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A comparative analysis of the three polymorphic structures H_3, O_{10} and H_{12} of FeRhP

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Abstract

The phosphide FeRhP, belonging to a large series of ternary pnictides, exhibits very unusual metal ordering characteristics, depending on the applied synthesis route. It is demonstrated that size and electronegativity difference, that are the main criteria to consider for metal atom ordering, cancel out each other with the iron–rhodium couple.

Keywords: Crystal structure; Polytypes; Transition metal phosphides; Magnetic properties

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1. Introduction

The polymorphic forms of the ternary FeRhP can be easily compared using a schematic representation developed in terms of polytype structures called H_3 (hexagonal), O_{10} (orthorhombic) and H_{12} (hexagonal). These polytype structures are built by linking 3, 10 and 12 modulus of a rhombohedral sub-cell that contains one elementary formula $MM'X = FeRhP$. Due to the large variety of polymorphic forms, special attention was paid to the FeRhP compound.

2. Experimental

The direct synthesis of all the three crystal types of FeRhP by using solid state diffusion at temperatures lower than 1050°C remained unsuccessful, contrary to most of the $MM'X$ compounds. In fact, only starting from the high temperature H_3-type, stable over than 1050°C, is it possible to stabilise the two other types – O_{10} and H_{12}.

2.1. Synthesis of H_3-FeRhP

The hexagonal structure H_3-FeRhP, of the Fe_2P structure type as synthesised at temperatures higher than 1050°C by solid state diffusion, can be stabilised by fast quenching. It is worth noting that a slight excess of phosphorus (e.g. 2%) leads to the synthesis of a vacant type of ternary phosphide which is shown to be even less stable.

2.2. Synthesis of O_{10}-FeRhP

The orthorhombic O_{10}-FeRhP, of the NbCoB structure type [1], is obtained by slow cooling the H_3 variant from 1050°C. A paramagnetic susceptibility analysis, as plotted in Fig. 1, shows the reversible transformation of the first order type $O_{10} \leftrightarrow H_3$ close to 1050°C.

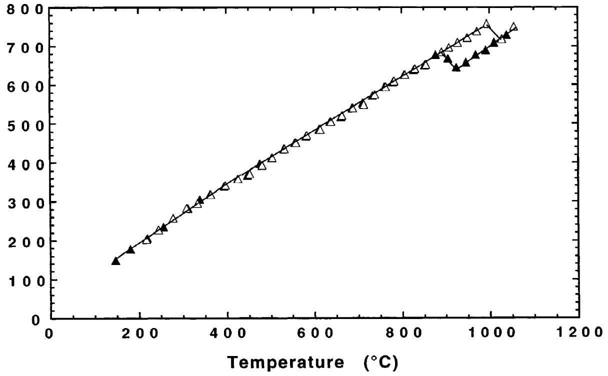

Fig. 1. Paramagnetic traces of the reversible transformation $H_3 \leftrightarrow O_{10}$ by slow rate heat treatment. The opened triangles correspond to the increase of temperature. The cooling treatment is represented by filled triangles.

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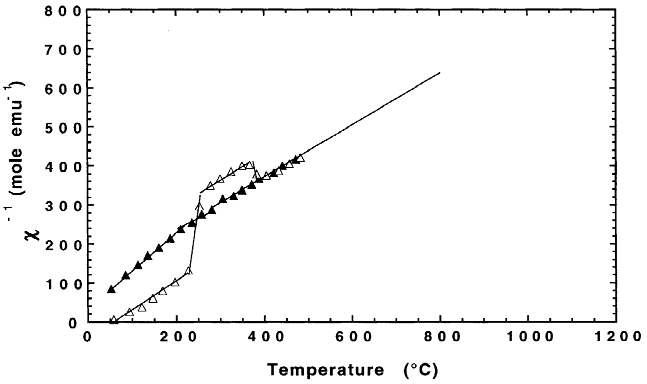

Fig. 2. Paramagnetic traces of the irreversible transformation from H_3 as initially stabilised by fast quenching from the high temperature to H_{12}, only stable from 230 to 570°C. The opened triangles correspond to the increase of temperature. The cooling treatment is represented by filled triangles. The high temperature range is not represented, being quite similar to that represented in Fig. 1.

2.3. *Synthesis of H_{12}-FeRhP*

The H_{12}-FeRhP type has been found isomorphous with the FePdP compound [2,3]. It was stabilised by long time annealing at temperatures just above 230°C, but it is irreversibly decomposed at temperatures lower than 570°C, as shown on the paramagnetic susceptibility analysis reported in Fig. 2.

