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1. Learning Outcomes

After studying this module, you shall be able to

- Know the relation between thermal energy and magnetic properties of any paramagnetic substance.
- Learn Van Vleck equations taking into account the first order and the second order Zeeman Effect.
- Modify the Van Vleck equations for the substances having the multiplet width large as compared to kT
- Modify the Van Vleck equations for the substances having multiplet width small as compared to kT
- Modify the Van Vleck equations for the substances having multiplet width comparable to kT
- Evaluate the magnetic properties of Lanthanides

2. Thermal Energy and Magnetic Moment

The magnetic property of a paramagnetic substance originates from the permanent magnetic dipoles present in it. On the application of a magnetic field:
1. The magnetic dipoles tend to align themselves along the field direction against the disrupting influence of temperature. As a result, the M_J levels symmetrically split into lower and upper levels. This splitting is known as the first order Zeeman Effect.
2. The orbitals get distorted via the introduction of some character of the excited state into the ground state. This is known as second order Zeeman Effect.

2.1 Van Vleck Equations

Using quantum mechanics, Van Vleck derived the analogous expression taking into account the two Zeeman effects;

$$\chi_M = \frac{N\bar{\bar{\mu}}_B^2}{3kT} + N\alpha \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots. (1)$$

Where $\bar{\bar{\mu}}_B^2$ is the square of the low frequency part of the magnetic moment vector, averaged over time, and this average being itself averaged over various normal states appropriately weighted according to the Boltzmann factor. Nα is the combined temperature independent contribution of the high frequency elements of the paramagnetic moment, and diamagnetic part. A convenient unit of atomic magnetic moment is the Bohr magneton, the magnitude of which is given by

$$\beta = \frac{eh}{4\pi mc} = 0.917 \times 10^{-20} \text{erg oersted}^{-1}$$

Now equation no 1 becomes

$$\chi_M = N\left(\frac{\beta^2 \bar{\bar{\mu}}_B^2}{3kT} + \bar{\alpha}\right) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

Where $\bar{\bar{\mu}}_B^2$ is the low frequency part of the magnetic moment expressed in Bohr magnetons. In general the magnetic moment of an atom consists of two parts

1. The orbital contribution, and
2. The electron spin contribution

In different normal states of the atom the inclination of orbital and spin contributions may be different. For many cases, the "permanent" magnetic moment is not invariant with temperature although it appears to be so. Also, "molecular" paramagnetism as contrasted with "atomic" paramagnetism, the orbital contribution appears to be quenched out for most of the cases. In evaluating μ_β^2 and α in terms of experimentally determinable quantities there are three cases for which different equations are required. A multi-electron system possesses several J levels; the ground state J being decided by Hund’s rule. The J levels of a given Russell-Saunders term together constitute a multiplet, and given J level is called a component of the multiplet. The energy gap between two successive J levels is known as the multiplet width. Normally, the magnetic property of a substance originates from its ground state. But this is not so when excited states lie close to the ground state, i.e., when the multiplet width is in the neighborhood of kT, the thermal energy. In such a situation, the excited state or states may be significantly populated as, for example, in samarium(III) and europium(III). Therefore, when deriving the magnetic moment equation, we need to also consider the population of the excited states. Such a consideration leads to three distinct situations, (Figure 1)

1. The multiplet width is large as compared to kT
2. The multiplet width is small as compared to kT
3. The multiplet width is comparable to kT.

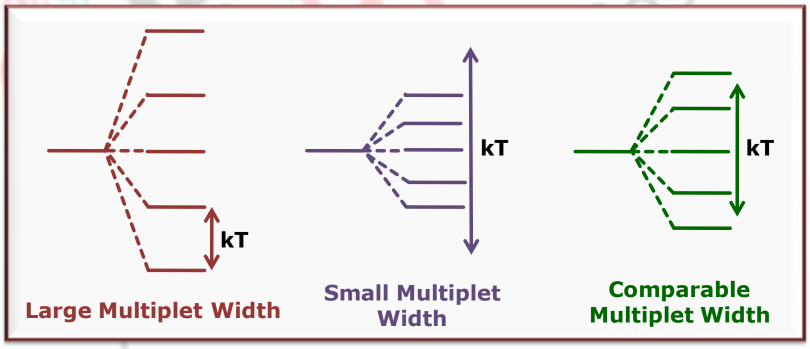

Figure 1

3. Multiplet Intervals Large Compared to kT

When the multiplet width is greater than kT, the L and S vectors interact strongly. This means that these vectors precess rapidly about the direction of the resultant J vector. In this situation, J becomes good quantum number such that the quantum numbers L and S no longer dictate the ultimate magnetic properties. Therefore, magnetic moment is given by

$$\mu_J = \sqrt{J(J+1)}\, g\beta \ldots\ldots\ldots\ldots\ldots\ldots\ldots.. (3)$$

