Origin of giant moments in non-stoichiometric FeRh alloys
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Résumé. — Nous étudions la structure électronique au niveau des premiers voisins d’un atome de fer substitué à un atome de rhodium dans un composé stoechiométrique de FeRh. La structure de bandes antiferromagnétique du composé binaire FeRh est décrite par une méthode de liaisons fortes. L’effet de la substitution est décrit par un potentiel perturbateur présentant des éléments de matrice intrasite et intersite limités à l’impureté et à ses premiers voisins. Notre modèle montre une tendance à un renversement de la direction du moment sur la moitié des premiers voisins de l’impureté, ceux qui étaient au départ antiparallèles à la direction du champ appliqué. Cet effet peut conduire à l’apparition de moments géants, ainsi qu’il a été suggéré expérimentalement.

Abstract. — Within a tight-binding scheme, we study the local electronic structure on the nearest-neighbours of a rhodium site which has been substituted by an iron impurity in the stoichiometric FeRh compound in its antiferromagnetic phase. The replacement of the rhodium atom is described by an extended perturbation potential which includes changes in the intrasite and intersite matrix elements up to the first nearest-neighbour shell of the point defect site. Our model shows that a spin-flip on the nearest-neighbour site of the substituted atom, antiparallel to the direction of the applied field is energetically favourable. This could lead to the nesting of a giant moment as has been suggested experimentally.

1. Introduction. — Since the work of Fallot [1] many detailed experimental studies have been made of the nearly equiatomic FeRh alloys. It is found that the nearly equiatomic ordered FeRh alloys exhibit a first order antiferromagnetic (AF)-ferromagnetic (F) phase transition at a critical temperature ($T_c$) of about 350 K and a second order ferromagnetic-paramagnetic (P) transition at a Curie temperature ($T_C$) somewhere between 600 and 700 K. The first order transition is very sensitive to the stoichiometry of the compound, as demonstrated by a sharp decrease in the critical temperature from about 350 K to zero by increasing the iron content by a few percent [2]. The critical temperature, $T_c$, can also be lowered by a magnetic field, but a very high magnetic field is required to significantly change $T_c$ [2]. The presence of giant moments responsible for magnetic inhomogeneity has been postulated for the nearly equiatomic iron rich alloys [2].

Attempt to elucidate the mechanism underlying the transition from the antiferromagnetic state to the ferromagnetic have been made recently [3-5]. Teraoka and Kanamori [3] have extended the Anderson model of 3d virtual states. By taking an antiferromagnetic exchange interaction, $E_{AF}$, between Fe atoms and a ferromagnetic exchange interaction, $E_{Fe}$, between Fe and Rh atoms, they were able to show that the mechanism underlying the transition is an increase of the magnetic polarizability of the Rh atoms and a decrease of $E_{Fe}$ with increasing temperature. Moriya and Usami [4] have shown that the coexistence of ferromagnetism and antiferromagnetism, which breaks the symmetry is possible in certain itinerant-electron systems where the wave-vector dependent susceptibility neglecting the electron-electron interaction has two peaks at $q = 0$ and $Q$, the antiferromagnetic wave-vector. For reasonable values of parameters within such a theory, they could explain the first order transition in FeRh alloys. More recently, Hasegawa [5], using a tight-binding single band model and an intraatomic electron-electron interaction has determined the free energy within a spin fluctuation theory. Hasegawa showed that by taking into account the effect of local spin fluctuations within the single site alloy analogy a first order transition takes place.
from one ordered state to a second ordered state. While these calculations are of interest they rely on parameters whose values may not be entirely meaningful because of the rough approximations used in these models.

The previous models have assumed a CsCl type ordering of Fe and Rh atoms with equal concentrations of Fe and Rh. Here we examine the case of non-stoichiometry by considering only the $T = 0$ case where the Hartree-Fock approximation is reasonably good. Our approach uses the d-bond model of Pettifor [6]. Our aim is to produce evidence of a local mechanism which could be responsible for the nucleation of ferromagnetism in an antiferromagnetic FeRh alloy. To do this we replace a Rh atom by an Fe atom in FeRh in its AF phase and we look for the effect of this non-stoichiometry on the magnetic behaviour of the nearest-neighbours of the substituted atom.

