THEORY OF MAGNETIC PHASE TRANSITIONS

MICHAEL E. MCHENRY AND DAVID E. LAUGHLIN

Carnegie Mellon University, Pittsburgh, PA, USA

The existence of magnetic order (also termed collective magnetism) that is the orderly arrangement of the magnetic spins appearing in materials below an ordering temperature (e.g., the Curie temperature, T_C, of a ferromagnet or the Neel temperature, T_N, of an antiferromagnet; see Magnetic Moment and Magnetization) points to a class of physical phenomena that can be described as magnetic phase transitions. The thermodynamics of these phase transitions can be described by energy functions (expressed in terms of intensive or extensive variables), in terms of magnetization–temperature (M–T) phase diagrams, or in terms of critical exponents that describe the variation of thermodynamic properties (as a function of the order parameter) as the ordering temperature is approached. In this article, we describe the thermodynamics of magnetic ordering transitions, the order of the transitions, critical exponents, and thermodynamic variables. We further describe magnetic phase transitions within the framework of the mean field Landau theory of phase transitions with discussion of several magnetic equations of state.

The discussion of thermodynamic properties begins with the definition of thermodynamic potential functions and their derivatives. For simplicity, we can take pressure and volume as being held constant and consider only magnetic work terms. In this case the entropy (S) and magnetization (M) are extensive variables, the temperature (T) and field (H) are intensive variables, and the different energy functions are the internal energy ($U(S, M)$), the enthalpy ($E(S, H)$) (many texts express enthalpy as H, but E is used here to avoid confusion with applied magnetic fields, H), the Helmholtz free energy ($F(T, M)$), and the Gibbs free energy ($G(T, H)$). The differentials of each are

$$
\begin{aligned}
dU &= T\,dS + H\,dM \\
dE &= T\,dS - M\,dH \\
dF &= -S\,dT + H\,dM \\
dG &= -S\,dT - M\,dH
\end{aligned}
\tag{1}
$$

Two specific heats, C_M and C_H, are defined as

$$
C_M = -T\left(\frac{\partial^2 F}{\partial T^2}\right)_M \quad \text{and} \quad C_H = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_H \tag{2}
$$

The adiabatic and isothermal susceptibilities are given, respectively, by

$$
\chi_S = \left(\frac{\partial M}{\partial H}\right)_S = -\left(\frac{\partial^2 E}{\partial H^2}\right)_S \quad \text{and} \quad \chi_T = \left(\frac{\partial M}{\partial H}\right)_T = -\left(\frac{\partial^2 G}{\partial H^2}\right)_T \tag{3}
$$

Phase transitions reflect discontinuities in certain derivatives of the free energy functions. The order of a phase transition is defined in terms of the smallest derivative of the free energy function for which a discontinuity occurs at the transition temperature. Figure 1a shows the functional dependence of the Helmholtz free energy on M and Figure 1b shows the same with the inclusion of a field (Zeeman) energy term. Figure 1a shows a second-order transition to occur when the parameter A (defined below) is zero ($A = 0$ at the Curie temperature) giving rise to the temperature-dependent magnetization of Figure 1c. Figure 1b shows a first-order transition to occur in a field, H, when the parameter A is zero.

The magnetization at constant temperature:

$$
M = -\left(\frac{\partial G}{\partial H}\right)_T \tag{4}
$$

in a ferromagnet at equilibrium is discontinuous at $H = 0$ for $T < T_C$ (Fig. 1d). At T_C, M is continuous, but the susceptibility is discontinuous between the ferromagnetic and paramagnetic states. The Helmholtz free energy (Fig. 1a) has a minimum only at $M = 0$ for $T > T_C$. For $T < T_C$, two minima occur at $\pm M_s$, the value of the spontaneous magnetization. The $H = 0$ ferromagnetic transition is second order (higher order), at T_C, while for $H \neq 0$ the transition is first order. The transition at $H = 0$ may be first order due to magnetostriction effects. See below.

From the above discussion it is clear that the spontaneous magnetization, M, or the reduced magnetization, $m = M/M_s$ (where M_s is the saturation magnetization), will serve as the order parameter in the ferromagnetic phase transition. In antiferromagnetic, ferrimagnetic, or helimagnetic systems, m is not spatially uniform on the atomic scale. The order parameter must therefore be taken as a spatial function of the local reduced magnetization, $m(r)$.

