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Influence of spin fluctuations on the specific heat and entropy of weakly itinerant ferromagnets

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From a theory including the effects of spin fluctuations via renormalization of the Landau coefficients, the magnetic contributions to the specific heat c_m and entropy S_m are calculated. In a generalization c_m and S_m are given for cases when the spin-fluctuation amplitude saturates for temperatures lower than or comparable with the Curie temperature. For the unsaturated case a model for the discontinuity of the specific heat at the Curie temperature is derived. A discussion of the predictions with respect to experimental results is given.

I. INTRODUCTION

During the past few years a great deal of progress has been made on the theory of spin fluctuations in itinerant systems.[1-10] It has become clear that the Stoner model involving the single-particle excitations of the itinerant electrons is insufficient for most systems and that collective excitations are also inevitably present to different degrees, depending on the temperature and the position in the ω,q plane. For ferromagnets the resulting contributions of spin waves to the bulk magnetization M is most easily envisaged for low temperatures and positions in this plane close to $q=0$, giving

$$1-\frac{M(T)}{M(0)}\sim T^{3/2},\quad \omega(q)\sim q^2 , \tag{1}$$

and the contribution of the specific heat and change in entropy, giving

$$c_m\sim T^{3/2},\quad \Delta S\sim T^{3/2} . \tag{2}$$

At higher temperatures and larger values of ω and q the early work of Murata and Doniach[11] and others[3,10] had made it clear that spin-fluctuation effects persist side by side with single-particle excitations but that it is difficult to describe these theoretically for realistic models of metals. Furthermore, it is also easy to deduce from experimental evidence the relative importance of single-particle excitations and spin fluctuations (see, for example, Ref. 12). Hence a very much simpler approach to the problem of spin fluctuations has been developed.[6-9] This retains the Stoner model in its equivalent expression as a Landau theory of phase transitions but takes account of the influence of spin fluctuations by appropriately renormalizing the corresponding Landau coefficients.

Lonzarich and Taillefer,[3] and more recently, Wagner,[4] gave a description of the inverse susceptibility derived from a Landau-Ginzburg free energy F:

$$\begin{aligned}F=&(A/2)[M^2+2\langle m_\perp^2\rangle+\langle m_\parallel^2\rangle]\\&+(B/4)[M^4+M^2(6\langle m_\parallel^2\rangle+4\langle m_\perp^2\rangle)\\&+8\langle m_\perp^2\rangle^2+3\langle m_\parallel^2\rangle^2+4\langle m_\perp^2\rangle\langle m_\parallel^2\rangle] ,\\ \frac{1}{M}\frac{\delta F}{\delta M}=&\frac{H}{M}=A+BM^2+B(3\langle m_\parallel^2\rangle+2\langle m_\perp^2\rangle) .\end{aligned} \tag{3}$$

Here A and B are the Landau coefficients for the Stoner theory, defined by

$$A=-\frac{1}{2\chi_0}\left[1-\frac{T^2}{(T_c^s)^2}\right],\quad B=\frac{1}{2\chi_0 M_0^2} , \tag{4}$$

$\langle m_\parallel^2\rangle$ and $\langle m_\perp^2\rangle$ are the mean values for the square of the parallel and transverse components of the locally fluctuating magnetic moments, respectively. The temperature dependence of the fluctuating magnetic moment was found to be linear for most systems[7] and is given by

$$\langle m^2\rangle=2\chi_0 k_B T . \tag{5}$$

As the parallel and transverse component of the fluctuating moment can, in lowest order, be considered equal[3] we derive an expression for the free energy

$$\begin{aligned}F=&\frac{M^2}{2}\left[\frac{1}{2\chi_0}\left[\frac{T^2}{(T_c^s)^2}-1\right]+\frac{1}{2\chi_0}\frac{T}{T_{\rm sf}}\right]+\frac{M^4}{4}\frac{1}{2\chi_0 M_0^2}\\&+\frac{6M_0^2}{20}\left[\frac{1}{2\chi_0}\left[\frac{T^2}{(T_c^s)^2}-1\right]\frac{T}{T_{\rm sf}}\right]+\frac{3M_0^2}{20}\frac{T^2}{2\chi_0 T_{\rm sf}^2} .\end{aligned} \tag{6}$$

with

$$T_{\rm sf}=M_0^2/10k_B\chi_0 \tag{7}$$

according to Ref. 6. Minimizing the free energy F [Eq. (6)] with respect to the static magnetization M gives

$$F=-\frac{M_0^2}{8\chi_0}\left[1-\frac{T^2}{(T_c^s)^2}-\frac{T}{T_{sf}}\right]^2+\frac{6M_0^2}{20}\left[\frac{1}{2\chi_0}\left[\frac{T^2}{(T_c^s)^2}-1\right]\frac{T}{T_{sf}}\right]+\frac{3M_0^2}{20}\frac{T^2}{2\chi_0 T_{sf}^2}, \tag{8}$$

which is the starting point for our calculation of the entropy and specific heat of fluctuating systems.

