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# Strong ferromagnets: Curie temperature and density of states

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**Abstract.** The Curie temperatures of magnetic 3d elements and yttrium intermetallics are investigated. Using densities of states obtained by self-consistent LMTO band-structure calculations, it is shown that the Curie temperatures in strong and nearly strong ferromagnets cannot be understood in terms of extensions of the theory of very weak itinerant ferromagnetism such as the Mohn–Wohlfarth approach. In particular, a knowledge of the partial densities of states  $D \uparrow (E_F)$  and  $D \downarrow (E_F)$  around the Fermi level is not sufficient to deduce the Curie temperature. Reasons for this are the non-analytic character of the density of states and  $k$ -space delocalization of the thermal excitations.

## 1. Introduction

For decades, the temperature dependence of the spontaneous magnetization of ferromagnets has been a major subject of interest. Despite much effort, we still have no detailed, quantitative understanding of Curie temperature trends in metallic ferromagnets [1, 2]. Even the Curie temperatures of simple ferromagnets such as Fe or Ni cannot be predicted by a coherent first-principles theory, i.e. exclusively from our knowledge of crystal and electronic structure. Present-day first-principles calculations are arbitrary in so far as they imply a selection of appropriate excitation mechanisms and approximations [3, 4]. For instance, attempts to go beyond the single-band Hubbard model have yielded a Curie temperature  $T_C \sim 2400$  K and a local magnetic moment  $\mu(T = T_C) = 3.29 \mu_B$  for Fe [5]. Another example is the approach used in [6], which reproduces reasonable Curie temperatures at the cost of a proper description of other physical properties such as specific heat and susceptibility (see [7] and references therein). Understanding the Curie temperature remains a serious challenge for most ferromagnetic metals although weak itinerant ferromagnets, such as  $ZrZn_2$  with  $T_C = 22$  K, are the exception [3, 8–10]. Modern permanent magnet intermetallics such as  $Nd_2Fe_{14}B$  [1] or  $Sm_2Fe_{17}N_3$  [11, 12] are nearly strong ferromagnets, like Fe, and cannot be understood in terms of weak itinerant ferromagnetism.

These difficulties are partly attributable to the complicated lattice and electronic structures of transition-metal-rich rare-earth intermetallics, but, to a larger extent, they stem from the complicated statistics of itinerant ferromagnets. Unlike ionic local-moment compounds, which are reasonably well described by the Heisenberg model, magnetic 3d metals and their alloys contain delocalized electrons and exhibit a very complex excitation structure [3, 14]. The simplest approach to estimate the Curie temperature of itinerant magnets is to consider Stoner excitations, which consist of transitions from  $\Psi_{k\uparrow}$  Bloch states to  $\Psi_{k\downarrow}$  Bloch states (see e.g. [10, 15]). Stoner excitations lead to a reduced magnetic moment, which finally vanishes at  $T = T_C$ . However, the Stoner model yields Curie temperatures  $T_S$  that are far too high, and there is much evidence that atomic moments persist above  $T_C$  [4, 10, 16]. Due to the strongly periodic character of Bloch functions,

Stoner excitations are much less effective in destroying magnetization than non-periodic spin fluctuations.

The archetypical approach to calculate the Curie temperature of very weak itinerant ferromagnets involves self-consistent renormalization of spin fluctuations [8]. In this approach, long-wavelength spin fluctuations are made responsible for the observed Curie temperature. Starting from a Gaussian trial Hamiltonian, the amplitude of the spin fluctuations at  $T_C$  is calculated in a self-consistent manner, and  $T_C$  itself is obtained from the condition  $\chi^{-1}(T_C) = 0$ . An extension of this approach is the spin-fluctuation theory of Lonzarich and Taillefer [9].

Unfortunately, spin fluctuations in strong or nearly strong itinerant magnets are fairly well localized. Though having a delocalized ground state, these systems exhibit a thermodynamic behaviour which is closer to local-moment magnets than to very weak itinerant ferromagnets [3, 4, 16] and cannot be properly described by a continuum theory. In addition, there is no well-based definition of the series expansion on which the spin-fluctuation theory of very weak itinerant ferromagnets is established. Using the Bogol'ubov inequality [17] it can be shown that  $T_C = 0$  unless the ground-state magnetization of the fully spin-polarized band is infinite [18, 19]. In very weak itinerant ferromagnets the magnetization of the fully spin-polarized state is much larger than the spontaneous magnetization so an *ad hoc* series expansion represents a reasonable approximation, but in strong ferromagnets the approach breaks down entirely.