LANDAU THEORY OF MAGNETIC PHASE TRANSITIONS

In our discussion we will rely on the Landau theory of the magnetic phase transitions. In the Landau theory, the Helmholtz free energy is expanded in a Taylor series where, for symmetry reasons (broken time inversion symmetry in magnetic materials), only even powers of the order parameter, M, are kept in the expansion. The temperature dependence is described in terms of expansion coefficients, of which $A(T)$ is a function of temperature. Near T_C, where the order parameter is small, only a few terms need to be kept in the expansion. Considering such an expansion, truncated at two terms and adding in a term to reflect the Zeeman contributions (i.e., potential energy of the magnetization in the internal field), the magnetic Helmholtz free energy (at constant temperature) can be expressed as

$$
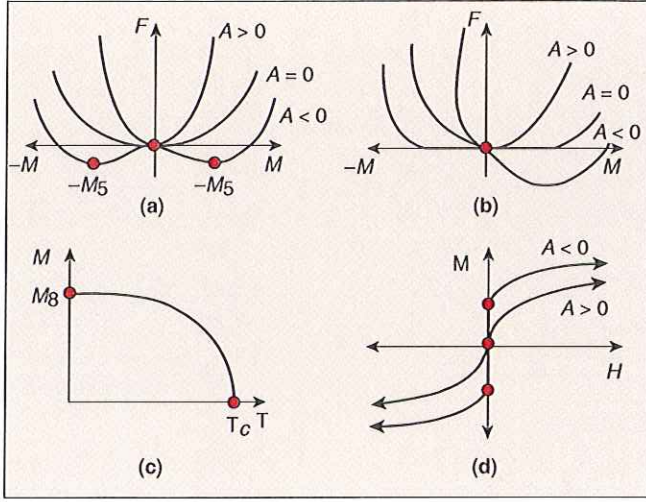F_M = \frac{1}{2}A(T)M^2 + \frac{1}{4}B(T)M^4 - \mu_0 MH \tag{5}
$$

Figure 1. **(a)** Helmholtz free energy functional dependence on M and **(b)** the same with the inclusion of a field (Zeeman) energy term. **(c)** Temperature, T, dependence of the magnetization, $M(T)$, in zero field and **(d)** fixed T magnetization versus field response above and below the ordering temperature, T_C. Adapted from Ausleos and Elliot (1983).

where $A(T)$ and $B(T)$ are the expansion coefficients in the Landau theory, and B is positive for stability. An equation of state can be derived by minimizing the free energy with respect to magnetization, the order parameter of the ferromagnetic material:

$$\frac{\partial F_M}{\partial M} = A(T)M + B(T)M^3 - \mu_0 H = 0 \qquad (6)$$

From this equation we obtain:

$$M^2 = -\frac{A(T)}{B(T)} + \frac{\mu_0 H}{B(T)M} \qquad (7)$$

By invoking a microscopic model of the magnetization (of which there are many), one can determine the specific coefficients $A(T)$ and B. For example, in the Stoner theory of itinerant ferromagnets, the magnetic equation of state and coefficients are expressed by the following equation (Gignoux, 1995):

$$M(H,T)^2 = M(0,0)^2 \left(1 - \frac{T^2}{T_C^2} + \frac{2\chi_0 H}{M(H,T)}\right) \qquad (8)$$

By equating coefficients of Equations 7 and 8, we get

$$B = \frac{\mu_0}{2\chi_0 M(0,0)^2} \quad \text{and} \quad A(T) = -\frac{\mu_0\left[1-\left(\frac{T}{T_C}\right)^2\right]}{2\chi_0} \qquad (9)$$

In this equation $M(0,0)$ is the magnetization when $H=0$ and $T=0$ and χ_0 is the magnetic susceptibility at 0 K. Notice that the Landau theory predicts a (Pauli) paramagnetic state, $M=0$ (no spontaneous magnetization), when the coefficient $A(T)>0$. On the other hand, a stable spontaneous magnetization is predicted for $H=0$ when $A(T)<0$. This spontaneous magnetization is

$$M^2 = -\frac{A(T)}{2B} \qquad (10)$$

In the presence of a field, and for the case $A(T)<0$, this model gives rise to a stable spontaneous magnetization, which is described by the equation of state (see Equation 7). From Equation 8 we can see that plots of $M^2(H, T)$ versus $H/M(H, T)$ are linear and that plotting different isotherms of M^2 versus H/M allows for the determination of $A(T)$ and $B(T)$. Moreover, since $A(T_C)=0$, that is, $A(T)$ vanishes at the Curie temperature, T_C, the Curie temperature can be determined as the isotherm with 0 as its intercept. Plots of M^2 versus H/M isotherms are called Arrott plots and are one method of determining the ferromagnetic ordering temperature from magnetization measurements.

