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The Onsager reaction field concept applied to the temperature dependent magnetic susceptibility of the enhanced paramagnets Pd and Pt

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Abstract

In this paper three different ways to calculate the temperature dependent susceptibility of the enhanced paramagnets Pd and Pt are presented and compared. Special attention is paid to the relative importance of one-particle and many-particle excitations. One of these methods has never been applied before to real itinerant systems. It is based upon Onsager's reaction field model, which seems to be a feasible and rigorous way to go beyond the mean field approximation, and it allows one to make quantitative statements. The backbone of this theory is the calculation of a temperature dependent Hubbard U due to thermal many-body excitations. In contrast to an earlier calculation we found a significant temperature dependence of U for Pd. The theoretical results are in fairly reasonable agreement with the experimental findings for both Pd and Pt.

1. Introduction

The temperature dependent magnetic susceptibility of enhanced paramagnets still attracts much interest and is studied extensively [1–7]. In this work three approaches are employed. One of the first microscopic treatments for the temperature dependence of the susceptibility was formulated within the framework of the Stoner theory. This theory essentially uses the density of states (DOS) of the material. The temperature dependence is provided by the derivative of the Fermi–Dirac distribution function and just one-particle excitations are considered. The only parameter needed is the Stoner parameter I , representing the interaction of electrons in a mean field manner.

A completely different approach is the phenomenological Murata–Doniach model. Nevertheless the underlying assumptions can at least be backed by more rigorous, microscopic

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considerations based upon a one-band Hubbard model [5]. In contrast to Stoner theory this approach emphasizes collective excitations.

During the course of our work, that is applying the three methods described above, we obtained quite reasonable results with the Stoner theory for the materials under consideration. According to common belief the relevant excitations are collective spin fluctuations as put forward by Moriya *et al* [8]. As will be shown, it is somewhat difficult to decide which approach—Stoner or spin fluctuation theory—is the better approximation.

Our new approach, using the Onsager reaction field theory, can give some hints for which cases the one-particle picture has to be corrected. The equation of the Onsager susceptibility is of exactly the same form as that of a mean field approximation. The only difference between the two approximations turns out to be the temperature dependence of the Hubbard parameter, i.e. $U = U(T)$. We use a self-consistent method to calculate $U(T)$ for enhanced paramagnets. Within the framework of this procedure a clear distinction between the one-particle effects and the collective effects is possible. One-particle properties simply enter through the DOS calculated within the local density approximation (LDA), whereas collective effects come into play through the correction of a mean field Hubbard U for the temperature range under consideration. The reaction field concept for itinerant electron magnetism [7] was developed in the same spirit as the self-consistent renormalization theory [8], and to the best of our knowledge we present the first quantitative results employing a theory like this. Another point is that we can compare two methods which take care of collective excitations. The first one is the classical Murata–Doniach (MD) model as already mentioned, the second one is the Onsager theory as a completely quantum mechanical description. Then both of them will be contrasted to the Stoner theory.

All calculations were done with realistic band structures and densities of states which were computed with the very accurate FLAPW method, using the Wien95 and Wien97 codes [9]. This is in contrast to the approaches of many authors who did calculations with nonrealistic models for the DOS. The investigations showed that the accuracy of the DOS is a decisive feature. The susceptibility is highly sensitive to even very small changes, for instance concerning the position of the Fermi energy. The above mentioned approaches will be described in more detail below. Beginning with the classical model we proceed to the more rigorous microscopic models.

2. Semi-empirical spin fluctuation theory—the Murata–Doniach approach

This section will give a brief account of the formulae that we apply to find the temperature dependent susceptibility within the classical MD model. The theory we actually use is an extension to the original work of Murata and Doniach. Details of this extended Murata–Doniach model can be found in former publications in this journal [2, 6]. For precursors of the extended Murata–Doniach model see [1, 10] and [11]. Some of the formulae we use for the numerical evaluations stem from a microscopic treatment [5]. In this context we mention the frequencies ω_{qv} of the spin fluctuations (SF), from which we get an expression for an indispensable cut-off wavevector q_c . This cut-off wavevector is parametrized by the Fermi wavevector k_F , which has to be adjusted in order to reproduce the experimental findings as well as possible.

All the calculations are performed within the framework of a classical model for the partition function

$$Z = \int D[\vec{m}(\vec{r})] e^{-\beta\gamma t[\vec{m}(\vec{r})]}. \quad (1)$$

The solid is considered as a continuous, isotropic medium. We are interested in the spin degrees of freedom only. A local deviation of the magnetization $\vec{m}(\vec{r})$ —a thermal excitation—at a place with homogeneous static magnetization \vec{M} leads to a total magnetization $\vec{M}(\vec{r}) = \vec{M} + \vec{m}(\vec{r})$. A system of equations that can easily be treated numerically reads:

$$\chi_{\text{SF}}^{-1}(\langle m^2 \rangle) = \frac{\sqrt{2/\pi}}{\langle m^2 \rangle^{3/2}} \int_0^\infty dm \left[\frac{B'(m)}{3} + \frac{2B(m)}{3m} \right] m^2 e^{-m^2/2\langle m^2 \rangle}, \quad (2)$$

$$\begin{aligned} \langle m^2 \rangle(T) &= \frac{k_{\text{B}} T V_{\text{c}}}{2\pi^2} \int_0^{q_{\text{c}}} dq \frac{q^2}{\chi_{\text{SF}}^{-1}(\langle m^2 \rangle) + \chi^{-1}(q) - \chi^{-1}(q=0)} \\ &= \frac{k_{\text{B}} T V_{\text{c}}}{2\pi^2} \int_0^{q_{\text{c}}} dq q^2 \chi_{\text{SF}}(T, q). \end{aligned} \quad (3)$$

In equation (2) the temperature dependence of χ^{-1} is implicitly given by $\langle m^2 \rangle$. Note the appearance of the cut-off wavevector q_{c} , which is indispensable for convergence of the q -space integral. Equation (2) also requires the knowledge of the wavevector dependent inverse susceptibility at $T = 0$. Calculations of this type have already been done by Stenzel and Winter [12]. We choose a parametrization

$$\chi^{-1}(q) = \chi^{-1}(T=0, q=0)(1 + \sigma^2 q^2), \quad (4)$$

where σ^2 serves to fit the *ab initio* calculation by Stenzel and Winter. The value of σ fitting the experimental curve equals $6.5 \frac{a}{2\pi}$. By use of the interpolation formula (4), equation (3) can be integrated leading to an analytical expression for $\langle m^2 \rangle(T)$.