3. Results

3.1. *Comparative organisation of the polytypes*

Up to now, several thousands of ternary phosphides, arsenides and related intermetallics of the formula MM′X (where M and M′ are transition or even rare earth metals, X=P, As . . . Si, Ge, Sn . . . , B, Al, Ga . . .) were found to

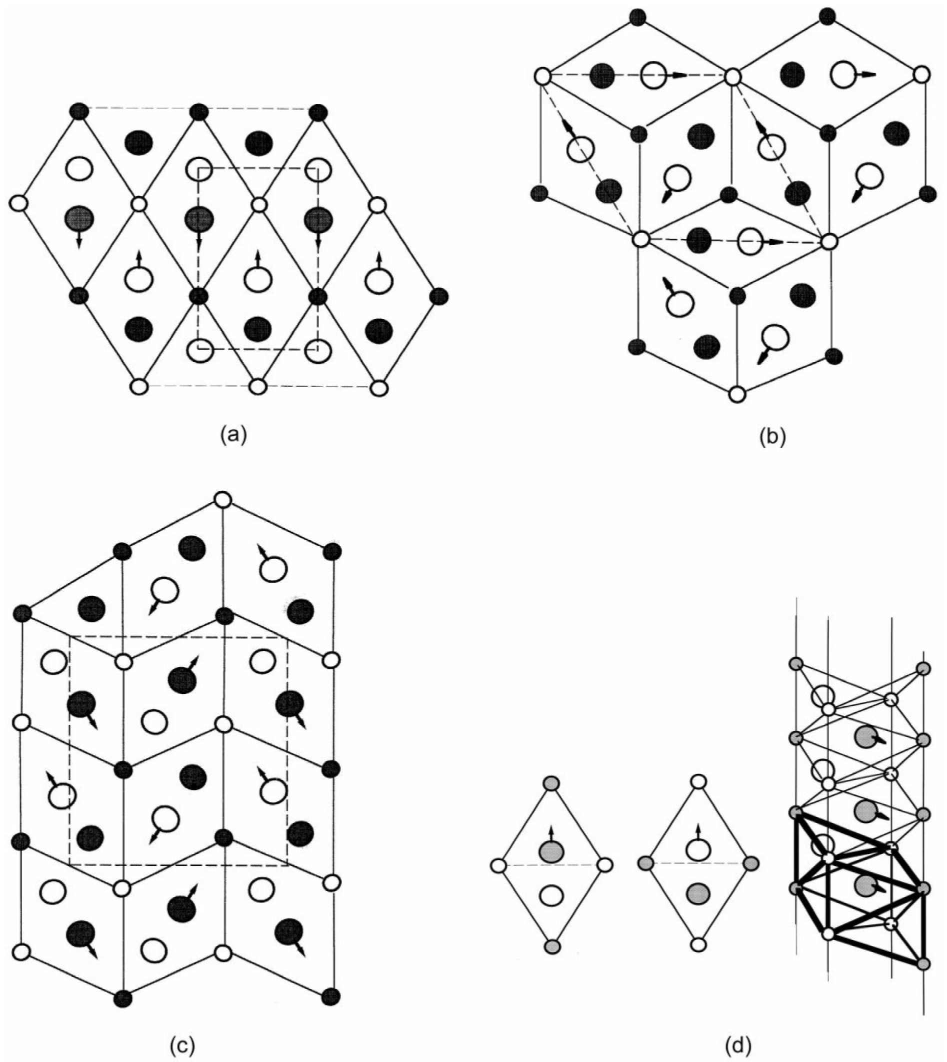

Fig. 3. Projections of the crystal structures of the three elementary polytypes of FeRhP: (a) T_2 (Fe_2As type), (b) H_3 (Fe_2P type) and (c) O_4 (Co_2P type). In the d/3-D view of the rhombohedral sub-cell that is the common structural element (containing one FeRhP formula unit) for all polytypes that are considered here. The metal atoms (large circles) exhibit either a five-fold P-coordination, and the attached arrows show the direction of the top of the corresponding pyramid, or a four-fold P-coordination (tetrahedron). Two projections of the sub-cell are represented apart, with the two possible relative positions along the triangular channels: $z=0$ with the empty circles and $z=1/2$ with the filled circles.

crystallise in one of the three closely related structure types – the polytypes T_2 (tetragonal, e.g. Fe_2As), H_3 (hexagonal, e.g. Fe_2P) and O_4 (orthorhombic, e.g. Co_2P). These prototypes are represented in Fig. 3. The FeRhP compound has the peculiarity in that it crystallises in the rarely found O_{10} and H_{12} higher order polytypes, while the H_3-type is stabilised with difficulty.

