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Using density functional theory to describe slowly varying fluctuations at finite temperatures: local magnetic moments in Gd and the ‘not so local’ moments of Ni

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Abstract

We briefly describe the density functional theory (DFT)-based ‘disordered local moment’ (DLM) picture for magnetism at finite temperatures. It shows how relatively slowly fluctuating local moments can emerge from the interacting electrons of many materials. Such entities have rigid magnitudes and fluctuate their orientations from atomic site to atomic site on a timescale long compared to other electronic times. We illustrate this theory with calculations of the magnetocaloric effect in Gd where we find excellent agreement with experiments. Fluctuating moments do not appear to establish naturally over such small regions for some other materials. We show how the DFT-DLM theory can be extended to these materials with the use of the Korringa–Kohn–Rostoker nonlocal coherent potential approximation (KKR-NLCPA) to allow for more extensive, slow magnetic fluctuations. We present the first application of this approach by revisiting the description of the magnetic fluctuations prevalent in the paramagnetic state of nickel. We find that local moments can emerge above T_c and that these form coherently over small clumps of atomic sites (4–8 sites).

Keywords: disordered materials, *ab-initio* electronic structure, magnetism

(Some figures may appear in colour only in the online journal)

1. Introduction

All real materials are disordered to some extent and *ab-initio* modelling needs to address the influence this disorder has on electronic structure [1]. Typically there is order over both small length scales, namely short-range order (SRO) [2] and also incomplete long-range order (LRO). Recently a method, the Korringa–Kohn–Rostoker nonlocal coherent potential approximation (KKR-NLCPA) [3–10] became available for the treatment of the effects of SRO and partial

LRO upon a material’s electronic structure together with its dependent properties within a DFT-based framework. The theoretical formalism and applications of this relatively new method have been extended to materials with multi-atom per unit cell lattices so that it is in principle possible to describe complex systems in which several ordering phenomena are present [11].

This new method gives opportunities for improving the description of materials’ interacting electrons at finite temperature. To improve upon the success of DFT for ground state properties, one effective approach is to identify some attributes of the interacting electrons that vary relatively slowly and then treat them as classical fluctuations. The disordered local moment (DLM) theory of magnetism [12, 13] is an example of this where local moments of roughly fixed magnitude, each



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associated with an atomic site, are assumed to slowly vary their orientations. In this paper we use the KKR-NLCPA to extend this concept to allow for short-ranged correlations between such fluctuations. We use our theory to describe the local moment fluctuations in the paramagnetic state of nickel in an effort to resolve the long-standing puzzle surrounding the magnetism of this metal. We find that the electronic structure of nickel can sustain local moments above the Curie temperature, T_c , but only if the moments form co-operatively on small clumps of sites.

In the next section we give a brief overview of DFT-DLM theory and illustrate it by presenting calculations for the magnetocaloric effect in gadolinium. We then outline the KKR-NLCPA and show how it can improve the current scope of DFT-DLM which we back up by initial calculations for the paramagnetic state of nickel.

2. Magnetism at finite temperatures and the disordered local moment picture

The assumption underpinning the Disordered Local Moment picture is that there are some fluctuations in the spin density of the interacting electrons of a magnetic material that vary slowly in comparison with the remaining electronic degrees of freedom. These fluctuations also influence the electronic structure from which they emerge. By picking out these collective electron entities by local spin polarisation axes fixed to each region around an atomic site, $\{\hat{\mathbf{e}}_i\}$ and using a generalisation of DFT [12] for prescribed non-collinear spin-polarisation, an *ab-initio* description of this picture can be produced [13–18]. Under the constraint of a particular orientational configuration $\{\hat{\mathbf{e}}_i\}$ there is a certain charge and magnetisation density, $\rho(\mathbf{r})$ and $\mathbf{M}(\mathbf{r})$ which minimises the electronic DFT Grand potential functional $\Omega[\rho(\mathbf{r}), \mathbf{M}(\mathbf{r}); \{\hat{\mathbf{e}}_i\}]$ [12]. Under this constraint $\mathbf{M}(\mathbf{r})$ is required to align according to the configuration $\{\hat{\mathbf{e}}_i\}$ so the magnetisation about a site i , $\mathbf{M}(\mathbf{r}_i) = \mu_i(\mathbf{r}_i; \{\hat{\mathbf{e}}_i\})\hat{\mathbf{e}}_i$, i.e. it has a magnitude μ_i . To date the DLM theory has been applied to systems in which these measures of local spin-polarisation are fairly independent of the orientations associated with the surrounding sites and are of roughly the same size as the magnetisation per site for the material when fully magnetically ordered at $T = 0$ K.

We will see later in this paper that this picture is not appropriate for some itinerant electron magnetic materials such as nickel where instead ‘not so local moments’ may establish themselves cooperatively over small clumps of sites. Before examining this outcome we first review the theory for ‘good’ local moment systems, e.g. bcc Fe, L1₀-FePt, transition metal oxides, heavy rare earth metals etc. [12], [14–18], where moments of roughly fixed magnitudes fluctuate their orientations. Here, although such local moments establish, interactions between them nonetheless depend on the type and extent of the long range magnetic order through the associated spin-polarized electronic structure which itself adapts to the extent of magnetic order and, in some cases, can trigger metamagnetic transitions [19, 20]. In our short recap of the DLM theory for a magnetic material in an external magnetic field \mathbf{H} at a temperature T [20] we show how entropy changes

that occur at magnetic transitions and thus the magnetocaloric effect (MCE), can also be calculated *ab-initio* and captured accurately. We illustrate this by presenting results for gadolinium, very much a ‘good local moment’ magnet, which possesses one of the highest MCE and has thus been used in prototype room temperature magnetic refrigerators [21].