Until now, there have only been semiempirical attempts to explain observed Curie temperature trends [1, 13, 20, 21]. Apart from a number of semiquantitative calculations, which nevertheless reveal interesting quantum-statistical details [3, 4], there is the semiempirical approach developed by Mohn and Wohlfarth [20]. This theory, which does not start from a well defined Hamiltonian, contains three parameters: saturation magnetization, Pauli susceptibility, and Stoner parameter. Despite its theoretical shortcomings, the Mohn–Wohlfarth approach has been quite widely used to evaluate experimental data on rare-earth intermetallics [16, 22–24].

In the Mohn–Wohlfarth theory

$$T_C^2/T_S^2 + T_C/T_{sf} = 1 \quad (1)$$

where  $T_S$  is the Stoner-model Curie temperature, and the spin-fluctuation temperature  $T_{sf}$  is given by

$$T_{sf} = (m^2/20k_B)(1/2D \uparrow(E_F) + 1/2D \downarrow(E_F) - I). \quad (2)$$

Here  $m$  is the transition-metal moment (in units of  $\mu_B$ ),  $D \uparrow(E_F)$  and  $D \downarrow(E_F)$  are the zero-temperature densities of states at the Fermi level of the spin-up and spin-down bands, and  $I$  is the Stoner parameter. Often  $T_S \gg T_{sf}$ , so  $T_C \sim T_{sf}$ .

It is worthwhile emphasizing that Mohn and Wohlfarth [20] start from a susceptibility given by Lonzarich and Taillefer [9] but neglect the wave-vector dependence of the spin fluctuations. Their approach could therefore be referred to as non-self-consistent spin-fluctuation theory. Furthermore, neither Murata and Doniach [8] nor Lonzarich and Taillefer [9] aimed at describing strong ferromagnets. The use of long-wavelength spin fluctuations to describe strong ferromagnetism by equations (1) and (2) is an innovation. It is therefore interesting to investigate to what extent the predictions of Mohn and Wohlfarth are actually realized in practice.

Here we use numerical electronic-structure data to investigate the applicability of the Mohn–Wohlfarth approach to a variety of strong and nearly strong ferromagnets and we give a qualitative explanation of our findings.

## 2. Band-structure calculations

In the past few years, great progress has been made with electronic-structure calculations. The crystal structure of transition-metal-rich rare-earth intermetallics of interest in magnetism is often complicated, so until quite recently calculations were restricted to non-self-consistent methods, but it is now possible to carry out self-consistent electronic-structure calculations for compounds with large unit cells, which reproduce the observed magnetization within about 5% [25, 26].

Here we have employed the linear muffin-tin orbital (LMTO) method [27, 28] with the atomic-sphere approximation (ASA). Exchange and correlation were treated with the local spin-density function (LSDF) approximation, using the form given by Von Barth and Hedin [29], with the parameters given by Janak [30]. The scalar-relativistic approximation of Koelling and Harmon [31] was used and spin-orbit interaction was neglected.

Within the ASA the crystal is subdivided into overlapping atomic spheres. The results will depend to some extent on the different choices for the atomic-sphere radii, particularly in interstitial compounds [32]. We used the radii ratio of 1.35:1.00:1.11:1.12:0.7 for Y, Fe, Ti, Mo and interstitial C or N atoms, which has proved reasonable in recent calculations [25, 26, 32, 33]. When the total volume and lattice parameters are based on the experimental results, the maximum overlap of the atomic spheres is always less than 25%.

The number of  $k$  points in the irreducible part of the Brillouin zone on which the calculation of the self-consistent potential was based is much smaller for systems with large unit cells than for systems with small unit cells. For Fe, Co, and Ni, for example, 625  $k$  points were used whereas for Y-Fe compounds with the 2:17 structure, which contain at least 38 atoms per unit cell, or Y-Fe compounds with the 1:12 structure, which contain at least 26 atoms per unit cell, 12 and 35  $k$  points respectively are sufficient. During the iteration procedure the total energy converged to within  $10^{-4}$  Ryd. Further details of the calculations are presented elsewhere [34].

