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# A method for the calculation of spin susceptibilities of itinerant systems for finite temperature

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**Abstract.** The temperature dependence of the magnetic properties of itinerant electron systems is mainly due to the excitation of spin fluctuations. In order to describe the energy of the spin fluctuation field, we use a functional that treats the fluctuation modes in the static limit and that includes the energy of the coupling between different modes in a local, i.e. wavevector-independent, way. We derive formulae for the free energy and the susceptibility of the system along the lines of the Murata–Doniach approach. Our energy functional is quite general, going beyond the Ginzburg–Landau expansion. It is possible to deal with arbitrary fluctuation amplitudes. Furthermore, the energy functional can be completely derived from first-principles calculations for the ground state of the system. Thermodynamic properties may thus be traced back to details of the band structure. We apply our method to the calculation of the temperature dependence of the susceptibility of Pd metal.

## 1. General theory

With the present state of spin fluctuation theory, magnetic properties of weakly correlated systems can be calculated from ground-state data obtained by band-structure calculations [1]. In this section, we briefly summarize the spin fluctuation theory first presented by Murata and Doniach [2]. The presentation is similar to a paper of Wagner [3].

Assuming isotropy of the system, the Hamiltonian may be written

$$\mathcal{H}(M,\{m(r)\}) = \int \mathrm{d}^3r\ E(M+m(r)) + \frac{1}{2}\int\int \mathrm{d}^3r\ \mathrm{d}^3r'\ \chi^{-1}(r-r')[m(r)m(r')-m^2(r)]. \tag{1}$$

Here $M$ indicates the homogeneous macroscopic magnetization and $m(r)$ the thermally induced fluctuations of the magnetization. Local mode–mode coupling is exactly taken into account through a local energy functional in the first term of (1), while non-local effects are approximated by a quadratic form in the fluctuating field, with the inverse susceptibility as a coupling function.

The system is completely characterized by the canonical partition function

$$Z = \int \mathcal{D}[m]\, \mathrm{e}^{-\beta\mathcal{H}(M,\{m\})} \tag{2}$$

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or, equivalently, by the free energy

$$F = -k_B T \ln Z \ . \tag{3}$$

In order to obtain analytical expressions, the Hamiltonian is approximated by a quadratic form in the magnetic fluctuations:

$$\mathcal{H}_0 = \sum_{i=1}^{3} \int\int \mathrm{d}^3 r \, \mathrm{d}^3 r' \, \Omega_i(r - r') m_i(r) m_i(r') \ . \tag{4}$$

The Peierls inequality sets an upper boundary for the free energy:

$$\begin{aligned} F &\leqslant F_0 + \langle \mathcal{H} - \mathcal{H}_0 \rangle \\ &= \int \mathrm{d}^3 r \, \langle E(M + m(r)) \rangle - \frac{k_B T}{2} \sum_{i,q} \left[ 1 + \ln \left( \frac{\pi}{2V \beta \Omega_{q,i}} \right) \right] \\ &\quad + \frac{k_B T}{4} \sum_{i,q} \frac{\chi^{-1}(q) - \chi^{-1}(0)}{\Omega_{q,i}} . \end{aligned} \tag{5}$$

The Fourier-transformed quantities

$$m_i(r) = \sum_q m_{q,i} \mathrm{e}^{\mathrm{i}qr} \qquad \Omega_i(r) = \frac{1}{V} \sum_q \Omega_{q,i} \mathrm{e}^{\mathrm{i}qr} \tag{6}$$

were used in (5), with $V$ as the volume of the macroblock; $\langle\,\rangle$ denotes the statistical mean with respect to the distribution function $(1/Z_0)\mathrm{e}^{-\beta \mathcal{H}_0}$.

Because of the translational invariance of $\mathcal{H}_0$, the average of an arbitrary function of $m$ is independent of the position vector $r$. It will be shown later that the result of the averaging process depends only on the three components of the mean-square fluctuations $\langle m_i^2 \rangle$.

The optimal frequencies $\Omega_{q,i}$ can be found by minimizing the right-hand side of (5), yielding

$$\Omega_{q,i} = \frac{\partial \langle E(M + m) \rangle}{\partial \langle m_i^2 \rangle} + \tfrac{1}{2} (\chi^{-1}(q) - \chi^{-1}(0)) \ . \tag{7}$$

The mean square of the fluctuations $\langle m_i^2 \rangle$ is related to the $\Omega_{q,i}$ through

$$\langle m_i^2 \rangle = \frac{k_B T}{2V} \sum_q \frac{1}{\Omega_{q,i}} \ . \tag{8}$$

Equations (7) and (8) determine the quantities $\langle m_i^2 \rangle$. To restrict the summation in (8), a cutoff wavevector is introduced in practical calculations. This is a shortcoming of the static approximation, which is based on the high-temperature limit $k_B T / \hbar\omega$ for the occupation number of the fluctuation modes.