The probability that a system’s local moments are configured according to $\{\hat{\mathbf{e}}_i\}$ is

$$P(\{\hat{\mathbf{e}}_i\}) = \frac{\exp[-\beta\Omega(\{\hat{\mathbf{e}}_i\})]}{\mathcal{Z}}, \quad (1)$$

where the partition function is $\mathcal{Z} = \prod_i \int d\hat{\mathbf{e}}_i \exp[-\beta\Omega(\{\hat{\mathbf{e}}_i\})]$, $1/\beta = k_B T$ (k_B is the Boltzmann constant) and the free energy $\mathcal{F} = -k_B T \ln \mathcal{Z}$. The ‘generalised’ electronic Grand potential $\Omega(\{\hat{\mathbf{e}}_i\}; \mathbf{H}, T)$ comes from the generalised DFT [12] and is suitably minimised for the appropriate charge and magnetisation densities. At this point it plays the role of a local moment or ‘spin’ Hamiltonian, but has a subtle electronic glue origin.

Expanding about a suitable reference ‘spin’ Hamiltonian [22], which is a sum of single site terms,

$$\Omega_0 = \sum_i \omega_i(\hat{\mathbf{e}}_i) = - \sum_i \mathbf{h}_i \cdot \hat{\mathbf{e}}_i, \quad (2)$$

gives a mean field theoretical estimate of the free energy [12]

$$\mathcal{F} = \bar{\Omega} - \sum_i \left(\mu_i \mathbf{m}_i \cdot \mathbf{H} - \frac{1}{\beta} \int d\hat{\mathbf{e}}_i P_i(\hat{\mathbf{e}}) \ln P_i(\hat{\mathbf{e}}) \right). \quad (3)$$

It comprises an internal energy $\bar{\Omega}$ from the interacting electron system, averaged over local moment orientations, a contribution from local moments interacting with the external magnetic field \mathbf{H} and $-T$ times the magnetic entropy, \bar{S}_{mag} . The probability of a local moment being oriented along $\hat{\mathbf{e}}_i$ on site i is set as

$$P_i(\hat{\mathbf{e}}_i) = \frac{\exp[\beta \mathbf{h}_i \cdot \hat{\mathbf{e}}_i]}{\int d\hat{\mathbf{e}}_i \exp[\beta \mathbf{h}_i \cdot \hat{\mathbf{e}}_i]}. \quad (4)$$

A magnetic state is specified by the set of local order parameters,

$$\left\{ \mathbf{m}_i = \int d\hat{\mathbf{e}}_i P_i(\hat{\mathbf{e}}_i) \hat{\mathbf{e}}_i = (\coth(\beta h_i) - 1 / (\beta h_i)) \hat{\mathbf{h}}_i \right\} \quad (5)$$

each of which has a size which can take values between 0 and 1. For a ferromagnetic state all the \mathbf{m}_i ’s are equivalent and specify the ferromagnetic order parameter, \mathbf{m} . The Weiss fields $\{\mathbf{h}_i\}$ satisfy

$$\mathbf{h}_i = - \frac{\partial \bar{\Omega}}{\partial \mathbf{m}_i} + \mu_i \mathbf{H}. \quad (6)$$

This ensures that the function $\mathcal{F}(\{\mathbf{m}_i\}; \mathbf{H}, T)$, shown in equation (3), is minimised with respect to the $\{\mathbf{m}_i\}$, at a temperature T and hence describes the free energy.

Particularly pertinent for our description of MCE [23] is the electronic entropy contained in $\bar{\Omega}$ of equation (3) [24], $\bar{\Omega} = \bar{E} - T \bar{S}_{\text{elec}}$. \bar{E} is the DFT-based energy averaged over local moment orientations [15, 19, 25, 26] with electronic density of states (DOS) at the Fermi energy $\bar{n}(E_F; \{\mathbf{m}_i\}; \mathbf{H})$ and \bar{S}_{elec} is the electronic entropy estimated as $\bar{S}_{\text{elec}} \approx \frac{\pi^2}{3} k_B^2 T \bar{n}(E_F)$

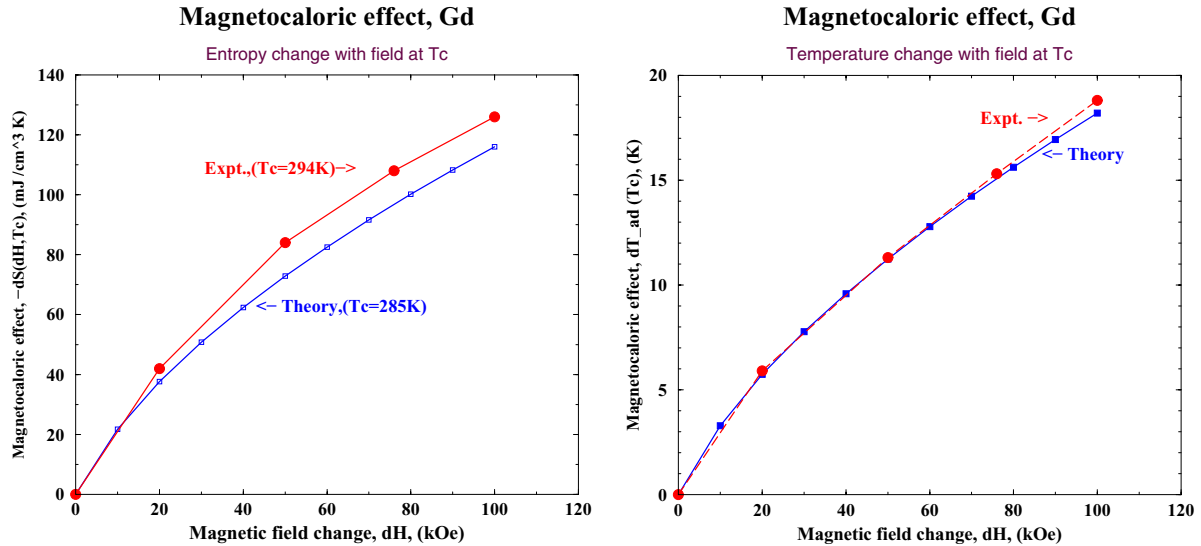


Figure 1. The MCE of Gd calculated by DFT-DLM theory and compared with experimental data of Gschneidner *et al* [21]. (a) The isothermal entropy change and (b) the adiabatic temperature change from an applied magnetic field.

