

Advanced Solid State Chemistry

“magnets: order vs disorder”

Magnet 磁性体
 Magnetic moment 磁気モーメント
 μ (axial vector)
 Magnetization M 磁化
 Spontaneous Magnetization M_s
 自発磁化
 Demagnetizing Field 反磁界
 Magnetic Hysteresis ヒステリシス
 Saturation Magnetization M_s 飽和磁化
 Remnant Magnetization M_r 残留磁化
 Coersive Field H_c 保磁力
 Domain ドメイン、磁区
 Curie / Neél temperature 転移温度

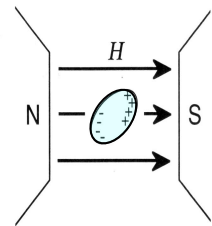
Dielectric 誘電体
 Electric dipole 電気双極子
 $\mu = qr$ (polarity vector)
 Polarization P 電気分極
 Spontaneous Polarization P_s
 自発分極
 Depolarizing Field 反電界, 脱分極電界
 Dielectric Hysteresis ヒステリシス
 Saturation Polarization P_s 飽和分極
 Remnant Polarization P_r 残留分極
 Coersive Field E_c 抗電界
 Domain ドメイン
 Curie / Neél temperature 転移温度

“Magnet” ?

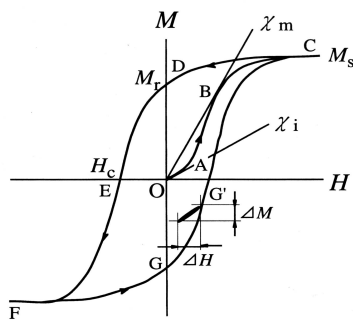
A magnet is a material that produces a magnetic field.

In other words, a magnet must have remnant magnetization.

Ferromagnet, Antiferromagnet, Ferrimagnet:
 defined by the mechanistic spin ordered structure.



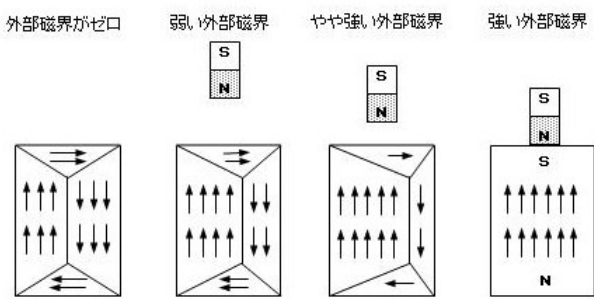
O→B→C: initial magnetization curve
 C→D: M_r or M_s (spontaneous)
 D→E: H_c
 C→D→E→F→G→C:
 Hysteresis Loop



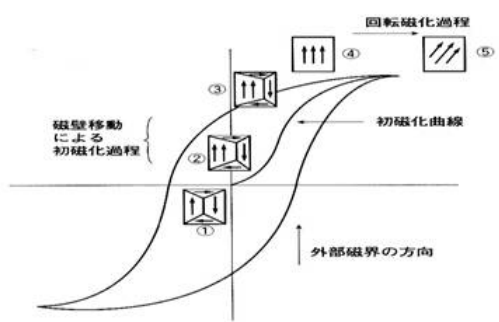
- H_c small: "soft" magnetic shield, transformer iron core
- H_c middle: "semi-soft" rewritable media
- H_c large: "hard" permanent magnet

A ferromagnet does not always behave as a magnet.

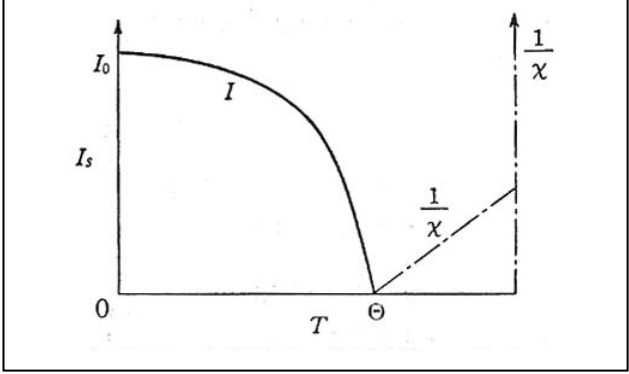
Why?



It is explained in terms of a *domain model*.



Spontaneous magnetization disappears at the Curie temperature (T_c). Above T_c , a substance is a paramagnet. Inverse susceptibility ($1/\chi$) is proportional to T , and the temperature intercept is approximately T_c in the $1/\chi$ vs T plot.



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-

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

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

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

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

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.

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

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

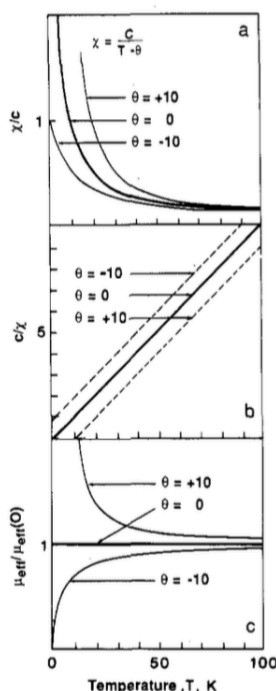


Figure 1. Susceptibility (χ) (a), reciprocal susceptibility (χ^{-1}) extrapolated from the high-temperature region (b), and effective moment (μ_{eff}) (c) as a function of temperature for independent $g = 2$, $S = 1/2$ spins as well as ferromagnetically coupled ($\theta = 10$ K) and antiferromagnetically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

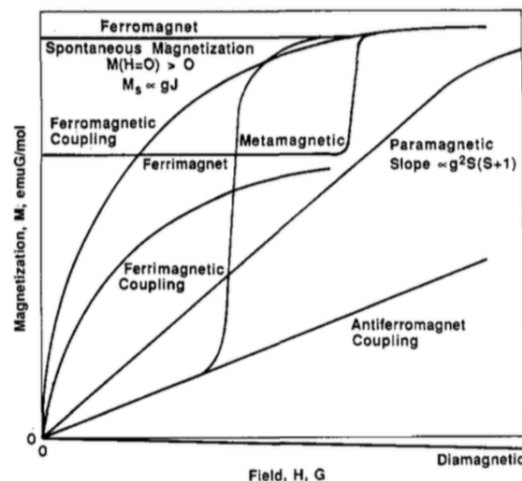


Figure 2. Schematic illustration of the magnetization (M) as a function of field (H) for several types of commonly observed magnetic behavior.

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 independent 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.