If the Landau expansion is extended to higher order, another free energy minimum for $M>0$ may exist, which could give rise to a so-called metamagnetic state. If $A(T)<0$ but small, a Pauli paramagnetic state may transform into a ferromagnetic state with small M. However, if $B(T)<0$, it is possible to have an additional minimum in the Helmholtz free energy at $H\neq 0$. This minimum may in fact be deeper than that at M_1. In such a case, application of a field causes the system to choose the second minimum (at M_2), giving rise to an $M(H)$ curve as depicted in Figure 2 for this first-order metamagnetic response. See Shimizu (1981).

Equation 5 can be expanded to include other order parameters, specifically strain, ε_S:

$$F_M = \frac{1}{2}A(T)M^2 + \frac{1}{4}B(T)M^4 - \mu_0 MH + C\lambda\varepsilon_S M^2 + \frac{1}{2}C_{EL}\varepsilon_S^2 \qquad (11)$$

where λ is the coupling parameter between the magnetization and strain, ε_S. By minimizing F_M with respect to strain and substituting back into Equation 11, we obtain:

$$F_M = \frac{1}{2}A(T)M^2 + \left(\frac{B}{4} - \frac{C^2\lambda^2}{2C_{EL}}\right)M^4 - \mu_0 MH \qquad .(12)$$

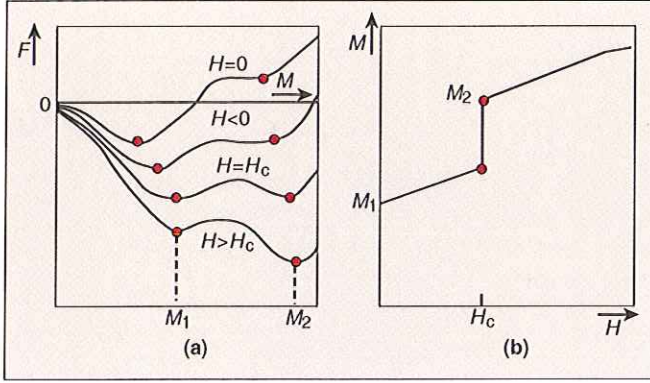**Figure 2. (a and b)** Magnetization curve showing a metamagnetic response. M_1 is the magnetization when $H < H_C$; M_2 is the magnetization in the metamagnetic state, for $H > H_C$. Note the first-order character of the transition from M_1 to M_2. Adapted from Shimizu (1981).

This shows that if the strain is large enough, the coefficient of the term M^4 can become negative, making the magnetic transition thermodynamically first order.

CRITICAL EXPONENTS IN MAGNETIC PHASE TRANSITIONS

One of the goals of thermodynamic treatments of magnetic phase transitions is to determine critical exponents associated with the phase transition. This involves describing power law exponents for the temperature dependence of thermodynamic quantities as the ordering transition is approached. Determination of critical exponents and scaling laws allows for closed-form representations of thermodynamic quantities with significant usefulness in prediction and/or extrapolation of thermodynamic quantities (Callen, 1985). To describe such scaling law behavior, the reduced temperature variance, ε, is defined as

$$\varepsilon = \frac{T-T_C}{T} \qquad (13)$$

ε approaches 0 as T approaches T_C from below or from above. For $T > T_C$ and $H=0$, the specific heat (C, which can be C_M or C_H; see Equation 2) and isothermal susceptibility obey the scaling laws:

$$C \sim \varepsilon^{-\alpha}, \qquad \chi_T \sim \varphi^{-\gamma} \qquad (14)$$

For $T < T_C$, the specific heat, the magnetization, and the isothermal susceptibility obey the scaling laws:

$$C \sim (-\varepsilon)^{-\alpha'}, \qquad \chi_T \sim (-\varepsilon)^{-\gamma'}, \qquad M \sim (-\varepsilon)^{\beta} \qquad (15)$$

At T_C the critical isotherm is described by

$$H \sim |M^{\delta}| \qquad (16)$$

Thermodynamic arguments, such as those of Rushbrooke (see Callen, 1985), allow us to place restrictions on the critical exponents. For example, defining

$$\alpha_H = \left(\frac{\partial M}{\partial T}\right)_H \sim (-\varepsilon)^{\beta-1} \qquad (17)$$

and using thermodynamic Maxwell relations, it is possible to show that

$$\chi_T(C_H - C_M) = T\alpha_H^2 \qquad (18)$$

which implies

$$C_H > \frac{T\alpha_H^2}{\chi_T} \qquad (19)$$

This then requires that, as T approaches T_C from below:

$$\alpha' + 2\beta + \gamma' \geq 2 \qquad (20)$$

See Stanley (1971).

Furthermore, if C_M/C_H approaches a constant (not equal to unity), then two more inequalities may be expressed:

$$\alpha' + \beta(1+\delta) \geq 2, \qquad \gamma' \geq \beta(\delta-1) \qquad (21)$$

Scaling theory predicts that these inequalities can be written as equalities.