from the Sommerfeld expansion. The isothermal entropy difference between states with and without a magnetic field applied, $\Delta S(\mathbf{H}, T)$, is therefore comprised of the sum of the \bar{S}_{mag} and \bar{S}_{elec} differences. Likewise the adiabatic temperature change, $\Delta T_{\text{ad}}(\mathbf{H}, T)$ can be estimated from

$$\bar{S}_{\text{mag}}(\mathbf{H}, T) + \bar{S}_{\text{elec}}(\mathbf{H}, T) + \bar{S}_{\text{latt}}(T) = \bar{S}_{\text{mag}}(0, T + \Delta T_{\text{ad}}) + \bar{S}_{\text{elec}}(0, T + \Delta T_{\text{ad}}) + \bar{S}_{\text{latt}}(T + \Delta T_{\text{ad}})$$

where \bar{S}_{latt} is the lattice vibration entropy and estimated, for example, by a simple Debye model.

Multiple-scattering (Korringa–Kohn–Rostoker, KKR) [15, 25, 26] formalism is used to describe the electronic structure and the averaging over local moment configurations is carried out via the Coherent Potential Approximation (CPA) [25] which is suited for the single site averages required by equation (4). Relativistic spin orbit coupling effects on the electronic motion are fully included by solving the Kohn–Sham–Dirac equations [27]. The electronic charge density and also the magnetisation density, which sets the moments' magnitudes, μ_i , are determined from a self-consistent field (SCF)-KKR-CPA [26]. For the heavy rare earth metal Gd and other materials where strong electron correlations need treatment beyond standard DFT prescriptions, methods such as the local self-interaction (L-SIC) [17, 18, 28] can be included.

Following on from our study of the magnetic order in the heavy rare earth metals [17] within this approach we show in figure 1 the isothermal entropy change caused by magnetic field change and adiabatic temperature drop for gadolinium in which we have used a Debye temperature θ_D of 173 K [29]. The agreement with experimental results [21] is very good.

Whilst effective for many magnetic materials, this DLM theory applied to nickel and some other metallic magnets finds that the magnetisation magnitude, $\mu_i(\mathbf{r}_i; \{\hat{\mathbf{e}}_i\})$, around a site i depends strongly on how the magnetisation is orientated on surrounding sites. Its averaging procedure over all configurations, as outlined above with the single site CPA, produces as a consequence no finite site-local magnetisation

in the paramagnetic state. As proposed by Balazs Györfly and others, it is however possible that instead a local moment might be sustained via short-ranged correlations of the orientations $\{\hat{\mathbf{e}}_i\}$ over small clusters of sites. The nonlocal extension to the CPA provides the electronic structure method to probe this idea. We summarise its basics in the next section before proceeding with the second investigation for nickel.

3. The KKR-NLCPA

For over forty years the coherent potential approximation [30] (CPA) has been a generally reliable method for dealing with the motion of an electron through a disordered system. However, being in essence a single-site mean-field theory, the CPA fails to take into account the effect of non-local correlations in the environment of each site and hence can miss some important physics. Consequently major effort was spent searching for ways to improve the CPA systematically particularly by some multi-site or cluster generalisation. This proved to be a surprisingly difficult problem [31, 32] but a tractable solution eventually emerged from the Dynamical Cluster Approximation [33] (DCA). Designed originally to describe dynamical spin and charge fluctuations in simple Hubbard models of strongly-correlated electron systems within the framework of the Dynamical Mean Field Theory [34, 35] (DMFT), the static version of this approximation was developed [33] and then later combined with realistic, *ab-initio* descriptions of systems of interacting electrons in disordered systems to produce the KKR-NLCPA [3].

Such a method is still an effective medium theory and it tries to address the main shortcoming of the CPA by resorting to a 'coarse-graining' procedure adapted from the DCA. The NLCPA approximates this effective medium by working in terms of clusters of atomic sites rather than single ones so that non-local correlations are included up to the range of the cluster size. It sets up a translationally invariant effective medium, which recovers the CPA in the limit of a 'cluster' of

just one site. The method is fully causal [31, 32, 36], allows the effects of short-range order to be modelled and can be implemented numerically for realistic systems [3].