In what follows we identify the optimized right-hand side of (5) with the free energy $F$. The inverse susceptibility of a paramagnetic system is obtained by taking the second derivative of $F$ with respect to $M$ at $M = 0$. Partial derivatives of $F$

with respect to $\Omega_{q,i}$ vanish due to the minimization procedure, and the expression for the inverse susceptibility reduces to

$$\chi^{-1} = \frac{\mathrm{d}}{\mathrm{d}M_i}\left(\frac{\partial}{\partial M_i}\langle E(M+m)\rangle\right)_{M=0}. \tag{9}$$

The subscript $i$ indicates a component of the magnetization.

The functional integration in the thermal average of the energy functional $\langle E(M+m)\rangle$ poses a difficult problem. Several authors [1–6] use a Landau expansion of $E(M)$, since the Gaussian average of any power of $m_i$ can be expressed by a power of $\langle m_i^2\rangle$. As mentioned before, data for $E(M)$ can be obtained from band-structure calculations for various values of $M$ with the fixed-spin moment method (FSM) [7,8]. To transform the numerical $E(M)$ data to the form of a Landau polynomial, fitting procedures have to be applied. The fit coefficients, however, depend strongly on details of the graph of $E(M)$ and, furthermore, on the $M$ range over which it is fitted. The coefficients of low order are not stable, if higher orders for the expansion are taken into account. In the following we present an exact formula in which the multidimensional phase-space integration in $\langle E(M+m)\rangle$ is replaced by a three-dimensional integral.

## 2. Exact treatment of the averaging process

The general formula for the averaged energy density is given by

$$\langle E(M+m(0))\rangle = \frac{1}{Z_0}\int \mathcal{D}[m]\, E(M+m(0))\, \mathrm{e}^{-\beta\mathcal{H}_0(M,\{m\})}. \tag{10}$$

Because of translational invariance of the mean value, evaluation at the origin of space does not mean any loss of generality. We write the magnetic field in its Fourier representation

$$M + m(r=0) = M + \sum_q m_q = M + 2\sum_{q_z>0} x_q \tag{11}$$

where

$$m_q = x_q + \mathrm{i}y_q.$$

Since $m(r)$ is real, only the real parts of the Fourier coefficients appear in equation (11). The term $\sum_{q_z>0}$ denotes summation over the positive semispace. In these terms we get

$$\langle E(M+m)\rangle = \left[\int \prod_{q_z>0} \mathrm{d}^3x_q \mathrm{d}^3y_q\, E\left(M+2\sum_{q_z>0}x_q\right)\exp\left(-2\beta V\sum_{i,q_z>0}\Omega_{qi}(x_{qi}^2+y_{qi}^2)\right)\right]$$
$$\times\left[\int\prod_{q_z>0}\mathrm{d}^3x_q\mathrm{d}^3y_q\exp\left(-2\beta V\sum_{i,q_z>0}\Omega_{qi}(x_{qi}^2+y_{qi}^2)\right)\right]^{-1} \tag{12}$$

where integrals over $y_{q,i}$ can immediately be eliminated.

The following relation holds for any function $f$:

$$\left[\int \prod_q \mathrm{d}x_q f\left(\sum_q x_q\right) \exp\left(-\sum_q a_q x_q^2\right)\right]\left[\int \prod_q \mathrm{d}x_q \exp\left(-\sum_q a_q x_q^2\right)\right]^{-1}$$
$$= \left(\int_{-\infty}^{+\infty} \mathrm{d}x f(x) \mathrm{e}^{-x^2/2\langle x^2\rangle}\right)\left(\int_{-\infty}^{+\infty} \mathrm{d}x \mathrm{e}^{-x^2/2\langle x^2\rangle}\right)^{-1}. \tag{13}$$

Here $\langle x^2\rangle$ means

$$\langle x^2\rangle = \left[\int \prod_q \mathrm{d}x_q \left(\sum_q x_q\right)^2 \exp\left(-\sum_q a_q x_q^2\right)\right] \exp\left[\int \prod_q \mathrm{d}x_q \exp\left(-\sum_q a_q x_q^2\right)\right]^{-1}.$$