II. ENTROPY AND SPECIFIC HEAT OF UNSATURATED SYSTEMS

The magnetic contribution to the specific heat c_m and the change in entropy ΔS_m are given by the thermodynamical relations

$$c_m=-T\frac{d^2F}{dT^2},\quad \Delta S_m=\int_{T=0}^{T=T_c}\frac{c_m}{T}dT. \tag{9}$$

With Eqs. (6) and (9) one easily obtains

$$c_m=-\frac{M_0^2}{2\chi_0 T_c}\frac{T}{T_c}t_c^2\left[1-\frac{(1-t_c^2)^2}{5t_c^2}-3\frac{T^2}{T_c^2}t_c^2-\frac{6T}{5T_c}(1-t_c^2)\right] \tag{10}$$

$$S_m=-\frac{M_0^2}{2\chi_0 T_c}\frac{T}{T_c}t_c^2\left[1-\frac{(1-t_c^2)^2}{5t_c^2}\frac{T^2}{T_c^2}t_c^2-\frac{3}{5}\frac{T}{T_c}(1-t_c^2)\right]. \tag{11}$$

In Eq. (10) and (11) we make use of the quantity t_c defined in Ref. 8 as $t_c=T_c/T_c^s$. The fraction T_c/T_c^s gives the deviation of the experimental T_c from the Curie temperature derived from pure Stoner theory T_c^s, and thus measures the relative importance of spin fluctuations. From this definition it is clear that the case $t_c^2=1$ refers to pure Stoner-type behavior (no spin fluctuations) and $t_c^2=0$ refers to pure spin-fluctuation behavior (no single-particle excitations). Although t_c seems to be a rather vaguely determined quantity, it has proved to be useful for a great number of systems.[7] In Ref. 7 t_c has been determined from band-structure calculations and was found to give reliable and physically reasonable results. A more elaborate discussion of the properties of t_c is given in Ref. 7. Using t_c as a parameter makes it very convenient to discuss the influence of spin fluctuations on both c_m and S_m.

For $t_c^2=1$ we get the "classical" result for pure Stoner theory, namely

$$S_m=-\frac{M_0^2}{2\chi_0 T_c}\frac{T}{T_c}\left[1-\frac{T^2}{T_c^2}\right],\quad \Delta S_m|_{T=0}^{T=T_c}=0, \tag{12}$$

$$c_m=-\frac{M_0^2}{2\chi_0 T_c}\frac{T}{T_c}\left[1-3\frac{T^2}{T_c^2}\right]. \tag{13}$$

Thus, c_m shows a negative linear and a positive cubic contribution to the total specific heat.

For $t_c^2=0$ we describe pure fluctuation behavior analogous to the theory formulated by Murata and Doniach:[11]

$$S=-\frac{M_0^2}{2\chi_0 T_c}\frac{T}{T_c}\left[-\frac{1}{5}\right], \tag{14}$$

$$c_m=-\frac{M_0^2}{2\chi_0 T_c}\frac{T}{T_c}\left[-\frac{1}{5}\right]. \tag{15}$$

Again we find a linear contribution in the specific heat. For these two extreme cases we obtain only linear or cubic contributions. Any experimentally determined specific-heat curve also contains linear dependences stemming from the electrons and the cubic Debye term. The similar power in T for these contributions and the magnetic ones makes it very hard to disentangle these two effects with any degree of certainty. In the general case for $0<t_c^2<1$, two further contributions arise: (i) a quadratic term proportional to $-(6T^2/5T_c^2)(1-t_c^2)t_c^2$, and (ii) a linear term equal to $-(T/T_c)[(1-t_c^2)^2/5]$, for the En-

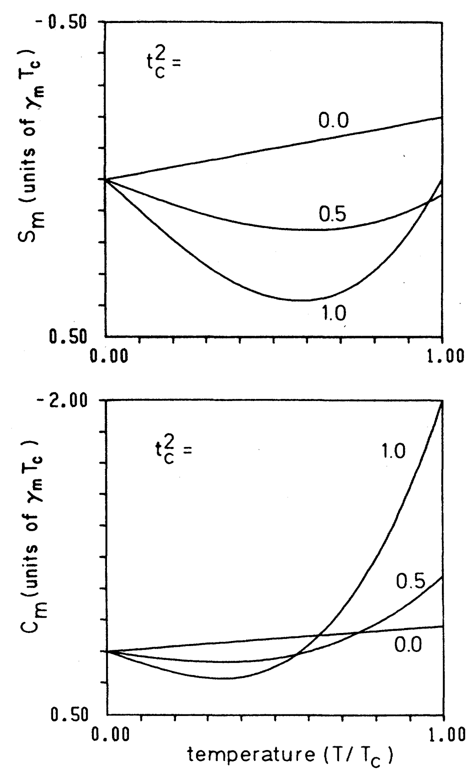

FIG. 1. Magnetic contribution to the specific heat C_m and the entropy S_m (both in units of $\gamma_m T_c$) as a function of the reduced temperature T/T_c. The curves are given for three values of t_c^2 corresponding to pure fluctuation, $t_c^2=0$; pure Stoner, $t_c^2=1$; and a general, $t_c^2=0.5$, case. Only for the general case $0<t_c^2<1$, is an additional T^2 term found. $\gamma_m=-M_0^2/2\chi_0 T_c^2$ is the Wohlfarth correction.

tropy S_m and the magnetic specific heat c_m. The additional quadratic term vanishes for both $t_c^2=0$ and $t_c^2=1$ and stands for the interaction between the single-particle excitations and the spin fluctuations considered in this theory.