The density of states at the Fermi level can be obtained from (i) the total density of states or (ii) the partial density of states averaged over all Fe or Co atoms. The former includes contributions from non-3d atoms. The data listed in table 1 were obtained with the second method. More than 300 points within about 1.5 Ryd were used to form the density-of-states curve. Interpolation was used to obtain the values as accurately as possible.

We can now use the data in table 1 to predict the Curie temperatures of strong and nearly strong ferromagnets. For the sake of simplicity we take the Stoner parameters given by Janak [35]:  $I = 0.93$  eV for Fe and Fe compounds,  $I = 0.99$  eV for Co and  $\text{YCo}_5$ , and  $I = 1.01$  eV for Ni. This causes a small degree of inexactness [16], but all inverse densities of states  $D_{\text{eff}}^{-1} = \{D \uparrow^{-1}(E_F) + D \downarrow^{-1}(E_F)\}/2$  are sufficiently different from  $I$  to introduce no large errors (table 1).

To determine the spin-fluctuation temperature  $T_{\text{sf}}$  from experimental Curie temperature data, we have to know the Stoner temperature  $T_S$ . In the Stoner model the phase transition at the Curie point is simply driven by the thermal smearing of the density of states at the Fermi surface. There are no generally accepted values of  $T_S$ , so we will compare two independently determined parameter sets: (i)  $T_S$  values given by Mohn and Wohlfarth [20] and (ii)  $T_S$  values obtained from the highly simplified narrow-band formula  $T_S = Im/4k_B$  [15]. The results are shown in figure 2: the spin-fluctuation temperatures deduced from the experimental Curie temperatures are reasonably independent of  $T_S$ . This statement remains valid if (1) is replaced by formulae with slightly different exponents, e.g.  $\frac{4}{3}$  instead of unity in the second term of the left-hand side [9].

