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E-NOTES

SUBJECT: CONDENSED MATTER PHYSICS

SUBJECT CODE: DPH31

UNIT : 4

SYLLABUS:

Free electron gas in three dimensions - Electronic heat capacity - Wiedmann-Franz law - Band theory of metals and semiconductors - Bloch theorem - Kronig-Penny model - Semiconductors - Intrinsic carrier concentration – Temperature dependence - Mobility - Impurity conductivity – Impurity states - Hall effect.

Unit - IV

Magnetism.

-On-
10/10/2023

Diamagnetism:

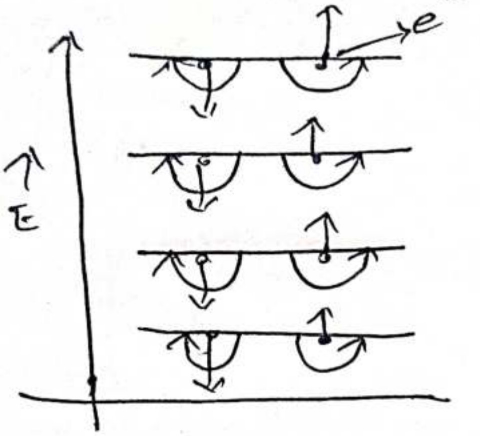

Fig (a)

Fig (b)

In a diamagnetic material the electron orbits are more or less random and mostly all the magnetic moments are cancelled. III^{ly}, all the spin moments are almost paired i.e) they have even no. of electrons and has equal no. of electrons spinning in two opposite direction as shown in (a)

Hence the net magnetic moment in the diamagnetic material is Zero. Most of these materials do not have magnetism in the absence of magnetic field.

properties!

→ They ~~irepel~~ ~~repul~~ rippel the magnetic lines of force. ~~Sucep~~ → susceptibility is negative it is independent of temperature and applied magnetic field strength

→ permeability is less than 1

→ There is no permanent dipole moment. So, they are called weak magnets.

→ When temperature is less than critical temperature, diamagnetics become normal material

Eg: Gold, Germanium, Silicon, etc.

Adiabatic Demagnetisation (paramagnetic cooling)

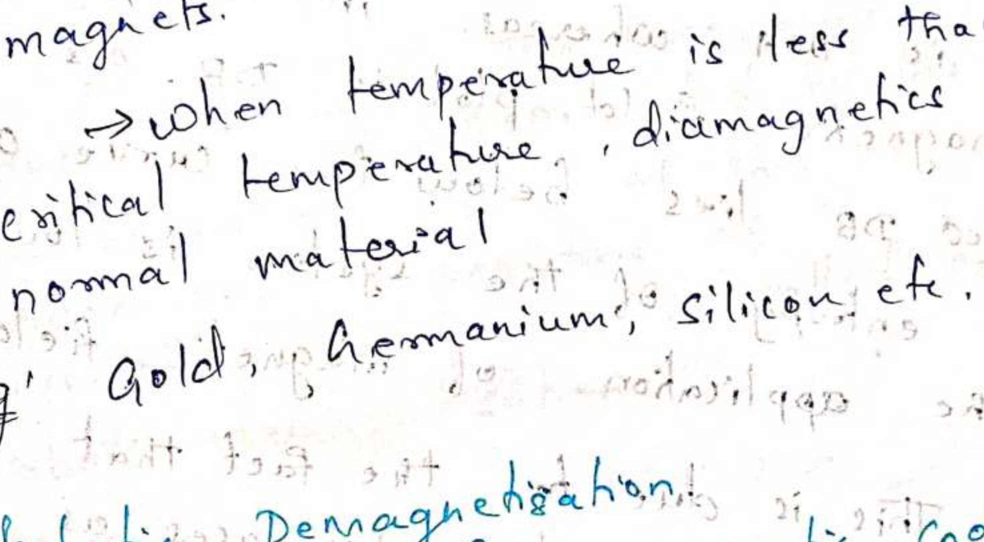

fig (1)

W. F. Giage developed a method of adiabatic demagnetisation to produce sufficiently low temperature, of the order of

0.001 K . The method is based on the fact that at a fixed temperature, the entropy of the system of the magnetic moments - a paramagnetic salt is lowered if a magnetic field is applied, as can be seen below. (1)

From fig (1), this is the plot of entropy vs temperature. In the absence of manetic field (H=0). plot is OCA whereas, in the presence of magnetic field plot is DB. as curved DB lies below the curve OCA, The entropy of the system is lowered by the application of magnetic field.

