Chapter Eleven  Diamagnetism and Paramagnetism

The story of magnetism begins with a mineral called magnetite “Fe$_3$O$_4$”. The first truly scientific study of magnetism was made by William Gilbert. His book “On the magnet” was published in 1600.

In 1820 Hans Christian Oersted discovered that an electric current produces a magnetic field.

In 1825 the first electromagnet was made by Sturgeon.

Each stores the same magnetic energy $\sim 0.4$J.
Magnetic susceptibility per unit volume

\[ \chi = \frac{M}{H} \]

- \( M \): magnetization, magnetic moment per unit volume
- \( B \): macroscopic magnetic field intensity
- \( \chi > 0 \): paramagnetic material
- \( \chi < 0 \): diamagnetic material

In general, paramagnetic material has a positive susceptibility (\( \chi > 0 \)). Diamagnetic material has a negative susceptibility (\( \chi < 0 \)).
Three principal sources for the magnetic moment of a free atom:

- Electrons’ spin
- Electrons’ orbital angular momentum about the nucleus
- Change in the orbital moment induced by an applied magnetic field

First two sources give paramagnetic contributions.
The last source gives a diamagnetic contribution.
Reviews, in CGS

\[ \vec{B} = \vec{H} + 4\pi \vec{M} = \mu \vec{H} \]

\[ \vec{M} = \bar{m} \frac{N}{V} \]

[magnetic dipole moment [emu/cm³]]

\[ \bar{m} = -\frac{e}{2m} \sum_i \vec{r}_i \times \vec{p}_i = -\frac{e\hbar}{2m} \vec{L} = -\mu_B \vec{L} \]

\[ \bar{m} = \mu_B g_o \sum_i \vec{s}_i = \mu_B g_o \vec{S} \]

Bohr magneton \( \mu_B = \frac{e\hbar}{2m} = 9.27 \times 10^{-24} \text{ J/T}; \quad 1 \text{T} = 1 \text{Vs/m}^2 \)

Electronic g-factor \( g_o = 2.0023 \)

L and S are quantum operators with no basis in classical physics.
Theory of diamagnetism was first worked out by Paul Langevin in 1905.

Negative magnetism present in an applied field even though the material is composed of atoms that have no net magnetic moment.

Motion of the electron is equivalent to current in the loop.

Faraday’s law

\[ \text{Emf} = -\frac{d\Phi_B}{dt} \]  

[volt]

Consider a circular loop with radius \( r \), the effect of applied field \( H \) is to change \( \mu \) by an amount \( \Delta \mu \) in negative direction.

\[ \chi = -\frac{N_A \rho e^2 Z}{A} \frac{e^2 Z}{6mc^2} \left\langle R^2 \right\rangle \]  

[emu/Oe-cm³]
The change in moment of a single orbit:

\[ E = \frac{Emf}{\ell} = -\frac{A}{\ell} \frac{dH}{dt} = -\frac{\pi r^2}{2\pi r} \frac{dH}{dt} = -\frac{r}{2} \frac{dH}{dt} \]

\[ a = \frac{dv}{dt} = \frac{eE}{mc} = -\frac{er}{2mc} \frac{dH}{dt} \]

\[ \Delta v = -\frac{er}{2mc} H \]

\[ \Delta \mu = \frac{er}{2c} \Delta v = -\frac{e^2 r^2}{4mc^2} H \]

the plane of the orbit is perpendicular to the applied field

All possible orientations in the hemisphere

\[ \langle r^2 \rangle = \langle R^2 \sin^2 \theta \rangle = R^2 \int \frac{\sin^2 \theta \, dA}{A} \]

\[ = \frac{R^2}{2\pi R^2} \int^\pi_0 \sin^2 \theta (2\pi R \sin \theta)(R \, d\theta) = \frac{2}{3} R^2 \]
A single electron with consideration of all possible oriented orbits,

\[ \Delta \mu = \frac{eR}{2c} \Delta v = -\frac{e^2 R^2}{6mc^2} H \]