Where, following the usual spectral notation, J is the vector sum of L and S; g, the Lande splitting factor is given by

$$g = 1 + \frac{S(S+1) + J(J+1) - L(L+1)}{2J(J+1)} \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4)$$

From equation 3, we get the equations for μ_L and μ_S easily. For orbital magnetic moment only, S=0, so that J= L and hence g=1. Therefore,

$$\mu_L = \sqrt{L(L+1)}\,\beta \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

For spin magnetic moment only, L=0, so that J = S and hence g=2. Therefore,

$$\mu_S = \sqrt{4S(S+1)}\,\beta \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots . (6)$$

Equation (2) then becomes

$$\chi_M = \frac{Ng^2\beta^2 J(J+1)}{3kT} + N\alpha \ldots\ldots\ldots\ldots . (7)$$

The term α no longer has the value zero (neglecting the diamagnetic part) but is given by

$$N\alpha = \frac{N\beta^2}{6(2J+1)}\left[\frac{F(J+1)}{h\nu(J+1;J)} - \frac{F(J)}{h\nu(J+1;J)}\right] \ldots\ldots\ldots\ldots\ldots\ldots . (8)$$

Where $F(J) = \frac{1}{J}[(S+L+1)^2 - J^2][J^2 - (S-L)^2] \ldots\ldots\ldots\ldots\ldots . (9)$

Equation (3) is used to evaluate the magnetic moment for most of the rare earth ions, elements and susceptibility of the same can be calculated by using equation (7).

4. Multiplet Intervals Small Compared to kT

When the multiplet width is quite small as compared to kT, virtually all the j levels may be assumed to be populated. Therefore,

$$\mu = \sqrt{4S(S+1) + L(L+1)}\,\beta \ldots\ldots\ldots\ldots\ldots\ldots . (10)$$

The magnetic moment arises from the sum total of the spin and orbital effects. Remembering that the magnetic susceptibility is additive and that the square of magnetic moment is additive. Moreover, the high-frequency elements of the paramagnetic moment are absent (neglecting the diamagnetic part). Equation (2) then becomes

$$\chi_M = \frac{N\mu_L^2}{3kT} + \frac{N\mu_S^2}{3kT} \ldots\ldots\ldots\ldots\ldots . (11)$$

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$$\chi_M = \frac{N}{3kT}(\mu_L^2 + \mu_S^2) \ldots\ldots\ldots\ldots.(12)$$

$$\chi_M = \frac{N\beta^2}{3kT}[4S(S+1) + L(L+1)] \ldots\ldots\ldots\ldots.(13)$$

where S and L are the resultant spin and orbital moments respectively. Therefore,

$$\mu_{L+S} = \sqrt{4S(S+1) + L(L+1)}\,\beta \ldots\ldots\ldots..(14)$$

5. Multiplet Intervals Comparable to kT

When the multiplet width is comparable to kT, then, to calculate the total magnetic susceptibility, it is advisable that the magnetic susceptibility due to each J level, along with the population of the J level, to be considered. This case involves summation of the contributions of atoms with different values of J. The number N_J, that is the number of atoms in a mole with a given value of J, is determined by the Boltzmann temperature factor. The Avogadro number N, is composite of N_J,N_{J+1},…….Thus, $\chi_M$is given by

$$\chi_M = \sum \frac{N_J g^2 \beta^2 J(J+1)}{3kT} + N_J \alpha_J \ldots\ldots\ldots\ldots.(15)$$

Each J level has as many as (2J+1) orientations, we have, for a J level having an energy E above the ground state J.