2.1. Self-consistent cut-off wavevector

Equation (3) contains a cut-off wavevector in order to limit the integral. This cut-off is chosen in a self-consistent fashion for each temperature T . We take the maximum frequency $\omega_{q_{\text{c}}}$ for the spin fluctuations from the microscopic treatment [5]. This choice is essentially equal to a $T^{\frac{1}{3}}$ cut-off. The necessity of a temperature dependent $T^{\frac{1}{3}}$ cut-off was already mentioned by Moriya [8].

The third-order equation for q_{c} is numerically solved for each T :

$$\begin{aligned} \omega_{q_{\text{c}}} &= \left[\frac{V_{\text{c}} \mu_{\text{B}}^2 k_{\text{F}}^2 q_{\text{c}}}{2\pi^2} \right] \left(\chi_{(\text{SF})}^{-1}(T) + \frac{D q_{\text{c}}^2}{\mu_{\text{B}}^2} \right) \\ &= \text{const} \times k_{\text{B}} T. \end{aligned} \quad (5)$$

2.2. Computational details

The function $B(M)$ in equation (2) is obtained from a fixed spin moment method [13]. What we are interested in is the external field B for a given magnetization M of the unit cell. To this end the number of electrons in each of the two spin-split bands is fixed. M and $B(M)$ are given by the following expressions:

$$\begin{aligned} M &= \mu_{\text{B}}(n_{\uparrow} - n_{\downarrow}), \\ n_{\uparrow/\downarrow} &= \int_{-\infty}^{\epsilon_{\text{F}}^{\uparrow/\downarrow}} d\epsilon \rho_{\uparrow/\downarrow}(\epsilon), \\ B(M) &= \frac{\epsilon_{\text{F}}^{\uparrow} - \epsilon_{\text{F}}^{\downarrow}}{2\mu_{\text{B}}}. \end{aligned} \quad (6)$$

For each point on the $B(M)$ curve a complete band structure calculation has to be done. We use a mesh of 51 magnetization values M .

The basis of our calculations are the equations (2), (3) and

$$0 = q_c^3 + \frac{\mu_B^2}{D} \chi_{(\text{SF})}^{-1}(T) q_c - \frac{2\pi^2 k_B T}{V_c k_F^2 D}, \quad (7)$$

which results from rearranging (5).

3. The Stoner theory

One of the different possible ways leading to the formula for the Stoner susceptibility uses the partial summation of a subset of ring diagrams. In principle the susceptibility is a sort of density–density correlation function. Of course it is a two-particle correlation function. A single-ring diagram (bubble) will represent the Pauli susceptibility. Taking the limit $\vec{q} \rightarrow 0$ and $\omega \rightarrow 0$, long wavelength and the static approximation are reached.

Starting with a proper definition for the finite temperature correlation function, $\chi(\vec{q}, \omega)$ can be calculated from the retarded correlation function. Using

$$\begin{aligned} \chi^{zz}(\vec{q}, i\omega) &= \int_0^\beta d\tau \langle T_\tau m_z(\vec{q}, \tau) m_z(-\vec{q}, 0) \rangle, \\ m_z(\vec{q}, \tau) &= -\mu_B \sum_{\vec{k}, \sigma} \sigma c_{\vec{k}\sigma}^+ (\tau) c_{\vec{k}+\vec{q}\sigma} (0) \end{aligned} \quad (8)$$

we can go on to calculate the interaction-free susceptibility (denoted by the index 0) by invoking Wick's theorem to disentangle the time ordered operator product. We end up with a sum over a product of two free Green functions:

$$\begin{aligned} \chi_0^{zz}(\vec{q}, i\omega) &= -\mu_B^2 \frac{1}{\beta} \sum_{\vec{k}, \sigma, n} G_\sigma^0(\vec{k} - \vec{q}, i\omega_n - i\omega) G_\sigma^0(\vec{k}, i\omega_n) \\ &= \mu_B^2 \sum_{\sigma} \Lambda_0^{zz}(\vec{q}, i\omega, \sigma) \\ &= 2\mu_B^2 \Lambda_0^{zz}(\vec{q}, i\omega). \end{aligned} \quad (9)$$

$\Lambda_0^{zz}(\vec{q}, i\omega)$ —defined as the product over two free propagators and the summation over all the internal degrees of freedom—can be visualized by a single-bubble diagram. We are interested in the static limit $i\omega = 0$. Summing over the internal Matsubara frequencies $i\omega_n$ leads to [14]

$$\chi_0^{zz}(\vec{q}, i\omega = 0) = -2\mu_B^2 \sum_{\vec{k}} \frac{n_F(\epsilon_{\vec{k}}) - n_F(\epsilon_{\vec{k}+\vec{q}})}{\epsilon_{\vec{k}} - \epsilon_{\vec{k}+\vec{q}}}. \quad (10)$$

Taking the limit $\vec{q} \rightarrow 0$ in equation (10) we can change the summation into an integration over the DOS, and get the formula

$$\chi_0^{zz}(0, 0) = -2\mu_B^2 \int d\epsilon n(\epsilon) f'(\epsilon), \quad (11)$$

known as the Pauli susceptibility. For $T = 0$ it simply reduces to $2\mu_B^2 n(E_F)$. In order to go beyond the interaction-free theory we include a Hubbard interaction. A general vertex representing the interaction would be V_{klmn} , which in the Hubbard case reads

$$V_{klmn} = \frac{U}{N} \delta_{k+l, m+n} \delta_{\sigma_k \sigma_n} \delta_{\sigma_l \sigma_m} \delta_{\sigma_k - \sigma_l}. \quad (12)$$

Ensuring four-momentum and spin conservation in the Feynman diagrams we can simply use $\frac{U}{N} \equiv I$ for the wiggle representing the interaction. It is important to note that only in the case

of the longitudinal susceptibility can another vertex be attached to the bubble. In the case of the transverse susceptibility the bubble itself completely defines the susceptibility.

The next step is the summation of bubble diagrams representing $\Lambda_0^{zz}(\vec{q}, i\omega, \sigma)$, each of them connected to the other by an interaction wiggle $V_{\text{Hubbard}} = I$. Two consecutive bubbles must have opposite spin directions. The result for the static, longitudinal susceptibility is the well known formula [15]

$$\chi^{zz}(\vec{q}) = \frac{\chi_0^{zz}(\vec{q})}{1 - \frac{I}{2\mu_B} \chi_0^{zz}(\vec{q})}. \quad (13)$$

For the numerical applications we use equation (11) for χ_0^{zz} in (13), thus applying the long wavelength limit. The restrictions to the long wavelength limit and to the static limit are not real restrictions in the case of enhanced paramagnets. These materials show excitations as quasiparticles which are called paramagnons. These paramagnons show up for example as peaks in neutron scattering cross section experiments. The closer we are to $q = 0$ and $\omega = 0$ the more pronounced the peak becomes [17], defining the appearance of a paramagnon.