The validity of (13) can be shown by induction over the number of integration variables. Taking the integrand of (12) successively as a function of $\sum_q x_{q,i}$, with $i=1,2,3$, and applying (13) three times, we get

$$\langle E(M+m)\rangle = \left(\prod_{i=1}^{3} \sqrt{2\pi\langle m_i^2\rangle}\right)^{-1} \int \mathrm{d}^3 m\, E(M+m) \exp\left(-\frac{1}{2}\sum_i \frac{m_i^2}{\langle m_i^2\rangle}\right). \tag{14}$$

The mean-square fluctuations of component $i$ are given by

$$\langle m_i^2\rangle = 4\left[\int \prod_{q_z>0} \mathrm{d}x_{q,i} \left(\sum_{q_z>0} x_{q,i}\right)^2 \exp\left(-2\beta V \sum_{q_z>0} \Omega_{qi} x_{qi}^2\right)\right]$$
$$\times \left[\int \prod_{q_z>0} \mathrm{d}x_{q,i} \exp\left(-2\beta V \sum_{q_z>0} \Omega_{qi} x_{qi}^2\right)\right]^{-1}. \tag{15}$$

It is obvious from equation (14), that the expectation value $\langle E(M+m)\rangle$ depends only on the three components of the mean-square fluctuations $\langle m_i^2\rangle$ and on $M$. Equation (9) can therefore be rewritten:

$$\chi^{-1} = \frac{\partial^2}{\partial M_i^2}\langle E(M+m)\rangle\Big|_{M=0} + \sum_j \frac{\partial^2\langle E(M+m)\rangle}{\partial\langle m_j^2\rangle \partial M_i} \frac{\partial\langle m_j^2\rangle}{\partial M_i}\Big|_{M=0}. \tag{16}$$

Using equation (14) it can be shown that

$$\frac{\partial\langle E(M+m)\rangle}{\partial\langle m_i^2\rangle} = \frac{1}{2}\frac{\partial^2\langle E(M+m)\rangle}{\partial M_i^2}. \tag{17}$$

For isotropic systems $E$ depends only on $|M|^2$. Hence the second term of equation (16) vanishes for the case $M = 0$, i.e. for a paramagnetic system. After transformation to polar coordinates an expression for the temperature-dependent inverse susceptibility is obtained from equations (14) and (16):

$$\chi^{-1}(\langle m^2\rangle) = \frac{4\pi}{3(2\pi\langle m^2\rangle)^{3/2}} \int_0^{\infty} \mathrm{d}m\, [m^2 E''(m) + 2m E'(m)] \mathrm{e}^{-m^2/2\langle m^2\rangle} \tag{18}$$

where

$$\langle m^2 \rangle = \langle m_1^2 \rangle = \langle m_2^2 \rangle = \langle m_3^2 \rangle \ .$$

To calculate $\langle m^2 \rangle$, we insert equations (7), (16) and (17) in (8). When the wavevector sum is replaced by an integral, we finally obtain

$$\langle m^2 \rangle = \frac{k_B T}{2\pi^2} \int_0^{q_c} \mathrm{d}q \, \frac{q^2}{\chi^{-1}(T, q=0) + \chi^{-1}(T=0, q) - \chi^{-1}(0,0)}. \tag{19}$$

The cut-off wavevector $q_c$ is the only free parameter of the theory and has to be adjusted to experimental data. The wavevector-dependent susceptibility for $T = 0$ is accessible, like the $E(M)$ data, from band-structure calculations or from neutron-scattering measurements.

For a given temperature $T \neq 0$, equations (18) and (19) can be solved for $\chi^{-1}$ and $\langle m^2 \rangle$ by an iterative procedure. Alternatively, and easier to implement, a set of $\langle m^2 \rangle$ values can be chosen to calculate the corresponding $\chi^{-1}(\langle m^2 \rangle)$ and $T(\langle m^2 \rangle)$.

## 3. Results

Formulae (18) and (19) were taken to calculate the temperature-dependent spin susceptibility of Pd metal. The experimental susceptibility of Pd against temperature shows a small maximum at about 85 K [9,10]. In our theory, this maximum turns out to correspond to a flat minimum of the function

$$E''(M) + 2E'(M)/M \tag{20}$$

at small $M$ values (see figure 1).

