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EFFECTS OF CLUSTERING ON THE MAGNETIC PROPERTIES OF TRANSITION METAL ALLOYS

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Résumé. — Un simple cadre théorique est présenté pour examiner les effets de rassemblement sur la formation d'un moment local et l'arrangement magnétique dans les alliages métalliques dans lesquels le soluté est un métal transition ferromagnétique pour qui un atome isolé dans le solvant ne porte pas nécessairement un moment magnétique (au sens de Hartree-Fock). Les conséquences du modèle sont discutées qualitativement et comparées avec l'expérience.

Abstract. — A simple theoretical framework is presented for examining the effects of clustering on local moment formation and magnetic ordering in metallic alloys in which the solute is a transition metal ferromagnetic in the bulk, but for which an isolated atom in the solvent does not necessarily carry a magnetic moment (in a Hartree-Fock sense). Consequences of the model are discussed and compared qualitatively with experiment.

Some transition metals exhibit spontaneous long range magnetic order, eg Ni, Co, Fe. These we shall call type A. Those which have no such spontaneous order, eg Pd, Rh, Pt, we shall call type B. Simple metals, such as Zn, Cu, Al, we shall refer to as type C.

We are interested in investigating theoretically the magnetic properties of BA and CA alloys at finite concentrations. We are particularly concerned with the effects of statistical (or metallurgical) clustering in producing «local moments» in alloys for which an isolated A atom (in B or C) is non-magnetic in a Friedel-Anderson or Hartree sense. We restrict our discussion to simple models and simple but non-trivial approximations.

As a model for a BA alloy, we take the d-electron Hamiltonian

$$\mathcal{H} = \sum_{ij} t_{ij} a_{i\sigma}^+ a_{j\sigma} + \sum_{i} V_i a_{i\sigma}^+ a_{i\sigma} + \sum_{i} U_i n_{i\uparrow} n_{i\downarrow}$$

where in general the parameters $t$, $V$, $U$ depend upon whether the atoms at $i$ and $j$ are A or B type. The problem may be simplified whilst retaining its essential features by assuming $t_{ij}$ independent of the type of atoms, by taking the constituents to have the same number of d-electrons per atom, by treating the local electron number in Hartree approximation, and by assuming $(V_i + U_i n/2) = \text{constant}$, due to sp charge transfer. We then obtain the simple model d-electron Hamiltonian

$$\mathcal{H} = \sum_{ij} t_{ij} a_{i\sigma}^+ a_{j\sigma} - \sum_{i} \frac{U_i}{4} S_i S_i$$

where

$$S_i = a_{i\uparrow}^+ \sigma_{\alpha\beta} a_{i\uparrow}$$

The only configuration-dependent variable is $U_i$ which takes the value $U_A$ or $U_B$ depending on whether the atom at site $i$ is A or B type:

$$U_A > (N(E_F))^{-1} > U_B.$$  (4)

The Hamiltonian in eq. (2) is in a convenient form to express the partition function as a functional integral over the magnetization fluctuations $m_i$ as $1, 2, 3$

$$Z = Z_0 \int \mathcal{D} \left( \frac{8U}{4\pi} \right)^{1/2} \exp \left\{ -\beta F[\{m\}] \right\}$$

where the free energy functional $F[\{m\}]$ has the expansion

$$F[\{m\}] = \frac{1}{4} \sum_{i} \sum_{\alpha} U_i m_i^\alpha (i\nu_a) m_i^\beta (-i\nu_a)$$

\begin{align*}
&- \frac{1}{4} \sum_{i} \sum_{j} \sum_{\alpha\beta} U_j m_j^\beta (i\nu_a) \chi^{(0)\beta\alpha}(i\nu_a) \\
&\times m_i^\alpha (-i\nu_a) U_j \\
&- \frac{1}{32} \sum_{i} \sum_{j} \sum_{\alpha\beta\gamma\delta} A^{(0)\beta\gamma\delta}(i\nu_a) \\
&\times (i\nu_a, i\nu_b, i\nu_c, -i\nu_a - i\nu_b - i\nu_c) \\
&\times U_i m_i^\beta (i\nu_a) U_j m_j^\alpha (i\nu_c) U_k m_k^\gamma (i\nu_b) \\
&\times \frac{1}{4} S_i S_i + \text{etc.} .
\end{align*}

Here $\mu^2 \chi^{(0)}$ is the bare susceptibility and $A^{(0)}$ the corresponding 4-point function. The Greek letters signify Cartesian coordinates.

Molecular field theory results from a static extremal
approximation to (5), yielding to lowest non-trivial order the Landau equation for the magnetization

$$m_i^\alpha - \sum_j \chi_{ij}^{(0)}(0) U_j m_j^\alpha - \frac{1}{4} \sum_{ijkl} A_{ijkl}^{(0)}(0) U_j m_j^\alpha U_k m_k^\alpha U_l m_l^\alpha = 0 .$$

(7)

Here $m$ denotes the local moment and $\chi^{(0)}(0)$ and $A^{(0)}(0)$ are the bare static susceptibility and 4-point functions.

Within molecular field approximation eq. (7) includes information both about moment formation on particular cluster arrangements and also about the long range ferromagnetic and generalized spin-glass types of behaviour which could occur due to the long range oscillatory character of $\chi^{(0)}$.

