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Theory of metallic magnetism at finite temperatures in bulk materials and thin films

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Abstract

A review of 'first-principles' theoretical work that describes the properties of magnetic metallic materials at finite temperatures is given. The key assumption is that a time-scale separation can be identified. There are the thermally induced spin fluctuations which are long-lived compared to the time electrons take to move from one lattice site to another. The dependence on the spin-polarised electronic structures of the systems is emphasised including the role of 'local exchange splitting' inferred even in the paramagnetic states. The disordered local moment picture which provides the basis of a mean field theory is discussed and its results for bulk transition metals and alloys recalled. Finally, new results for this picture in metallic thin films are reported. In particular comparison with calculated magnetic ordering temperatures of iron films on copper substrates is made with those deduced from experiment and an interpretation in terms of the electronic structure is given.

Keywords: Theoretical magnetism; Electronic structure; Transition metals

1. Introduction

As a metallic magnet is heated up, spin fluctuations are induced which eventually destroy the long-range magnetic order and, hence, the 'global' spin polarisation of the system. These collective electron modes interact as the temperature is raised and are dependent upon and can affect the underlying electronic structure. In many materials such spin fluctuations can be modelled by 'local moments' which produce local magnetic fields on the lattice sites. The moments are assumed to vary their orientations slowly on the time scale of the electronic motions and to be self-consistently maintained by them. The average over the local moments' orientations produces zero overall magnetisation in the paramagnetic state, but, nonetheless, the electronic structure is affected by this local moment disorder. The disordered local moment (DLM) picture [1], when implemented by the KKR–CPA method [2,3], is a material specific and yet parameter-free, mean-field theory of this picture of metallic magnetism.

Over the last few years there has been much work on the growth and engineering of ultrathin ferromagnetic films. Fascinating new properties [4]

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have been revealed by intensive experimental scrutiny which demand a theoretical description. Such thin film systems include layers of the 3d ferromagnetic transition metals Fe, Co on and embedded in Cu and W substrates. At low temperatures their magnetic properties can be described successfully and, in some cases, predicted by 'first principles' electronic structure calculations, e.g. Ref. [5]. Experimental studies, however [6], have shown that the magnetic properties of these systems at finite temperatures cannot be parameterised simply in terms of the temperature-dependent magnetisation $M(T)$ and that a 'first principles' theoretical approach is needed here as well. The DLM method provides such an approach. It works well for bulk Fe and Co and their alloys [7] and it is of fundamental interest to test its applicability to thin films comprising these materials and to use film thickness, d, as a tuneable, new thermodynamic variable.

The DLM picture is based on assuming a separation between fast and slow degrees of freedom in the interacting many-electron system. For times, τ, long in comparison with an electronic hopping times, $\hbar/w$ ($\approx 10^{-15}$ s), where w represents a relevant band-width, but short when compared with typical spin fluctuation times, the spin orientations of the electrons leaving an atomic site are sufficiently correlated with those arriving that the magnetisation integrated over a unit cell and averaged over τ is non-zero. These are the 'local moments' which can change their orientations (described by a set of unit vectors $\{\hat{e}_i\}$ labelled by the site index i) on a time scale longer than τ while their magnitudes fluctuate rapidly on the time scale τ. This time-scale demarcation has been invoked in much recent work [8] on bulk systems and we have recently examined and tested it in thin film systems. We have carried out case studies of ultra-thin films of Fe on a BCC W substrate, Co on a FCC Cu substrate [9] and Fe on and also embedded in a Cu(1 0 0) substrate [10].