4. The Onsager concept

The idea is to go beyond Stoner theory for the longitudinal susceptibility. This will be achieved at least approximately by adding a correction term $\lambda(T)$ to U , thus giving an effective temperature dependent interaction parameter $U_{\text{eff}}(T)$.

The idea of a temperature dependent Stoner parameter $I(T)$ was already proposed in 1979 by Liu *et al* [16]. To our knowledge these authors were the first to combine the single-particle density of states with temperature dependent many-body effects. In their paper a general formula for the temperature dependent susceptibility was derived, which has exactly the form as the Stoner equation (13) presented above, with the additional feature of a temperature dependent interaction parameter. No special assumption concerning the form of the temperature dependent exchange–correlation was necessary. The approach [16] made use of a finite temperature spin density functional formalism, the essential feature being a free energy exchange correlation functional $F_{\text{xc}}(T)$.

The theory evaluated in this paper makes use of a temperature dependent free energy too. In the following we describe the steps to get a correction to the mean field free energy due to temperature dependent many-body effects. Finally we succeeded in treating real materials and making quantitative statements.

The molecular field \vec{B} felt by a spin is corrected by the Onsager reaction field B_{R} leading to $B_{\text{eff}} = \vec{B} - B_{\text{R}}$, taking into account that even for a paramagnet there is certainly some kind of short range correlation. Any spin will influence its own molecular field. For the Heisenberg model this concept has been known for some time [17]. The generalization to itinerant magnetism has been proposed only recently [7].

Starting from the concept described, a self-consistent, microscopic method can be developed to calculate the longitudinal susceptibility for itinerant metals, using the Hubbard U as the only parameter. A necessary input is the DOS of the material under consideration. The essential quantity to be calculated is the correction term $\lambda(T)$ which gives $U_{\text{eff}}(T) = U - \lambda(T)$. This is done numerically by calculating the second derivative of a free energy term $\Delta F(M, T)$. This $\Delta F(M, T)$ is in principle an exact supplement to a mean field free energy. For the actual calculation of $\Delta F(M, T)$ we make use of a rigid band approximation, which works very well for small values of the magnetization M , as will be shown.

We start with an expression for the total magnetization M due to an effective magnetic field B_{eff} , which includes the molecular field as well as the Onsager reaction field. We write

$$\begin{aligned} M &= \chi_0 B_{\text{eff}} \\ &= \chi_0 (B + \alpha M - \lambda M). \end{aligned} \quad (14)$$

Using the definition $\chi^{-1} = \frac{dB}{dM}$ for the inverse susceptibility we get

$$\begin{aligned} \chi^{-1} &= \chi_0^{-1} - \alpha + \lambda \\ &= \chi_{\text{mf}}^{-1} + \lambda, \end{aligned} \quad (15)$$

which defines the correction to the mean field susceptibility. Integrating (15) with respect to M (assuming λ to be independent of M , $\chi^{-1} = \frac{\partial^2 F}{\partial M^2}$) results in

$$\lambda = \frac{\partial^2 \Delta F}{\partial M^2}, \quad (16)$$

with the total free energy written as $F = F_0 + \Delta F$. Now the task is to get the free energy correction. This can be done in the framework of the Hubbard model. We use

$$\begin{aligned} \mathcal{H}(U) &= \mathcal{H}_0 + U \sum_i n_{i\uparrow} n_{i\downarrow} \\ &= \mathcal{H}_0 + \frac{U}{4} \sum_i (n_i^2 - m_i^2) \end{aligned} \quad (17)$$

with $n_i = n_{i\uparrow} + n_{i\downarrow}$ and $m_i = n_{i\uparrow} - n_{i\downarrow}$. Neglecting the first term in $\mathcal{H}(U)$ we are left with the magnetization dependent part of the Hamiltonian. This in turn can be rewritten with $s_i^z = \frac{1}{2}(n_{i\uparrow} - n_{i\downarrow})$ as

$$\mathcal{H}_{\text{int}} = -\frac{U}{2} \sum_i [s_i^z, s_i^z]_+. \quad (18)$$

A Fourier transformation yields a Hamiltonian which the fluctuation dissipation theorem can be applied to. Thus the susceptibility comes into play. We have ($\frac{U}{N} \equiv I$)

$$\begin{aligned} \langle \mathcal{H}_{\text{int}} \rangle &= -\frac{I}{2} \sum_{\vec{q}} \langle [s_z(\vec{q}), s_z(-\vec{q})]_+ \rangle, \\ \langle [s_z(\vec{q}), s_z(-\vec{q})]_+ \rangle &= \frac{1}{\pi} \int d\omega \coth\left(\frac{\omega}{2T}\right) \text{Im} \chi^{zz}(\vec{q}, \omega + i\eta), \\ \chi^{zz}(\vec{q}, \omega) &= i \int_0^\infty dt e^{i\omega t} \langle [s_z(\vec{q}, t), s_z(-\vec{q}, 0)]_- \rangle. \end{aligned} \quad (19)$$

The susceptibility χ^{zz} is defined as a retarded correlation function. With the help of a coupling constant integral [8] we get the desired ΔF [8]:

$$\begin{aligned} \Delta F(M, T) &= \int_0^I dI \left\langle \frac{\partial \mathcal{H}_{\text{int}}}{\partial I} \right\rangle_{M, I} \\ &= -\frac{1}{2} \int_0^I dI \sum_{\vec{q}} \langle [s_z(\vec{q}), s_z(-\vec{q})]_+ \rangle_{M, I} \\ &= -\frac{1}{2\pi} \sum_{\vec{q}} \int d\omega \int_0^I dI \coth\left(\frac{\omega}{2T}\right) \text{Im} \chi_{M, I}^{zz}(\vec{q}, \omega + i\eta). \end{aligned} \quad (20)$$

The statistical average is taken for certain values of M and I denoted by $\langle \rangle_{M, I}$. So far this is an exact treatment—in principle. Later on this formula will be the starting point for our numerical treatment. On setting $I = 0$ in $\chi_{M, I}^{zz}$, ΔF reduces to the mean field free energy.