Figure 1 shows the calculated curves for S_m and c_m for various values of t_c^2. In Ref. 7 a value of $t_c=0.5$ was used to distinguish between systems with single-particle excitations as leading effects ($t_c \geq 0.5$) and systems mainly determined by collective excitations ($t_c \leq 0.5$). If we apply a similar consideration, meaning that for fluctuation systems the magnetic specific heat should always be positive throughout the whole temperature range, we get a value for $t_c=0.38$.

It has been shown in Ref. 7 that most of the ferromagnetic systems considered therein are found to have t_c values ranging from 0.3 to 0.52 (e.g., Y_2Fe_{17}, Y_6Fe_{23}, YFe_3, $Y_2Fe_{14}B$, FeB, Y_2Co_{17}, YCo_5, Y_2Co_7, Fe, Ni); only very few systems are close to Stoner-type behavior, most prominent amongst which are members Co ($t_c=0.62$) and $ZrZn_2$ ($t_c=0.78$).[6] For the usual t_c range between 0.3 and 0.52 we would therefore predict a quadratic contribution to the magnetic specific heat of $0.09T^2/T_c^2$ up to $0.24T^2/T_c^2$ in units of $M_0^2/2\chi_0 T_c$.

III. EFFECTS OF SATURATION OF THE FLUCTUATION AMPLITUDE

The idea of a saturation of the fluctuation amplitude has been introduced by Moriya.[13] He bases his assumptions on a local charge neutrality condition because of the limited number of electrons per atom. The upper bond for one parallel component $\langle m_\parallel^2 \rangle$ is then given by $M_c^2/3$ where M_c is the number of electrons or holes in the band, whichever is smaller.

From our definition of the temperature dependence of the fluctuating magnetic moment [Eq. (5)], it is clear that saturation effects of the parallel components of the fluctuating moment will only appear for systems with almost or hardly filled bands and/or large high-field susceptibility χ_0. An example for this situation has been found in $ZrZn_2$ (Ref. 6), where the magnetic moment is carried by Zr. The Zn atoms have an almost completely filled $3d$ band[14,15,16] and a high value of the density of states at the Fermi energy causing a value for χ_0 and γ at least 10 times larger than those of Fe (see, e.g., Tables I and II). For $ZrZn_2$, $\langle m_\parallel^2 \rangle$ saturates well below the Curie temperature of 28 K so that this effect has to be considered for an analysis of the specific heat and the entropy.

Taking account of this saturation effect of the parallel component via a maximum amplitude of the fluctuating moment m' one obtains[6]

$$\langle m_\parallel^2 \rangle = \frac{k_B T}{|A|} f(T) = 2x_0 k_B T f(T) ,$$
$$f(T) = 1 - \frac{\frac{2}{\sqrt{\pi}}\sqrt{\Theta/T}\, e^{-\Theta/T}}{\operatorname{erf}(\sqrt{\Theta/T})} , \tag{16}$$

where Θ is a characteristic temperature for the saturation of the fluctuation amplitude, given by $\Theta = m'^2|A|/2k_B$. Again assuming that only the parallel component saturates the free energy F [Eq. (3)] now reads

$$\begin{aligned} F = (A/2)\{M^2+\langle m^2\rangle[2+f(T)]\} \\ +(B/4)\{M^4+M^2\langle m^2\rangle[6+4f(T)] \\ +\langle m^2\rangle^2[8+3f^2(T)]+\langle m^2\rangle^2 4f(T)\} . \end{aligned} \tag{17}$$

As the quantities A, M, $\langle m^2\rangle$, and $f(T)$ depend on the temperature, the analytic expressions for c_m and S_m become extremely complicated. We thus restrict ourselves to the presentation of the results, plotted in Fig. 2. The curves shown are all calculated for $t_c=0$, meaning spin fluctuations only. The temperature scale is defined by making use of the Curie temperature given by[7]

$$\frac{T_c^2}{(T_c^s)^2} + \frac{T}{T_{sf}} - 1 = 0 , \tag{18}$$

describing the Curie temperature of the referenced unsaturated curves (see Fig. 1).

The main difference between the curves with and without an upper bound for the fluctuation amplitude is

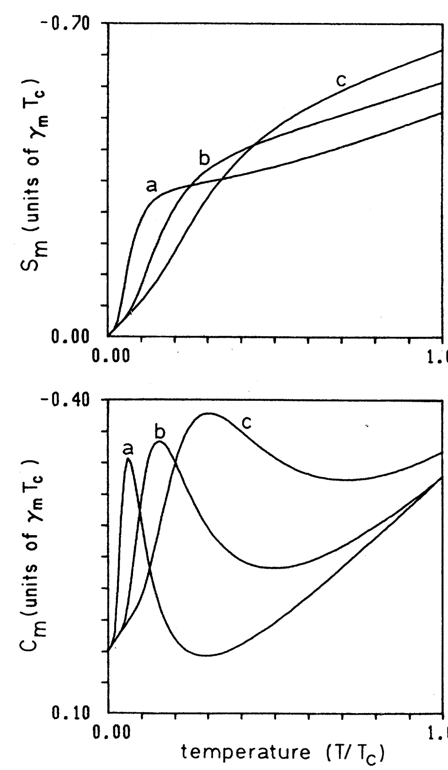

FIG. 2. Magnetic contribution to the specific heat C_m and the entropy S_m (both in units of $\gamma_m T_c$) as a function of the reduced temperature T/T_c for saturating parallel fluctuation. The curves a, b, and c, correspond to three different values of $\Theta/T_c=0.2$, 0.5, and 1.0, respectively.