The outline of this paper is as follows. In section 2, we derive a general tight-binding formalism to describe the variation of the local magnetic moment on an Fe site, $i$, the first nearest-neighbour to an Fe substituted Rh atom at site $S$. In this section, we take into account the intersite Green functions. Section 3 develops the results obtained with the approximations used in section 2. We retain only the intrasite element of the host Green function $G^0$ in section 4. Section 5 presents numerical results while the final section (6) is devoted to conclusions and discussions concerning further improvements of the theory and possible future developments.

2. General formalism. — The tight-binding band structure of an ordered FeRh alloy [7] is first calculated in the (P) phase. For the computation of the energy bands in the magnetic phases, a spin dependent potential is introduced such that the magnetic moments on the Fe and Rh sites are in agreement with the experimental values. In the AF phase of the FeRh alloy all the magnetic moments are localized on Fe atoms. The Fe$^1$ and Fe$^+$ atoms indicating oppositely oriented magnetic moments are arranged on two interleaved face-centred cubic lattices (cf. the distribution of Na and Cl in NaCl). The unit cell contains two atoms of Fe, with magnetic moments of $\pm 3.1 \mu_B$ (Fig. 1). Let $H_0$ be the Hamiltonian of the stoichiometric ordered AF phase of FeRh. The eigenfunctions of $H_0$ are:

$$\varphi_m^\sigma(k, r) = \sum_m a_m^\sigma(k) |mk\sigma\rangle \quad (2.1)$$

where $a_m^\sigma(k)$ are the coefficients of normalization for the $\sigma$th band and $|mk\sigma\rangle$ is a Bloch function of symmetry $m$ constructed from the atomic orbitals at site $R$, namely $|m\sigma\rangle \equiv xy, yz, zx, x^2 - y^2, 3z^2 - r^2$, with spin $\sigma$. The resulting density of states is shown in figure 2.

Let us now consider a single iron atom substituted at a rhodium site $S$. The Hamiltonian of the alloy is then given by:

$$H = H_0 + \left\{ \sum_{\nu m'} \delta f_{\nu m'} < \nu m' | + \text{h.c.} \right\} +$$

$$+ \sum_{m,m'} \delta v_m^\sigma < Sm\sigma | \sum_{vm} \delta v_m^\sigma < vm\sigma |. \quad (2.2)$$

270

251

211

-0.2 -0.1 0 0.1 0.2

Energy (Ryd) $E_F$

0.1

0.2

Electrons / Ry/FeRh

Fig. 1. — The antiferromagnetic structure of the FeRh alloy. $H_{ext}$ is the magnetization field. ○ Rh S site, • Fe$_x$ site, □ Fe. $H_{ext}$

Fig. 2. — a) Density of states of FeRh in the antiferromagnetic phase: ---- total density of states of majority spin electrons; --- partial density of states of majority spin electrons; partial density of states of minority spin Fe electrons in the AF phase [7].

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Fig. 2. — a) Density of states of FeRh in the antiferromagnetic phase: ---- total density of states of majority spin electrons; --- partial density of states of majority spin electrons; partial density of states of minority spin Fe electrons in the AF phase [7].
The impurity introduces an extended perturbation potential, where the change in the matrix elements, both intrasite ($\delta \epsilon_{v}$ and $\delta \epsilon_{s}$) and intersite (the hopping integrals $\delta \beta_{v}$), are considered up to the first nearest-neighbour shell ($v$ sites) of the substituted atom. The expression (2.2) is more general than that used previously by Khwaja and Nauciel Bloch [8]. The matrix elements of the Green function $G$ of the perturbed system are deduced from the unperturbed Green function $G^{0}$ with the help of Dyson’s equation and the perturbation potential $V = H - H_{0}$:

$$G = G^{0} + G^{0} VG.$$  

(2.3)

The change in the local magnetic moment, $\delta \mu_{R}$ on a site $R$, due to the perturbation potential $V$ is given by:

$$\delta \mu_{R} = \mu_{B}(\delta n_{R} - \delta n_{R}^{\uparrow})$$

where $\mu_{B}$ is the Bohr magneton and $\delta n_{R}$ is the change in the number of electrons of spin $\sigma$ on site $R$, given by,

$$\delta n_{R} = - \frac{1}{\pi} \text{Im} \int_{E_{F}}^{E_{F}} \{ G_{RR}^{mm}(E) - G_{RR}^{mm}(E') \} dE$$