A comparison of the three different polytype structures shows a specific arrangement of the elementary sub-cell in the design of a local six-arms star which takes a very particular place in the structural reorganisations of FeRhP, as seen in Figs. 4a–c. Close to the central phophorus atom of such a star-like arrangement, the rhodium atom density is found particularly high in the H_{12}-polytype: surprisingly the large Rh atoms completely fill the smallest sites, the P-tetrahedra close to the centre of the star. Contrary to that, the star-like arrangement observed in the H_3 high temperature polytype reveals an almost perfect random metal distribution in both the tetrahedral and pyramidal P-sites. Within this scheme, the O_{10}-polytype appears as the representative of an intermediate state between the H_3 and the H_{12}-polytypes in terms of rhodium clusters. Moreover the six-arms star has not got exact hexagonal symmetry, in a direct relationship with the local rhodium concentrations.

Table 1
Magnetic properties of the metallic H_3, O_{10}, H_{12} polytypes

FeRhP	H_3	O_{10}	H_{12}
M_{sat} (μ_B/fu)	2.02	1.46	1.09
T_c (K)	355	235	120
M_{para} (μ_B/fu)	2.50	2.35	2.18

3.2. Magnetic properties

The three H_3, O_{10} and H_{12}-polytypes of FeRhP exhibit ferromagnetic properties [4]. The magnetic characteristics of the compounds are gathered in Table 1 while Fig. 5 displays the magnetisation curves recorded under a magnetic field of 20 T. The intermediate O_8-phase exhibits intermediate properties with respect to the H_3 and H_{12}-compounds.

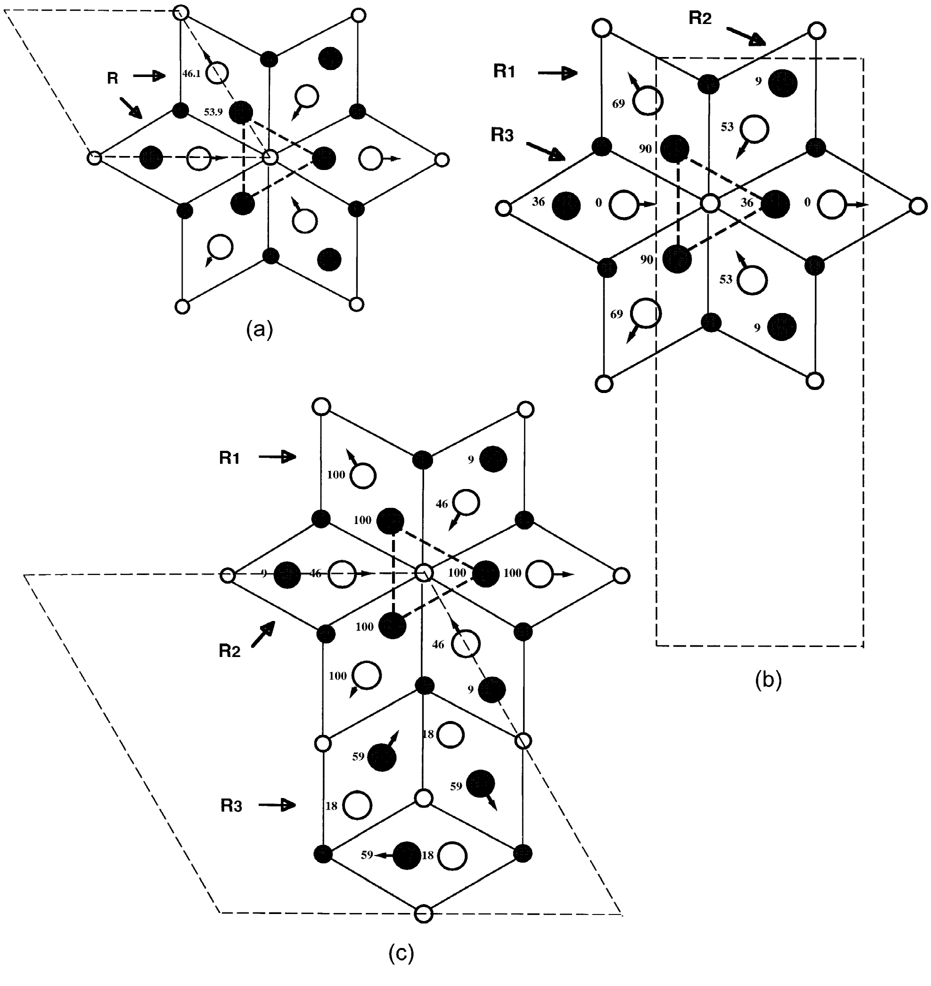

Fig. 4. Projections of the crystal structures evidencing the six-arms star formed around the P atom belonging to a group of three tetrahedral sites (dashed lines triangle) in the: (a) H_3 high temperature disordered phase of Fe_2P type; (b) O_{10}, orthorhombic and partly disordered phase, exhibiting a differentiated concentration of Rh atoms in the 6-arms star; (c) H_{12} hexagonal phase exhibiting a full occupation of the tetrahedral sites by Rh atoms in the six-arms star. The projection of the unit cell is represented by thin dashed lines.