This is due to the fact that disorder in the system decreases as most of magnetic dipoles align along field direction and the entropy decreases as the disorder decreases.

At a fixed temperature Ti, if we proceed along the curve AB then it would mean an isothermal change (system is to be kept in good thermal contact with the surroundings).

from a zero field value to a field value, say, H.

Thus entropy will fall along AB. Now if field is switched off (H=0) and the system is isolated from the surroundings then the state of affair will be represented by an adiabatic process represented by the curve BC (The magnetic field is removed without changing the entropy of the system).

As a result, the temperature is reduced to T_f (represented by the point C). Thus, repeated cycle of this nature will reduce the temperature of the system very much. The process is called cooling by Adiabatic demagnetisation.

Rare Earth Ions:

Rare earth elements are relatively plentyfull in the earth's crust, with cerium being the 25th most abundant element at 68 parts per million. This makes it as abundant as copper. Because of the geochemical properties, rare earth elements are typically dispersed. This means they are not often found in concentrated enough clusters to make them viable to mine.

It was the Scarcity of this minerals that led to them being called rare earths

Rare earth's (57 71) are a group of 15 elements in the periodic table known as the Lanthanide series. Rare earth are categorised into light elements (57-62) (Lanthanum to Samarium) and heavy elements (63 71) (Europium to Lutetium).

The later are less common and consequently more expensive.

REE - Applications.

Lathanum - Batteries, catalyst for petroleum refining

Cerium - Autocatalyst, chemical catalyst, glass polishing, metal alloys.

Neodymium - High power magnets

Europium - Flurroscent lightning

Dysprosium - High power high temperature magnets, lasers.

Yetterbium ~~Yttebium~~ - Fibre optic cable, solar panels.

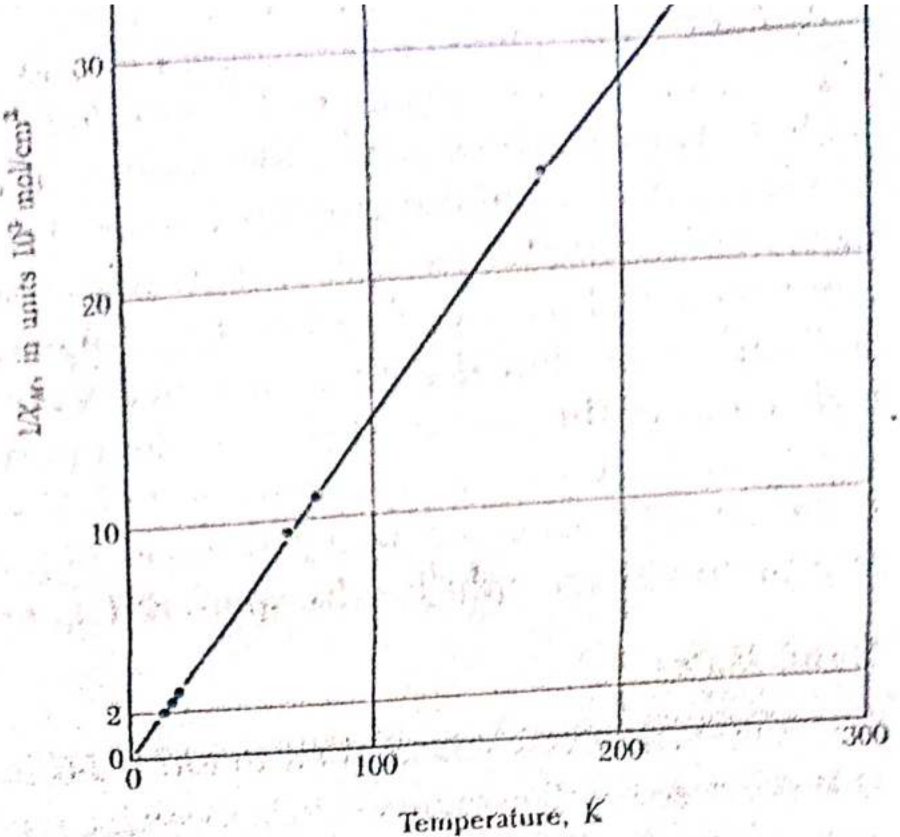

Figure 5 Plot of $1/\chi$ *vs* T for a gadolinium salt, $Gd(C_2H_5SO_4)_3 \cdot 9H_2O$. The straight line is the Curie law. (After L. C. Jackson and H. Kamerlingh Onnes.)