Former approaches [1–6] used a Landau expansion of $E(M)$ to calculate the expectation value (14). To reproduce a maximum of the susceptibility curve, the energy function has to be expanded up to sixth order in $M$. The coefficient of $M^2$ has to be positive, that of $M^4$ negative, and that of $M^6$ positive. In contrast to [6], our own attempts to fit the $E(M)$ data in this way failed because the coefficients of the fitting polynomial depend too strongly on the range of the fit and the order of the expansion. Nor could the sign of the coefficients be determined reliably. Thus calculations on Pd obtained with the Landau expansion method suffer from a high degree of arbitrariness.

In our method an arbitrary parametrization of (20) can be used, because no assumptions on function (20) were made. We chose a parametrization of $E'(M)$ with a cubic spline function in order to evaluate (20) and to perform the integration in (18). To this end the magnetic field $B(M) = E'(M)$ was taken from our band-structure program.

The self-consistent band-structure calculations were carried out with the augmented spherical wave (ASW) formalism [11] under the constraint of a fixed-spin moment [7,8]. In order to evaluate (19) data for the wavevector-dependent susceptibility at 0 K were taken from *ab initio* calculations performed by Stenzel and Winter [12–14].

Figures 2 and 3 show the $E(M)$ as well as the $B(M)$ graphs for several lattice parameters. From the latter function we obtain the dependence $\chi^{-1}(\langle m^2 \rangle)$ using

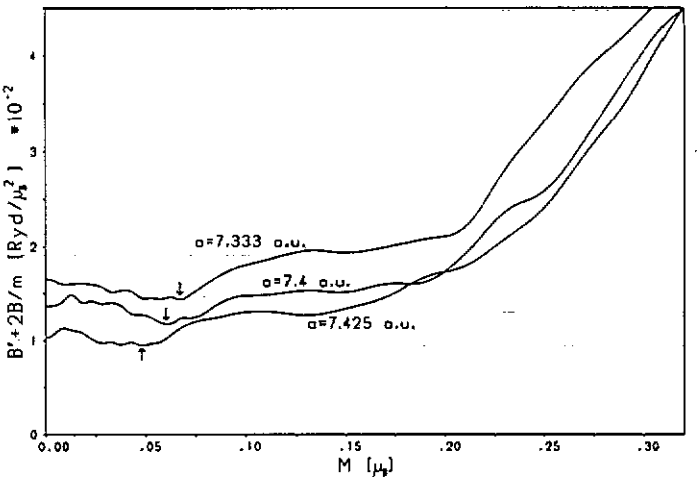


**Figure 1.** Integrand $B'(M) + 2B(M)/M$ against magnetization $M$. The arrows indicate small minima responsible for the maxima in the temperature-dependent susceptibility.

equation (18). In a second step we apply (19) to get $\chi^{-1}(T)$. The free parameter $q_c$ affects only the relation between $\langle m^2 \rangle$ and $T$ by formula (19). For a fixed value of $\langle m^2 \rangle$, the corresponding temperature decreases with increasing $q_c$ and vice versa. Therefore $q_c$ scales the temperature axis, i.e. increasing $q_c$ shifts the susceptibility curve to lower temperatures. For our calculations we chose a constant cut-off wavevector $q_c$ in such a way, that we achieved the best possible correspondence between experimental and theoretical results for $T > 150$ K.

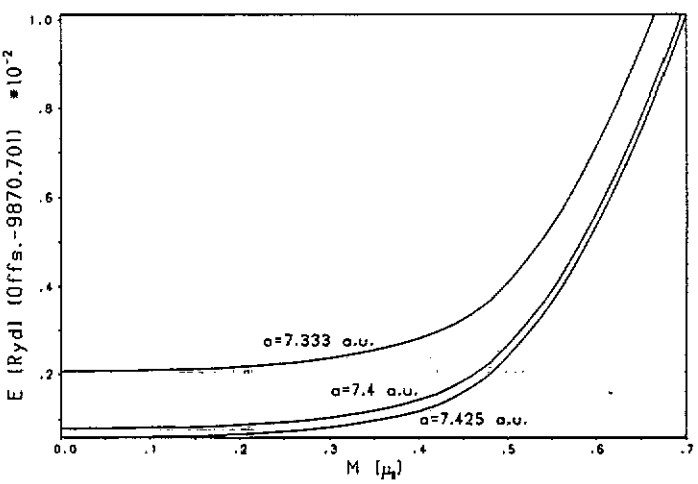


**Figure 2.** Magnetization-dependent ground-state energy per Pd atom ($a$: lattice parameter).

The $\chi(T)$ plots for various lattice parameters and the experimental results are given in figure 4. The equilibrium lattice parameter provided by the ASW program is 7.42 au Note that our classical spin fluctuation model fails in the limit $T \rightarrow 0$.