the saturation behavior of the entropy, leading to a maximum in the specific heat. This effect can be understood from the underlying assumption for the mechanism responsible for the saturation. By introducing a maximum value m'^2 for the fluctuating amplitude one describes a system similar to a Schottky two-level model. For low temperatures, the fluctuation amplitude follows the relation for unsaturated systems. For rising temperatures, the upper limit for the m'^2 in the Maxwell-Boltzmann distribution function acts as an upper level which becomes more and more occupied. Expanding $f(T)$ for high temperatures $(\Theta/T<1)$ indeed gives the well-known decrease of c_m proportional to T^{-2}. In the low-temperature range c_m increases exponentially. A very similar model has been introduced by Hahn and Wohlfarth[17] to explain the specific-heat contribution of the anisotropy in superparamagnetic clusters.

In our theory we assumed that only the parallel component of the fluctuating moment show a saturation. Only this component can *a priori* be described to depend directly on the band-structure information, and only for this component the actual band shape enters in our theory. For the transverse component $\langle m_\perp^2 \rangle$ no such saturation is expected, so that for $\langle m_\perp^2 \rangle$ the validity of Eq. (5) is assumed for the whole temperature range. It has to be pointed out that the maximum in c_m occurs, even if the saturation temperature Θ is of the order of T_c. We want to stress the fact that the saturation of the parallel component of the fluctuating moment may rather often occur in weakly itinerant systems with almost or hardly filled bands or a gap which then acts as a delimiter.

An example for this behavior of c_m is found in FeSi.[18,19] The particular shape of the density of states curve leads to a saturation of the fluctuating magnetic moment around 500 K.[18] The specific heat rises exponentially to a maximum around 250 K and falls off proportional to T^{-2} for temperatures above.[20] The density of states of FeSi is characterized by a band gap above the d states about 0.12 eV wide. This band gap causes the saturation of the fluctuation amplitude. Once the local charge neutrality criterion, discussed in Ref. 3, is fulfilled no more electronic states are available to become occupied by the long-wavelength fluctuations.

IV. THE DISCONTINUITY OF THE SPECIFIC HEAT AT T_c

In the case of pure single-particle excitations (Stoner theory) the magnetic states below and above T_c are clearly defined. Below T_c one assumes spin-split bands and vanishing spin splitting exactly at T_c. Above T_c the system is in a truely paramagnetic state, i.e., no spin splitting exists. This behavior implies that the magnetic contribution of the specific heat drops to zero above T_c giving, according to (13),

$$\Delta C_m = \frac{M_0^2}{\chi_0 T_c} = -2\gamma_m T_c \ . \tag{19}$$

In the more general case, where spin fluctuations persist side by side with single-particle excitations, the Curie temperature is only the temperature where the macroscopic magnetic moment disappears. Spin fluctuations do exist above T_c and thus have to be taken into account. Our description of the behavior above T_c assumes that fluctuations are still present and contribute to c_m. From the fact that the bulk magnetization M and all its derivatives with respect to the temperature vanish for $T>T_c$, one derives from Eq. (3):

$$c_m(T>T_c) = -\frac{M_0^2}{2\chi_0 T_c}\frac{T}{T_c}t_c^2 \times \left[\frac{9}{5}(1-t_c^2)\frac{T}{T_c}+\frac{3(1-t_c^2)^2}{10t_c^2}\right] , \tag{20}$$

$$S_m(T>T_c) = -\frac{M_0^2}{2\chi_0 T_c}\frac{T}{T_c}t_c^2 \times \left[\frac{9}{10}(1-t_c^2)\frac{T}{T_c}+\frac{3(1-t_c^2)^2}{10t_c^2}\right] . \tag{21}$$

In the presence of spin fluctuations c_m will not drop to zero at T_c, because these fluctuations, if not saturated, will always contribute to the specific heat.

Combining the results of Eqs. (10) and (11), valid for $T<T_c$ and from Eqs. (20) and (21), one derives for the change of the entropy and the specific heat at T_c:

$$\Delta S_m = \frac{M_0^2}{2\chi_0 T_c}\left(\tfrac{1}{2}-\tfrac{1}{2}t_c^2\right) , \tag{22}$$

$$\Delta c_m = \frac{M_0^2}{2\chi_0 T_c}\left(\tfrac{1}{2}t_c^4+t_c^2+\tfrac{1}{2}\right) . \tag{23}$$

In our model the discontinuity of c_m varies from a peak behavior (for $t_c^2=1$) to an ordinary discontinuity (for $t_c^2=0$). Our result is very similar to the discontinuity found by Murata and Doniach.[11] The remaining difference in the actual behavior of c_m is caused by the fact that we assume a strictly linearly temperature dependence of the mean square of the fluctuating magnetization. Figures 3(a) and 3(b) show a three-dimensional plot of the entropy and specific heat as a function of the temperature T and our parameter t_c^2. From the entropy plot (3a) one clearly sees how the obvious discontinuity in c_m in the Stoner case $(t_c^2=1)$ is caused by the change dS/dT from a finite value to zero at T_c. In the other extreme $(t_c^2=0)$ dS/dT below and above T_c have different signs, so that Δc_m jumps from a positive to a negative value. In (3b) the corresponding plot for c_m gives exactly these features.