The constant C is known as the **Curie constant.** The form (19) is known as the Curie-Brillouin law, and (22) is known as the **Curie law.** Results for the paramagnetic ions in a gadolinium salt are shown in Fig. 5.

Rare Earth Ions

The ions of the rare-earth elements have closely similar chemical properties, and their chemical separation in tolerably pure form was accomplished only long after their discovery. Their magnetic properties are fascinating: the ions exhibit a systematic variety and intelligible complexity. The chemical properties of the trivalent ions are similar because the outermost electron shells are identically in the $5s^2 5p^6$ configuration, like neutral xenon. In lanthanum, just before the rare earth group begins, the $4f$ shell is empty; at cerium there is one $4f$ electron, and the number of $4f$ electrons increases steadily through the group until we have $4f^{13}$ at ytterbium and the filled shell $4f^{14}$ at lutecium. The radii of the trivalent ions contract fairly smoothly as we go through the group from 1.11 Å at cerium to 0.94 Å at ytterbium. This is the famous "lanthanide contraction." What distinguishes the magnetic behavior of one ion species from another is the number of $4f$ electrons compacted in the inner shell with a radius of perhaps 0.3 Å. Even in the metals the $4f$ core retains its integrity and its atomic properties: no other group of elements in the periodic table is as interesting.

The preceding discussion of paramagnetism applies to atoms that have a $(2J + 1)$-fold degenerate ground state, the degeneracy being lifted by a magnetic field. The influence of all higher energy states of the system is neglected. These assumptions appear to be satisfied by a number of rare-earth ions, Table 1. The calculated magneton numbers are obtained with g values from the Landé result (13) and the ground-state level assignment predicted by the Hund theory of spectral terms. The discrepancy between the experimental magneton numbers and those calculated on these assumptions is quite marked for Eu^{3+} and Sm^{3+} ions. For these ions it is necessary to consider the influence of the high states of the L–S multiplet, as the intervals between successive states of the multiplet are not large compared to k_BT at room temperature. A multiplet is the set of levels of different J values arising out of a given L and S. The levels of a multiplet are split by the spin-orbit interaction.

Hund Rules

The Hund rules as applied to electrons in a given shell of an atom affirm that electrons will occupy orbitals in such a way that the ground state is characterized by the following:

for 2 marks.

1. The maximum value of the total spin S allowed by the exclusion principle;
2. The maximum value of the orbital angular momentum L consistent with this value of S;
3. The value of the total angular momentum J is equal to $|L - S|$ when the shell is less than half full and to $L + S$ when the shell is more than half full. When the shell is just half full, the application of the first rule gives $L = 0$, so that $J = S$.

The first Hund rule has its origin in the exclusion principle and the coulomb repulsion between electrons. The exclusion principle prevents two electrons of the same spin from being at the same place at the same time. Thus electrons of the same spin are kept apart, further apart than electrons of opposite spin. Because of the coulomb interaction the energy of electrons of the same spin is lower—the average potential energy is less positive for parallel spin than for antiparallel spin. A good example is the ion Mn^{2+}. This ion has five electrons in the $3d$ shell, which is therefore half-filled. The spins can all be parallel if each electron enters a different orbital, and there are exactly five different orbitals available, characterized by the orbital quantum numbers $m_L = 2, 1, 0, -1, -2$. These will be occupied by one electron each. We expect $S = \frac{5}{2}$, and because $\Sigma m_L = 0$ the only possible value of L is 0, as observed.

Table 1 Effective magneton numbe

(Near room temperature)