(2.5)

where

$$G_{RR}^{mm}(E) = \langle R \sigma | G | R' m' \sigma \rangle.$$  

$$G_{RR}^{mm}(E) = \langle R \sigma | G^{0} | R' m' \sigma \rangle.$$  

(2.5)

The quantities, $G_{RR}^{0mm}(E)$, are derived from the $\alpha'^{2}(k)$ defined in equation (2.1). The diagonal matrix elements, $\delta \epsilon_{v}$, $\delta \epsilon_{s}$ on the impurity site and $\delta \epsilon_{v}$, $\delta \epsilon_{s}$ on the iron site $\lambda$ of type $A$ (the $A$ site has a moment antiparallel to the direction of the external applied field) are related through the usual exchange equation:

$$J_{S}^{eff} G_{SS}^{0mm} \delta n_{R} = \delta \epsilon_{v} + J_{S}^{eff} \delta n_{R}^{\uparrow}$$

(2.6)

$J_{S}^{eff}$ is an exchange parameter which takes the value $J_{S}^{eff}$ on the substituted rhodium site and $J_{S}^{eff}$ on the iron site. $J_{S}^{eff}$ is known from a band structure calculation [7]. $J_{S}^{eff}$ is adjusted so as to have a magnetic moment of about 2.6 $\mu_{B}$ on the $S$ site [8].

It is non-trivial to obtain the expression, $G_{RR}^{0mm}$, required to determine the change in the magnetic moment on the site $R$, so we have made the following approximations:

(i) Perturbations on the iron sites are restricted to the $A$ sites;

(ii) The intersite matrix elements of $G^{0}$ and $V$ are retained only up to the first nearest-neighbours of the substituted impurity atom;

(iii) We have used the spherical approximation by replacing $\delta \epsilon_{v}$ by $\delta \epsilon_{s}$;

(iv) In the expansion of the Dyson equation we retain only intersite terms up to second order.

The following results are obtained for the intrasite Green functions on the $S$ and $\lambda$ sites:

$$G_{SS}^{0mm} = \frac{G_{SS}^{0mm} + R_{SS}^{0mm}}{D_{SS}^{0mm}}$$

(2.7)

with

$$D_{SS}^{0mm} = D_{S}^{0mm} - \sum_{vm} G_{Sv}^{0mm} \delta \beta_{sv} - T_{SS}^{0mm}$$

(2.8)

$$R_{SS}^{0mm} = \sum_{vm} \frac{1}{D_{v}^{0mm}} \{ G_{Sv}^{0mm} \delta \epsilon_{v} + G_{SS}^{0mm} \delta \beta_{sv} \} G_{sv}^{0mm}$$

(2.9)

$$T_{SS}^{0mm} = \sum_{vm} \frac{1}{D_{v}^{0mm}} \{ G_{Sv}^{0mm} \delta \epsilon_{v} + G_{SS}^{0mm} \delta \beta_{sv} \} \{ G_{sv}^{0mm} \delta \epsilon_{v} + G_{vv}^{0mm} \delta \beta_{vv} \}$$

(2.10)

$$D_{R}^{0mm} = 1 - G_{RR}^{0mm} \delta \epsilon_{R}^{g}$$

(2.11)

The following relations for the site $\lambda$ can be obtained from equations (2.7) to (2.10) by simply exchanging $S$ and $\lambda(\nu)$.

3. Numerical results. — The change in the hopping integrals $\delta \beta_{sv}$ between the impurity at site $S$ and its nearest-neighbours $v$ can be expressed [7] in terms of changes in the two-centre integrals $d_{\sigma}^{\nu}, d_{\sigma}^{\nu},$ and $d_{\sigma}^{\nu}$ (using the notation of Slater and Koster [9]).