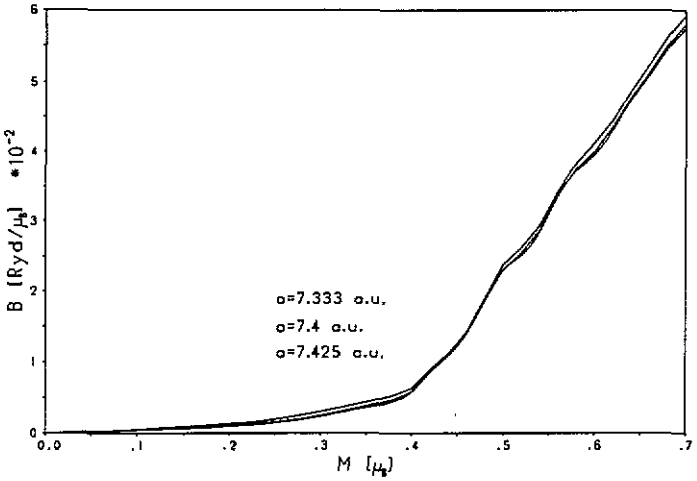


**Figure 3.** Magnetic field $B$ against magnetization $M$.

Hence the slopes of the susceptibility curves are finite at $T = 0$ K, in contrast to the third law of thermodynamics. By comparing the results with experiment two major shortcomings are evident. These are as follows.

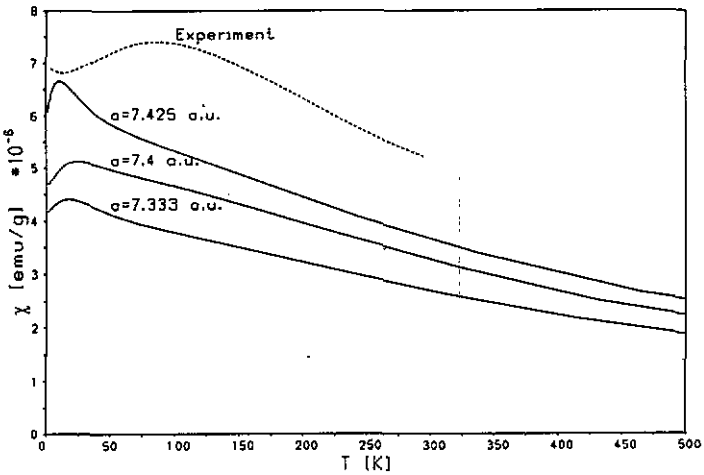


**Figure 4.** Temperature-dependent susceptibility for lattice parameters 7.333, 7.4, 7.425 au Corresponding $q_c$: 0.73, 0.63, 0.53 $\times 2\pi/a$. Experimental results [10].

First, the calculated susceptibility values are too small, and second, the maximum of the susceptibility appears at too low temperatures. We believe that the first discrepancy has its origin in the non-relativistic treatment of the band-structure calculations. It is well known [12], that relativistic effects shift the d bands to higher energies. This results in a considerable increase of the exchange enhancement, on account of a moderate increase of the density of states at the Fermi level.

With regard to the second deficiency we would like to emphasize that the cut-off wavevector should be temperature dependent. In the classical treatment the cut-off

wavevector has to be introduced as a boundary for the highest occupied fluctuation modes. This limit should increase with temperature. A temperature-dependent $q_c$ will shift the maximum of the susceptibility to larger temperatures without affecting the curves in the high-temperature regime. Better agreement of theoretical and experimental curves might then be achieved. In addition, when $q_c$ is set proportional to $T^\gamma$, $\gamma > 0$, the susceptibility curves will start with a horizontal slope at $T = 0$ K, as the third law of thermodynamics requires.

## 4. Summary

We treated the susceptibility of itinerant electron systems, for which spin fluctuations are the predominant thermal excitations. Our method starts with the model Hamiltonian from (1), and applies an approximation for the free energy in terms of a quadratic form with renormalized mode frequencies. Without further approximations a method for the calculation of the susceptibility of a paramagnetic system results. The only data required is the magnetization-dependent ground-state energy and the $q$-dependent susceptibility for $T = 0$ K. Both are accessible from band-structure calculations. The small curvature of $E(M)$ for low $M$ values in Pd metal is a critical test for the quality of our method.

With the exception of equation (18), the formalism is quite general and also applicable to itinerant ferromagnetic systems.

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