For complexity in magnetic systems this last material is unsurpassed [11]. How the films grow, their structure and morphology are profoundly intertwined with their magnetic properties and a satisfactory description of these systems has become a benchmark for theories of thin film magnetism. Below a critical thickness of 10–12 monolayers (ML) the films take on the FCC structure of the substrate while thicker films revert to the BCC structure of bulk iron. In the ultra thin regime when there are fewer than 4–5 ML a ferromagnetic (FM) phase is observed whilst the thicker films of 6–11 ML seem to be antiferromagnetic (AF) with a net moment across the film. Adding covering layers of Cu to the films has a marked effect upon their magnetic properties. A single Cu monolayer suppresses the magnetic ordering temperatures T_c whilst the T_c's of 2 ML Cu-capped films are partly restored. In fact T_c oscillates weakly as further Cu layers are added [12]. A recent highlight of our work has been the excellent agreement of our calculations with these findings coupled with an interpretation in terms of the underlying electronic structure of the films [10].

2. Disordered local moment (DLM) theory

The DLM theory uses an adaptation of standard electronic spin density functional theory [13,3] to describe the generalised electronic grand potential $\Omega\{\hat{e}_i\}$ of the system constrained to have local moment configuration $\{\hat{e}_i\}$. By choosing a suitable reference 'spin' Hamiltonian $\Omega_0\{\hat{e}_i\}$ and expanding about it using the Feynman–Peierls' inequality [14], an approximation to the free energy is obtained,

$$F \leqslant F_0 + \langle \Omega - \Omega_0 \rangle^0 = \check{F} \tag{1}$$

with

$$F_0 = -(1/\beta) \ln \prod_i \int \mathrm{d}\hat{e}_i \exp(-\beta\Omega_0) \tag{2}$$

and

$$\langle X \rangle^0 = \prod_i \int \mathrm{d}\hat{e}_i \, X \exp(-\beta\Omega_0) \Big/ \prod_i \int \mathrm{d}\hat{e}_i \exp(-\beta\Omega_0) = \prod_i \int \mathrm{d}\hat{e}_i \, P_0\{\hat{e}_i\} X\{\hat{e}_i\}. \tag{3}$$

With Ω_0 in the form

$$\Omega_0 = \sum_i \omega_i^{(1)}(\hat{e}_i) + \sum_{i,j,i\neq j} \omega_{ij}^{(2)}(\hat{e}_i, \hat{e}_j) + \cdots, \qquad (4)$$

a scheme is set up which can, in principle, be systematically improved. Minimising $\check{F}$ to obtain the best estimate of the free energy gives $\omega_i^{(1)}$, $\omega_{ij}^{(2)}$, etc., as expressions involving restricted averages of $\Omega\{\hat{e}_i\}$ over the orientational configurations [2].

A type of mean-field theory, which turns out to be equivalent to a 'first principles' formulation of the DLM picture, is produced by taking the first term only in the equation above. Using a generalisation of the SCF–KKR–CPA method [15] introduced originally in the context of compositional disorder in alloys, explicit calculations were performed first for BCC Fe and FCC Ni. The average magnitude of the local moments, $\langle \mu_i(\{\hat{e}_j\})\rangle_{\hat{e}_i} = \mu_i(\hat{e}_i) = \bar{\mu}$, in the paramagnetic phase of iron was $1.91\mu_B$ [2] (The total magnetisation is zero since $\langle \mu_i(\{\hat{e}_j\})\hat{e}_i\rangle = 0$.) This value is of roughly the same magnitude as the magnetisation per atom in the low-temperature ferromagnetic state. The uniform, paramagnetic susceptibility, $\chi(T)$, followed a Curie–Weiss dependence upon temperature as observed experimentally and the estimate of the Curie temperature T_c was found to be 1280 K, also comparing well with the experimental value of 1040 K. In nickel, however, $\bar{\mu}$ was found to be zero and the theory reduced to the conventional SDF version of the Stoner model with all its shortcomings [16,7].

This mean-field DLM picture of the paramagnetic state has been improved by including the effects of correlations between the local moments to some extent. This has been achieved by integrating the consequences of Onsager cavity fields into the theory [7]. T_c for Fe is now 1015 K and a reasonable description of neutron scattering data is given. This approach has recently been generalised to alloys [17]. A first application to the paramagnetic phase of the 'spin glass' alloy $Cu_{85}Mn_{15}$ showed that the magnetic interactions between the Mn local moments fell off exponentially with distance and were oscillatory. This was in agreement with extensive neutron scattering data and the underlying electronic mechanisms were also identified [17]. It has since been applied successfully to a number of Fe and Co alloys [18] where good local moments form in the paramagnetic states.

