CU-2008/1(i), 7

The Classical theory of paramagnetism -

The static paramagnetism susceptibility -

Consider a medium containing N magnetic dipole moments μ per unit volume. Suppose the interacti between the dipoles is weak, so that the field in which a given dipoles find itself assume that the magnetic field is constant or varies very slowly with time. In the classical theory, the dipoles are assumed to be freely rotating Hence, the resulting magnetic moment M per unit volume can be calculated in exactly the same way as the polarisation P for a dipolar gas.

Thus, according to the Langevin-Debye theory. we find -

$$M = N\mu L(\mu H/kT) \quad \text{.....(1)}$$

where, $L(x)$ is the Langevin function.

As long as $\mu H \ll kT$, this reduces to the simple expression -

$$\left.\begin{aligned} M &\simeq N\mu^2 H/3kT \\ \text{or,}\quad \frac{M}{H} &= \chi = N\mu^2/3kT \end{aligned}\right\} \quad \text{.....(2)}$$

Note that μ is of the order of one Bohr magneton $\simeq 10^{-20}$ erg/gauss, so that for a field of 10^4 gausses, $\mu H \simeq 10^{-16}$ erg. At room temp,

$\frac{kT}{3} \simeq 10^{-14}$ erg., so that the condition $\mu H \ll kT$ is satisfied except for very low temperatures. The relation $\chi = \frac{\text{Constant}}{T}$ is known as the Curie Law.

H - 2008 Q.5; 2009

The Quantum Theory Of Paramagnetism: According to the quantum theory, the permonet magnetic moment of a given atom or ion is not freely rotating, but restricted to a finite set of orientation relative to the applied field. Let us thus consider a medium containing N atoms per unit volume, the total angular momentum quantum number of each atom being J (this combines the total orbital angular momentum L and the total spin S of the electronic system per atom). According to the equ^{n}(2), this give rise to the possible components of the magnetic moment,

$M_J g \mu_B$ where, $M_J = J, (J-1) \ldots -(J-1) \ldots -1$ ... (3)

Here,

M_J is the magnetic quantum number associated with J.

The potential energy of a magnetic dipole with a component $M_J g \mu_B$ along H is $-M_J g \mu_B H$, so that, according to the statistical mechanics, the magnetisation is given by -

$$M = N \frac{\sum_{-J}^{J} M_J g \mu_B \exp(M_J g \mu_B H / RT)}{\sum_{-J}^{J} \exp(M_J g \mu_B H / RT)} \quad \ldots\ldots (4)$$

V.I.R.

The coefficient of N on the right hand side is the statistical average of the magnetic moment component per atom along H.

Case I- $M_J g \mu_B H/kT \ll 1$

Under these circumstances the exponentials in equ^n(4) may be approximated by $(1+M_J g \mu_B H/kT)$ and by writing out the sums, one readily finds for the paramagnetic susceptibility,

$$\chi = \frac{M}{H} = N g^2 J(J+1) \mu_B^2 / 3kT \quad \ldots\ldots (5)$$

This result is identical with the classical result of equ^n(2) because the total magnetic moment μ_J associated with J is given by -

$$\mu_J^2 = g^2 J(J+1) \mu_B^2 \quad \ldots\ldots (6)$$

We note that from susceptibility measurements in the range where the Curie law holds, it is possible to determine the effective number of Bohr magnetons.

$$P_{eff} = g [J(J+1)]^{1/2} \quad \ldots\ldots (7)$$

Case II- At low temperatures and strong magnetic fields the condition imposed under where the Case I may not be satisfied, and the equ^n(4) must be calculated without approximating the exponentials. After some algebraic

by the sum of the applied field and the field due to the polarization of the surroundings. On the other hand, in the derivation of the magnetic susceptibility, the field acting on a dipole in a paramagnetic solid was assumed to be equal to the applied field H. The justification for this is the following: the order of the magnitude of the internal field is given by -

$$H + rM = H(1 + rX) \qquad \text{where } r \simeq 4.$$

It should finally be mentioned that there exists also a temperature-independent paramagnetic contribution to the susceptibility at low temp. This is called Van Vleck paramagnetism.

Since $p_{eff} = g[J(J+1)]^{1/2}$

This is called the Van Vleck expression.

Thus in terms of the effective Bohr magneton,

$$\chi = \frac{N p_{eff}^2 \mu_B^2}{3kT}$$

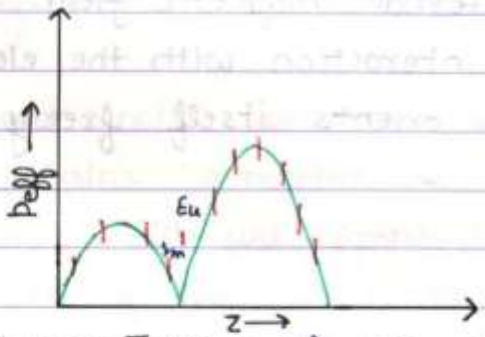
Li - 2009, 2008

Comparison of theory and experiment for paramagnetic salts - It was noted that paramagnetism requires the existance of partly filled electronic shell. Thus paramagnetic compounds are essentially those containing transition group elements of these, the rare earth group (incomplete 4f shell)

and the iron group (incomplete 3d shell) have been investigated most extensively.