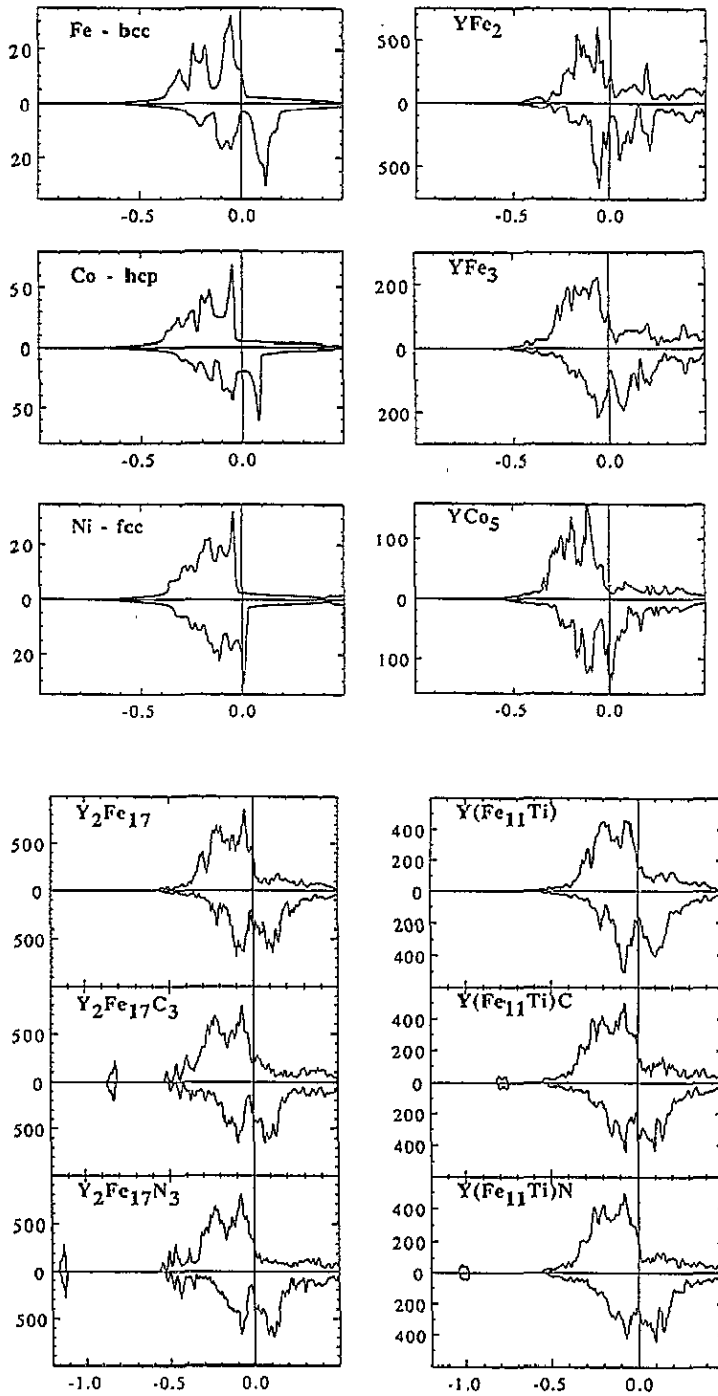


Figure 1. Typical spin-up (upper part of each panel) and spin-down (lower part of each panel) densities of states for Fe, Co, Ni, and some Y-Fe, Y-Co intermetallics, and  $Y_2Fe_{17}Z_3$  ( $Z = C, N$ ),  $Y(Fe_{12-x}M_x)Z$  ( $M = Ti, Z = C, N, x = 1$ ;  $M = Mo, Z = N, x = 1, 2, 3, 4$ ) interstitial intermetallics, obtained from LMTO band-structure calculations. The scale of the density of states (dos) is in  $Ryd^{-1}spin$ . The energy scale is in Rydbergs (1 Ryd = 13.6 eV).

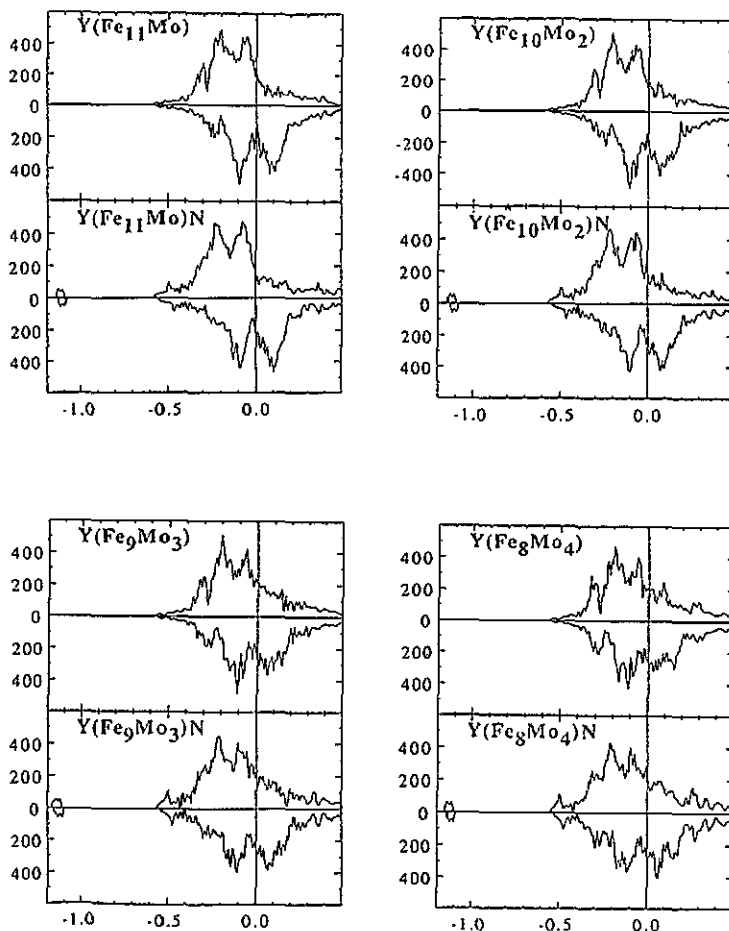


Figure 1. (Continued)

### 3. Discussion

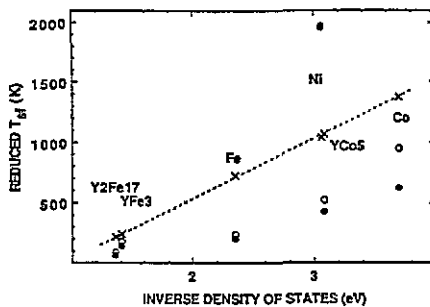
We see in figures 2 and 3 that the Mohn–Wohlfarth theory equation (2) gives a poor account of the experimental results. It is certainly possible to readjust the factor  $\frac{1}{20}$  for any particular group of materials, for instance Fe-rich rare-earth intermetallics, but then magnets such as Ni lie far beyond any acceptable error. Moreover, even within a restricted group of Fe-rich rare-earth intermetallics there is no clear linear dependence (figure 3). At best it may be possible to account for the ratios of Curie temperatures of closely related pairs of compounds.