Table 2
Metal distribution onto the tetrahedral (T) and pyramidal (P) sites for the MRhAs series

Compound	Structure type	Site T	Site P	Volume per fu (A^3)
TiRhAs	Co_2P–O_4	Rh	Ti	44.65
VRhAs	Co_2P–O_4	Rh	V	43.11
CrRhAs	Fe_2P–H_3	Rh	Cr	43.74
MnRhAs	Fe_2P–H_3	Rh	Mn	45.05
FeRhAs	Fe_2P–H_3 (O_8, H_{12})	disorder	disorder	41.76
CoRhAs	Co_2P–O_4	Co	Rh	38.96
NiRhAs	Fe_2As–T_2	Ni	Rh	39.15

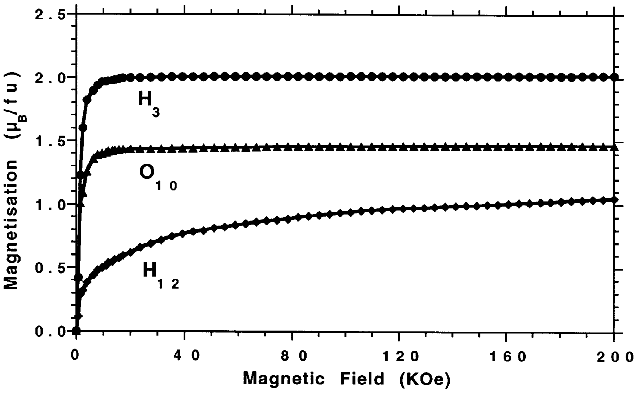

Fig. 5. Magnetisation measurements versus field performed at 4 K of the H_3, O_{10} and H_{12}-phases showing a progressive decreasing of the saturation magnetisation with the increasing concentration of Rh atoms in the linked tetrahedra (dashed line triangle) around the centre of the six-arms star.

4. Discussion

In most of the ternary MM′P and MM′As compounds the M and M′ metal atoms are fully ordered, respectively, in the two pyramidal and tetrahedal sites of phosphorus (arsenic). On the contrary, the two compounds of the Fe_2P-type, FeRhAs and, more recently, FeRhP were found to have almost disordered metal arrangements. Moreover, in the MRhAs series (M=Ti–Ni), which is more extended than the corresponding phosphides series, a reverse ordering is found. Such a phenomenon occurs for FeRhAs as it is shown in Table 2.

With more electropositive metals than Fe (as Ti, V, Cr, Mn) the large Rh atom occupies the smallest site (T-tetrahedal site). Conversely, with less electropositive metals (as Co, Ni), Rh occupies the largest and P-pyramidal site. Reverse ordering effects result from the competing parameters as the difference of radius and the difference of electronegativity. These contributions are opposite and cancel each other out in FeRhAs and H_{12}-FeRhP. The volumes per formula unit for the compounds containing the large Rh atom in the smallest T-site (Ti to Mn compounds) are especially large. They are markedly reduced when the largest Rh atom occupies the larger P-site (Co and Ni compounds). For the intermediate element, M=Fe, the formula unit volume is intermediate and atomic disordering is found.

The dramatic reduction of magnetisation in the O_{10}, and even more in the H_{12}-phase, is to be correlated with the filling of the 3d states (with a gain of stability for both the considered phases) and the formation of diamagnetic clusters. In fact in the solid solution Co_2P–Ni_2P the metal atom distribution (within partly disordered T-clusters of a H_3-structure type) leads to diamagnetic characteristics which are enhanced near to the $Co_{0.8}Ni_{1.2}P$ composition [5].

5. Conclusion

Both the ordering factors which are the difference of radius and the difference of electronegativity of the M and M′ atoms, act oppositely and cancel out each other in the H_3-FeRhP. This yields a selective redistribution of these atoms, thus forming the O_{10}-FeRhP and the H_{12}-FeRhP clusters of diamagnetic characteristics.

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