(4-2008(5))

Rare Earth Ions - Fig(1) shows the group, where the full curve represents the effective number of Bohr magnetons calculated by Van Vleck from expression (*) the J values and g were obtained from Hund's rules and from Lande's formula. The vertical lines correspond to observed values of p_{eff}, obtained from measurements of the temperature of X. The ions Sm^{3+} and Eu^{3+} do not obey the simple theory. However, it has been shown by Van Vleck and Frank that these discrepancies can be explained satisfactorily if one considers the special situation with regard to the energy levels of these ions.



(4-2008(5)) fig (1)

* Iron Group Ions - If one calculates the effective number of Bohr magnetons for the ions of the iron group from expression (*), the results do not agree at all with the experimental values obtained from Curie Law. This may be seen from fig(2), where the vertical lines represent experimental values and the dashed curve represents (*) However, if one assumes that only the electron spins contribute to

the magnetization, i.e if one replaces (*) by -

$$P_{eff} = 2[S(S+1)]^{1/2} \quad \cdots\cdots (8)$$

One obtains quite good agreement with experiment. Thus, the iron group ions behave as if the orbital magnetic moment does not contribute at all. This is called the quenching of the orbital momentum.
Lu - 2011, 2010

Stoner suggested the following explanation for the different behaviour of the iron groups. In the iron group, the paramagnetic 3d electrons are the outermost electrons are the outermost electrons and these are therefore fully exposed to the crystalline field. Consequently, the orbital motion is locked into the field of the neighbours and cannot orient itself in an external magnetic field. The electron spin has no direct interaction with the electrostatic field and thus orients itself freely in an external magnetic field.

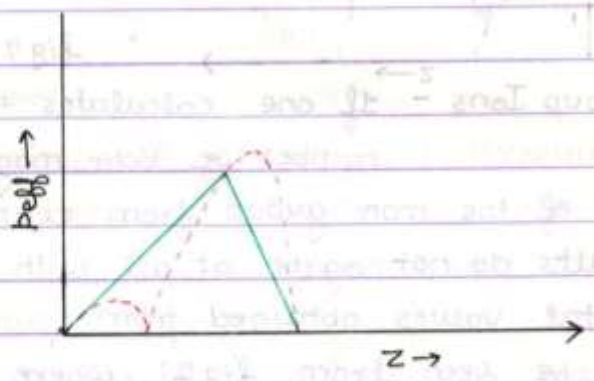


fig (2)

+ P456 Gupta and Kumar (9mp)

Ferromagnetism - Of the elements, only Fe, Ni, Co Gd and Dy are ferromagnetic, although there are a relatively large number of ferromagnetic alloys and oxides. Above a critical temperature θ_f, known as the ferromagnetic curie temperature, the spontaneous magnetization vanishes and the material becomes paramagnetic. Above the curie temperature the susceptibility follows the curie - weiss law.

$$\chi = \frac{C}{T-\theta} \quad \ldots\ldots (1)$$

where, C is the curie constant; the temperature θ is called the paramagnetic curie temperature and is usually some degrees higher than θ_f.

The theory of ferromagnetism is put forward in 1907 by weiss.

1. A feroomagnetic speciman of macroscopic dimensio-ns contains a number of small regions (domains) which are spontaneously magnetized; the magnitude of the spontaneous magnetization of the specimen is determined by the vector sum of the magnetic moments of the individual domains.

2. With in each domain the spontaneous magnetization is due to the existence of a "molecular field" which tends to produce a parallel alignment of the atomic dipoles.

As a particular example of a hysteresis curve given in fig (1) the magnetization curve for a single crystal of Silicon-iron. It is observed that a very weak field (of the order of 10^{-2} gauss) is sufficient to produce a magnetization $M = \frac{B}{4\pi} = 10^3$ gausses. Assuming atomic dipoles of the order of one Bohr magneton the value of M is of the order of 10^3 gausses.

On comparing with a paramagnetic field which is in the same field of 10^{-2} gauss would give a magnetisation $M = 10^{-6}$ gauss at room temperature; this is smaller by a factor of 10^9 (10^9 = 1 dipole).

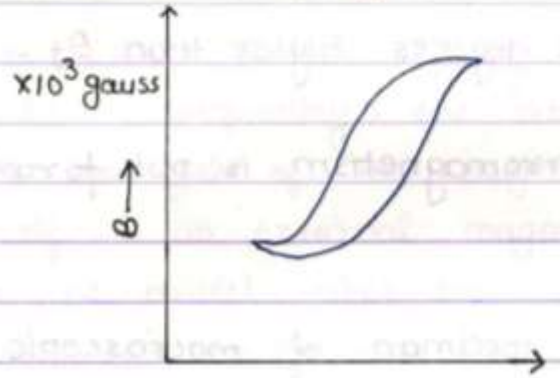


fig (1)