In order to demonstrate the applicability of our model, we compare in Tables I and II calculated and experimental values of Δc_m for Fe, Co, Ni and weak ferromagnetic materials. The key quantity $-\gamma_m = M_0^2/2\chi_0 T_c^2$ representing the linear contribution to the magnetic-heat capacity can simply be derived from the spontaneous magnetization M_0, the Curie temperature T_c, and the initial ferromagnetic susceptibility χ_0. As long as the material under consideration exhibits weakly ferromagnetic

TABLE I. Saturation magnetization M_0, Curie temperature T_c, high-field susceptibility χ_{hf}, experimental electronic specific-heat coefficient γ, the specific-heat jump Δc_m at T_c, and the calculated Wohlfarth correction $\tilde{\gamma}_m$, Δc_m, and $\Delta\tilde{c}_m$ for iron, cobalt, and nickel with and without the correction due to fluctuations via the parameter t_c, respectively. t_c is the ratio between the experimental Curie temperature and the Stoner Curie temperature T_c^s.

	Fe	Co	Ni	Reference
M_0 (emu/g)	221.7	162.5	58.6	22
T_c (K)	1039	1377	630	22
χ_{expt} (10^{-6} emu/g)	4.76	4.3	1.96	22
χ_{theor} (10^{-6} emu/g)	2.41	0.679	0.273	
t_c	0.41	0.62	0.35	
$\tilde{\gamma}_m=-M_0^2/(2\chi_0 T_c^2)$ (mJ/mol K^2)	−26.7	−9.53	−13	
$\tilde{\gamma}_m^*[t_c^2-(1-t_c^2)^2/5]$ (mJ/mol K^2)	0.79	2.82	−0.49	
γ (expt) (mJ/mol K^2)	4.74	4.38	7.03	30
$\Delta\tilde{c}_m=-2\tilde{\gamma}_m T_c$ (J/mol K)	55.4	26.3	16.4	
$\Delta c_m=-\tilde{\gamma}_m T_c(\frac{1}{2}t_c^4+t_c^2+\frac{1}{2})$	18.9	12.6	5.2	
Δc_m band theory	35.8	60.9	31.5	
Δc_m (expt) (J/mol K)	43.2	22.2	10.1	21

properties characterized by linear Arrott plots (M^2 versus H/M) over a wide temperature range down to low temperatures, $1/(2\chi_0)$ can easily be determined from the intercept of the extrapolated M^2 versus H/M graph with the negative H/M axis. This quantity is sometimes called high-field susceptibility (χ_{hf}) since it represents the susceptibility due to the band splitting. In the case where Arrott plots are nonlinear (caused by, e.g., spin fluctuations, metallurgy, etc.), the model for weak itinerant ferromagnetism is no longer valid in its simple form, and we derive the high-field susceptibility from M versus H measurements in high fields at low temperatures. An appreciable source of uncertainty is introduced from the evaluation of χ_0 since various contributions like the orbital, van Vleck, and diamagnetic susceptibilities add up to the grand total susceptibility. Because of the uncertainty in decomposing the experimental susceptibility into the above-mentioned terms, which are usually estimated to be of the same order of magnitude as the spin susceptibility, we therefore, in the tables, use either the uncorrected ferromagnetic initial susceptibility from Arrott plots (χ_A) or the differential high-field susceptibility (χ_{hf}) at low temperatures.

Δc_m values of Fe, Co, and Ni derived from magnetic measurements and corrected for fluctuations, via

$$\Delta c_m=-\gamma_m T_c(\tfrac{1}{2}t_c^4+t_c^2+\tfrac{1}{2}) , \tag{24}$$

using t_c from Ref. 6, which are by a factor of 2 smaller than the experimental Δc_m values of Braun and Kohlhaas.[21] The reason for this discrepancy arises from the experimental χ_{hf} values taken from Ref. 22, which consist of the above-mentioned two contributions of the same order of magnitude. Experimentally only the total susceptibility is easily available. An estimation of the spin susceptibility is, e.g., derived from measurements of the Knight Shift, where the Pauli susceptibility enters linearly. As the model presented in this paper is formulated for spin-dependent quantities, one should use the spin susceptibility χ_0 to calculate c_m. However, using the uncertain estimates for χ_0 from Ref. 22 results in a much better agreement between theory and experiment. Calculated values of Δc_m, using the same band-structure data as in Ref. 6 are in the same order of magnitude for Fe but do not fit well, for Co and Ni. In Ref. 6 the spin susceptibilities of these three compounds were calculated from a rigid-band model to account for experimental values of the spin splitting. Furthermore, we want to emphasize that our model is formulated for weakly itinerant systems, meaning that it should work much better for Fe than for Co and Ni. This example also demonstrates that both the experimental and theoretical results depend sensitively on χ_0. However, χ_0 in both cases is found to be a rather poorly determined quantity. Experimentally this uncertainty arises from the necessary decomposition, which is usually omitted. A theoretical investigation in determining reliable values of χ_0 too often lacks a satisfactory description of exchange and correlation as discussed in Ref. 7.