$$N_J = C(2J+1)e^{\frac{-E}{kT}}$$

Where C is proportionality constant. Substituting the value of $N_J$in equation (15), we get

$$\chi_M = C\frac{\sum_{J=|L-S|}^{L+S}\left\{\left[g_J^2\beta^2 J(J+1)(2J+1)e^{\frac{-E}{kT}}\right]\right\}}{3kT} + C\sum(2J+1)e^{\frac{-E}{kT}}\alpha_J \ldots\ldots\ldots\ldots\ldots..(16)$$

Since $N = \sum N_J = C\sum(2J+1)e^{\frac{-E}{kT}}$, Therefore,

$$C = \frac{N}{\sum(2J+1)e^{\frac{-E}{kT}}}$$

Thus, the final expression for χ_M is given by

$$\chi_M = \frac{N\beta^2}{3kT}\frac{\sum_{J=|L-S|}^{L+S}\{[g_J^2 J(J+1)] + \alpha_J\}(2J+1)e^{\frac{-E}{kT}}}{\sum(2J+1)\,e^{\frac{-E}{kT}}} \ldots\ldots\ldots\ldots.(17)$$

Therefore, magnetic moment is given by

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$$\mu = \sqrt{\frac{\sum_{J=|L-S|}^{L+S}\{[g_J^2\beta^2 J(J+1)] + \alpha_J\}(2J+1)e^{\frac{-E}{kT}}}{\sum(2J+1)\,e^{\frac{-E}{kT}}}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots..(18)$$

It is clear from the above discussion that when the multiplet intervals are small or large compared to kT the Curie law should be obeyed, except for the relatively small temperature independent high frequency elements. But where multiplet intervals are comparable to kT we get a Boltzmann distribution of various "normal" states together with some rather striking departures from the Curie law.

6. Magnetic Properties of Lanthanides

The Lanthanides belongs to the inner transition series. These elements are generally trivalent, having electronic configuration –[Pd] $4f^{0-14}5s^2 5p^6$. The paramagnetism in these elements arises from the 4f electrons. These electrons are effectively shielded from external influence (surrounding coordinating ligand) by filled 5s and 5p sub-shells. Evidence that 4f electrons, responsible for the paramagnetism, are relatively free from external influence is given by the facts that the Lanthanides are remarkably alike chemically, and that their absorption bands and magnetic susceptibilities are little affected by change of ionic environment as by change of compound or of solvent. The crystal field effect in lanthanides is about 1/100 of that observed in the first transition series. This suggests that for lanthanides the spin-orbit coupling constant is quite high (spin-orbit coupling >> ligand field splitting), so that the L and S vectors couple effectively to give the J vector. Thus for lanthanides, J is a good quantum number. As we realize now this is simply equivalent to assuming the multiplets all very wide compared to kT. The magnetic moment will be given by the following equation (7)

$$\mu_J = \sqrt{J(J+1)}\, g\beta$$

Where

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

On simplifying this equation we get

$$g = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}$$

J = L+S, L+S-1,……L-S.

For the calculation of g value, we use minimum value of J for the configurations having up to half-filled f orbitals; i.e. J = L−S for f^0-f^7 configurations

And maximum value of J is used for configuration with more than half-filled f orbitals; i.e. J = L+S for f^8-f^{14} configurations. For f^0, f^7, and f^{14}, L = 0, hence μ_J becomes μ_S. Now let us calculate Landè factor g and μ_J for a Pr^{3+} ion.

Pr^{3+} has electronic configuration - $[Xe]4f^2$

Ground State from Hund's Rules is shown in figure 2

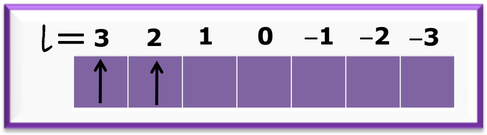

Figure 2

Thus, total spin quantum number (S) = 1/2 + 1/2 = 1
Spin multiplicity(2S+1) = 3
Total angular momentum number (L) = 3 + 2 = 5
J = 6, 5, 4. ^3H state splits into $^3H_4$, $^3H_5$ and $^3H_6$ states. According to Hund's rule $^3H_4$ is the ground state and energies of these states increase in the order $^3H_4 < ^3H_5 < ^3H_6$. Thus, J =4 is chosen for f^2

$$g = \frac{3}{2} + \frac{1(1+1) - 5(5+1)}{2 \times 4(4+1)}$$

$$g = \frac{3}{2} + \frac{2 - 30}{40} = 0.8$$

$$\mu_J = 0.8\sqrt{4(4+1)}\ B.M$$

$$\mu_J = 0.8\sqrt{20}\ B.M$$

$$\mu_J = 3.58\ B.M$$

This calculated value is very close to the experimental value μ_J = 3.4 – 3.6 B.M.
Similarly, we can calculate Landè factor g and μ_J for all the lanthanides(III) ions. The calculated and observed magnetic moment for the trivalent lanthanides are given in the table 1