3. Locally exchange split electronic structure

When the DLM theory was used to study bulk magnetic metals, it was found that the electronic structure can possess a 'local exchange' splitting even in the paramagnetic state [2]. This means that an electron spin-polarised parallel to a local moment will have a different density of states to that polarised anti-parallel. When all orientations of the moments are averaged over in the paramagnetic state the electronic structure is inevitably unpolarised but consequences from the presence of local moments can still be identified. This local exchange splitting is the cause of the establishment of a local moment. Photoemission and inverse photoemission (IPES) experiments [19] have found these qualitative features in BCC Fe. In our generalisation of the DLM theory to layered systems we found a layer dependence of similar features in the electronic structures of paramagnetic Fe and Co grown on substrates [10,9] which drive the onset and type of magnetic order and the form of the magnetic interactions.

In Fig. 1 we show an example of our results. We show the electronic density of states, layer resolved, for a three layer Fe system on a Cu(1 0 0) substrate at a temperature above its Curie temperature i.e. in its paramagnetic state. A 'local exchange' splitting is evident which varies from layer to layer. The local moments supported by this electronic structure reflect this dependence—the topmost layer has a moment per site of $2.53\mu_B$, the middle layer $1.70\mu_B$ and the layer next to the copper substrate $2.20\mu_B$. Results for films of varying thicknesses show similar features: the moments on the topmost layer are always the largest at around $2.5\mu_B$ followed by the moments on the Fe layer closest to the substrate next at roughly $2.2\mu_B$. In the interior of the film the moments are reduced to $1.7\mu_B$ close to what was found for FCC-Fe for this lattice spacing [20].

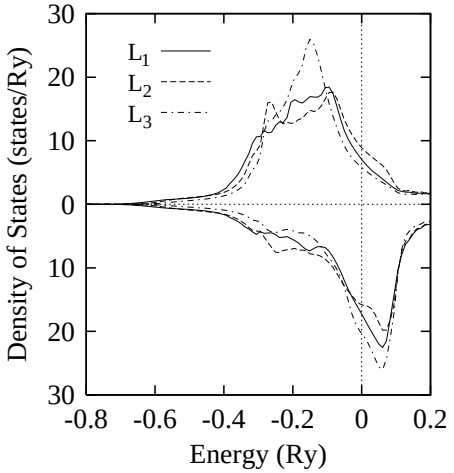

Fig. 1. The density of states (DOS) in each of the Fe layers of a $Fe_3Cu(1\,0\,0)$ system. The full line shows the topmost layer whilst the dashed line shows the DOS in the second layer and the dotted line shows the DOS for the Fe layer next to the Cu substrate. The upper half of the figure shows the DOS for an electron spin-polarised parallel to the local moment on a site whereas in the lower half the DOS of an electron-polarised anti-parallel is shown.