In Table II we give an estimate for Δc_m for some weak or nearly weak ferromagnetic materials with T_c below room temperature, where only for three of them experimental Δc_m values exist. Unfortunately, for most of the compounds discussed in Ref. 7 with T_c much larger than room-temperature, specific-heat measurements up to T_c are not yet available. Although we believe that fluctuations are present in those materials, Δc_m is not corrected for fluctuations since band-structure data to determine t_c are not yet available except for $ZrZn_2$.[14] For $ZrZn_2$ we obtain nearly the experimental Δc_m value assuming parallel fluctuations being saturated as in Ref. 6. Δc_m value derived from magnetic measurements[23–25] range from 138 up to 840 mJ/mol K, in comparison with the heat-capacity result of 420 mJ/mol K for the best sample, while values down to 80 mJ/mol K have also been observed by Viswanathan.[24] This example further demonstrates that the experimental results depend sensitively upon the method deriving the susceptibility and also upon the sample purity. For YNi_3 we estimated $\Delta c_m = 0.1$ J/mol K which is smaller than the experimental resolution of the measurement (± 0.15 J/mol K) and could therefore not be detected.[26] The agreement in the case of UNi_2 using polycrystalline data is rather good; however, it should be considered with reservation, since Frings[27] showed that a UNi_2 single crystal exhibits a large anisotropy which influences the slope of the Arrott plot and the differential high-field susceptibility.

Furthermore, we examine in the tables the measured electronic specific-heat coefficient γ and the estimated linear magnetic contribution to the heat capacity $-\tilde{\gamma}_m = M_0^2/2\chi_0 T_c^2$. The so-called Wohlfarth correction $\tilde{\gamma}_m$—usually neglected—was estimated by Brommer[28] for weak ferromagnetic materials to be typically of the order of (-0.5 mJ/mol K^2, i.e.,) -10% of the electronic term γ of a usual metal. Without considering fluctuations this term is negative and by a factor of 2–5 times larger than γ_{expt} for Fe, Co, and Ni and the other compounds in Table II. The large deviation for Fe, Co, and Ni indicates the limited applicability of the Stoner model at finite temperatures. Fluctuations reduce the bare $\tilde{\gamma}_m$ value via the factor $[t_c^2 - (1-t_c^2)^2/5]$ leading either to a positive or a negative contribution to the experimental heat capacity (see Table I). In particular, the reduction is large at $t_c = 0.38$, where this factor changes its sign.