Clearly the mean field part later on has to be subtracted in order to get the supplement for a mean field theory. For χ^{zz} we use

$$\chi^{zz} = \frac{\chi_0^{zz}}{1 - U\chi_0^{zz}}, \quad (21)$$

where we set $\frac{1}{2} = U$ (additionally $\mu_B^2 \equiv 1$ will be used henceforth). U is essentially a parameter which has to be chosen in a meaningful way. With this mean field form for χ^{zz} we get from equation (15) for the total susceptibility, now extended to depend on M ,

$$\chi_{M,U}^{zz}(\vec{q}, \omega) = \frac{\chi_{0,M}^{zz}(\vec{q}, \omega)}{1 - (U - \lambda)\chi_{0,M}^{zz}(\vec{q}, \omega)}. \quad (22)$$

The form of equation (22) results from (15) and will be called the Onsager susceptibility. The generalization of χ_0^{zz} to $\chi_{M,0}^{zz}$ is necessary for an evaluation of equation (20). Further approximations to equation (20) are necessary to get a practicable formula for the free energy. We make use of a high temperature approximation $\coth(\frac{\omega}{2T}) \approx \frac{2T}{\omega}$ and change the integration variable from dI to $\frac{U}{N} dx$ with $x \in [0, 1]$ and consequently $(U - \lambda) \rightarrow x(U - \lambda)$. With these changes we insert (22) into (20) and subtract the interaction-free $U = 0$ part. The ω integration is done by a principal value integration using the Kramers–Kronig relations. We get

$$\Delta F(M, T) = \frac{1}{\beta} \frac{1}{N} \sum_{\vec{q}} \frac{U}{U - \lambda} \ln[1 - (U - \lambda)\chi_{M,0}^{zz}(\vec{q}, 0)] + U\chi_{M,0}^{zz}(\vec{q}, 0). \quad (23)$$

Still a few more approximations are necessary. The \vec{q} dependence of $\chi_{M,0}^{zz}$ is taken into account in analogy to section 2 as [12]

$$\chi_{M,0}^{-1}(q) = \chi_{M,0}^{-1}(q = 0)(1 + \sigma^2 q^2). \quad (24)$$

We assume an isotropic system and change the summation to an integration over the first Brillouin zone. This results in

$$\begin{aligned} \Delta F(M, T) = & \frac{1}{\beta} \frac{V_c}{2\pi^2} \frac{U}{U - \lambda} \int_0^{q_{\text{BZ}}} dq q^2 \ln \left[1 - (U - \lambda) \frac{\chi_{M,0}^{zz}}{(1 + \sigma^2 q^2)} \right] \\ & + U \frac{1}{\beta} \frac{V_c}{2\pi^2} \int_0^{q_{\text{BZ}}} dq q^2 \frac{\chi_{M,0}^{zz}}{(1 + \sigma^2 q^2)}. \end{aligned} \quad (25)$$

The \vec{q} -space integration over the first Brillouin zone is approximated by an spherical average with the same volume. We use

$$q_{\text{BZ}} = \sqrt{\frac{3 \cdot 6\pi^2}{a^3}}. \quad (26)$$

At this point let us say some words concerning the simplifications we made in order to come to the final result, namely equation (25). The approximations of importance we should mention here are

- the high temperature approximation;
- the assumption of an isotropic system with a spherical Brillouin zone.

Concerning the high temperature approximation we have two aspects to be aware of. The first is a mathematical one. The application of the Kramers–Kronig relations obviously depends on the usage of the high temperature approximation, that is $\omega \ll k_B T$. But as we already mentioned, the excitation energy of the quasiparticle under consideration tends to zero where it shows up. Clearly this argument will break down at exactly $T = 0$, but in this case the correction to the free energy is equal to zero anyway (note that $\Delta F(M, T) \sim T$). For $T > 0$ it should be a reasonable approximation.

The second approximation deals with the assumption of an isotropic system. As we deal with paramagnets the magnetic moments will fluctuate at finite temperature but their fluctuations will be around vanishing moments. In this case the assumption of isotropy makes sense. Using a spherical boundary for the first Brillouin zone is of course a crude approximation for the shape of the Brillouin zone itself. But in our case it has nearly no influence. The reason is that a paramagnon is restricted to the region of $q = 0$, which in turn means that we expect the dominant contributions to the free energy integral around the vicinity of $q = 0$. In fact it can be shown by an expansion ($q \gg 1$) of the logarithmic part of the free energy that the resulting term just compensates the last one. This means that there should be no crucial contributions to the free energy correction from the border of the Brillouin zone. Additionally we tested it numerically, and we found our arguments convincingly confirmed.

4.1. Self-consistent determination of $\lambda(T)$

Equation (25), along with (16), is the basis for a self-consistent determination of $\lambda(T)$. Notice that $\lambda(T)$ enters both equations. We are interested in an evaluation of equations (25) and (16) in the vicinity of $M = 0$, because this is the region where paramagnons should contribute. The only input that enters equation (25) is the longitudinal free susceptibility for a certain value of magnetization, always at $I = 0$. In the case of $M = 0$, $I = 0$ and $T = 0$ one gets the Pauli susceptibility $2n(E_F)$.

Note that we are not restricted to zero temperature when we insert $\chi_{M,0}^{zz}$ into equation (25). This is an important point. The overall temperature dependence of equation (25) is not $\sim T$ resulting from the high temperature approximation. Instead using $\chi_{M,0}^{zz}(T)$, the temperature dependence becomes nonlinear.

Our attention is focused on the susceptibility for the general case where $M \neq 0$ and $T \neq 0$. A rigid band model is used where

$$\begin{aligned}\chi^{-1}(T) &= \frac{1}{4} \sum_{\sigma} \chi_{0,\sigma}^{-1}(T) - \frac{I}{2}, \\ \chi_{0,\sigma}(T) &= - \int d\epsilon f'_{\sigma}(\epsilon) n_{\sigma}(\epsilon).\end{aligned}\quad (27)$$

The spin sum represents the Pauli part. Including the $-\frac{I}{2}$ term would give the mean field correction, i.e. the Stoner susceptibility. With equation (27) we have

$$\chi_{M,I}^{-1}(T=0) = \frac{1}{4} \left(\frac{1}{n(E_F^+)} + \frac{1}{n(E_F^-)} \right) - \frac{I}{2}, \quad (28)$$

where \pm denote spin up and down. Setting $I = 0$ clearly leads to the interaction-free Pauli susceptibility (with $n(E_F^-) = n(E_F^+)$ for a paramagnet).