The spin fluctuation temperature  $T_{sf}$  determined from the density of states at the Fermi level via (2) is typically three times greater than that determined from the experimental Curie temperature using (1). Since  $(T_C/T_S)^2 \ll 1$ , the theory predicts  $T_C \sim T_{sf}$ . In order to explain the observed magnitudes of the Curie temperature using the Mohn–Wohlfarth theory it would be necessary for the calculation to have underestimated the density of states for Fe and Co compounds by about a factor of two. This is most unlikely.

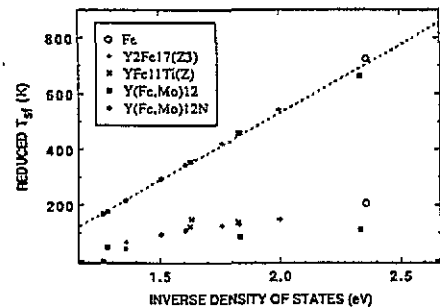
The Curie temperature of a metallic ferromagnet is a very complex quantity. Let us consider the free-electron gas to see what interaction mechanism actually causes the parallel coupling between spins. A very simple mechanism is illustrated in figure 4. The free-

**Table 1.** Band-structure parameters obtained in self-consistent LMTO band calculations on some 3d metals and intermetallics. Spin fluctuation temperatures  $T_{sf}$  deduced from the density of states at the Fermi level are compared with experimental Curie temperature results  $T_C^{expt}$ .

Compound	$m^{calc}$ ( $\mu_B$ )	$I$ (eV)	$D_{\uparrow}^{\dagger}$ ( $eV^{-1}$ /d atom)	$D_{\downarrow}$	$T_{sf}$ (K)	$T_C^{expt}$ (K)
Fe	2.28	0.93	0.876	0.280	3769	1043
Co	1.60	0.99	0.166	0.729	3523	1410
Ni	0.62	1.01	0.181	1.667	401	656
YFe <sub>2</sub>	1.79	0.93	0.832	0.469	1200	535
YFe <sub>3</sub>	2.00	0.93	0.834	0.617	976	569
YCo <sub>5</sub>	1.55	0.99	0.178	1.815	2569	987
Y <sub>2</sub> Fe <sub>17</sub>	2.20	0.93	0.723	0.749	1055	324
Y <sub>2</sub> Fe <sub>17</sub> C <sub>3</sub>	2.12	0.93	0.353	0.859	2442	660
Y <sub>2</sub> Fe <sub>17</sub> N <sub>2</sub>	2.35	0.93	0.501	0.655	2332	694
Y(Fe <sub>11</sub> Ti)	2.06	0.93	0.619	0.610	1503	524
Y(Fe <sub>11</sub> Ti)C	2.22	0.93	0.424	0.770	2252	678
Y(Fe <sub>11</sub> Ti)N	2.25	0.93	0.510	0.766	1809	742
Y(Fe <sub>11</sub> Mo)	2.04	0.93	0.598	0.358	2756	472
Y(Fe <sub>10</sub> Mo <sub>2</sub> )	1.93	0.93	0.493	0.608	1717	323
Y(Fe <sub>9</sub> Mo <sub>3</sub> )	1.65	0.93	0.644	0.991	484	138
Y(Fe <sub>8</sub> Mo <sub>4</sub> )	1.48	0.93	0.679	0.948	372	—
Y(Fe <sub>11</sub> Mo)N	2.26	0.93	0.437	0.726	2344	664
Y(Fe <sub>10</sub> Mo <sub>2</sub> )N	2.08	0.93	0.590	0.657	1491	477
Y(Fe <sub>9</sub> Mo <sub>3</sub> )N	1.90	0.93	0.518	0.921	1060	342
Y(Fe <sub>8</sub> Mo <sub>4</sub> )N	1.76	0.93	0.590	0.983	671	140



**Figure 2.** Reduced spin-fluctuation temperature  $T_{sf}/m^2$  as a function of inverse DOS at Fermi level  $D_{eff}^{-1}$ : experimental data based on  $T_S = mI/4k_B$  (full circles), experimental data based on  $T_S$  given in [20] (open circles), and predictions of the Mohn-Wohlfarth theory [20] (dashed line).