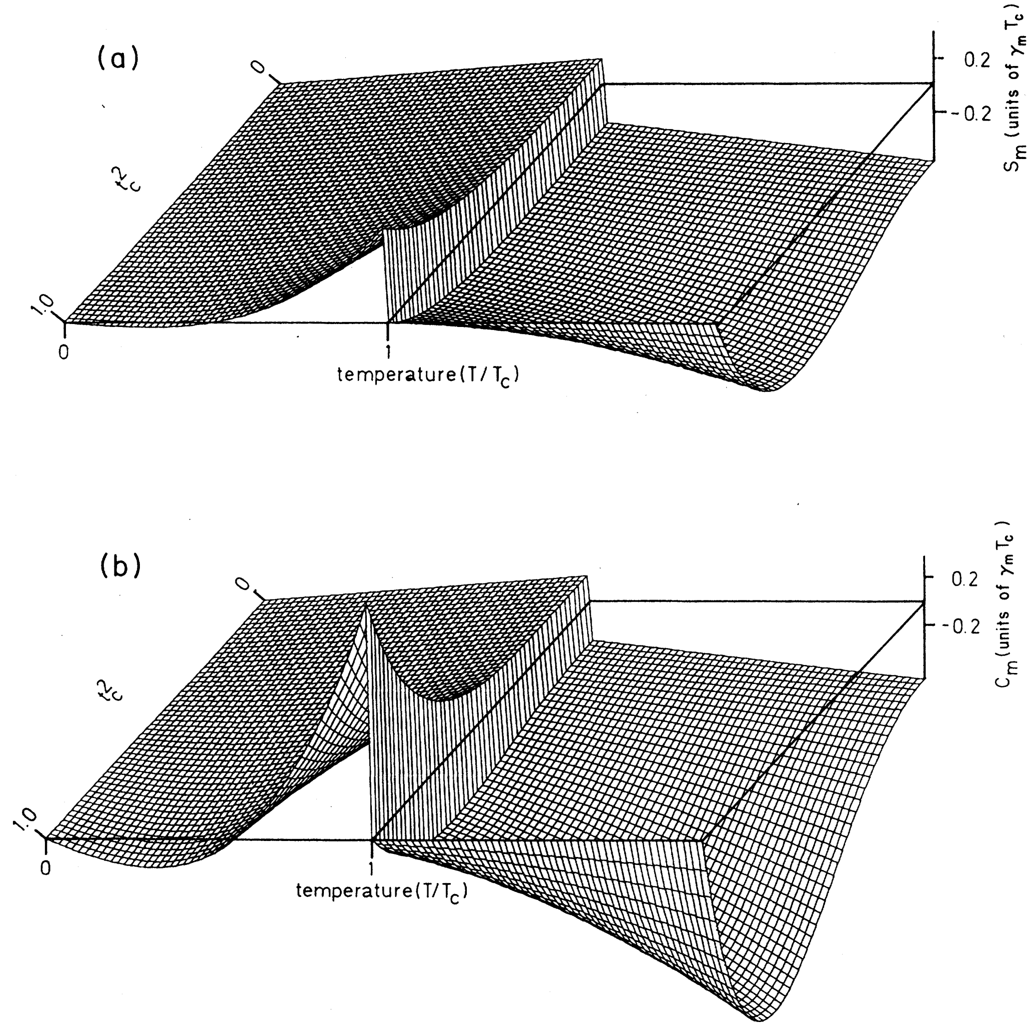

FIG. 3. Three-dimensional plot of the entropy S_m (a) and the specific-heat c_m (b) as a function of the normalized temperature T/T_c, and the fluctuation parameter t_c^2. The vertical axis is in units of $-\gamma_m T_c$ as in Fig. 1.

TABLE II. Comparison of the same experimental and calculated quantities (also same units) as in Table I for nearly weak ferromagnetic materials, but without corrections due to fluctuations. χ_A and χ_{hf} denote that either the initial susceptibility from an Arrott plot or the high-field susceptibility is used.

P	M_0	T_c	χ	$\tilde{\gamma}_m$	γ_{exp}	$\Delta\tilde{c}_m$	Δc_m exp
$ZrZn_2$							
Ref. 23	2.45	17.3	$\chi_A 5.5\times10^{-5}$	-4		0.138	
Ref. 24				-6.4	26–40	0.280	0.420
			$\chi_{hf} 4.4\times10^{-4}$	-0.5			
Ref. 25			$\chi_{hf} 9.5\times10^{-6}$	-24		0.840	0.080
Ref. 14						0.300-0.400	
		(band-structure data)				(0.405 for $t_c=0.78$)	
YNi_3							
Ref. 26	2.35	31	$\chi_A 5.7\times10^{-5}$	-1.7	31	0.104	<0.3*
$CeFe_2$	57	230	$\chi_A 3.45\times10^{-5}$	-22	53	10.12	
			$\chi_{hf} 2.27\times10^{-5}$	-32		14.72	
UFe_2	17.8	160	$\chi_A 9.7\times10^{-6}$	-22	55	7.04	
Ref. 31			$\chi_{hf} 7\times10^{-6}$	-29		9.28	
UNi_2	0.69	23	7.45×10^{-7}	-21	70	0.97	0.96

Generally, for a single compound it is very difficult to unscramble the magnetic-heat capacity of itinerant electrons, including fluctuations from the experimental specific-heat data, because even in the simplest case (no fluctuations) the magnetic terms follow the same power law as the electronic and the lattice-heat capacity at low temperatures. At finite temperatures spin waves and fluctuations become important. Therefore, it is hardly possible to give experimental evidence for our small additional term proportional to T^2, introduced by the interaction between fluctuations and single-particle excitations, especially if spin waves with a $T^{3/2}$ dependence also exist side by side.

In contrast to a single compound, a series of alloys as pseudobinary systems, where substituting one element with another induces a magnetic moment, offers the possibility to disentangle the additional magnetic contribution to the heat capacity from the electronic and Debye term as the onset of magnetism occurs. A systematic analysis of the magnetic-heat capacity and magnetic entropy in (Ho,Y)Co_2 and other heavy rare-earth Laves phases (R,Y)Co_2 gives experimental evidence for the occurrence of the negative $\tilde{\gamma}_m T$ term:[29] starting from YCo_2, an exchange-enhanced Pauli paramagnet, the substitution of Y by Ho causes the freezing of the localized Ho moments while for Ho concentrations larger than 20% an itinerant Co moment is induced, which attains 1 μ_B and remains constant for $x>0.5$. In Fig. 4 we present the magnetic entropy of (Ho,Y)Co_2. Up to $x=0.2$ the $S_m(T)$ plots exhibit a negative curvature while positive curvatures occur for $x>0.2$, just at this composition where the itinerant Co moment is gradually induced. This change of curvature can be attributed to the negative $\tilde{\gamma}_m$ term in the specific heat and the magnetic entropy equations (10) and (11), which is intimately correlated with the appearance of an itinerant moment. However, a quantitative estimation of $\tilde{\gamma}_m$ was not possible, since various types of moments with different mechanisms contribute to the bulk moment and total susceptibility.

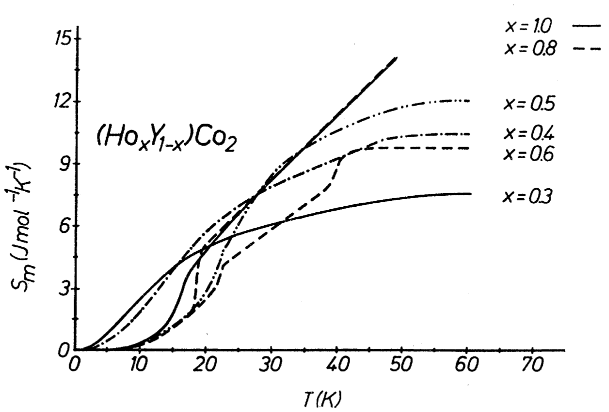

FIG. 4. Magnetic entropy of $(Ho_xY_{1-x})Co_2$ as a function of temperature. The various concentrations are labeled in the figure.