For an atom that contains \( Z \) electrons,

\[ \Delta \mu = \sum_{i=1}^{Z} -\frac{e^2 R_i^2}{6mc^2} H = -\frac{e^2 H}{6mc^2} \sum_{i=1}^{Z} R_i^2 \]

\( R_i \) is the radius of the \( i \)th orbit

The number of atoms per unit volume:

\[ \rho = \frac{N_A \rho/A}{A} \]

\( N_A \) is Avogadro’s number

On the volume basis,

\[ \Delta \mu = -\frac{N_A \rho}{A} \frac{e^2}{6mc^2} \left( \sum_{i=1}^{Z} R_i^2 \right) H \]

Susceptibility, \( \chi = -\frac{N_A \rho}{A} \frac{e^2 Z}{6mc^2} \left\langle R^2 \right\rangle \)

Classical Langevin result

Carbon (radius = 0.7 Å)

\[ \chi = -\frac{6.02 \times 10^{23} \left(2.22 \text{g/cm}^3\right)}{12.01 \text{g}} \times \frac{\left(4.80 \times 10^{-10} \text{esu}\right)^2}{6 \left(9.11 \times 10^{-28} \text{g}\right) \left(3 \times 10^{10} \text{cm/s}\right)^2} \left(0.7 \times 10^{-8} \text{cm}\right)^2 \]

\[ \chi = -1.5 \times 10^{-6} \text{emu/Oe} - \text{cm}^3 \]

Experimental value: \(-1.1 \times 10^{-6} \text{emu/Oe-cm}^3\)
The agreement between calculated and experimental values for other diamagnetic materials is generally not that good, but it is at least within an order of magnitude.

This classical theory of Langevin is a good example of the use of a simple atomic model to quantitatively explain the bulk properties of a material.

Negative susceptibility
magnitude : $10^{-5} \sim 10^{-6}$ cm$^3$/mole

The other consistency is that $\chi$ is independent of temperature for most diamagnetic materials.

Quantum theory of diamagnetism results in the same expression.
Diamagnetic materials

Closed-shell electronic structures result in no net moment
  The monatomic rare gases He, Ne, Ar, …
  Polyatomic gases, H₂, N₂, …
  Some ionic solids, NaCl, …
  Some covalent solids, C, Si, Ge, …

Superconductors: Meissner effect

The first systematic measurements of susceptibility of a large number of substances over an extended range of temperature were made by Pierre Curie and reported by him in 1895.

-- mass susceptibility is independent of temperature for diamagnetics, but that it vary inversely with temperature for paramagnetics.

\[ \chi = \frac{C}{T} \quad \chi = \frac{C'}{T - \theta} \quad \text{in general} \]

Curie law               Curie-Weiss law (1907)
Quantum theory of diamagnetism

Hamiltonian
\[ H = \frac{1}{2m} \left( \vec{p} - \frac{Q}{c} \vec{A} \right)^2 + QV \]

Terms due to the applied field
\[ \vec{B} = \nabla \times \vec{A} \]

\[ H' = \frac{i \hbar}{2mc} \left( \nabla \cdot \vec{A} + \vec{A} \cdot \nabla \right) + \frac{e^2}{2mc^2} A^2 \]

In the uniform magnetic field
\[ \vec{B} = B \hat{k} \]

\[ \nabla \times \vec{A} = \left( \frac{\partial}{\partial x} \hat{i} + \frac{\partial}{\partial y} \hat{j} + \frac{\partial}{\partial z} \hat{k} \right) \times \left( A_x \hat{i} + A_y \hat{j} + A_z \hat{k} \right) \]
\[ = \left( \frac{\partial A_z}{\partial y} - \frac{\partial A_y}{\partial z} \right) \hat{i} + \left( \frac{\partial A_x}{\partial z} - \frac{\partial A_z}{\partial x} \right) \hat{j} + \left( \frac{\partial A_y}{\partial x} - \frac{\partial A_x}{\partial y} \right) \hat{k} \]

One solution
\[ \vec{A} = -\frac{yB}{2} \hat{i} + \frac{xB}{2} \hat{j} + 0 \hat{k} \]

\[ H' = \frac{i\hbar B}{4mc} \left( x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) + \frac{e^2B^2}{8mc^2} \left( x^2 + y^2 \right) \]

\[ \vec{L}_z \]
z-component of angular momentum

\[ \tilde{L}_z = -i\hbar \left( x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) \]

\[ \rightarrow \text{ paramagnetism} \]

For diamagnetic materials with all electrons in filled core shells, the sum \( \sum \langle L_z + 2S_z \rangle \) over all electrons vanishes.

