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Magnetocaloric effect in itinerant magnets around a metamagnetic transition

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ABSTRACT

The phase diagram and magnetocaloric effect in itinerant magnets is explored within the Stoner theory, which yields a reasonable description of the metamagnetic transition observed in various compounds. We obtain the phase diagram as a function of temperature and magnetic field, identifying the region of metastability around the first-order ferromagnetic transition. The impact on the magnetocaloric properties has been verified through the calculation of the isothermal entropy change ΔS, which is computed from two alternative methods based on specific heat or magnetization data. From the direct comparison between the two methods, we observe that the second one is strongly dependent on the process, and we explain under what conditions they become equivalent by using the Clausius-Clapeyron equation. We also discuss the effect of metastable states on the curves of ΔS. The evolution of the transition from first to second order is in good agreement with the phenomenological approach based on the Landau expansion. The results can be applied to different magnetic compounds such as RCo_2, $MnAs_{1-x}Sb_x$, and $La(Fe_xSi_{1-x})_{13}$.

1. Introduction

The magnetocaloric effect (MCE) in intermetallic compounds containing rare-earth R and transition metal M ions is a subject of renewed interest, which deserves a detailed theoretical examination. Such study requires a coherent description of the emergence of itinerant magnetism, the order of the magnetic phase transitions, and how the thermodynamic properties depend on temperature, pressure, and magnetic field.

Magnetic compounds undergoing a first-order magnetic transition may exhibit an augmented MCE, as reported for $Gd_5Ge_2Si_2$ [1]. The MCE around a first-order magnetic phase transition has been studied in Ref. [2] from a microscopic localized model of magnetism. A phenomenological description of the problem is provided by the Landau-Devonshire expansion [3,4].

Itinerant electron metamagnetism (IEM) is observed in various compounds showing a large MCE, e.g., RCo_2 [5,6], MnAs [7], $MnFeP_{1-x}As_x$ [8], $MnAs_{1-x}Sb_x$ [9], and $La(Fe_xSi_{1-x})_{13}$ [10,11]. It can be understood in terms of the Wolfarth-Rhodes-Shimizu theory, which is also based on a Landau expansion of the free energy up to sixth order in the magnetization [12,13]. The temperature dependence of the coeficients can be determined by the spin fluctuations within the Ginzburg-Landau theory [14–16].

A simple microscopic description of itinerant magnetism is provided by the Stoner theory. Some well known drawbacks of this mean-field approach are discussed, e.g., in Refs. [17,18]. Nevertheless, it has been systematically evoked in the description of IEM [19–22,24] and magnetocaloric properties of intermetallic compounds [23]. Here we show that the results obtained in the Stoner theory are compatible with the Shimizu description, and in good agreement with experiments.

The evaluation of the isothermal entropy change ΔS from magnetization data has been a subject of intense debate when first-order transitions are involved [25–32,6]. The context here is suitable to explore this point, through a direct comparison with the alternative method based on calorimetric data.

In the next section we present the microscopic Hamiltonian and some basic thermodynamic formulas. The obtained numerical results are reported in Sections 3 and 4. The discussion is concluded in the last section.

2. Theoretical model and thermodynamics

In presence of a magnetic field $\boldsymbol{B}$, the band Hamiltonian in the Stoner theory can be written as

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$$\mathcal{H} = -\sum_{ij\sigma} t_{ij} c^{\dagger}_{i\sigma} c_{j\sigma} - \sum_{i\sigma} h^{\mathrm{eff}}_{\sigma} n_{i\sigma}, \tag{1}$$

where t_{ij} is the hopping parameter, $h^{\mathrm{eff}}_{\sigma} = \sigma h - U\langle n_{i\bar{\sigma}}\rangle$ is the local effective field, U is the on-site Coulomb interaction, and $h = \mu_B B$. This Hamiltonian can be derived from the Hubbard model [33] in a Hartree-Fock approximation. The electron interaction is taken into account by a spin-dependent molecular field $-U\langle n_{i\bar{\sigma}}\rangle$ which implies a self-consistent rigid band shift.

The magnetic enthalpy per site

$$E = \langle\mathcal{H}\rangle/N - U\langle n_{i\uparrow}\rangle\langle n_{i\downarrow}\rangle$$

can be evaluated by means of the integral

$$E = \sum_{\sigma} \int \varepsilon f(\varepsilon)\rho_0(\varepsilon + h^{\mathrm{eff}}_{\sigma}) d\varepsilon, \tag{2}$$

where

$$\langle n_{i\sigma}\rangle = \int f(\varepsilon)\rho_0(\varepsilon + h^{\mathrm{eff}}_{\sigma}) d\varepsilon, \tag{3}$$

$\rho_0(\varepsilon)$ is bare the density of states (in absence of U and h), and $f(\varepsilon)$ is the Fermi-Dirac distribution function.

The isothermal entropy change can then be obtained by $\Delta S(T,h) = S(T,h) - S(T,0)$, where the entropy per site is given by

$$S(T,h) = \int_0^T \frac{c_h(T)}{T} dT, \tag{4}$$

and $c_h(T) = \left(\frac{\partial E}{\partial T}\right)_h$ is the heat capacity.