The Green function \bar{G}_{ij} describes the average motion of an electron through the lattice from a site at lattice vector \mathbf{R}_i to one at \mathbf{R}_j and is written in terms of a self-energy, $\bar{\Sigma}_{ij}$. The goal of the theory is to restore, on average, the periodicity of the lattice so that, in reciprocal \mathbf{k} -space, at an energy E :

$$\bar{G}(\mathbf{k}, E) = G_0(\mathbf{k}, E) + G_0(\mathbf{k}, E) \bar{\Sigma}(\mathbf{k}, E) \bar{G}(\mathbf{k}, E) \quad (7)$$

where $G_0(\mathbf{k}, E)$ describes the free electron propagation through the lattice. In this formulation, the bar over the top specifies an effective medium quantity. We briefly outline the derivation of the NLCPA, full details of which can be found in references [3, 7, 33, 37]. We consider a specific cluster of N_c sites with positions \mathbf{R}_I under periodic Born–von Karman boundary conditions so that there are N_c evenly spaced points, \mathbf{K}_n , in reciprocal space and these can be taken to identify N_c tiles of Brillouin zone. We write a lattice Fourier transform:

$$\frac{1}{N_c} \sum_{\mathbf{K}_n} e^{i\mathbf{K}_n \cdot (\mathbf{R}_I - \mathbf{R}_J)} = \delta_{I,J} \quad (8)$$

(N.B. The choice of \mathbf{K}_n 's is not unique; here we limit ourselves to choosing one set, i.e. a single phase [7], $\phi = 0$, when coarse graining reciprocal space, but remark how the multi-phase reformulation which involves averaging over several phases made by Rowlands *et al* [7] can also be made.)

As required by equation (7), averaged cluster quantities must be translationally invariant, i.e. the coarse-grained self-energy of the effective medium is written [37] for an arbitrary site I :

$$\bar{\Sigma}(\mathbf{K}_n, E) = \sum_{J=1}^{N_c} \bar{\Sigma}_{IJ}(E) e^{-i\mathbf{K}_n \cdot (\mathbf{R}_I - \mathbf{R}_J)}, \quad (9)$$

$$\bar{\Sigma}_{IJ}(E) = \frac{1}{N_c} \sum_{\mathbf{K}_n} \bar{\Sigma}(\mathbf{K}_n, E) e^{i\mathbf{K}_n \cdot (\mathbf{R}_I - \mathbf{R}_J)}. \quad (10)$$

with which the electronic Green function for the effective medium is

$$\bar{G}_{IJ}(E) = \frac{1}{N_c} \sum_{\mathbf{K}_n} \bar{G}(\mathbf{K}_n, E) e^{i\mathbf{K}_n \cdot (\mathbf{R}_I - \mathbf{R}_J)} \quad (11)$$

$$\bar{G}(\mathbf{K}_n, E) = \frac{N_c}{\Omega} \int_{\Omega_{\mathbf{K}_n}} [(G_0(\mathbf{k}))^{-1} - \bar{\Sigma}(\mathbf{K}_n, E)]^{-1} d\mathbf{k} \quad (12)$$

where the integration extends over the tile centred on \mathbf{K}_n in the Brillouin zone and $\Sigma(\mathbf{k}, E) = \Sigma(\mathbf{K}_n, E) \forall \mathbf{k} \in \Omega_{\mathbf{K}_n}$. (Evidently $\bar{G}(\mathbf{K}_n, E)$ satisfies a coarse-grained version of equation (7).). A procedure for determining the self-energy needs to be developed. One way of achieving this is to establish a cluster cavity Green's function (equivalent to the impurity projector formalism used Faulkner and Stocks and others [10, 32, 38]).

$$\bar{G}_{IJ}(E) = (\bar{G}^{-1}(E) + \bar{\Sigma}(E))_{IJ}^{-1}, \quad (13)$$

where \bar{G} and $\bar{\Sigma}$ denote matrices in cluster space, ($N_c \times N_c$). To compute these we can write down an impurity cluster Green function in which the cavity is filled by an appropriate arrangement (labelled by γ) of potentials, \underline{v}^γ . Thus

$$G_{IJ}^\gamma(E) = (\bar{G}(E) - \underline{v}^\gamma)_{IJ}^{-1}, \quad (14)$$

where \underline{v}^γ is a matrix with elements $v_i^\gamma \delta_{i,j}$. Summing over these with an appropriate probability distribution function $P(\gamma)$ gives an expression for $\bar{G}_{IJ}(E)$:

$$\bar{G}_{IJ}(E) = \sum_{\gamma} P(\gamma) G_{IJ}^\gamma(E). \quad (15)$$

The self-consistent solution of the above equations (9)–(15) enables the effective medium to be determined and relevant averaged properties to be calculated. $P(\gamma)$ is the probability of a configuration γ occurring and can include the effects of multi-site short-range ordering or clustering up to the cluster size. It reduces to the usual concentration of the single-site CPA in the $N_c = 1$ limit

This procedure can be expressed in a multiple scattering framework for our magnetic systems with their local spin-polarisation orientational disorder. The free space propagation from site to site in the material is now specified in terms of the KKR structure constants $\underline{g}(\mathbf{R}_i - \mathbf{R}_j; E)$ which have lattice Fourier transform

$$\underline{g}(\mathbf{k}, E) = \frac{1}{N} \sum_j \underline{g}(\mathbf{R}_i - \mathbf{R}_j; E) e^{-i\mathbf{k} \cdot (\mathbf{R}_i - \mathbf{R}_j)}, \quad (16)$$

in which the underline refers to the usual angular momentum and spin matrix notation. Following [3] we identify the site diagonal part of the self energy $\bar{\Sigma}_{II}(E)$ with the inverse of an effective medium t-matrix, $\bar{t}_I(E)$ whilst the off-diagonal part can be viewed as effective corrections to the structure constants, $\bar{\delta}\underline{g}(\mathbf{R}_I - \mathbf{R}_J; E)$. The KKR version of the self-energy is denoted \bar{M}_{IJ} and, just like in equation (9), has coarse grained reciprocal space components $\bar{M}(\mathbf{K}_n, E)$. The scattering path operator [39] between sites within the NLCPA cluster is written:

$$\begin{aligned} \bar{\tau}_{IJ}(E) &= \frac{1}{\Omega} \sum_{\mathbf{K}_n} \int_{\Omega_{\mathbf{K}_n}} [\bar{M}(\mathbf{K}_n, E) - \underline{g}(\mathbf{k}, E)]^{-1} d\mathbf{k} e^{i\mathbf{K}_n \cdot (\mathbf{R}_I - \mathbf{R}_J)} \\ &= \frac{1}{N_c} \sum_{\mathbf{K}_n} \bar{\tau}(\mathbf{K}_n, E) e^{i\mathbf{K}_n \cdot (\mathbf{R}_I - \mathbf{R}_J)}. \end{aligned} \quad (17)$$