For a spherically symmetric system

\[ \langle x^2 + y^2 \rangle = \frac{2}{3} \langle r^2 \rangle \]

the additional energy

\[ E' = \frac{e^2 B^2}{8mc^2} \langle x^2 + y^2 \rangle = \frac{e^2 \langle r^2 \rangle}{12mc^2} B^2 \]

the associated magnetic moment

\[ \mu = -\frac{\partial E'}{\partial B} = -\frac{e^2 \langle r^2 \rangle}{6mc^2} B \]

in agreement with the classical Langevin result.
Vibrating Sample Magnetometer (VSM)

→→ measuring sample’s magnetic moment

- oscillate sample up and down
- measure induced emf in coils A and B
- compare with emf in coils C and D from known magnetic moment
Classical theory of paramagnetism

In 1905, Langevin also tried to explain paramagnetism qualitatively. He assumed that paramagnetic materials have molecules or atoms with the same non-zero net magnetic moment $\mu$.

In the absence of magnetic field, these atomic moments point at random and cancel one another. $M=0$

When a field is applied, each atomic moment tends to align with the field direction; if no opposing force acts, complete alignment would be produced and the material demonstrates a very large moment. But thermal agitation of atoms tends keep the atomic moments pointed at random. Partial alignment and small positive $\chi$.

As temperature increases, the randomizing effect of thermal agitation increases and hence, $\chi$ decreases.

This theory leads naturally into the theory of ferromagnetism.
A unit volume material contains $n$ atoms with a magnetic moment $\mu$ each.

$$E = -\vec{\mu} \cdot \vec{H} = -\mu H \cos \theta$$

Let the direction of each moment be presented by a vector, and let all vectors be drawn thru. the center of the sphere.

$$dn = KdA \exp \left( \frac{-E}{k_BT} \right) = K2\pi \sin \theta d\theta e^{\frac{\mu H \cos \theta}{k_BT}} \quad \# \text{at angle } \theta \rightarrow \theta + d\theta$$

$$n = \int dn = K2\pi \int_0^\pi d\theta \sin \theta e^{\frac{\mu H \cos \theta}{k_BT}} \quad \text{total } #$$

$$M = \int_0^n dn \mu \cos \theta = K2\pi \mu \int_0^\pi d\theta \cos \theta \sin \theta e^{\frac{\mu H \cos \theta}{k_BT}}$$

Let $a = \frac{\mu H}{k_BT}$,

$$M = \frac{n \mu \int_0^\pi d\theta \cos \theta \sin \theta e^{a \cos \theta}}{\int_0^\pi d\theta \sin \theta e^{a \cos \theta}}$$

$$= \frac{n \mu \int_{-1}^1 dx \, xe^{ax}}{\int_{-1}^1 dx \, e^{ax}} = n \mu \left( \frac{e^a + e^{-a}}{e^a - e^{-a}} - \frac{1}{a} \right) = n \mu \left( \coth(a) - \frac{1}{a} \right)$$
Langevin function $L(a) = \coth(a) - \frac{1}{a}$

$L(a)$ can be expressed in series,

$$L(a) = \frac{a}{3} - \frac{a^3}{45} + \frac{2a^5}{945} - \ldots$$

When $a$ is small ($<0.5$), $L(a)$ is a straight line with a slope $1/3$.

When $a$ is large, $L(a) \to 1$.

Two conclusions:

1. Saturation will occur at large $a$ implying that at large $H$ and low $T$ the alignment tendency of field is going to overcome the randomizing effect of thermal agitation.