To examine the effects of clustering on moment formation (aside from the long range ordering effects) (7) is studied with suitable cut-off or decaying boundary conditions. For simplicity let us consider only the possibility in which all the spins in a moment bearing cluster are ordered ferromagnetically. By redefining as variable (for all $U \neq 0$)

$$M_i = U_i m_i$$

all the explicit $U$-dependence may be formally included in the first term as

$$U_i^{-1} M_i - \sum_i \chi_{ii}^{(0)}(0) M_i - \frac{1}{4} \sum_{ijkl} A_{ijkl}^{(0)}(0) M_j M_k M_l M_i = 0 .$$

(9)

The explicit solution of this equation (plus boundary condition) for particular cluster distributions is straightforward. We may also note the analogy of eq. (9) with the Schrödinger equation for an electron in a disordered potential distribution as described by Anderson's model,

$$e_i \varphi_i + \sum_{ji} t_{ij} \varphi_j - E \varphi_i = 0$$

(10)

where $e_i$ varies from site to site but $t_{ij}$ is often assumed constant (for simplicity). Taking

$$e_i = U_i^{-1} , \quad t_{ij} = - \chi_{ij}^{(0)}(0) ,$$

and noting that

$$\sum_{ijkl} A_{ijkl}^{(0)}(0) < 0 ,$$

(11)

we see that magnetic solutions to (9) occur essentially for BA distributions such that the eigenvalues $E$ of (10) are negative. If the concentration of A in B is far below the uniform enhancement approximation value for ferromagnetism, then the magnetic solutions of (9) correspond to the band tail solutions of (10), which are better understood than those near the mobility edge. When $U_A, U_B$ are both close to $(N(E_F))^{-1}$, so that correlation lengths are long, (9) may be transformed into a Ginzburg-Landau type of equation.

Further analogies for this case have been considered [4].

For high A concentrations (7) or (9) may be used analogously to study magnetic hole clusters.

As mentioned earlier (7) also contains information necessary to examine long range ordering within molecular field theory. Above some A concentration ferromagnetism is expected whilst below it there exists the possibility of a cluster generalization of the spin glass phase found for example in CuMn or AuFe. The ferromagnetic limit could be related to that at which suitable percolation paths exist in which all A spins on the path have sufficient similar neighbours to maintain the moment locally. In a spin glass phase associated with n-clusters, and ignoring Kondo lifetime effects, one might expect by analogy with « good moment » spin glasses, where as a function of concentration the ordering temperature varies a little more slowly than linearly, that the ordering temperature $T_n^k(c)$ will vary roughly as $P_n(c)$, the concentration of n-atom clusters.

Kondo or spin fluctuation lifetime effects limit the validity of such molecular field descriptions. If the Kondo temperature of an n-cluster is $T_n^k$ then one would expect spin glass behaviour to be restricted to concentrations for which $T_n^k(c) \lesssim T_n^k$ whilst for lower concentrations the lifetime effects will prevent ordering and allow only paramagnetism. For clusters with strong moments the Kondo lifetime may be investigated within the functional integral formulation by analogy with Hamann's hopping path procedure [1], whilst for weak clusters the same type of theoretical difficulties will be experienced as occur for weak single local moments [5].

The picture presented above leads to typical phase diagrams as illustrated schematically in figure 1. In figure 2, we show the phase diagram of RhCo [6] for comparison. The theoretical picture is clearly in qualitative accord with experiment, the ferromagnetic percolation limit suggesting that moments form on Co clusters in Rh with about 5 nearest or 8 next nearest neighbours. The phase diagram of PdNi [7] is shown.

**Fig. 1.** Typical theoretical phase diagram for a transition metal alloy BA. The abscissa measures the concentration of A. The dashed line refers to the fictitious good cluster moment spin glass ordering temperature.
in figure 3 and suggests that HF moments will occur on even next nearest neighbour pairs, in accord with crude estimates from (9). The absence of a spin glass phase is presumably due to a relatively high Kondo temperature.

CA alloys are more appropriately described by an Anderson-type Hamiltonian

\[H = \sum_{\mathbf{k}\sigma} \varepsilon(\mathbf{k}) \uparrow \downarrow a^\dagger_\mathbf{k}\sigma d_\mathbf{k}\sigma + \sum_{\mathbf{i}\sigma} \varepsilon_d \uparrow \downarrow d^\dagger_\mathbf{i\sigma} d_\mathbf{i\sigma} + \sum_{\mathbf{i}\mathbf{j}\sigma} \tilde{t}_{ij} \uparrow \downarrow d^\dagger_\mathbf{i\sigma} d_\mathbf{j\sigma} + \sum_{\mathbf{k}\mathbf{i}\sigma} (V_{\mathbf{k}\mathbf{i}} \uparrow \downarrow a^\dagger_\mathbf{k\sigma} d_\mathbf{i\sigma} e^{i\mathbf{k} \cdot \mathbf{R}_i + \mathbf{h} \cdot \mathbf{c}}) + \sum U n_{\mathbf{d}\uparrow} n_{\mathbf{d}\downarrow}. \]

(12)

\( \mathbf{k} \) is a Bloch label and runs over its usual values. \( i, j \) are d-site labels and run only over A-atom sites. A modified functional integral procedure may be used to examine local moment behaviour in this case. The d-electron magnetization is given by an equation with the same form as eq. (7) except that the sum runs only over A-sites and \( \chi^{(0)} \) and \( A^{(0)} \) are determined with an effective overlap integral

\[\tilde{t}_{ij} = t_{ij} + \sum_{\mathbf{k}} \frac{|V_{\mathbf{k}\mathbf{j}}|^2}{(\varepsilon_d - \varepsilon_k + i\delta)} e^{i\mathbf{k} \cdot (\mathbf{R}_i - \mathbf{R}_j)}. \]

(13)

To lowest order the s-electron magnetization is simply obtained from an expression of the form

\[m_s^i = \sum_{\mathbf{i}} \mathbb{I}_{\mathbf{i}\mathbf{i}} U_1 m^d_1 \]

(14)

where \( \mathbb{I}_{\mathbf{i}\mathbf{i}} \) is independent of \( U \).

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References