In the Landau theory (mean field), it can be determined that

$$\alpha' = \alpha = 0, \qquad \beta = \frac{1}{2}, \qquad \gamma' = \gamma = 1, \qquad \delta = 3 \qquad (22)$$

For example, the critical exponent β in the Landau theory can be found as follows:

$$A(T) = a(T-T_C) \text{ since it is } > 0 \text{ above } T_C \text{ and } < 0 \text{ below } T_C$$

$$F_M = \frac{1}{2}a(T-T_C)M^2 + \frac{1}{4}BM^4 - \mu_0 HM$$

In zero field:

$$F = \frac{1}{2}a(T-T_C)M^2 + \frac{1}{4}BM^4$$

$$\frac{\partial F}{\partial M} = a(T-T_C)M + BM^3 = 0 \text{ at equilibrium}$$

Thus:

$$M = \left(\frac{a(T_C - T)}{B}\right)^{1/2} = \left(\frac{aT_C(-\varepsilon)}{B}\right)^{1/2}$$

Therefore:

$$\beta = \frac{1}{2}$$

Also, the critical exponent of the isotherm can be determined as follows:

$$F_M = \frac{1}{2}a(T - T_C)M^2 + \frac{1}{4}BM^4 - \mu_0 HM$$

$$\frac{\partial F}{\partial M} = a(T - T_C)M + BM^3 - H$$

Therefore, on the critical isotherm, $T = T_C$:

$$M^3 = \frac{H}{B} \quad \text{and} \quad \delta = 3$$

Chikazumi (1997) has reported that the well-known Ising model in 3D for two spins gives rise to the following critical exponents:

$$\alpha' = 0.063, \quad \alpha = 0.125, \quad \beta = 0.313, \quad \gamma' = 1.31,$$

$$\gamma = 1.25, \quad \delta = 5.2 \tag{23}$$

These values that are predicted from models are not always found experimentally. The values have been found in the range:

$$-0.2 < \alpha < 0.2$$
$$-0.2 < \alpha' < 0.3$$
$$0.3 < \beta < 0.4$$
$$1.2 < \gamma < 1.4$$
$$1 < \gamma < 1.2$$
$$4 < \delta < 5$$

See Callen (1985).

If we consider a vector magnetization, and allow for a spatially varying local magnetization, then the Landau theory must be extended to a more complicated form. Further, it is often necessary to add terms $\sim (\nabla M)^2$ to the energy functional. In such cases, $T_C = T_C(\mathbf{k})$ and $\chi = \chi(\mathbf{k})$ can be taken as reciprocal space expansions and the spatial dependence of the susceptibility, $\chi(\mathbf{r})$, can be determined as the Fourier transform of $\chi(\mathbf{k})$. In these cases a correlation length, ζ, for the magnetic order parameter is defined, which diverges at T_C. Further

discussion of the spatial dependence of the order parameter is beyond the scope of this article.

APPLICATIONS

Of particular current interest in application of the theory of magnetic phase transitions has been the development of materials exhibiting large magnetocaloric effects. The magnetocaloric effect (MCE) explains the fact that magnetic materials heat when placed in a magnetic field and cool on removal from the field. This effect was first observed by Warburg (1881) in iron. The magnitude of the effect in elemental ferromagnets, Fe, is 0.5–2°C per *Tesla*.

Recently, Gd–Ge–Si alloys have been shown to have much larger effects of $\sim$3–4°C per *T*. The search for new magnetocaloric effect materials is an active area of current research. A large MCE is the figure of merit for the efficacy of a magnetic refrigerant. With an increasing field, the magnetic entropy decreases and heat is transferred from the magnetic system to the environment in an isothermal process. With a decreasing field, the magnetic entropy increases and heat is absorbed from the lattice system to the magnetic system in an adiabatic process. The Arrott–Noakes (Arrott and Noakes, 1967) equation of state, expressing scaling behavior in terms of critical exponents, β and γ.

$$H^{1/\gamma} = a(T - T_C)M^{1/\gamma} + bM^{(1/\gamma)+(1/\beta)} \tag{24}$$

has recently been used to scale magnetocaloric data for the magnetic entropy change in the ferromagnetic to paramagnetic phase transition for a variety of materials onto a single master curve (Franco et al., 2007) allowing for the comparison of materials for this application.

Equation 24 also shows that if $H^{1/\gamma}$ is plotted against $M^{(1/\gamma)+(1/\beta)}$, the result should be a straight line at the Curie temperature. For mean field values this is the Arrott plot, discussed above.

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