2. At small $a$, $L(a)$ depends linearly on $a$ implying that $M$ varies linearly with $H$. 
The Langevin theory also leads to the Curie law.

For small $a$,

$$M = \frac{n\mu a}{3} = \frac{n\mu}{3} \frac{\mu H}{k_B T}$$

$$\chi = \frac{M}{H} = \frac{n\mu^2}{3 k_B T} = \frac{C}{T}$$

$$C = \frac{n\mu^2}{3 k_B}$$

Oxygen is paramagnetic and obeys the Curie law w/ $\chi = 1.08 \times 10^{-4} \text{emu/gOe}$.

$$\mu = \sqrt{\frac{3 k_B T \chi}{n}} = \sqrt{\frac{3(32 \text{g/mole})(1.38 \times 10^{-16} \text{erg/K})(1.08 \times 10^{-4} \text{emu/gOe})}{6.02 \times 10^{23}}}$$

$$= 2.64 \times 10^{-20} \text{erg/Oe} - \text{mole}$$

$$= 2.85 \mu_B$$

Even in heavy atoms or molecules containing many electrons, each with orbital and spin moments, most of the moments cancel out and leave a magnetic moment of only a few Bohr magnetons.

Typically,

$$a = \frac{\mu H}{k_B T} = \frac{(2.64 \times 10^{-20} \text{erg/Oe})(10000 \text{Oe})}{(1.38 \times 10^{-16} \text{erg/K})(300 \text{K})} = 0.0064 < 0.5$$

smaller enough

$L(a) = a/3$
The Langevin theory of paramagnetism which leads to the Curie law, is based on the assumption that individual carrier of magnetic moment do not interact with one another, but are acted on only by applied field and thermal agitation.

However, many paramagnetic materials obey the more general law, considering the interaction between elementary moments.

Weiss suggested that this interaction could be expressed in terms of a fictitious internal field, “molecular field $H_M$”. In addition to $H$.

The total field acting on material $H + H_M = H + \gamma M$

$$\chi = \frac{M}{H_{tot}} = \frac{M}{H + \gamma M} = \frac{C}{T} \quad \Rightarrow \quad (T - C\gamma)M = CH$$

$$\chi = \frac{M}{H} = \frac{C}{T - C\gamma} = \frac{C}{T - \theta}$$

where $\theta (=C\gamma)$ is a measure of the strength of the interaction.
Theoretical predictions

\[ \frac{1}{\chi} = \frac{T - \theta}{C} = \frac{1}{C} \frac{T - \theta}{C} \]

Intercept reveals information of \( \theta \)

\( \theta (\text{FeSO}_4) < 0, \quad \theta (\text{MnCl}_2) > 0 \)

\( \theta > 0 \) indicates that the molecular field aids the applied field, makes elementary moments align with H, and tends to increase \( \chi \).

\( \theta < 0 \) indicates that the molecular field opposes the applied field, makes elementary moments disalign with H, and tends to decrease \( \chi \).
Precession of atomic magnetic moments about $H$, $\vec{\tau} = \vec{\mu} \times \vec{H}$

like gyroscope, angular momentum in the presence of gravitation.

$$\vec{\tau} = \vec{r} \times m\vec{g} = \frac{d\vec{L}}{dt}$$

If the atom was isolated, the only effect of an increase in $H$ would be an increase in the rate of precession, but no change in $\theta$.

For a system with many atoms, all subjected to thermal agitation, there is an exchange of energy among atoms. When $H$ is applied, the exchange of energy disturbs the precessional motion enough so that the value of $\theta$ for each atom decreases slightly, until the distribution of $\theta$ values becomes appropriate to the existing values of field and temperature.
Quantum theory of Paramagnetism

The central postulate of QM is that the energy of a system is discrete, improving the quantitative agreement between theory and experiment.

\[ \theta \text{ is continuous variable.} \]

\[ \theta \text{ is restricted to certain variables.} \]