To get an idea of the quality of the rigid band approximation we compare a $B(M)$ curve calculated with the FSM method to a $B(M)$ curve calculated for $T = 0$ with the formulae

$$\begin{aligned}B(M) &= \frac{E_F^+ - E_F^-}{2} - \frac{IM}{2}, \\ \chi_{M,I}^{-1} &= \frac{\partial B(M)}{\partial M}.\end{aligned}\quad (29)$$

It is important to realize that the Fermi energies depend on the magnetization. At least for small values of M this should be in reasonable agreement with a fully self-consistent $B(M)$ curve of section 2. The value of I which we have to use in (29) for a meaningful comparison stems from

$$I = 2(\chi_{M=0,I=0}^{-1} - \chi_{M=0,I}^{-1}), \quad (30)$$

evaluated at zero temperature. $\chi_{M=0,I}^{-1}$ has to be calculated from the output of a FSM calculation of section 2 in combination with (29), in the neighbourhood of small M , thus actually from the differential quotient. This results in quite reasonable values for I . It is remarkable that the two different $B(M)$ curves agree even for higher values of M , as can be seen in figure 1.

For $T \neq 0$ it is necessary to calculate the chemical potential $\mu_\sigma(T_i)$ for the Fermi distribution function f . Practically this is done by solving the equations

$$\begin{aligned} \int d\epsilon f_+(\epsilon)n(\epsilon) - \frac{N+M}{2} &= 0, \\ \int d\epsilon f_-(\epsilon)n(\epsilon) - \frac{N-M}{2} &= 0. \end{aligned} \quad (31)$$

N defines the total number of valence electrons for the material. These equations have to be solved for each temperature $T = T_i$ and the chemical potential $\mu_\sigma(T_i)$ is inserted in (27).

We evaluate equation (25) and its second derivative $\lambda(T)$ (16) with the help of the temperature dependent Pauli susceptibility at small values of M . For the second derivative near $M = 0$ the numerics is done with three consecutive values of a small M .

4.2. The self-consistency cycle

First of all we have to choose a value for U . There are different methods for getting the interaction parameter. One member of our group calculated the Stoner I for palladium and platinum [18] with the method of Janak [19] and the method of Gunnarson [20]. The results for palladium are 5.16×10^{-2} and 5.33×10^{-2} Ryd, respectively. The value of the parameter I used in the present paper is very close to the last one. Another possibility for getting $U \equiv \frac{I}{2}$ would be to use equation (30). Using either one of these methods makes a fitting of the interaction parameter superfluous. Nevertheless we feel free to use the interaction parameter as a fit parameter, because the values of *ab initio* methods obviously differ too much.

Now for three values of M (near $M = 0$) a self-consistency cycle runs as follows: for each T_i we calculate the free energy (25) and then take the second derivative with respect to M in order to get $\lambda(T)$. Then $\lambda(T)$ is inserted back into the expression for the free energy. This procedure is repeated until convergence is reached for each T .

We end up with $\lambda(T)$ for the temperature range under consideration. Finally the temperature dependent Onsager susceptibility is given by

$$\chi_{\text{ons}}(T) = \frac{\chi_{\text{p}}(T)}{1 - U(T)\chi_{\text{p}}(T)} \quad (32)$$

where $U(T) = U - \lambda(T)$ and χ_{p} means the Pauli susceptibility.

5. Results

The experimental values were taken from [21, 22] and [23]. All results presented in this section are based on FLAPW calculations. There are different possibilities for doing the band structure calculations. Many authors use the experimental lattice constant for their calculations. In our opinion this is inconsistent with the fact that band structures are (usually) calculated at $T = 0$. So we decided to use the equilibrium lattice constants as derived from the LAPW program ($a = 7.264$ au for Pd, $a = 7.365$ for Pt). 1059 k -points were used in the irreducible part of the Brillouin zone. All our computations use the scalar relativistic option. Figures 2–9 show the results for Pd, figures 10–12 those for Pt.

Figure 1 gives an impression of the validity of the rigid band model that we use for the Onsager theory. We compare a self-consistent fixed spin moment calculation with a much

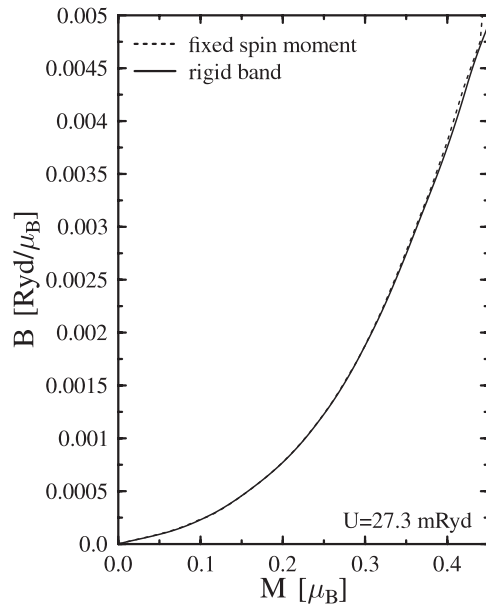


Figure 1. $B(M)$ from a rigid band model compared to a fixed spin moment calculation for Pd.

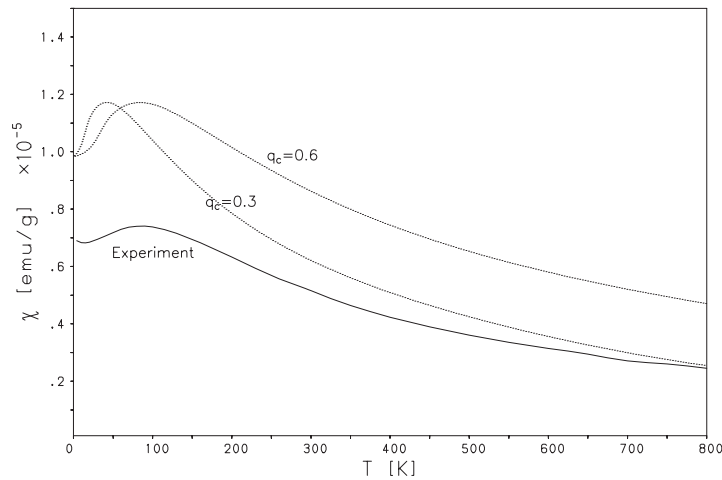


Figure 2. $\chi(T)$ from classical spin fluctuation theory. Two different cut-offs are used. Results for Pd.

simpler rigid band shift. The agreement is very convincing up to even relatively large values of magnetization.