4. Onset of magnetic order

In order to study the onset of magnetic order in metallic magnets, we consider the application of a small, external spin-only magnetic field $\{\mathbf{h}_i\}$, varying from site to site, layer to layer which induces a magnetisation by the local moments changing their orientations to align with the field. For layered systems with two-dimensional translational symmetry the magnitudes of the 'local moments', $\{\mu_i\}$, assume one value μ_P per site in a given layer labelled P but vary from layer to l ayer and the paramagnetic spin susceptibility can be written as, $\chi^{PQ}(\mathbf{q}_\parallel) = (\beta/3)\mu_P^2\delta_{PQ} + (\beta/3)\sum_S S^{(2)}_{PS}(\mathbf{q}_\parallel)\,\chi^{SQ}(\mathbf{q}_\parallel)$ where, $\mathbf{q}_\parallel$ is a wave vector in the 2D layer Brillouin zone, and $S^{(2)}_{PS}(\mathbf{q}_\parallel)$ a 2D layer Fourier transform of a direct correlation function or effective 'exchange interactions' between layers P and Q. Once the $S^{(2)}_{PS}(\mathbf{q}_\parallel)$'s have been obtained from convolution integrals of electronic structure quantities over this zone, they are loaded into a $n \times n$ matrix, $S^{(2)}(\mathbf{q}_\parallel)$ (where n is the number of layers in the film), and the susceptibility obtained by a matrix inversion. For films in which the intralayer exchange coupling is ferromagnetic, as for the Fe films on Cu, W and Co on Cu the magnetic ordering temperature T_c is specified by the condition $\|3k_B T_C I - S^{(2)}(\mathbf{q}_\parallel = 0)\| = 0$ or in terms of the largest eigenvalue of $S^{(2)}(\mathbf{q}_\parallel = 0)$ [9,10]. Our calculations of the electronic structure of thin films of Fe on BCC W of thicknesses up to eight Fe layers also showed significant local exchange splittings and local moments associated with all layers. The moments were enhanced at the surface and diminished at the Fe-substrate interface. From the calculations of the susceptibility we found that the Curie temperature rose monotonically to the bulk value as the film thickness was increased. The interactions between the local moments were found to be very closely confined to nearest neighbours only. Another study of films of Co on FCC Cu produced a different picture. Here the local moments at both the film surface and the substrate interface were enhanced noticeably over those in the film's interior. The local moment 'exchange' interactions (the $S^{(2)}_{PQ}$'s) were of longer range and the magnetic ordering temperatures displayed oscillations about the bulk 3D value as the film thickness was increased [9].

We subjected the system comprising Fe layers on and embedded in FCC Cu to the most detailed study. For the uncapped films the magnetic ordering temperatures reduce monotonically to a constant value of 485 K for six Fe monolayers onwards. The intralayer 'exchange interactions' (the $S^{(2)}_{PP}$'s) are FM throughout. The layer at the top of films and the layer nearest the Cu substrate have the largest values owing to their reduced effective coordination. It is the interlayer couplings that show an important and interesting trend. The top two layers are strongly ferromagnetically (FM) coupled (positive values) whereas the coupling to nearest-neighbour layers within the films is AF. There is also significant coupling to subsequent layers which alternates between FM and AF. In Table 1 we show these intra- and interlayer interactions for a system comprising four Fe layers on Cu(1 0 0) and present a comparison with analogous values for a three layer system. Adding a copper cap to these films alters these results profoundly. Excellent agreement was obtained with the trends extracted from extensive

Table 1
Intra- and inter-layer effective 'exchange' interactions in meV between layers in an uncapped $Fe_4/Cu(1\,0\,0)$ system with the values for $Fe_3/Cu(1\,0\,0)$ shown for comparison in brackets

No.	L_1	L_2	L_3	L_4
1	108.0 (108.4)	−5.5	9.5 (−10.9)	0.2 (25.1)
2	−5.5	20.9	−8.2	12.5
3	9.5 (−10.9)	−8.2	33.7	53.4
4	0.2 (25.1)	12.5	53.4 (53.8)	96.0 (96.7)

The Fe layer L_1 is adjacent to the substrate and layer L_n is the top layer.

experimental data. Moreover, we were able to give a detailed analysis in terms of the electronic structures of the films [10].

5. Summary

In this paper we have briefly reviewed a 'first-principles' mean-field theory of metallic magnetism at finite temperatures and have indicated how it can provide a good description of the onset of magnetism in both bulk and thin film systems. Indeed the latter class of systems present a particularly useful testing ground for the theory. The variation of the local moments in such metallic systems are caused by the motion of the electrons not of course confined to atoms but restricted by the geometry of the sample. Consequently, the physics is similar to that underpinning other phenomena in layered metallic systems such as the oscillatory magnetic coupling in metallic multilayers [21].

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