Space Quantization
The orbital and spin magnetic moments for an electron

\[ \vec{\mu}_{\text{orbit}} = \frac{e\hbar}{4\pi mc} = \frac{e}{2mc} \frac{\hbar}{2\pi} = -\frac{e}{2mc} \vec{p}_{\text{orbit}} \]

\[ \vec{\mu}_{\text{spin}} = \frac{e\hbar}{4\pi mc} = \frac{e}{mc} \frac{1}{2} \frac{\hbar}{2\pi} = -\frac{e}{mc} \vec{p}_{\text{spin}} \]

In general

\[ \vec{\mu} = -g \frac{e}{2mc} \vec{p} \]

where \( g \) is spectroscopic splitting factor, or \( g \)-factor

\( g = 1 \) for orbital motion and \( g = 2 \) for spin

In a multiple-electron atom, the resultant orbital angular momentum and the resultant spin momentum are characterized by quantum numbers \( L \) and \( S \). Both are combined to give the total angular momentum that is described by the quantum number \( J \).

\[ \mu = g \frac{e}{2mc} \sqrt{J(J+1)} \hbar = g \sqrt{J(J+1)} \mu_B \]

In the direction of \( H \),

\[ \mu_H = g \frac{e}{2mc} m_J \hbar = gm_J \mu_B \]

There are \( 2J+1 \) numbers of allowed azimuthal quantum number \( m_J \):

\( J, J-1, \ldots, -(J-1), -J \).
For a free atom, the g factor is given by the Landé equation

\[
g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}
\]

The energy levels of the system in a magnetic field

\[
E = -\mu \cdot \vec{H} = m_J g \mu_B H
\]

For a single spin with no orbital moment, \( m_J = \pm 1/2 \) and \( g = 2 \).

The equilibrium population for the two level system:

\[
\frac{N_1}{N} = \frac{\exp(\mu H/k_B T)}{\exp(\mu H/k_B T) + \exp(-\mu H/k_B T)} \quad \text{lower level}
\]

\[
\frac{N_2}{N} = \frac{\exp(-\mu H/k_B T)}{\exp(\mu H/k_B T) + \exp(-\mu H/k_B T)} \quad \text{upper level}
\]

Total number of atoms is conserved.

\[ N = N_1 + N_2 = \text{constant} \]
The resultant magnetization for $N$ atoms per unit volume

$$M = (N_1 - N_2)\mu = N\mu \frac{e^x - e^{-x}}{e^x + e^{-x}} = N\mu \tanh(x) \quad \text{where} \quad x = \frac{\mu H}{k_B T}$$

For $x<<1$, $\tanh(x) \sim x$ and $M \approx N\mu x = N\frac{\mu^2 H}{k_B T}$

For a system with known $g$ and $J$,

Potential energy of each moment in $H$

$$U = -m_J g\mu_B H$$

The probability of an atom w/ energy $U$

$$e^{-U/k_B T} = e^{m_J g\mu_B H/k_B T}$$

Boltzmann statistics

$$\sum m_J g\mu_B e^{m_J g\mu_B H/k_B T}$$

Therefore,

$$M = N \sum_{m_J} m_J g\mu_B e^{m_J g\mu_B H/k_B T}$$

$$M = NgJ\mu_B \left[ \frac{2J + 1}{2J} \coth \left( \frac{(2J + 1)x}{2J} \right) - \frac{1}{2J} \coth \left( \frac{x}{2J} \right) \right]$$

$$= NgJ\mu_B B_J(x)$$

Brillouin function

where $x = \frac{gJ\mu_B H}{k_B T}$
The saturation magnetization \( M_0 = N \mu_H = N gJ \mu_B \)

The maximum moment of each atom in the direction of \( H \)

\[
\frac{M}{M_0} = B_j(x) = \frac{2J + 1}{2J} \coth \left( \frac{(2J + 1)x}{2J} \right) - \frac{1}{2J} \coth \left( \frac{x}{2J} \right)
\]

Brillouin function, 1927

When \( J=\infty \), the classical distribution, the Brillouin function reduces to the Langevin function.

\[
\frac{M}{M_0} = \coth(x) - \frac{1}{x}
\]

