplings, the Monte Carlo method, as implemented in the program MCMAG[14], can be used to extract the magnetic properties. Details of the crystai structure, anisotropies, easy axis etc, may be simply included using this program.

The general case where both sublattices contribute to the magnetic properties is more complicated, see fig. 4a. If the high temperature behaviour is to be described, in particular the Curie temperature, sophisticated methods should be used. A rough description of he procedure[15] is the following: the B sublattice must be described using the functional integral formalism, but suitably adapted to include the effect of rare earth spins of A sublattice.

Itinerant electrons of hybrid character, associated to the A (5d states) and B (usually 3d states), are coupled to the localized 4f states via the interaction $J_{df} < S_f^z >$. The thermal average of the f-spin must be obtained self-consistently, including the interaction with the itinerant electrons. The functional integral method is used to calculate the itinerant electron magnetization $< m_d(T) >$ and

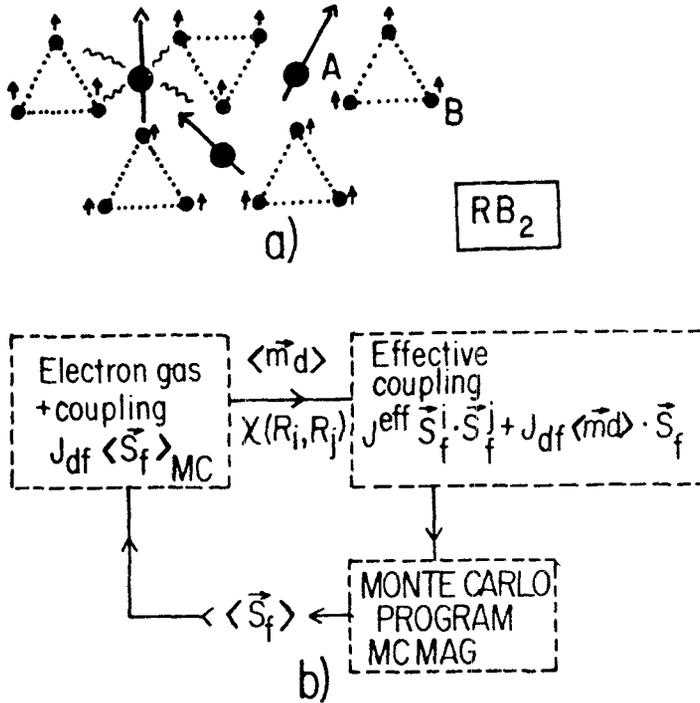*J.* E. Schmidt, S. Zamora, C. *M.* da Silva, *A. A.* Gomes

Fig. 4 – Rare earth transition metal compounds: a) Schematic representation of the lattice. b) Flow chart for self-consistency.

the real space local susceptibility $X_d(R-R'; T)$. The classical static approximation, combined with the CPA, is used for solving the functional integral problem. The itinerant electron quantities like m_d and X_d implicitly contain a dependence on the thermal averages of the localized f moments at the temperature T.

Once these quantities are obtained, the Monte Carlo method is used to recalculate, in terms of the d magnetization and susceptibility X, the new values for the thermal average of the localized f-moment. Again the effective RKKY coupling is given by $J_{df}^2 X_d(R-R'; T)$, which is one of the entry data of the MCMAG program. Self consistency is achieved when both thermalaverages converge.A schematic flow chart for these computations is shown in fig. 4b, together with a scheme for the

Two-sublattice intermetallics

AB$_2$ lattice and the corresponding local magnetic moments.

iii) Actinide-transition metal interrnetallics

Examples are AM$_2$ compounds with A an actinide like U and M may be Fe, Co or Ni. This is a complex case which will not be discussed here in detail. We only mention a qualitative version ignoring relativistic and orbital magnetic moments[16]. The interesting magnetic behaviour of these intermetallics is the crossover from magnetism carried by the 3d electrons in UFe$_2$ to the case of UNi$_2$ where U atoms at the A sites are responsible for the magnetic moments. On the contrary, UCo$_2$ is a strongly exchange enhanced Pauli paramagnet (see[16] for the experimental references). These results can be qualitatively understood in tems of a strong d-f hybridization between states originated from the U atoms at the A and the 3d atoms at the B sites.