We define a cavity function as $\bar{\Delta}(\mathbf{K}_n, E) = \bar{M}(\mathbf{K}_n, E) - [\bar{\tau}(\mathbf{K}_n, E)]^{-1}$ and a cluster impurity scattering path operator as

$$\underline{\tau}_{IJ}^\gamma(E) = [\underline{m}^\gamma(E) - \bar{\Delta}(E)]_{IJ}^{-1} \quad (18)$$

where $\underline{m}^\gamma(E)$ has matrix elements in cluster space $\underline{t}_I^{-1}(\hat{\mathbf{e}}_I = \gamma(I)) \delta_{IJ}$ in which $\hat{\mathbf{e}}_I$ denotes the orientation of the spin polarisation of the scatterer occupying a site in the cluster at \mathbf{R}_I for the configuration $\gamma = \{\hat{\mathbf{e}}_1, \hat{\mathbf{e}}_2, \dots, \hat{\mathbf{e}}_{N_c}\}$ and $\underline{t}_I^{-1}(\hat{\mathbf{e}}_I = \gamma(I))$ is the inverse of the scattering t-matrix. The KKR-NLCPA condition is

$$\bar{\tau}_{IJ}(E) = \sum_{\gamma} P(\gamma) \underline{\tau}_{IJ}^\gamma(E) \quad (19)$$

which enables a new \bar{M} to be generated,

$$\bar{M}(E) = [\bar{\tau}(E)]^{-1} + \bar{\Delta}(E) \quad (20)$$

with which an iterative procedure for determining the NLCPA effective medium is defined.

Once this iterative process has produced a solution to equations (12)–(15), averaged observables can be found from the Green function [3, 38]. For an impurity cluster local moment configuration γ , the propagation from position \mathbf{r}_I in the Voronoi cell space surrounding the site at \mathbf{R}_I to \mathbf{r}'_J in the space around \mathbf{R}_J is given by the Green function

$$G_{IJ}^{\gamma}(\mathbf{r}_I, \mathbf{r}'_J; E) = Z(\mathbf{r}_I, E; (\hat{\mathbf{e}}_I = \gamma(I))) \tau_{IJ}^{\gamma}(E) Z(\mathbf{r}'_J, E; (\hat{\mathbf{e}}_J = \gamma(J))) - Z(\mathbf{r}_I^{\leftarrow}, E; (\hat{\mathbf{e}}_I = \gamma(I))) J(\mathbf{r}_I^{\rightarrow}, E; (\hat{\mathbf{e}}_I = \gamma(I))) \delta_{IJ}, \quad (21)$$

where $Z(\mathbf{r}_I, E; (\hat{\mathbf{e}}_I = \gamma(I)))$, $J(\mathbf{r}_I, E; (\hat{\mathbf{e}}_I = \gamma(I)))$ are the regular and irregular solutions to the single site problem and a trace over the angular momentum and spin indices is implied. The charge and magnetisation densities and densities of states for these configurations are obtained from the Green function.

4. Disordered local moments and the KKR-NLCPA

We want to use this framework to study the impact of short-ranged ordering effects on systems with disorder. In particular, for the paramagnetic state of a magnet, we formulate a way to determine the size of the clump over which a fluctuating local moment can emerge naturally from its interacting electrons. To do this we improve upon the choice of reference ‘spin’ Hamiltonian used to estimate the free energy of the system, equation (2), so that short-ranged coupling between the moment orientations, $\{\hat{\mathbf{e}}_i\}$, can be included. As in section 2 we start by considering a particular configuration $\{\hat{\mathbf{e}}_i\}$ over the lattice where DFT can give a formal specification of the electronic Grand potential $\Omega\{\hat{\mathbf{e}}_i\}$ of a system which has this configuration imposed on it (using constraining fields if necessary [12]). This is a functional of charge and magnetisation densities $\rho_i(\mathbf{r}; \{\hat{\mathbf{e}}_i\})$, $\mu_i(\mathbf{r}; \{\hat{\mathbf{e}}_i\})$ which themselves depend on the particular configuration $\{\hat{\mathbf{e}}_i\}$. The i subscript denotes the nearest atomic site. We now select a ‘spin’ Hamiltonian of the form

$$\Omega_0 = \sum_C \omega_C(\hat{\mathbf{e}}_1, \hat{\mathbf{e}}_2, \dots, \hat{\mathbf{e}}_{N_C}) \quad (22)$$

where the lattice has been split into many equal size clusters, labelled by index C and each containing N_C contiguous sites. ω_C is therefore a function of the orientations of each of the sites within the cluster labelled C . The probability of this cluster having its sites with orientations $\hat{\mathbf{e}}_1, \hat{\mathbf{e}}_2, \dots, \hat{\mathbf{e}}_{N_C}$ is given by

$$P_C(\hat{\mathbf{e}}_1, \hat{\mathbf{e}}_2, \dots, \hat{\mathbf{e}}_{N_C}) = \frac{\exp(-\beta\omega_C(\hat{\mathbf{e}}_1, \hat{\mathbf{e}}_2, \dots, \hat{\mathbf{e}}_{N_C}))}{\int d\hat{\mathbf{e}}'_1 \int d\hat{\mathbf{e}}'_2 \dots \int d\hat{\mathbf{e}}'_{N_C} \exp(-\beta\omega_C(\hat{\mathbf{e}}'_1, \hat{\mathbf{e}}'_2, \dots, \hat{\mathbf{e}}'_{N_C}))}. \quad (23)$$