When \( J=1/2 \), the magnetic moment consists of one spin per atom.

\[
\frac{M}{M_0} = \tanh(x) \quad x << 1
\]

\[
M \approx N \mu_H x = N g^2 J^2 \frac{\mu_B^2 H}{k_B T} = N \frac{\mu^2 H}{k_B T}
\]
The Brillouin function, like the Langevin, is zero for $x$ equals to zero and tends to unity as $x$ becomes large. The course of the curve in between depends on the value of $J$ for the atom involved.

\begin{align*}
\text{classical} \quad x &= \frac{\mu H}{k_B T} \\
\text{quantum} \quad x &= \frac{g J \mu_B H}{k_B T} = \frac{\mu_H H}{k_B T}
\end{align*}

$\mu$: net magnetic moment in the atom

Henry, Phys. Rev. 88, 559 (1952)
When H is large enough and T low enough, a paramagnetic can be saturated.

For example, KCr(SO$_4$)$_{12}$H$_2$O at H=5Tesla and T=4.2K

only magnetic ion Cr$^{3+}$, J=3/2, L=3, and S=3/2  →  g=2/5

the lower curve shown in the figure

→ data does not follow this predicted curve

The data is well described by the quantum model with J=S=3/2 and g=2.

→ L=0 no orbital component

\[
\mu = gJ\mu_B = g\sqrt{J(J+1)}\mu_B = 2\sqrt{\frac{3}{2}\left(\frac{3}{2}+1\right)}\mu_B = 3.87\mu_B
\]

“Spin-only” moment
Gd(C₂H₃SO₄)₃•9H₂O
What magnetic moment a metal should have?

Hund’s rule: incorporate coupling of magnetic moment to determine the magnetic state

(1) Maximize $S = \sum m_s$ subject to the Pauli exclusion principle

$$m_s = \pm 1/2 \quad \text{put spins (in different states) parallel}$$

(2) Maximize $L = \sum m_\ell$ subject to the Pauli exclusion principle

$$m_\ell = -\ell, -\ell+1, \ldots, \ell-1, \ell \quad \text{fill higher } m_\ell \text{ state preferentially}$$

(3) \[ J = \begin{cases} L - S & \text{when shell is less than half full} \\ L + S & \text{when shell is more than half full} \end{cases} \]

\[ J = L - S, L - S + 1, \ldots, L + S - 1, L + S \quad \text{allowed values} \]

Whether it is a minimum or maximum in the ground state depends on filling function.
Magnetic state $^{2S+1}L_J$

$L : 0, 1, 2, 3, 4$
$S, P, D, F, G$

Examples

(1) Full shells : $L=0$, $S=0$, and hence, $J=0$

(2) Half filled shells : $L=0$ and $S=(2\ell+1)(1/2)$

Eg. Gd$^{3+}$ $4f^7 5s^2 5p^6$

(n=4, $\ell=3$)

$L=0$ and $S=7/2$

$J=L+S=7/2$
Eg. Cs$^{3+}$ 4f$^{1}5s^{2}5p^{6}$  
(n=4, ℓ=3)  
L=3 and S=1/2  
J=L-S=5/2  
Eg. Pr$^{3+}$ 4f$^{2}5s^{2}5p^{6}$  
(n=4, ℓ=3)  
L=5 and S=1  
J=L-S=4  
Eg. Dy$^{3+}$ 4f$^{9}5s^{2}5p^{6}$  
(n=4, ℓ=3)  
L=5 and S=5/2  
J=L+S=15/2
For Sm$^{3+}$ and Eu$^{3+}$, there are discrepancies between experimental $p$ and theoretically calculated value.