3. Effects of impurities in the B sublattice

We separate in this paragraph the case of transition and sp impurities, selectively dissolved in the B sublattice. A classical experimental example of magnetic order induced in a otherwise paramagnetic B sublattice is provided by Gd (Ir$_{1-x}$ Co$_x$)$_2$ [17]. The intermetallic Lu Ir$_2$ is expected to belong to the class of paramagnetic intermetallics, since Lu is non magnetic and Ir does not develop enough Coulomb correlations to magnetize the B sublattice. The ferromagnetism of Gd Ir$_2$ is thus entirely associated to the RKKY interaction. In the pseudo-binary Lu (Ir$_{1-x}$ Co$_x$)$_2$ one expects that for high enough Co concentration, magnetic order may appear. This follows from the fact that the Coulomb interactions U satisfy[18] the relation $U(3d) > U(5d)$, and thus for an adequate concentration x, the criterion or the occurrence of magnetism is satisfied. In the case of Gd (Ir$_{1-x}$Co$_x$)$_2$, it was experimentally demostrated that ferrimagnetism is induced due to the appearance of magnetic order in the B sublattice, as shown in *fig* 5. Clearly two effects are present: an extra magnetic field of exchange character due to the Gd atms and acting in the sublattice B, together with the local enhancement of the Coulomb interaction. The treatment of this case is still more complicated than the

J. E. Schmidt, S. Zamora, C. M. da Silva, A. A. Gomes

general case described above, since besides the fluctuating fields of the functional integral, impurity dísorder should be introduced; a double CPA calculation should then be performed.
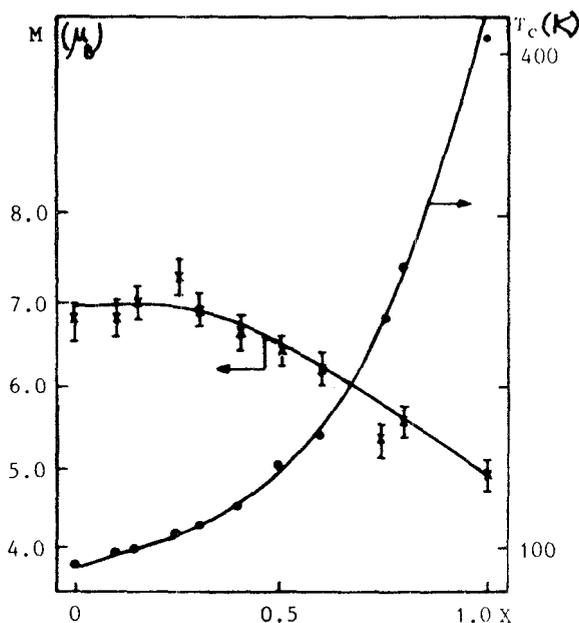

Fig. 5 – Magnetization and transition temperature of Gd(Ir,Co) Results from reference 17.

The case of sp impurities like Si and Al in the B sublattice will be discussed now in more detail. It has been shown that these pseudobinaries exhibit a systematic behaviour concerning tht: lattice parameters (see fig. 6), magnetic properties (see fig 7), and crystal structure (see table 1). This type of impurity, contrary to the others mentioned above, has the feature of eliniinating most of the d character at its site[19]. However, although very close in the periodic table, Si and Al introduce different modifications in the lattice parameter behaviour, in the stability region of the C15 or C14 phases. In connection with the C14-C15 phase stability the magnetization of the pure C14 phase may be approximately determined as a function of concentration. In figs. 6a and 7 we show the structural parameters