Exploiting the Feynman–Peierls’ inequality [12, 22] to find the ‘best’ Ω_0 leads to an estimate for the free energy of the system so that

$$\mathcal{F} = \overline{\Omega} - \sum_C \left(\mathbf{H} \cdot \mathbf{M}_C - \frac{1}{\beta} \int d\hat{\mathbf{e}}'_1 \int d\hat{\mathbf{e}}'_2 \dots \int d\hat{\mathbf{e}}'_{N_C} P_C(\hat{\mathbf{e}}'_1, \hat{\mathbf{e}}'_2, \dots, \hat{\mathbf{e}}'_{N_C}) \ln P_C(\hat{\mathbf{e}}'_1, \hat{\mathbf{e}}'_2, \dots, \hat{\mathbf{e}}'_{N_C}) \right) \quad (24)$$

(i.e. sum of ‘internal energy’, interaction with external field and $-T$ times the local fluctuation entropy) and where \mathbf{M}_C is the average magnetisation of cluster C . The ‘internal energy’, $\overline{\Omega}$, is the electronic Grand potential $\Omega\{\hat{\mathbf{e}}_i\}$ averaged using cluster probability distributions $P_C(\hat{\mathbf{e}}_1, \dots, \hat{\mathbf{e}}_{N_C})$. Finding the cluster Weiss fields according to

$$\omega_C(\hat{\mathbf{e}}_1, \hat{\mathbf{e}}_2, \dots, \hat{\mathbf{e}}_{N_C}) = \frac{\partial \overline{\Omega}}{\partial P_C(\hat{\mathbf{e}}_1, \hat{\mathbf{e}}_2, \dots, \hat{\mathbf{e}}_{N_C})} \quad (25)$$

ensures that \mathcal{F} is minimised.

We now refer to reference [6] to obtain a prescription for $\overline{\Omega}$ from DFT and KKR-NLCPA which we need to vary with respect to probability distribution P_C to obtain our Weiss cluster fields in equation (25). $\overline{\Omega}$ comprises an average over the usual single particle energies and double-counting terms of DFT. As such it is a charge and magnetisation density functional which is minimised for the correct charge and magnetisation densities. Using γ again as shorthand to denote a particular set of orientations, $\{\hat{\mathbf{e}}_1, \hat{\mathbf{e}}_2, \dots, \hat{\mathbf{e}}_{N_C}\}$ for the sites in a cluster, we adapt equation (29) and equations (A2) and (A7) from [6], which explains how the KKR-NLCPA is used within DFT. With the property of $\overline{\Omega}$ that it is stationary with respect to charge and magnetisation densities, $\rho^C(\mathbf{r}; \gamma)$, $\mu^C(\mathbf{r}; \gamma)$, for each configuration γ in the DFT sense we obtain the following expression for $\frac{\partial \overline{\Omega}}{\partial P_C(\gamma)}$ which determines $\omega_C(\gamma)$ *ab-initio*. (As before I labels a site within a cluster from 1 to N_C .)

$$\frac{\partial \overline{\Omega}}{\partial P_C(\gamma)} = \int f(E - \nu) \frac{1}{\pi} \text{ImTr} \cdot (\ln(\overline{\mathcal{E}}^{\gamma}(E))^{-1} - \ln(\overline{\mathcal{E}}(E))^{-1})_C dE + \sum_{I=1}^{N_C} \left(\overline{U}_I^C(\gamma) + \mathbf{H} \cdot \int \mu^C(\mathbf{r}; \gamma) \hat{\mathbf{e}}_I^{\gamma} d\mathbf{r}_I \right) \quad (26)$$

where ν is the system’s chemical potential. The first term derives from varying the single particle energy part of the electronic Grand potential and the Fermi–Dirac function shows that single particle excitations can be included. The second term, \overline{U}_I^C , comes from the variation of the double-counting term and is given as

$$\begin{aligned} \overline{U}_I^C(\gamma) = & - \int (\rho^C(\mathbf{r}; \gamma) v^C(\mathbf{r}; \gamma) - \mu^C(\mathbf{r}; \gamma) b^C(\mathbf{r}; \gamma) - \rho^C(\mathbf{r}; \gamma) \epsilon_{xc}(\mathbf{r}; \gamma)) d\mathbf{r}_I \\ & + \frac{1}{2} \int \sum_J \int \frac{\rho^C(\mathbf{r}; \gamma) [\rho^C(\mathbf{r}'; \gamma) - 2Z\delta(\mathbf{r}_J')]}{|\mathbf{r}_I - \mathbf{r}_I + \mathbf{R}_{I,J}|} d\mathbf{r}_J d\mathbf{r}_I \\ & + \frac{1}{2} \int \sum_{C' \neq C} \sum_{\gamma'} P_{C'}(\gamma') \sum_J \int \frac{(\rho^C(\mathbf{r}; \gamma) - Z\delta(\mathbf{r}_I)) (\rho^{C'}(\mathbf{r}'; \gamma') - Z\delta(\mathbf{r}_J'))}{|\mathbf{r}_I - \mathbf{r}_J' + \mathbf{R}_{C,I,C',J'}|} d\mathbf{r}_J' d\mathbf{r}_I - \sum_{C,I} \mathbf{H}_{C,I}^{\text{cons}} \cdot \hat{\mathbf{e}}_I. \end{aligned} \quad (27)$$