V. CONCLUSION

The theory presented in this paper is based on the treatment of fluctuations in weakly ferromagnetic systems via the renormalization of the Landau coefficients yielding a satisfactory description of the magnetic-heat capacity and entropy. It was shown that for systems where spin fluctuations are unsaturated the parameter t_c—ranging between 1 and 0—measuring the extent of spin fluctuations give a continuous transition from the classical result for the pure Stoner theory with single-particle excitations only to the pure fluctuation behavior formulated by Murata and Doniach.[11] Although the model is primarily designed for weak or nearly weak ferromagnetic materials and contains no real free parameter, since only quantities derived from band structure or from the experiment are required, we apply the theory to different ferromagnetic materials and estimate Δc_m also for Fe, Co, Ni, and weak or nearly weak ferromagnetic compounds. For all systems considered the experimental Δc_m values lay between an upper and lower bound given by pure itinerant and pure fluctuation behavior. Again the quantity t_c interpolates between these two extreme cases. We therefore deduce that theories neglecting the influence of single-particle excitations around the Curie temperature should be considered very carefully. Experimentally, however, it is very difficult to determine γ_m unambiguously for a single compound, but we could give experimental evidence for the occurrence of the negative γ_m in a series of intermetallic compounds.

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APPENDIX: COMPARISON WITH MURATA'S AND DONIACH'S RESULTS

In the limit $t_c=0$ we can compare our result for the specific heat with the earlier work by Murata and Doniach.[11] Assuming only parallel components of the fluctuating magnetic moment, they derive a relation for the discontinuity of the specific heat:

$$c_m(T)=\begin{cases} +\frac{B}{2}6\langle m^2\rangle\frac{\partial\langle m^2\rangle}{\partial T} & T<T_c \qquad \text{(A1)}\\ -\frac{B}{2}3\langle m^2\rangle\frac{\partial\langle m^2\rangle}{\partial T} & T>T_c\ . \qquad \text{(A2)}\end{cases}$$

Following the paper by Wagner,[4] who includes both parallel and transverse fluctuations, one obtains contributions due to both symmetries so that c_m is given by the sum

$$c_m=\sum_i c_{\langle m_i^2\rangle}\ , \tag{A3}$$

with $i=1$ and 2 for transverse components and $i=3$ for the parallel case.

$$c_{\langle m_\parallel^2\rangle}=+\frac{B}{2}\langle m_\parallel^2\rangle\left[6\frac{\partial\langle m_\parallel^2\rangle}{\partial T}+4\frac{\partial\langle m_\perp^2\rangle}{\partial T}\right],\quad T<T_c \tag{A4}$$

$$c_{\langle m_\perp^2\rangle}=+\frac{B}{2}\langle m_\perp^2\rangle\left[2\frac{\partial\langle m_\parallel^2\rangle}{\partial T}-2\frac{\partial\langle m_\perp^2\rangle}{\partial T}\right],\quad T<T_c \tag{A5}$$

$$c_{\langle m_\parallel^2\rangle}=-\frac{B}{2}\langle m_\parallel^2\rangle\left[3\frac{\partial\langle m_\parallel^2\rangle}{\partial T}+2\frac{\partial\langle m_\perp^2\rangle}{\partial T}\right],\quad T>T_c \tag{A6}$$

$$c_{\langle m_\perp^2\rangle}=-\frac{B}{2}\langle m_\perp^2\rangle\left[1\frac{\partial\langle m_\parallel^2\rangle}{\partial T}+4\frac{\partial\langle m_\perp^2\rangle}{\partial T}\right],\quad T>T_c\ . \tag{A7}$$

It is easy to see that Eqs. (A4)–(A7) reduce to the Murata-Doniach result if $\langle m_\perp^2\rangle$ and subsequently its derivative with respect to the temperature is zero. In Eqs. (A6) and (A7) we still distinguish between parallel and transverse components, although these terms become identical above T_c. However, this makes it more convenient to trace the different terms.

If we assume that around T_c the parallel and transverse components and their temperature derivatives are equal, we derive

$$c_m(T)=\begin{cases} +\frac{B}{2}10\langle m^2\rangle\frac{\partial\langle m^2\rangle}{\partial T} & T<T_c \qquad \text{(A8)}\\ -\frac{B}{2}15\langle m^2\rangle\frac{\partial\langle m^2\rangle}{\partial T} & T>T_c\ . \qquad \text{(A9)}\end{cases}$$

With the explicit dependence of $\langle m^2\rangle$ [Eq. (5)] we rederive our formula for Δc_m [Eq. (23)] in the limit $t_c=0$.

Comparing the Murata-Doniach result with Eqs. (A8) and (A9) demonstrates how strongly the presence of transverse fluctuations influences the result. These additional terms enhance the discontinuity of Δc_m at T_c so that the influence of the transverse fluctuations must always be taken into account.

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