

3. Thermodynamics

3.1 Introduction

It is clear from the preceding chapters that the relative population of the lowest energy levels of paramagnetic ions depends on both the temperature and the strength of the external magnetic field. The equilibrium states of a system can often be described by three variables, of which only two are independent. For the common example of the ideal gas, the variables are pVT (pressure, volume, temperature). For magnetic systems, one obtains HMT (magnetic field, magnetization, temperature) as the relevant variables and the thermodynamic relations derived for a gas can be translated to a magnetic system by replacing p by H and V by $-M$. In the next section we review a number of the thermodynamic relations. Then, two sections are used to demonstrate the usefulness of these relations in analyzing experiments. In fact the simple thermodynamic relations are often applicable, even to magnetic systems that require a complicated model to describe the details of their behavior [1].

3.2 Thermodynamic Relations

The first law of thermodynamics states that the heat dQ added to a system is equal to the sum of the increase in internal energy dU and the work done by the system. For a magnetic system work has to be done on the system in order to change the magnetization, so the first law of thermodynamics may be written as

$$dQ = dU - HdM,$$

where H is the applied field and M is the magnetization. Remembering that the entropy S is related to Q by $TdS = dQ$, the first law can be written as

$$dU = TdS + HdM. \quad (3.1)$$

The energy U is an exact differential, so

$$\left(\frac{\partial T}{\partial M}\right)_S = \left(\frac{\partial H}{\partial S}\right)_M. \quad (3.2)$$

The enthalpy E is defined as $E = U - HM$, thus

$$dE = dU - HdM - MdH = TdS - MdH,$$

and, as E is also an exact differential

$$\left(\frac{\partial T}{\partial H}\right)_S = -\left(\frac{\partial M}{\partial S}\right)_H. \quad (3.3)$$

The Helmholtz free energy F is defined as $F = U - TS$, so

$$dF = dU - TdS - SdT = -SdT + HdM,$$

and the exact differentiability leads to

$$\left(\frac{\partial S}{\partial M}\right)_T = -\left(\frac{\partial H}{\partial T}\right)_M. \quad (3.4)$$

The Gibbs free energy is $G = E - TS$, thus

$$dG = dE - TdS - SdT = -SdT - MdH$$

and

$$\left(\frac{\partial M}{\partial T}\right)_H = \left(\frac{\partial S}{\partial H}\right)_T. \quad (3.5)$$

Equations (3.2)–(3.5) are the Maxwell relations in a form useful for magnetic systems.

The specific heat of a system is usually defined as dQ/dT , but it also depends on the particular variable that is kept constant when the temperature changes. For magnetic systems, one has to consider both c_M and c_H , the specific heats at constant magnetization and field, respectively. From $dQ = TdS$ and the definitions of U and E one obtains

$$c_M = \left(\frac{\partial Q}{\partial T}\right)_M = T \left(\frac{\partial S}{\partial T}\right)_M = \left(\frac{\partial U}{\partial T}\right)_M \quad (3.6)$$

and

$$c_H = \left(\frac{\partial Q}{\partial T}\right)_H = T \left(\frac{\partial S}{\partial T}\right)_H = \left(\frac{\partial E}{\partial T}\right)_H. \quad (3.7)$$

Now let the entropy, which is a state function, be a function of temperature and magnetization, $S = S(T, M)$. Then, an exact differential may be written

$$dS = \left(\frac{\partial S}{\partial T}\right)_M dT + \left(\frac{\partial S}{\partial M}\right)_T dM.$$

Multiplying through by T , and using the Maxwell relation given by Eq.(3.4),

$$TdS = T \left(\frac{\partial S}{\partial T}\right)_M dT - T \left(\frac{\partial H}{\partial T}\right)_M dM$$