The C, C', \dots label the NLCPA clusters into which the material is divided, each with N_C sites. $\mathbf{R}_{I,J}$ sets the separation

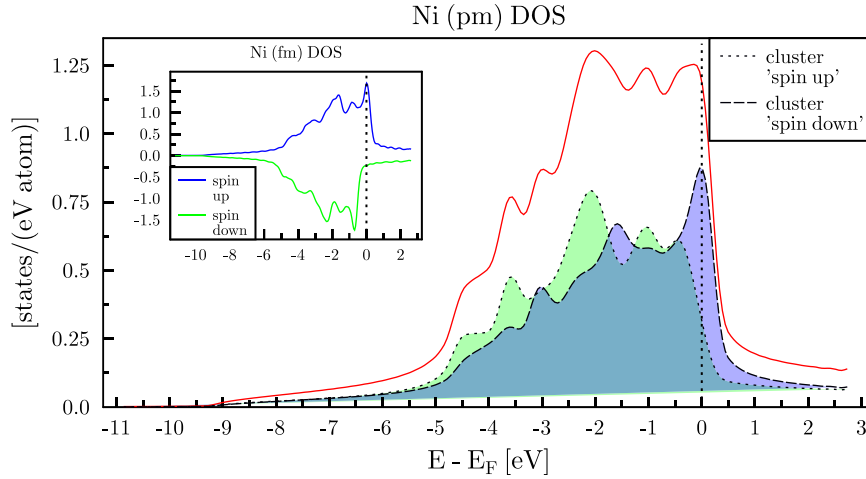


Figure 2. The density of states, DOS, (states/atom/eV) of paramagnetic nickel in which there are disordered clump moments of eight sites. The components of the DOS for an electron spin-polarised parallel (dashed) and anti-parallel (dotted) to the orientation of the clump moment are also shown. The average over all orientations produces the total DOS (red full line) which is non-spin polarised. The inset shows, for comparison, the spin-polarised DOS for ferromagnetic Ni.

between sites within a cluster and $\mathbf{R}_{C, I; C' J'} = \mathbf{R}_{I; J'} + \mathbf{R}_C - \mathbf{R}_{C'}$ where \mathbf{R}_C is the position of a cluster. Z is the nuclear charge per site and the $\mathbf{H}_{C, I}^{\text{cons}}$ refer to constraining magnetic fields to hold a non-collinear magnetic state [12], $\{\hat{\mathbf{e}}_1, \hat{\mathbf{e}}_2, \dots, \hat{\mathbf{e}}_{N_c}\}$. $v_\gamma^C(\mathbf{r}_I)$ and $b_\gamma^C(\mathbf{r}_I)$ are the Kohn–Sham effective potentials for the configuration γ in cluster C in the region around site I (see [6]).

Our *ab-initio* theory for including effects of short-ranged correlations between the orientational fluctuations $\{\hat{\mathbf{e}}_I\}$ can now be implemented as follows:

- Guess an initial set of probability weights, $P_c(\gamma)$ for the configurations $\{\gamma\}$ for a selected temperature T and value of external field.
- Carry out a DFT-KKR-NLCPA calculation for this system to produce the charge and magnetisation densities $\rho^C(\mathbf{r}_I; \gamma)$, $\mu^C(\mathbf{r}_I; \gamma)$ for all N_c sites I in the cluster and for all configurations, γ , together with the constraints $\mathbf{H}_{C, I}^{\text{cons}}$ to set the configurations.
- Calculate the $\omega_C(\gamma)$ according to equations (25) and (6). Hence a new set of probability weights, $P_c(\gamma)$'s is generated.
- Repeat the above steps (b) and (c) until a self-consistent solution is found.
- Calculate the required properties of the material. For example, for the paramagnetic state of a ferromagnetic metal, the regular ‘disordered local moment’ (DLM) picture will result if $P_c(\hat{\mathbf{e}}_1, \hat{\mathbf{e}}_2, \dots, \hat{\mathbf{e}}_{N_c})$ ends up as $\left(\frac{1}{4\pi}\right)^{N_c}$, which describes an equal uncorrelated chance of finding any configuration and the magnetisations (local moment magnitudes) $\mu^C(\mathbf{r}_I; \hat{\mathbf{e}}_1, \hat{\mathbf{e}}_2, \dots, \hat{\mathbf{e}}_{N_c}) = \mu^C(\mathbf{r}_I)$, are independent of configuration. If, on the other hand, we find that the configurations that have the highest weight are those where all the $\hat{\mathbf{e}}_I$ are aligned, it will show that local moments can only be established cooperatively on a cluster of sites. We investigate this scenario for nickel in the next section.

5. The ‘not so local’ moments of paramagnetic Ni

For many magnetic metals the usual DLM picture works well [12, 13]. The onset of magnetic order and transition temperatures is calculated reliably for many materials [17, 18] by the DLM-DFT formalism outlined in section 2, temperature dependent magnetic anisotropy can be quantitatively estimated [14] and guidance for tuning metamagnetic transitions in potential magnetic refrigerants given [19, 20] etc. In each case the starting point is the paramagnetic state where there is an equal chance of a ‘local moment’ pointing in any direction. The DFT for this scenario results in a local magnetisation magnitude, $\bar{\mu}$, being sustained self-consistently by a ‘local exchange splitting’ of the paramagnetic electronic structure [12]. In b.c.c. Fe, for example, $\bar{\mu}$ is nearly $2\mu_B$, close to the value of the saturation magnetisation per site at $T = 0$ K.