Figure 2 shows the results from the classical spin fluctuation theory of section 2. The overall agreement of the SF curve with the characteristics of the experimental curve is satisfying. Nevertheless there is a strong dependence of the results on the choice of the cut-off vector for the q -space integration. This makes it quite difficult to compare the theory to the experiment. One common way to choose the cut-off is to force the theoretical curve to match the experimental one at high temperatures because the theory makes use of the high temperature approximation.

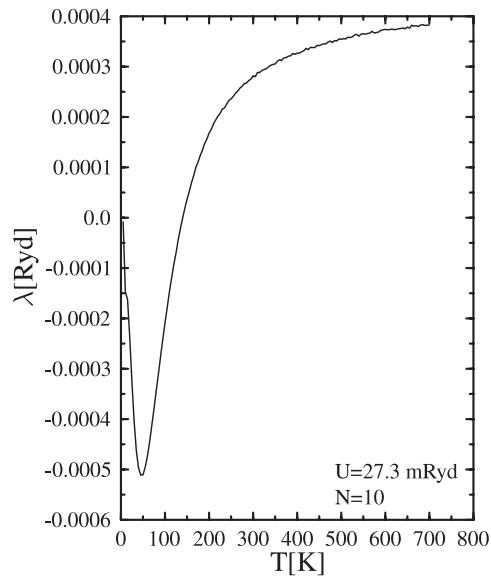


Figure 3. The correction factor $\lambda(T)$ for a calculated U value for Pd.

Figure 3 shows the temperature dependence of the correction factor λ with a value for U calculated with equation (30). Thus there is no fit parameter at all. It has to be emphasized that the temperature variation of λ is very delicate. Liu *et al* [16] could not find a variation of $I(T)$ which was strong enough to reproduce the experimental curve, claiming that a variation of $\approx 2\%$ (in a temperature range from 0 to 300 K) seems to be necessary (Pd). That is exactly in accordance with what we found, namely a variation of $\lambda(T)$ in that temperature range of $\approx 1.5\%$ relative to the values of the Stoner factor for $T = 0$. It depends somewhat on the value of U that one uses (compare figures 3 and 4).

Figures 5 and 6 show the results obtained with the Stoner and Onsager theory, respectively. The Stoner theory obviously gives quite reasonable results. This seems to stress the importance of single-particle effects, which enter the band structure DOS. The experimental characteristics are reproduced quite well, whereas the temperature of the maximum is somewhat too high (≈ 115 K). Inclusion of the temperature dependence of U gives a lower temperature of the maximum (20 K off experiment), but the absolute value of χ is exaggerated if the calculated interaction parameter is used. By choosing a smaller U we can remedy this disagreement, thus treating U as a fit parameter. The value of U drastically influences the absolute values of χ , but the position of the maximum is apparently unaffected.

The results are highly sensitive to the structure of the density of states near E_F (see figure 9). In order to show this, we shifted E_F by changing the number of electrons in our calculations. Using 9.99 instead of 10 electrons we get the results shown in figures 7 and 8.

The results for Pt are similar to those for Pd ‘grosso modo’. Yet there are some striking differences in detail. As can be seen in figure 11 the minimum value for the correction term λ is roughly one order of magnitude smaller compared to that for Pd. As a consequence the influence of λ on the Onsager susceptibility is much less pronounced. Another important feature of Pt is the density of states near E_F (see figure 10). The number of states there is much smaller compared to Pd, whereas the value for U (25.2 mRyd for Pt) is about the same. This means a much smaller enhancement factor for Pt, thus making Pt much less sensitive.

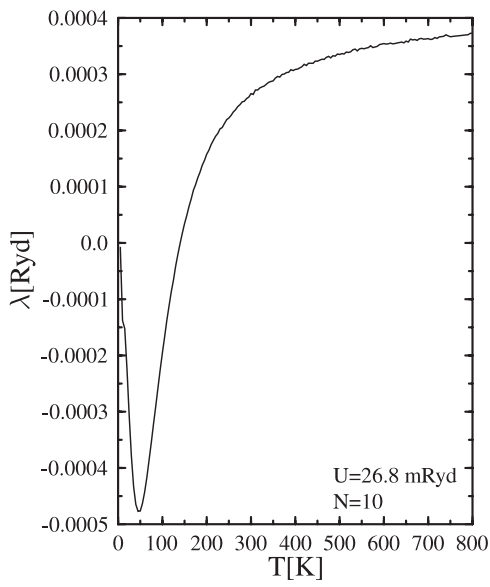


Figure 4. The correction factor $\lambda(T)$ for a smaller value of U for Pd.

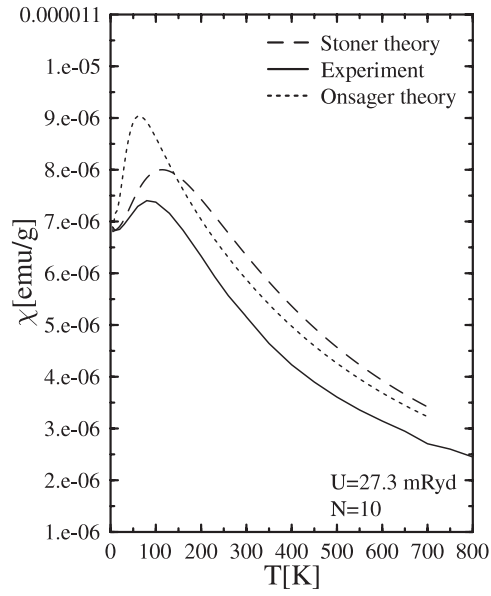


Figure 5. $\chi(T)$ based on a calculated U for Pd.

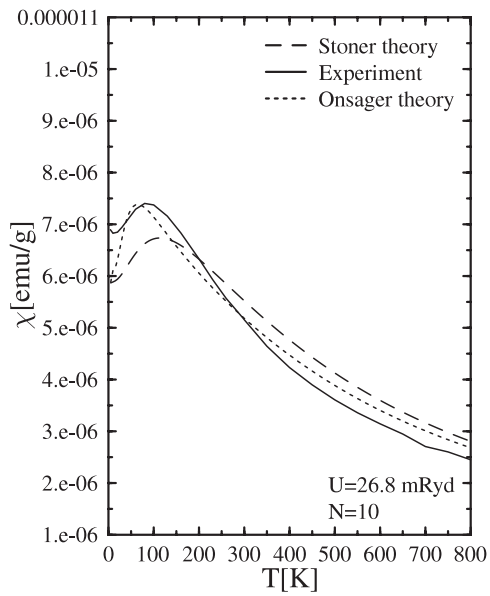


Figure 6. $\chi(T)$ based on a fitted U for Pd.