Table 1

No of f electrons	M^{3+}	L	S	Ground State Term	g	Calculated μ_J (B.M)	Observed μ_J (B.M)
0	La	0	0	$^1S_0$	1	0	Diamagnetic
1	Ce	3	1/2	$^2F_{5/2}$	6/7	2.54	2.3 – 2.5
2	Pr	5	1	$^3H_4$	4/5	3.58	3.4 – 3.6
3	Nd	6	3/2	$^4I_{9/2}$	8/11	3.62	3.5 – 3.6
4	Pm	6	2	$^5I_4$	3/5	2.68	2.9 (observed for Nd^{2+})
5	Sm	5	5/2	$^6H_{5/2}$	2/7	0.84	1.5 – 1.6
6	Eu	3	3	$^7F_0$	1	0	3.4 – 3.6
7	Gd	0	7/2	$^8S_{7/2}$	2	7.94	7.8 – 8.0
8	Tb	3	3	$^7F_6$	3/2	9.72	9.4 – 9.6
9	Dy	5	5/2	$^6H_{15/2}$	4/3	10.63	10.4 – 10.5
10	Ho	6	2	$^5I_8$	5/4	10.60	10.3 – 10.5
11	Er	6	3/2	$^4I_{15/2}$	6/5	9.57	9.4 – 9.6
12	Tm	5	1	$^3H_6$	7/6	7.63	7.1 – 7.4
13	Yb	3	1/2	$^2F_{7/2}$	8/7	4.50	4.4 – 4.9

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14	Lu	0	0	$^1S_0$	1	0	Diamagnetic

Landé formula fits well with observed magnetic moments for all the lanthanides except Sm^{3+} and Eu^{3+}.The magnetism of these two ions is best studied in combination with that of promethium (III) and terbium (III). The J values for these four ions are shown in figure 3. As we know that the energy separation between the ground state and the first excited state is 5λ for Pm^{3+}, (7/2)λ for Sm^{3+}, λ for Eu^{3+} and 6λ forTb^{3+}. λ is the spin-orbit coupling constant, is about 1000 cm^{-1} for all the lanthanides except Sm^{3+} and Eu^{3+}. However, λvalue for Eu^{3+} and Sm^{3+} is about 230 cm^{-1}, that means the energy separation between the states is about 230 cm^{-1} for Eu^{3+}(very close to kT~200 cm^{-1} at T= 300 K) and for Sm^{3+} is about 840 cm^{-1} which is also a small value. The magnitude of separation between the adjacent states of a term indicates the strength of the spin-orbit coupling, and in all cases, except Sm^{3+} and Eu^{3+}, it is sufficient to render the first excited state of the Ln^{+3} thermally inaccessible, and so the magnetic properties are determined only by their ground state. However, for Sm^{3+}at room temperature, the first excited state and for Eu^{3+}, the first excited state and even the second and third excited states are populated. In each of these ions, the J value is higher than that of the ground state and μ_J is expected to be greater than that of only the ground state. The magnetism of these ions is expressed by equation (17).