Nickel remains stubbornly resistant to this simple picture. No finite size local moment can be self-consistently supported and the paramagnetic state reduces to that of the conventional Stoner type [13]. So we investigate whether a local moment entity that persists on a small cluster of sites can emerge consistently from nickel’s interacting electrons instead using the ideas of the last section and hence form a basis for the understanding of its magnetism. To this end we study f.c.c. Ni and use our DFT-KKR-NLCPA theory where we divide the lattice in clusters of $N_c = 1, 2, 4, 8$ and 32 sites.

The application requires equation (25) for $\omega_C(\hat{\mathbf{e}}_1, \hat{\mathbf{e}}_2, \dots, \hat{\mathbf{e}}_{N_c})$ to be used in which constraining fields are included to set the local moment orientational configurations. There are charge and magnetisation densities for each impurity cluster associated with a specified N_c local moment orientational configuration $\gamma = \{\hat{\mathbf{e}}_i\}$. Carrying out steps from the end of the last section, where the configuration phase space of the orientations is adequately sampled, will in principle lead to an improved picture. For the paramagnetic state, one of the sites’ orientation, e.g. $\hat{\mathbf{e}}_1$, can be used as a reference and we can assume ω_C has no dependence on it. Averages are then taken over all

possible, equally weighted $\left(\frac{1}{4\pi}\right)$ orientations of $\hat{\mathbf{e}}_1$ to ensure a paramagnetic state. The relative orientations of the other sites are varied. Hence, above T_c , $\omega_c = \omega_c(\hat{\mathbf{e}}_1 \cdot \hat{\mathbf{e}}_2, \hat{\mathbf{e}}_1 \cdot \hat{\mathbf{e}}_3, \dots, \hat{\mathbf{e}}_1 \cdot \hat{\mathbf{e}}_{N_c})$, i.e. a function of how orientational vectors are aligned with an overall cluster orientation.

We have implemented a preliminary, ‘proof of principle’ scheme to see if it gives new insight into the magnetic fluctuations in the paramagnetic state of nickel. To this end, we start with $N_c = 2$ clusters and sample just the collinear configurations, e.g. $(\uparrow), (\downarrow)$ with equal probabilities $\left(\frac{1}{2}\right)$, ($\hat{\mathbf{e}}_1$ varies over all directions with probability $\left(\frac{1}{4\pi}\right)$). \uparrow means the two orientations are aligned, \downarrow —they are antiparallel. We find that neither configuration sustains a finite local cluster moment. This situation changes dramatically when we move to $N_c = 4$ clusters. We again sample the collinear configurations $(\uparrow, \uparrow, \uparrow), (\downarrow, \uparrow, \uparrow), (\uparrow, \downarrow, \uparrow), (\uparrow, \uparrow, \downarrow), (\downarrow, \downarrow, \uparrow), (\uparrow, \downarrow, \downarrow), (\downarrow, \uparrow, \downarrow), (\downarrow, \downarrow, \downarrow)$ starting with equal probabilities $\left(\frac{1}{2}\right)^3$. $\hat{\mathbf{e}}_1$ varies equally over all directions as before to describe the paramagnetic state. This time the only configuration that supports a finite local cluster moment is where all moments are aligned with each other, i.e. $(\uparrow, \uparrow, \uparrow)$. These cluster moments have a magnitude $0.43 \mu_B$ per site, 68% of the saturation magnetisation, M_s , per atom in the ferromagnetic state at $T = 0$ K. If larger clusters of eight contiguous sites are examined in the same way a local moment per site of $0.54 \mu_B$ establishes which is 85% of M_s saturation magnetisation of the ferromagnetic state. This increases to just $0.57 \mu_B$ for a 32 atom cluster.

We propose therefore that, above T_c in Ni, small clumps of 4–8 sites align the orientations of their moments with a clump-local spin-polarisation direction. The clump direction slowly fluctuates and captures the essence of the important collective electron magnetic fluctuations of paramagnetic Ni. Figure 2 shows the density of states for a cluster of eight sites embedded in the paramagnetic system which is spin polarised both parallel and anti-parallel to a local cluster moment orientation $\hat{\mathbf{e}}_1$. The overall electronic structure is not spin-polarised since an average over all directions is taken but figure 2 shows the source of a local exchange splitting in the electronic structure. A calculation of the paramagnetic susceptibility and the Curie temperature T_c is in progress which is based on an examination of the response of this model of the paramagnetic state of Ni to the application of a small magnetic field. The effect of conventional Stoner particle-hole excitations are also likely to affect the local cluster magnetisation and is being included.

6. Conclusions

Apart from at very low temperatures, it is often possible to extract out from all the interacting electrons of a material those electronic degrees of freedom which are fluctuating much more slowly than most of the others. These can

then be modelled as classical entities and their statistical mechanics written down, as long as a way of determining how the remaining electronic degrees of freedom depend on them can be found. In many magnetic materials fluctuating local moments associated with each atomic site naturally emerge from the electronic glue and the DFT-DLM method provides an *ab-initio* way of implementing this picture. We have illustrated this further here by describing the magnetocaloric effect in gadolinium which has local moments derived directly from the metal’s f-electrons. For some other materials it is more difficult to identify the pertinent slowly varying magnetic fluctuations. We have used the KKR-NLCPA method to test the idea that these fluctuations may be still be regions where a local magnetisation orientation can be defined but be comprised of a small number of atomic sites. In this paper we have described a tractable strategy for this task and have taken the first steps in implementing it in order to understand nickel’s magnetism better. We find that fluctuating local magnetic moments can emerge self-consistently in nickel’s paramagnetic state but that these form coherently over contiguous clusters of a small number of atomic sites. These disordered cluster moments affect the electronic structure sustaining them and consequently the metal’s properties. Work is now underway to calculate these details and to investigate how long range ferromagnetic order grows with decrease in temperature.

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