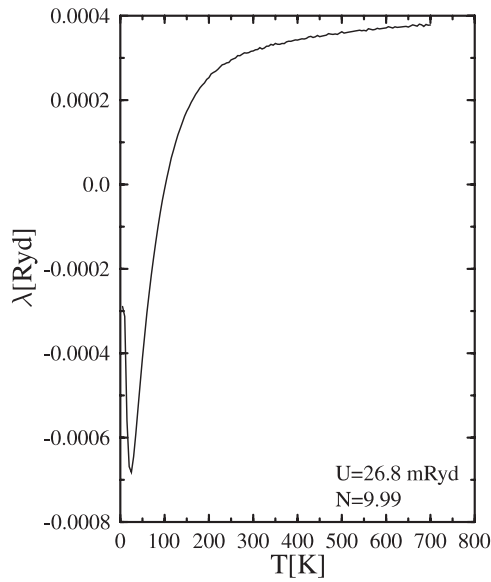


Figure 7. $\chi(T)$ with a shifted Fermi energy for Pd.

Figure 12 shows the results for Pt. As expected, the correction due to a temperature dependent U is apparently non-existent. In this case the Stoner theory is a very good description.

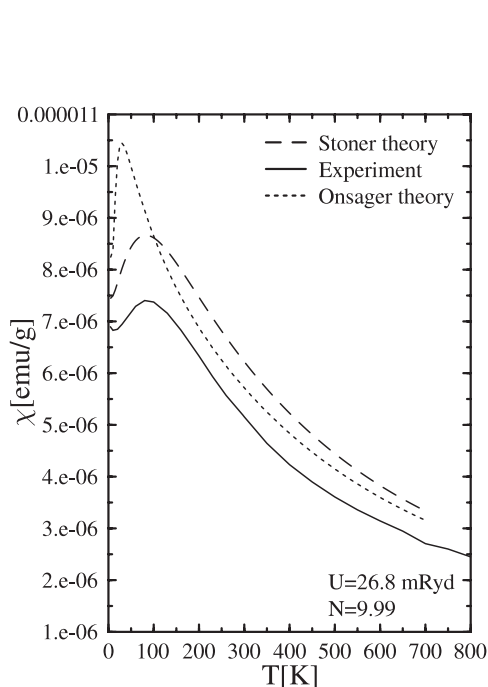


Figure 8. $\chi(T)$ based on a shifted Fermi energy for Pd.

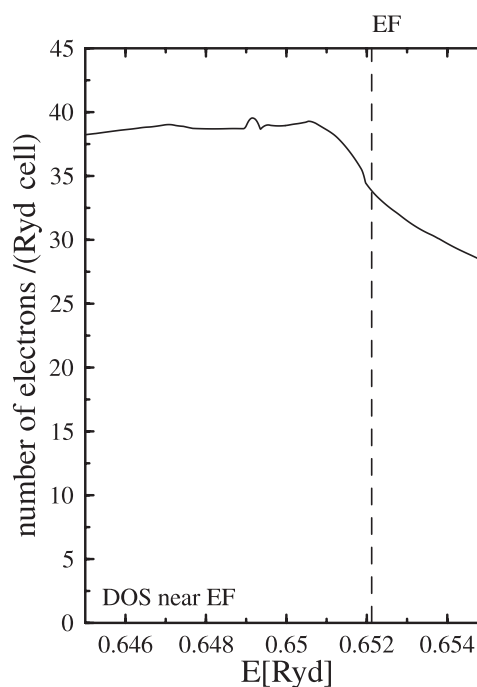


Figure 9. The density of states for Pd.

6. Discussion and conclusions

In this paper the influence of thermal many-body excitations (spin fluctuations) on the temperature dependence of the susceptibility was investigated. We have applied three different models to compute the temperature dependent susceptibility of Pd and Pt. The classical spin fluctuation theory is basically capable of reproducing the significant maximum in the temperature dependence of the susceptibility. Nevertheless the results are not quite satisfactory, because the dependence of the results on the cut-off parameter seems to be a severe problem, which limits the predictive power of this theory considerably.

The Stoner theory is a simple and rigorous theory. The only input needed is the density of states. Calculating *ab initio* values for I there are no other parameters at all. The results show that the Stoner theory gives good results for both Pd and Pt.

Using the Onsager concept we performed realistic calculations of the temperature dependent interaction parameter $U(T)$. We found out that U changes only little ($\approx 0.75\%$) in the temperature range of interest. These changes can be ascribed to spin fluctuations. Though very small, they have a significant influence on the temperature behaviour for Pd. The Onsager concept turns out to be a theory which makes it easy to distinguish between one-particle excitations and many-body excitations. This kind of distinction is somewhat difficult within the framework of the classical spin fluctuation theory. Altogether we could show that the temperature dependence of the susceptibility is a very intricate interplay of one-particle and many-body effects. The many-body excitations are strongly influenced by single-particle effects, as expressed by equation (23).

In our opinion it is somewhat difficult to decide whether there is a real need to invoke many-body excitations to explain the typical temperature dependence of the susceptibility.

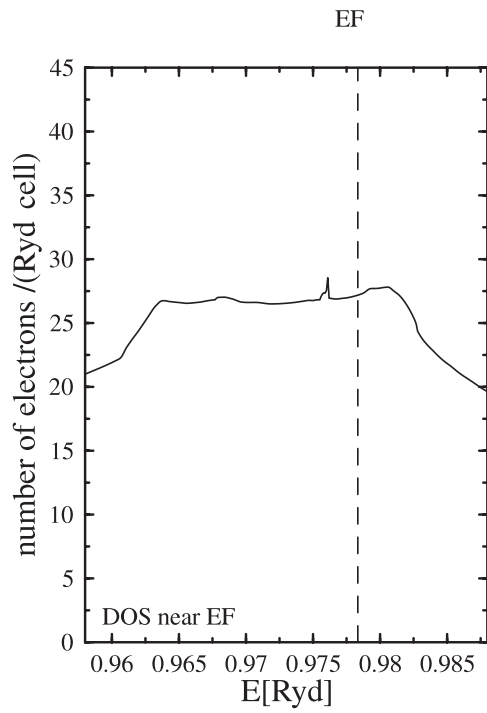


Figure 10. The density of states for Pt.