and the measured saturation magnetization at room temperature and at 77 K, the obtained crystallographic phases being shown in Table 1. It is observed that in Zr Fe$_2$ doped with Al or Si, the measured saturation magnetization follows nearly a site dilution behaviour. We interpret such behaviour as indicating the existence of a single phase, since the effect of the impurities is only to empty the d-orbitals, the transferred magnetization from the sp states of the host being expected to be small. The case of Hf compounds is more complex, in the sense that there is phase coexistence is present in some concentration ranges. In the case of Hf(Fe,Si)$_2$ coexistence of the C14 and C15 phases does occur for Si concentrations lower than 0.03 as mentioned in table 1. Some previous studies at the microscopic level, using Mossbauer spectroscopy of these mixed phase systems, were unable to determine the magnitude of the magnetization in the C14 phase[20]. The origin of this complexity comes from the existence o two distinct crystallographic sites in the hexagonal C14 phases. The combination of spectra arising from Fe pobes in the C14 and C15 phases gives rise to a rather complex Mossbauer spectrum. The unicity of the fit of the spectrum is dubious and consequently from such poorly derived hyperfine fields, the magnetization can hardly be estimated.

Table I

Compound	Mixed: C14+C15	Pure: C15	Pure: C14
Zr(e,Al)$_2$	–	$0. \leq x \leq .20$	–
Zr(Fe,Si)$_2$	–	$0. \leq x \leq .17$	$.17 \leq x \leq .20$
Hf(Fe,Al)$_2$	$10. \leq x \leq .131$	–	$.13 \leq x \leq .20$
Hf(Fe,Si)$_2$	$10. \leq x \leq .031$	$.03 \leq x \leq .13$	$.13 \leq x \leq .20$

In this case the technique of X-ray step scan was used to determine the concentration of C14 phase-as a function of Si concentration in Laves-phase Hf compounds. The results of this procedure are shown in fig. 8. It is important to recall that Al impurities cannot stabilize the C14 phase in all the concentration range, as indicated in Table 1. Once the amount of C15 phase is obtained from these results, an esimate of the magnetization of the C14 phase can be made. From the
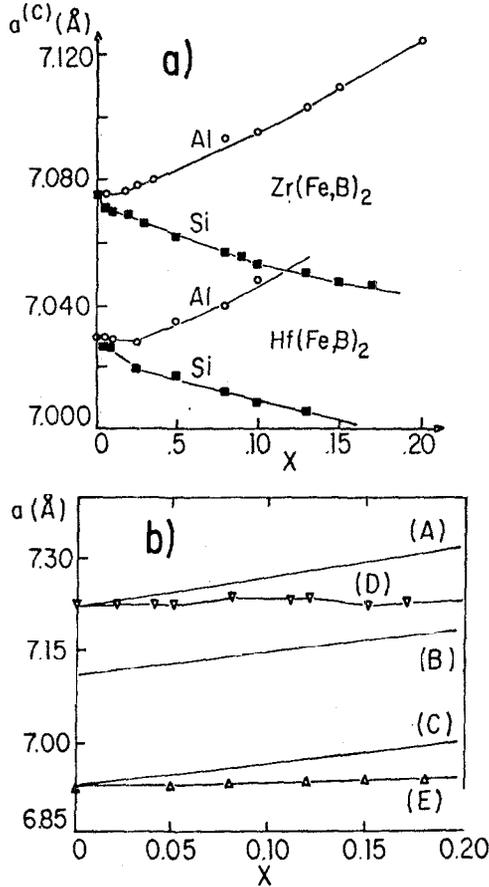
J. E. Schmidt, S. **Zamora,** *C. M. da Silva, A. A.* **Gomes**

Fig. *6* – Lattice parameters: a) Zr(Fe,Al)$_2$, Zr(Fe,Si)$_2$, Hf(Fe,Al)$_2$, Hf(Fe,Si)$_2$; b) (A) Y(Co,Al)$_2$, (B) Lu(Co,Al)$_2$, (C) Sc(Co,Al)$_2$ (D) Y(Co,Si)$_2$, (E) Sc(Co,Si)$_2$. In (b) data from reference 26.