High states of the L-S multiplet.
Quenching of the orbital angular momentum: Iron group ions

<table>
<thead>
<tr>
<th>Ion</th>
<th>Configuration</th>
<th>Basic level</th>
<th>$p(\text{calc}) = g[J(J+1)]^{1/2}$</th>
<th>$p(\text{calc}) = 2[S(S+1)]^{1/2}$</th>
<th>$p(\text{exp})$</th>
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<tr>
<td>Ti$^{3+}$, V$^{4+}$</td>
<td>$3d^1$</td>
<td>$^2D_{3/2}$</td>
<td>1.55</td>
<td>1.73</td>
<td>1.8</td>
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<tr>
<td>V$^{3+}$</td>
<td>$3d^2$</td>
<td>$^3F_2$</td>
<td>1.63</td>
<td>2.83</td>
<td>2.8</td>
</tr>
<tr>
<td>Cr$^{3+}$, V$^{2+}$</td>
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<td>$^4F_{3/2}$</td>
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<td>3.87</td>
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<td>$^5D_0$</td>
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<td>4.9</td>
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<tr>
<td>Fe$^{3+}$, Mn$^{2+}$</td>
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<td>$^6S_{5/2}$</td>
<td>5.92</td>
<td>5.92</td>
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<td>$^2D_{5/2}$</td>
<td>3.55</td>
<td>1.73</td>
<td>1.9</td>
</tr>
</tbody>
</table>

Effective number of Bohr magneton

\[ p = 2\sqrt{S(S+1)} \quad \text{and} \quad p = g\sqrt{J(J+1)} \]

In the iron group ions, the 3d shell, the outermost shell, is responsible for the paramagnetism and experiences the intense inhomogeneous electric field produced by neighboring ions, called “the crystal field”

- breaking L-S coupling ($J$ is meaningless)
- splitting $2L+1$ sublevels (diminishing the contribution of orbital motion to magnetic moment)
An atom w/ L=1 is placed in the uniaxial crystalline electric field of two positive ions along the z-axis. Take S=0 to simplify the problem.

In a free atom, a single electron in a p-state.

\[ R_{n\ell}(r)Y_{1,1}(\theta\phi) \propto f(r) \left[ \frac{x + iy}{\sqrt{2}} \right] \]

\[ R_{n\ell}(r)Y_{1,0}(\theta\phi) \propto f(r) \ z \]

\[ R_{n\ell}(r)Y_{1,-1}(\theta\phi) \propto f(r) \left[ \frac{x - iy}{\sqrt{2}} \right] \]

Three degenerate p states
In a crystal of orthorhombic symmetry the charges on neighboring ions will produce an electrostatic potential $\varphi$ about the nucleus,

$$e\varphi = Ax^2 + By^2 - (A + B)z^2$$

Reconstructing unperturbed ground state

$$U_x = xf(r), \quad U_y = yf(r), \quad U_z = zf(r) + \text{perturbed term } e\varphi$$

Non-diagonal elements

$$\langle U_x | e\varphi | U_y \rangle = \langle U_y | e\varphi | U_z \rangle = \langle U_z | e\varphi | U_x \rangle = 0$$

Diagonal elements

$$\langle U_x | e\varphi | U_x \rangle = \int |f(r)|^2 x^2 [Ax^2 + By^2 - (A + B)z^2]dxdydz$$

$$= \int |f(r)|^2 [Ax^4 - Ax^2y^2]dxdydz$$

$$= A(I_1 - I_2)$$
\[ \langle U_y | e\varphi | U_y \rangle = \int |f(r)|^2 y^2 [Ax^2 + By^2 - (A + B)z^2] dx dy dz \]
\[ = \int |f(r)|^2 [By^4 - By^2 z^2] dx dy dz \]
\[ = B(I_1 - I_2) \]
\[ \langle U_z | e\varphi | U_z \rangle = \int |f(r)|^2 z^2 [Ax^2 + By^2 - (A + B)z^2] dx dy dz \]
\[ = \int |f(r)|^2 (A + B)[y^2 z^2 - z^4] dx dy dz \]
\[ = (A + B)(I_2 - I_1) \]

The orbital moment of each of the states
\[ \langle U_x | L_z | U_x \rangle = \langle U_y | L_z | U_y \rangle = \langle U_z | L_z | U_z \rangle = 0 \]

Crystal field splits the original degenerate states into non-magnetic states separated by energies \( \gg \mu H \).