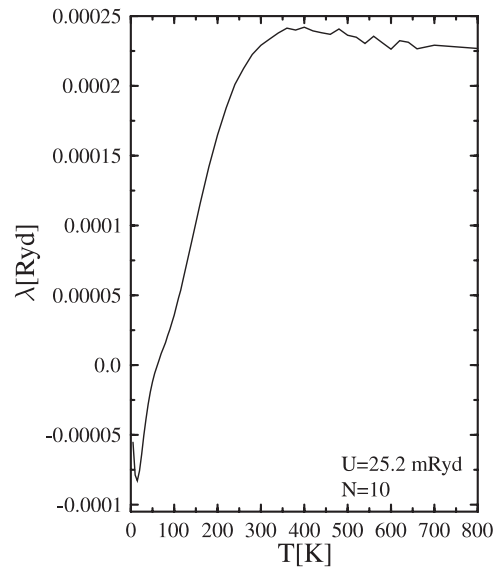


Figure 11. $\lambda(T)$ for Pt.

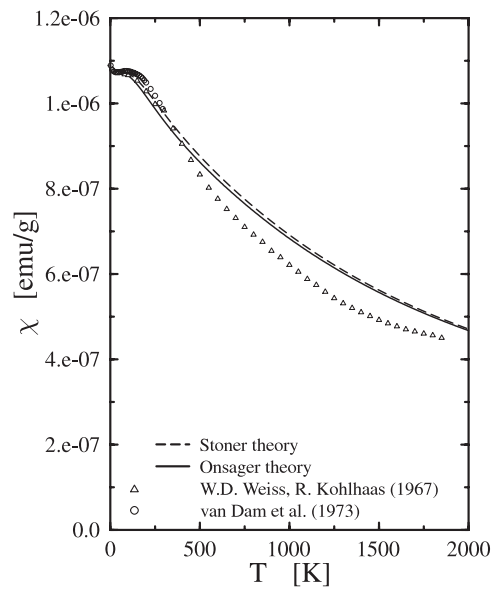


Figure 12. $\chi(T)$ for Pt.

Nevertheless our results for Pd give us some important hints concerning the influence of spin fluctuations for Pd and Pt. That is:

- Spin fluctuations shift the position of the maximum to lower temperatures. The Onsager maximum appears at about 65 K compared to about 115 K with the Stoner theory. The experimental maximum shows up at 85 K.
- The influence of spin fluctuations is much less pronounced for Pt than for Pd; this can be seen from the absolute values for λ .
- Within the Onsager theory we can understand our surprisingly good agreement of the Stoner theory with the experimental findings. This is obviously because of the small absolute change of the interaction strength U as a function of the spin–spin correlation for $T \neq 0$.

Also we made real progress by dealing with spin fluctuations within the framework of the Onsager theory compared to the treatment with the classical Murata–Doniach model. At this point we should mention:

- The Onsager theory is a completely quantum mechanical description.
- There is no need to invoke a cut-off wavevector which shifts the maximum temperature as well as changing the shape of the theoretical curve. Within the Onsager theory the maximum appears as a stable effect.
- Compared to the Murata–Doniach model we have a much better agreement with the experimental curve.
- Last but not least, the Onsager theory provides a feasible way to do calculations for realistic materials. The computational effort is basically not much different to that of band structure calculations.

As we have shown, the sensitivity of the calculations to tiny changes in e.g. E_F is very high.

So it might be possible that just more accurate band structure calculations will lead to even better results in the framework of the Stoner theory. The explanation of the temperature behaviour of the susceptibility of Pd without spin fluctuations was already proposed by Irkhin *et al* [24].

Acknowledgments

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References

- [1] Murata K K and Doniach S 1972 *Phys. Rev. Lett.* **29** 285
- [2] Kirchner B, Weber W and Voitländer J 1994 *J. Phys.: Condens. Matter* **6** 2603
- [3] Pamyatnykh E, Poltavets A and Shabalin M 1997 *J. Phys.: Condens. Matter* **9** 715
- [4] Bai Y, Ryu C, Kim C, You S and Nahm K 1996 *Phys. Rev. B* **54** 33
- [5] Weber W, Kirchner B and Voitländer J 1994 *Phys. Rev. B* **50** 1090
- [6] Kirchner B, Weber W and Voitländer J 1992 *J. Phys.: Condens. Matter* **4** 8097
- [7] Cyrot M and Kaga H 1997 *Phys. Rev. Lett.* **77** 5134
- [8] Moriya T 1982 *Spin Fluctuations in Itinerant Electron Systems (Springer Series Solid-State Sciences vol 56)* (Berlin: Springer)
- [9] Blaha P, Schwarz K, Dufek P and Augustyn R WIEN95
Blaha P, Schwarz K and Luitz L 1999 *WIEN97, A Full Potential Linearized Augmented Plane Wave Package for Calculating Crystal Properties* ed K Schwarz (Techn. Univ. Wien. Vienna ISBN 3-9501031-0-4)
Blaha P, Schwarz K and Luitz L 1990 *Comput. Phys. Commun.* **59** 339 (updated version)
- [10] Wagner D 1989 *J. Phys.: Condens. Matter* **1** 4635

- [11] Mohn P and Schwarz K 1992 *J. Magn. Magn. Mater.* **104–107** 685
- [12] Stenzel E and Winter H 1986 *J. Phys. F: Met. Phys.* **16** 1789
- [13] Singh D J 1994 *Planewaves, Pseudopotentials and the LAPW Method* (Dordrecht: Kluwer)
- [14] Mahan G D 1981 *Many-Particle Physics* (New York: Plenum) p 157
- [15] White R M 1983 *Quantum Theory of Magnetism (Springer Series in Solid-State Sciences vol 32)* 2nd edn (Berlin: Springer) p 132
- [16] Liu K L, MacDonald A H, Daams J M and Vosko S H 1979 *J. Magn. Magn. Mater.* **12** 43
- [17] Fulde P 1995 *Electron Correlations in Molecules and Solids (Springer Series in Solid State Sciences vol 100)* 3rd edn (Berlin: Springer) pp 245–51
- [18] Deng M 1997 unpublished results, University of Munich
- [19] Janak J F 1977 *Phys. Rev. B* **16** 255
- [20] Gunnarson O 1976 *J. Phys. F: Met. Phys.* **6** 587
- [21] Weiss W D and Kohlhaas R 1967 *Z. Angew. Phys.* **23** 175
- [22] Jamieson H C and Manchester F D 1972 *J. Phys. F: Met. Phys.* **2** 323
- [23] Van Dam J E, Gubbens P C M and Van Den Berg G J 1973 *Physica* **70** 520
- [24] Irkhin Y P, Noskova L M and Rozenfeld E V 1984 *Sov. Phys.—Solid State* **26** 475