**Figure 3.** Reduced spin-fluctuation temperature  $T_{sf}/m^2$  as a function of inverse DOS at Fermi level  $D_{eff}^{-1}$  for Fe-rich intermetallics. To calculate  $T_{sf}$ ,  $T_S = mI/4k_B$  is assumed. According to the Mohn-Wohlfarth theory, all points should lie on the dashed straight line. The points in the line are calculated values. The experimental points for each compound are much lower.

electron gas is subject to an inhomogeneous magnetic field  $H_z(r) = H_0 \cos k \cdot r$ , which will modulate the spin-up and spin-down densities. In the long-wavelength case  $|k| \ll k_F$ , the magnetic energy can be written as [9, 36, 37]

$$E = \frac{N_{el}}{V} \int \left( \frac{1}{48D(E_F)k_F^2} (\nabla s)^2 + \frac{1}{4D(E_F)^2} s^2 - \mu_0 \mu_B H(r) s \right) dr \quad (3)$$

where  $|s| = |M_z|/M_0 \ll 1$  is the reduced magnetization. Note that the coupling represented by the first term in (3) is not to be confused with exchange coupling: a free-electron gas is not subject to exchange. The term simply describes the increase of kinetic energy  $(\hbar^2/2m)\nabla^2$  upon modulation of the wavefunction. As a matter of fact, a small  $D(E_F)$  or, more precisely, a large  $D_{\text{eff}}^{-1}(E_F)$  enhances this ferromagnetic coupling and the Curie temperature and offers some quantitative justification of the Mohn–Wohlfarth approach.

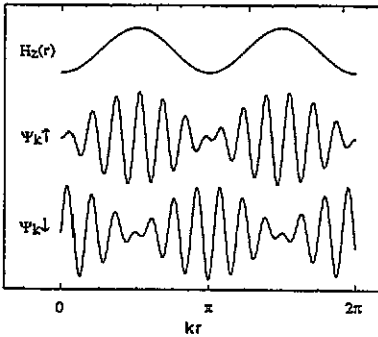


Figure 4. Modulations of spin-up and spin-down wave functions by a periodic external field. The energy of these long-wavelength excitations is proportional to  $D_{\text{eff}}^{-1}$ .

On the other hand, we know that exchange coupling is also an important factor in 3d elements and alloys [3, 10]. For instance, attempts to calculate the spin-wave stiffness of Fe, Co, and Ni from the band structure have failed due to the neglect of exchange interaction [10]. This leads us to a more subtle argument [3]. While the ground state of a strong or nearly strong metallic ferromagnet is delocalized, its thermodynamical behaviour near  $T_C$  is controlled by local excitations. This can be discussed most simply in terms of the spin-1 Ising model, with the spin states  $s_i = \{-1, 0, 1\}$  [18, 19]. If the energy of the non-magnetic state is very high, as can be assumed for strong ferromagnets, then non-magnetic states ( $s_i = 0$ ) are suppressed and the system behaves as a local-moment magnet with  $s_i^2 = 1$ . Local-moment excitations, however, are localized in real space but delocalized in  $k$  space. This means that the knowledge of  $D(E)$  in a narrow region around  $E_F$  is not sufficient to predict the Curie temperature, and all attempts to do so are bound to fail. Note, finally, that the density of states is generally a non-analytical function so series expansion around  $E_F$  is not a good way to describe the overall behaviour of the density of states [18, 19].

#### 4. Conclusions

We conclude that it is not possible to deduce the Curie temperatures of strong ferromagnets from the density of states at the Fermi level. There is a general tendency for a low  $D(E_F)$  to increase the cost of long-wavelength spin fluctuations and thereby stabilize the ferromagnetic state, but both exchange interactions and short-wavelength excitations are misinterpreted in a fully delocalized approach. In particular, the widely used Mohn–Wohlfarth theory is shown to disagree with experimental results, giving Curie temperatures typically in error by a factor of two to four in either sense. Earlier successes of the theory are attributed to inexact band-structure calculations.



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