Quenching of the orbital angular momentum
Paramagnetic susceptibility of conduction electrons

- Conduction electrons are not bound to atoms so that they are not included in atomic magnetization.

- Each electron has $\mu = \pm \mu_B$.

- Curie-type paramagnetic contribution (electron spins align w/ H)

$$M = n\mu_B^2H/k_BT$$

where $n$ is # of conduction electrons

This requires each electron spin align w/ H, independent of all others.

**Fermi-Dirac distribution**

- Pauli pointed out that only electrons near $E_F (\pm k_B T)$ can flip over.
Fraction of electron participating

\[ \frac{k_B T}{\varepsilon_F} = \frac{T}{T_F} \]

\[ M = \left( n \frac{T}{T_F} \right) \left( \frac{\mu_B^2 H}{k_B T} \right) = \frac{n\mu_B^2 H}{k_B T_F} \]

independent of temperature

Consider the density of states \( D(\varepsilon) \) in the presence of \( H \)

Spin \( \uparrow \) electrons lowered in energy by \( \mu H \) in \( H \uparrow \)

Spin \( \downarrow \) electrons raised in energy by \( \mu H \) in \( H \uparrow \)

flip spins
The concentration of electrons w/. magnetic moment parallel to H

\[ N_\uparrow = \left( \frac{1}{2} \right) \int_{-\mu H}^{\varepsilon_F} d\varepsilon D(\varepsilon + \mu H) \approx \frac{1}{2} \int_{-\mu H}^{\varepsilon_F} d\varepsilon D(\varepsilon) + \frac{1}{2} D(\varepsilon_F) \mu H \]

\( H^\uparrow, \quad T=0K \)

The concentration of electrons w/. magnetic moment antiparallel to H

\[ N_\downarrow = \left( \frac{1}{2} \right) \int_{-\mu H}^{\varepsilon_F} d\varepsilon D(\varepsilon - \mu H) \approx \frac{1}{2} \int_{-\mu H}^{\varepsilon_F} d\varepsilon D(\varepsilon) - \frac{1}{2} D(\varepsilon_F) \mu H \]

Pauli spin magnetization

\[ M = \left( N_\uparrow - N_\downarrow \right) \mu = \mu D(\varepsilon_F) \mu H = \frac{3N}{2\varepsilon_F} \mu^2 H = \frac{3N}{2k_B T_F} \mu^2 H \]

valid when \( k_B T << \varepsilon_F \) independent of temperature
References:


Spin-dependent Transport in Magnetic Nanostructures, Edited by Maekawa and Shinjo, Taylor & Francis, 2002.
Cooling by isentropic demagnetization

Entropy: A measure of the disorder of a system

The greater the disorder, the higher is the entropy. In the magnetic field the moments will be partly lined up (partly ordered), so that the entropy is lowered by the field.

The entropy is lowered if the temperature is lowered, as more of the moments line up.

When the material is demagnetized at constant entropy, entropy can flow from the system of lattice vibrations into the spin system.

\[ S = k_B \ln Z \]

where \( Z \) is the partition function

\[ Z = \sum_{m=-I}^{m=I} \left( \exp \left( \frac{\mathcal{E}_M}{k_B T} \right) \right)^N \]
Entropy for a spin $\frac{1}{2}$ system depends only for the population distribution.

- $a \rightarrow b$ : the system is magnetized isothermally.
- $b \rightarrow c$ : the magnetic field is turned off adiabatically.

$$T_f = T_i \left( \frac{H_{\Delta}}{H} \right)$$

where $H_{\Delta}$ is the effective field

If we start at $H=5T$ and $T_i=10mK$ \[
\frac{\mu H}{k_B T} \approx 0.5
\]

$T_f \sim 10^{-7}K$

The first nuclear cooling was done on Cu, $T_i=20mK$

$T_f \sim 1.2 \times 10^{-6}K$
Cu nuclei in the metal

\[ T_f = T_i \left( \frac{3.1}{B} \right) \]

where \( B_\Delta = 3.1 \text{Oe} \).

The present record for a spin temperature is about 280pK.

PRL70, 2818 (1993).