results of Fig.7, one may extract the best straight line describing the site dilution decrease of the saturation magnetization of Hf(Fe,Si)$_2$, in the concentration range indicated by the arrows where the cubic C15 phase is stable. Extrapolating this straight line to zero Si concentration and assuming that the extrapolated line adequately describes the C15 phase for the entire measured concentration range, the magnetization of the C14 phase can be derived from the phase concentration measurements. In fact the measured magnetization at any concentration is the weighted sum of the phase concentrations times phase magnetization. Using the
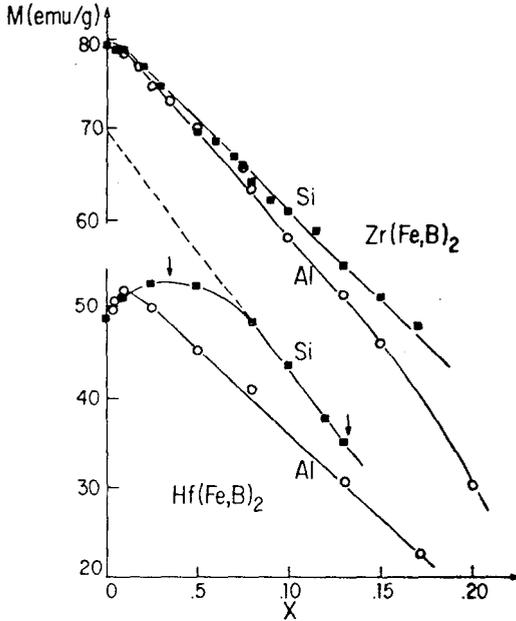
Fig. 7 – Saturation magnetization for $Zr(Fe,Al)_2$, $Zr(Fe,Si)_2$, $Hf(Fe,Al)_2$, $Hf(Fe,Si)_2$. The arrows indicate the range of Si impurities where the pure C15 phase is stable.

straight line for the C15 phase the magnetization of the disordered C14 phase can be obtained. The result of this procedure is shown in Fig.8. These experimental results suggest an interesting application of the tight-binding CPA first principies method[21], for the description of these chemically disordered phases. Once one obtains a theoretically precise result for the magnetization of this disordered C14 phase, a good test for the simple dilution picture is possible for these Hf compounds.

Besides the stability changes in pseudobinaries with Hf and Fe, these sp impurities may introduce more drastic effects. It has been recently shown experimentally that Al impurities stabilize weak ferromagnetism in otherwise paramagnetic compounds. It is well know that $ScCo_2$, YCo_2, $ZrCo_2$ and $LuCo_2$ are paramagnetic compounds. It has been verified that adequate concentrations of Al induce a weak ferromagnetism in these materials[22-27].
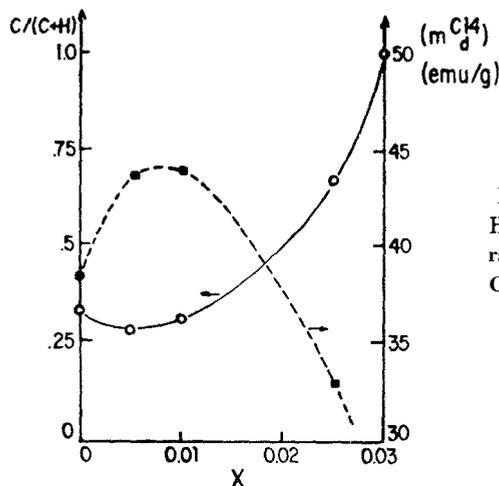
J. E. Schmidt, S. Zamora, C. *M.* da Silva, A. A. **Gomes**

Fig. 8 – Concentration of the C15 phase for Hf(Fe,Si)$_2$ intermetallics as extracted from X-ray step scan (left scale) Magnetuation of the C14 phase (nght scale).

On the contrary, Si impurities are unable to induce magnetic order. Both impurities however alter the lattice parameter behaviour in a way similar to the case of Fe compounds mentioned above, and are shown in fig .6b. In references 22-26, macroscopic methods of measurement were used in contrast to[2'] were NMR experiments have been.

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J. E. Schmidt, S. Zamora, C. M. da Silva, A. A. **Gomes**

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Resumo

Algumas propriedades estruturais e magnéticas de sistemas de Laves e duas subredes, puros ou pseudo binários são discutidas. Alguns resultados experimentais originais são apresentados assim como desenvolvimentos teóricos pertinentes a estes resultados.