Another method assumes the Maxwell relation

$$\left(\frac{\partial S}{\partial h}\right)_T = \left(\frac{\partial m}{\partial T}\right)_h, \tag{5}$$

where $m = \langle n_{i\uparrow}\rangle - \langle n_{i\downarrow}\rangle$ is the magnetization per site. It allows the determination of ΔS directly from the magnetization curves $m(T)$ as

$$\Delta S(T,h) = \int_0^h \left(\frac{\partial m}{\partial T}\right)_{h'} dh'. \tag{6}$$

The use of Eqs. (4)–(6) requires special attention in presence of first-order transitions, as will be discussed in connection with the results in Section 4. The magnetic Gibbs potential per site $G(T,h) = E - TS$ can be computed from Eqs. (2) and (4).

3. Metamagnetic transition

The following results correspond to a tight-binding band with nearest-neighbor hopping on a simple cubic lattice at half-filling. The nearest-neighbor hopping parameter t is taken as the energy unit.

Fig. 1 shows the magnetization isotherms $m(h)$ obtained in the self-consistent calculation, which exhibit the standard odd symmetry $m(-h) = -m(h)$. For lower values of U, the system is in a paramagnetic (PM) state. The curves are monotonically increasing, starting from zero and showing a marked plateau at $m \approx 0.6$. The magnetization continue to increase slowly towards much higher values of the magnetic field, eventually ataining the saturation value $m = 1$, when the minoritary spin band is empty.

For sufficiently large values of U, a ferromagnetic (FM) solution with spontaneous magnetization emerges at low temperature, according to the Stoner criterium $U\rho(E_F) > 1$. It is satisfied at the value $U_0 = 7.0092t$ (the density of states at the Fermi level being $\rho(E_F) = 0.14267$), where the PM solution becomes unstable for $h = 0$. This corresponds to a divergent paramagnetic susceptibility $\chi = \left(\frac{\partial m}{\partial h}\right)_T$, as can be verified from the respective curve in Fig. 1.

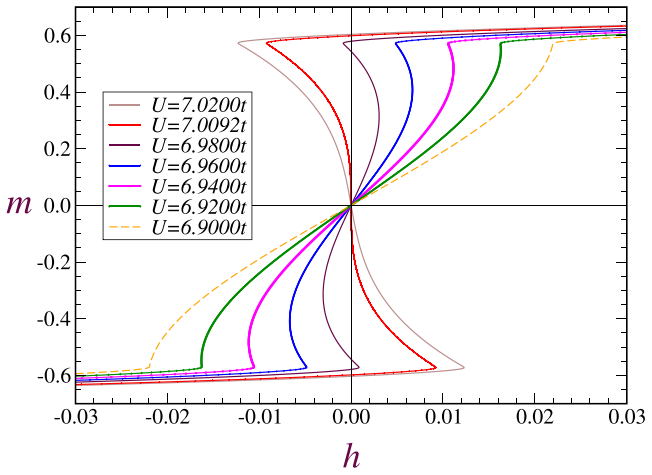

Fig. 1. Magnetization isotherms at low temperature ($T = 0.005t$) for different values of U.

For intermediate values of U, the curves in Fig. 1 exhibit a reentrant S-like shape, so that, for some range of h, multiple solutions are found for m, and the corresponding Gibbs potential $G(T,h)$ is multivalued. The portion of the isotherms where the slope of $m(h)$ is negative corresponds to unstable solutions, and the remaining FM and PM solutions may be stable or metastable.

The variation of the Gibbs potential

$$\Delta G(T,h) = -\int_0^h m(T,h) dh \tag{7}$$

as a function of h for fixed T is illustrated in Fig. 2, which corresponds to a standard first-order transition [34]. We can identify the PM portion of the curve at low h, the FM portion of the curve at high h, and the region of metastablility, where the Gibbs potential can assume three different values for a given h. The crossing of the PM and FM segments of the curve occurs at h^*, where the PM and FM solutions have the same Gibbs potential $G_{PM}(T,h^*) = G_{FM}(T,h^*)$. The value of h^* must be determined by a Maxwell construction.

For values of U just below U_0, the PM solution is metastable for $h = 0$. A modified Stoner criterium for the stability of the FM phase is provided by the condition $h^* = 0$, which is verified for

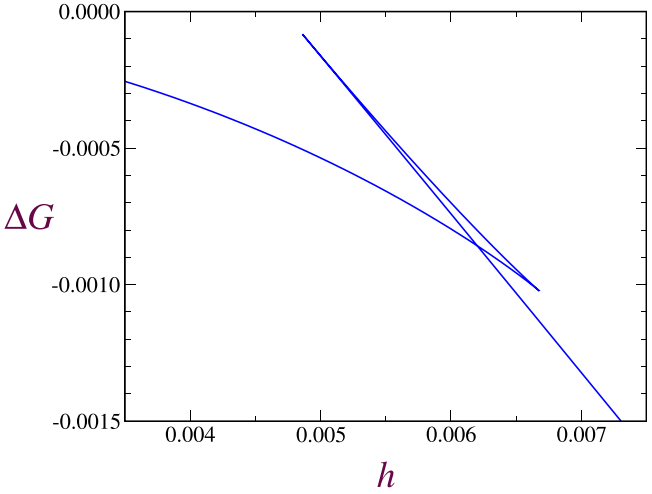

Fig. 2. Magnetic Gibbs potential as a function of the magnetic field at $T = 0.005t$ for $U = 6.96t$.