The matrix elements of the Green function $G_{Sv}^{0mm}(E)$ can be deduced from $H_{0}$. From group theoretical considerations, it can be shown that $G_{Sv}^{0mm}(E)$ can be expressed in terms of five basis elements:

$$G_{Sv}^{011e} = G_{Sv}^{0e}; G_{Sv}^{044e} = G_{Sv}^{0e}; G_{Sv}^{012e} = G_{Sv}^{0e}; G_{Sv}^{015e} = G_{Sv}^{0e};$$

$$G_{Sv}^{021e} = G_{Sv}^{0e} \text{ and } G_{Sv}^{051e} = G_{Sv}^{0e}.$$
As a result of the local symmetry at $S$ we obtain the corresponding expressions to equations (2.7) to (2.11), except that in these expressions there are no intersite Green functions. Thus we obtain

$$ G_{SS}^{\text{me}}(E) = G_{SS}^{\text{mono}}(E) $$

(4.1)

$$ D_{SS}^{\text{me}} = D_{SS}^{\text{ma}} - \sum_{\sigma} \frac{1}{2} D_{SS}^{\text{ma}} \cdot G_{SS}^{\text{me}}(E) \cdot \delta \beta_{SV}^{\text{me}} \cdot G_{VV}^{\text{me} \cdot \text{me}}(E) \cdot \delta \beta_{SV}^{\text{me}}. $$

(4.2)

The lack of local symmetry at site $\lambda$ compared to site $S$, means that the general expression for $G_{Sl}^{\text{me}}$ is lengthy and complicated. However for the particular case of symmetry $m$, we obtain:

$$ G_{Sl}^{\text{me}}(E) = G_{Sl}^{\text{ma}}(E) = G_{Sl}^{\text{ma}}(E) $$

(4.3)

and

$$ G_{Sl}^{\text{me}}(E) = G_{Sl}^{\text{ma}}(E) $$

(4.4)

$$ G_{Sl}^{\text{me}}(E) = G_{Sl}^{\text{me}}(E) \{ 1 + A_{Sl}^{1\sigma}(B_{1}^{2} + 2B_{2}^{2}) + A_{Sl}^{1\sigma}(B_{2}^{2}) \} $$

(4.5)

$$ G_{Sl}^{\text{me}}(E) = G_{Sl}^{\text{me}}(E) \{ 1 + A_{Sl}^{1\sigma}(B_{1}^{2} + 2B_{2}^{2}) + A_{Sl}^{1\sigma}(B_{2}^{2}) \} $$

(4.6)

The $B_i$'s are given by $B_1 = \delta \beta_{Sl}^{1\sigma}$; $B_2 = \delta \beta_{Sl}^{1\sigma}$; $B_3 = \delta \beta_{Sl}^{1\sigma}$ and $B_4 = \delta \beta_{Sl}^{1\sigma}$ where $S = (0, 0, 0)$ and $\lambda = a/2 (1, 1, 1)$. $D_{SS}^{\text{me}}$ is defined as in equation (2.11) and $A_{Sl}^{\text{me}}$ are written as:

$$ A_{Sl}^{\text{me}} = G_{Sl}^{\text{mono}}(E) \cdot G_{Sl}^{\text{me} \cdot \text{me}}(E) $$

(4.7)

$$ P_{Sl}^{\text{me}} = D_{Sl}^{\text{me}} - 4 \cdot G_{Sl}^{\text{mono}}(E) \cdot N_{Sl}^{\text{me}} $$

(4.8)

$N_{Sl}^{\text{me}}$, for $n = 1, 2$ or 3, is given by:

$$ N_{Sl}^{1\sigma} = \frac{G_{Sl}^{\text{me}}(E) \cdot [B_{1}^{2} + 2B_{2}^{2}] + G_{Sl}^{\text{me}}(E) \cdot B_{2}^{2}}{D_{Sl}^{\text{me}}} $$

(4.9)

and for $n = 4$ or 5 by:

$$ N_{Sl}^{5\sigma} = \frac{G_{Sl}^{\text{me}}(E) \cdot \frac{3}{2} B_{2}^{2} + G_{Sl}^{\text{me}}(E) \cdot B_{2}^{2}}{D_{Sl}^{\text{me}}} $$

(4.10)

To be physically self-consistent the model should be in agreement with Friedel's screening rule. The change in the number of outer electrons in the present case is equal to $-1$, so that we have

$$ \sum_{\sigma, \mu} \delta n_{\mu}^{\sigma} = -1 $$

(4.11)

where $\mu$ is a metallic site. To simplify this rather complicated sum, we replace the summation over the sites, where a perturbation potential is present ($S$ and $\lambda$ sites), as follows

$$ \sum_{\sigma} \{ \delta n_{S}^{\sigma} + 4 \delta n_{\lambda}^{\sigma} \} \approx -1. $$

(4.12)