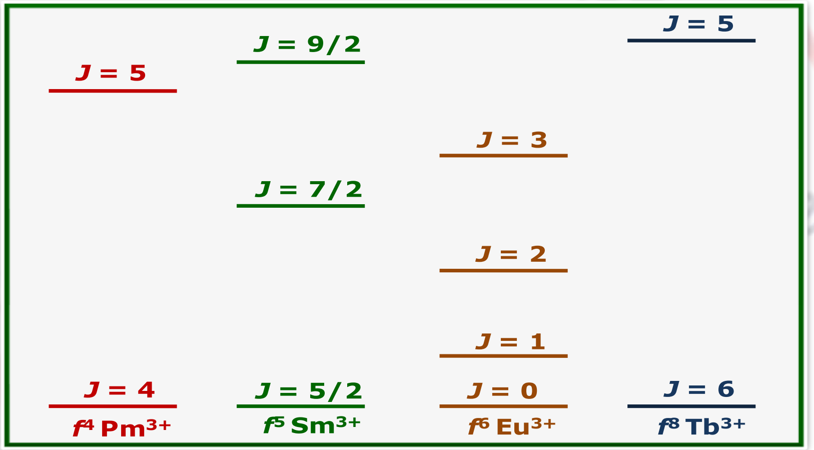

Figure 3

For Sm^{3+}, we have L= 5, J= 5/2, g = 0.286 for the ground state and g = 0.825 for the J= 7/2 level. Neglecting, α_J, we can writeequation (17) as

$$\chi_M = \frac{N\beta^2}{3kT}\left[\frac{A}{B}\right] \ldots\ldots\ldots\ldots\ldots (17)$$

Where A= $(0.286)^2\times(5/2)\times(7/2)\times6 \times \exp(0)+(0.825)^2\times(7/2)\times(9/2)\times6 \times\exp[(-7/2)\times\lambda/kT]+\ldots\ldots$,(E for J level is = 0, for J+1 level is = (-7/2)×λ)

And B = $[2\times(5/2)+1] \exp(0)+[2\times(7/2)+1] \exp[(-7/2)\times\lambda/kT]+\ldots\ldots$

From this, μ_J = 1.3 B.M. is calculated at 300K. This value agrees well with the experimental values. Similarly for $Eu^{3+}\mu_J$ = 3.5 B.M. is calculated at 300K using the same equation. This again agrees well with the experimental values.

Theoretical effective Bohr magneton numbers calculated from the appropriate equations of Van Vleck are in extraordinarily good agreement with observed values. In figure 4, the averages of all recent experimental values at room temperature have been shown.

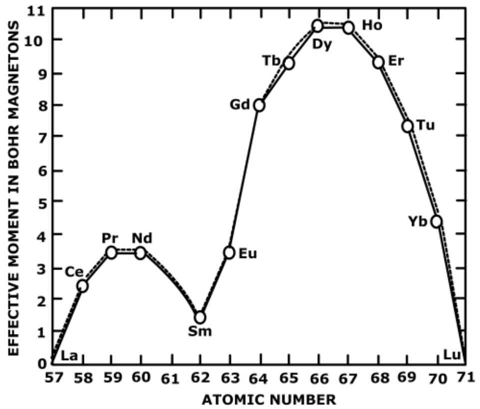

Figure 4

6.1 Use of Lanthanides Magnetic Moment

1. NMR Shift Reagents - paramagnetism of lanthanide ions is utilized to spread resonances in ^{1}H NMR of organic molecules that coordinate to lanthanides.
2. Lanthanide metals and alloys have interesting ordered magnetism effects. For example, $SmCo_5$and$Nd_2Fe_{14}B$ show ferromagnetic properties. Thus they are permanent magnets having following interesting properties;
a)They are light weight.
b) High saturation moments.
c) High coercivity.
d) High magneto crystalline anisotropy.
e) Superior performance magnets for magnetic bearings / couplings / wave tubes.
3. Synthetic rare earth garnets e.g. $Ln_3Fe_5O_{12}$ and $Y_3Fe_5O_{12}$ show interesting ferrimagnetism.

7. Summary

In this module, we discussed that,

- The Van Vleck equations taking into account the first order and the second order Zeeman Effect.
- The magnetic property of a substance originates from its ground state. But this is not so when the excited states lie close to the ground state, i.e., when multiplet width is close to kT, the thermal energy. There is a need to also consider the population of excited states. Such a consideration leads to three distinct situations: (1) the multiplet width is large as compared to kT, (2) the multiplet width small as compared to kT, and (3) the multiplet width comparable to kT.
- The three distinct situations give rise to different magnetic moments and susceptibilities equations.
- The magnetic properties of Lanthanides
- For the lanthanides the spin-orbit coupling constant is quite high, so that L and S vectors couple effectively to give the J vector. Thus for lanthanides, J is a good quantum number and the multiplets all very wide compared to kT.

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