

III. Magnetic Phenomena

All substances exhibit a magnetic moment, M , upon application of a magnetic field, H , which is related to H by $M = \chi H$, where χ is the magnetic susceptibility.^{13,14a-c} Open-shell paramagnetic compounds have their induced moment aligned parallel to the field. For noninteracting independent spins the magnetic moment is inversely proportional to temperature (T) and the susceptibility can be modeled by the Curie expression (eq 1) where $x = g\mu_B H/k_B T$ or the more general Brill-

$$\chi = C/T \quad (1)$$

$$C = Ng^2\mu_B^2 S(S+1)/3k_B T = (0.375 \text{ (emu K)/mol})(S(S+1)g^2)/3T$$

$$\chi = Ng\mu_B J B_J(x)/H \quad (2)$$

$$B_J(x) = \frac{2J+1}{2J} \operatorname{ctnh} \left(\frac{(2J+1)x}{2J} \right) - \frac{1}{2J} \operatorname{ctnh} \left(\frac{x}{2J} \right)$$

ouin (eq 2) expressions, where N is Avogadro's number, g is the Lande factor, μ_B is the Bohr magneton, $J = S + L$, $x \equiv gJ\mu_B B/k_B T$, and k_B is the Boltzmann constant.^{14a-c} Closed-shell diamagnetic compounds have their induced moment aligned antiparallel to the field. This latter phenomenon is temperature independent.

In some circumstances these spins experience an effective parallel (or antiparallel) exchange (molecular or Weiss) field due to the neighboring spins which leads to an increase (or decrease) in the measured susceptibility from that predicted for independent spins. The high-temperature susceptibility data often may be expressed by the Curie-Weiss¹⁴ law (eq 3), where for ferromagnetic (parallel) and antiferromagnetic (antiparallel) interactions θ is respectively greater or less than zero.

$$\chi = C/(T - \theta) \quad (3)$$

$$\mu_{\text{eff}} = (3\chi k_B / NT)^{1/2} = 2.823(\chi T)^{1/2} = \mu_B [g^2 S(S+1)]^{1/2} \quad (4)$$

The magnitude of χ is temperature dependent and chemists frequently report the effective moment,^{14c} μ_{eff} (eq 4). The susceptibility, reciprocal susceptibility (χ^{-1}), and effective moment possess characteristic temperature dependencies. The magnetization (M) also possesses a characteristic field dependency, which enables the rapid qualitative determination of the magnetic behavior. These dependencies are illustrated for in-

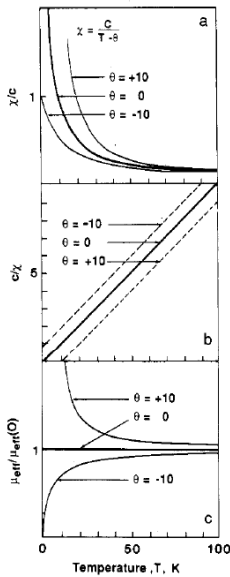


Figure 1. Susceptibility (χ) (a), reciprocal susceptibility (χ^{-1}) extrapolated from the high-temperature region (b), and effective moment (μ_{eff}) (c) as a function of temperature for independent $g = 2$, $S = 1/2$ spins as well as ferromagnetically coupled ($\theta = 10$ K) and antiferromagnetically coupled ($\theta = -10$ K) spins.

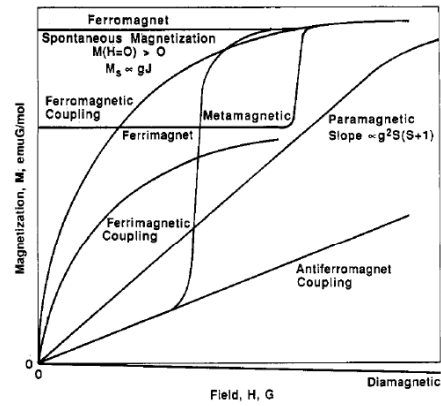


Figure 2. Schematic illustration of the magnetization (M) as a function of field (H) for several types of commonly observed magnetic behavior.

dependent spin (Curie), ferromagnetic, and antiferromagnetic behaviors in Figures 1 and 2.

At sufficiently low temperature the spins may order. If they align parallel to each other (ferromagnet), then a macroscopic spontaneous magnetization at zero applied field [i.e., $M(H_{\text{app}} = 0) > 0$] is present with a characteristic saturation moment, M_s (e.g., 1.22×10^4 (emu G)/mol for Fe),^{14d} in a finite applied field. The saturation magnetization, M_s , can be calculated from eq 5. If neighboring spins are aligned antiparallel

$$M_s = NgS\mu_B \quad (5)$$

(antiferromagnet), then there is no net macroscopic moment in zero applied field and the susceptibility is anisotropic below the Néel temperature. Ferrimagnetism occurs when the antiferromagnetically aligned spins have differing local moments resulting in incomplete cancellation of the parallel and antiparallel spin sublattices leading to a reduced, but nonzero, moment. The saturation magnetization for a ferrimagnet can be calculated from eq 6 or 7 depending if incomplete

$$M_s = N\Delta gS\mu_B \quad (6)$$

$$M_s = Ng\Delta S\mu_B \quad (7)$$

cancellation of sublattice magnetic moments arises from differences in g or S , respectively. Application of a magnetic field to a ferromagnet leads to alignment of the ferromagnetic domains and $M(H)$ exhibits a hysteresis behavior with a characteristic coercive field (e.g., ~ 1 G for Fe)^{14e} necessary to move the domain walls. Metamagnetism is the field-dependent transformation from an antiferromagnetic state to a high-moment ferromagnetic state. Like the gas/liquid critical behavior, the onset of cooperative magnetic behavior near the Curie temperature, T_c , can be scaled with critical exponents; i.e., the phenomena can be modeled by $(T - T_c)^\lambda$, where λ is the critical exponent.¹⁵ The critical exponents can be compared against theoretical expectations to elucidate the dimensionality and anisotropy of the dominant spin interactions.

磁気転移温度が室温より低い場合、温度を下げたら秩序磁性相に入る、というスタンスで書いてある。転移温度が室温より高い通常の磁石は、もちろん温度をそれより上げると無秩序磁性相になる。