5. Numerical results for substitutional Fe atom at the Rh atom site in the intrasite approximation for $G_{Sl}^{\text{me}}$.—

First, we studied the effect of the substitution on the $S$ site using the method discussed by Khwaja and Nauciel-Bloch [8]. The perturbation potential $\delta n_{S}^{\sigma}$ is varied to find the most likely magnetic moment on this site by solving the exchange equation,

$$ \delta n_{S}^{\uparrow} + J_{S}^{\text{eff}} \delta n_{S}^{\downarrow} = \delta n_{S}^{\uparrow} + J_{S}^{\text{eff}} \delta n_{S}^{\downarrow} $$

(5.1)

Khwaja and Nauciel-Bloch find a moment of $2.6 \mu_{B}$ [8] on the iron site for a perturbation located almost in the minority spin band. Table I gives the values of the different physical quantities associated with this magnetic moment. We then studied the effect of $\delta n_{S}^{\sigma}$ on the site $\lambda$, using $\delta n_{\lambda}^{\sigma}$ as an adjustable parameter to give a spin-flip on this site, but ensuring that Friedel's sum rule (equation (4.12)) is satisfied. In order to make this calculation, we allowed $J_{\lambda}^{\text{eff}}$ to vary by a small amount from its value in pure FeRh [7]. Table I gives the values of the parameters associated with a spin-flip on an $A$ site.

Within the cluster of nine atoms consisting of the $S$ site and its nearest-neighbour iron sites, the magnetic moment in the stoichiometric compound is $0$ for the $S$ site, $+3.1 \mu_{B}$ for the $B$ site and $-3.1 \mu_{B}$ for the $A$ site. From table I, it can be seen that the cluster of atoms has a giant moment of $\approx 17 \mu_{B}$.

Table I. — Physical parameters to obtain the spin-flip. At site $R$, $\delta n_{R}^{\sigma}$ is the change in the local potential (Ry), $J_{R}^{\text{eff}}$ the effective exchange parameter (Ry), $\delta n_{R}^{\sigma}$ the change in the number of electrons and $\delta \mu_{R}$ the change of the Bohr magneton number [10].

<table>
<thead>
<tr>
<th>Site</th>
<th>(substituted Rh)</th>
<th>(antiparallel to applied field)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S$ site</td>
<td>$N_{1}^{1\sigma}$</td>
<td>$N_{1}^{5\sigma}$</td>
</tr>
<tr>
<td>$\lambda$ site</td>
<td>$J_{\lambda}^{\text{eff}}$</td>
<td>$J_{\lambda}^{\text{eff}}$</td>
</tr>
<tr>
<td>$\delta n_{S}^{\uparrow}$</td>
<td>-0.000 8</td>
<td>$\delta n_{S}^{\downarrow}$</td>
</tr>
<tr>
<td>$\delta n_{S}^{\downarrow}$</td>
<td>0.075</td>
<td>$\delta n_{S}^{\uparrow}$</td>
</tr>
<tr>
<td>$J_{S}^{\text{eff}}$</td>
<td>0.029</td>
<td>$J_{S}^{\text{eff}}$</td>
</tr>
<tr>
<td>$\delta n_{\lambda}^{\uparrow}$</td>
<td>-2.58</td>
<td>$\delta n_{\lambda}^{\downarrow}$</td>
</tr>
<tr>
<td>$\delta n_{\lambda}^{\downarrow}$</td>
<td>2.60</td>
<td>$\delta \mu_{\lambda}$</td>
</tr>
</tbody>
</table>

6. Conclusion. — In this paper we have shown that within a purely electronic model, it is quite possible to obtain a giant moment in Fe rich FeRh alloys using reasonable values of the change in local potentials. However the calculation was restricted to $T = 0$ within a Hartree-Fock approximation using the available band structure for the pure compound. Further understanding could be gained by:
i) Introducing a model with an arbitrary number
\( n (1 \leq n \leq 8) \) of Fe substituted Rh sites along the
lines proposed by Parlebas [11] for the case of Ni
clusters in Cu to see if the magnetic properties are
sensitive to the impurity-impurity interaction within
a cluster;

ii) Replacing a Rh site by a vacancy. In this case the
variation \( \delta \rho_{\text{mm'}} \) can be approximated by \( \delta \rho_{\text{mm'}} \) [12]
which may be an important term for the spin-flip
mechanism.

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