Ion	Configuration	Basic level	$p(\text{calc}) = g[J(J+1)]^{1/2}$	$p(\text{exp})$, approximate
Ce^{3+}	$4f^1 5s^2 p^6$	$^2F_{5/2}$	2.54	2.4
Pr^{3+}	$4f^2 5s^2 p^6$	$^3H_4$	3.58	3.5
Nd^{3+}	$4f^3 5s^2 p^6$	$^4I_{9/2}$	3.62	3.5
Pm^{3+}	$4f^4 5s^2 p^6$	$^5I_4$	2.68	—
Sm^{3+}	$4f^5 5s^2 p^6$	$^6H_{5/2}$	0.84	1.5
Eu^{3+}	$4f^6 5s^2 p^6$	$^7F_0$	0	3.4
Gd^{3+}	$4f^7 5s^2 p^6$	$^8S_{7/2}$	7.94	8.0
Tb^{3+}	$4f^8 5s^2 p^6$	$^7F_6$	9.72	9.5
Dy^{3+}	$4f^9 5s^2 p^6$	$^6H_{15/2}$	10.63	10.6
Ho^{3+}	$4f^{10} 5s^2 p^6$	$^5I_8$	10.60	10.4
Er^{3+}	$4f^{11} 5s^2 p^6$	$^4I_{15/2}$	9.59	9.5
Tm^{3+}	$4f^{12} 5s^2 p^6$	$^3H_6$	7.57	7.3
Yb^{3+}	$4f^{13} 5s^2 p^6$	$^2F_{7/2}$	4.54	4.5

The second Hund rule is best approached by model calculations. Pauling and Wilson,[1] for example, give a calculation of the spectral terms that arise from the configuration p^2. The third Hund rule is a consequence of the sign of the spin-orbit interaction: For a single electron the energy is lowest when the spin is antiparallel to the orbital angular momentum. But the low energy pairs m_L, m_S are progressively used up as we add electrons to the shell; by the exclusion principle when the shell is more than half full the state of lowest energy necessarily has the spin parallel to the orbit.

Consider two examples of the Hund rules: The ion Ce^{3+} has a single f electron; an f electron has $l = 3$ and $s = \frac{1}{2}$. Because the f shell is less than half full, the J value by the preceding rule is $|L - S| = L - \frac{1}{2} = \frac{5}{2}$. The ion Pr^{3+} has two f electrons: one of the rules tells us that the spins add to give $S = 1$. Both f electrons cannot have $m_l = 3$ without violating the Pauli exclusion principle, so that the maximum L consistent with the Pauli principle is not 6, but 5. The J value is $|L - S| = 5 - 1 = 4.$ for Sm.

Iron Group-Ions

Table 2 shows that the experimental magneton numbers for salts of the iron transition group of the periodic table are in poor agreement with (18). The values often agree quite well with magneton numbers $p = 2[S(S+1)]^{1/2}$ calcu-

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[1] L. Pauling and E. B. Wilson, *Introduction to quantum mechanics*, McGraw-Hill, 1935, pp. 239–246.

Table 9.7 Magnetic susceptibilities of some paramagnetic materials at room temperature

Material	$\chi \simeq (\mu_r - 1)$	*Material*	$\chi \simeq (\mu_r - 1)$
Air	0.038×10^{-5}	Ebonite	1.4×10^{-5}
Aluminium	2.3×10^{-5}	$MnSO_4$	360×10^{-5}
Magnesium	1.2×10^{-5}	Fe_2O_2	140×10^{-5}
Tungsten	6.8×10^{-5}	$FeCl_2$	370×10^{-5}
Platinum	30×10^{-5}	$NiSO_4$	120×10^{-5}
Oxygen	1.94×10^{-6}	CoO	580×10^{-5}
Nitrogen	0.0013×10^{-5}	Titanium	7.06×10^{-5}

Paramagnetism in general is a relatively small effect that has found a few technical appl
e.g., paramagnetic salts have been used in obtaining very low temperature of the order of 10
adiabatic demagnetisation. They are also essential materials used in the solid state MASER.

XVII. HUND RULES

It is required to obtain the characteristics of the ground state of an atom or iron whose ele
configuration is known through *L-S* coupling. The orbital angular momenta of the *Z* electrons
atom are vectorially added to obtain the total orbital angular momentum of the atom,

$$L = L_1 + L_2 + ...$$

The contribution from the electrons in the closed shell vanishes, and so the summation has
carried only over the electrons outside the closed shells. In a similar manner the total spin *S* of the
atom is obtained by summing over the spins of the electrons outside the closed shell. Finally, *L* and *S*
are coupled to give the total angular momentum $J = L + S$. For example, tungsten, ^{74}W, has a d^4 configur
Since the *d* subshell can hold 10 electrons of which 5 can have the same spin, the greatest *S* for
ground state ($4 \times 1/2 = 2$). Since all the four electrons have the same spin, they must have differen
m_l and the biggest possible M_L is then

$[2 + 1 + 0 + (-1) = 2]$. With $L = 2$ and $S = 2$, the smallest *J* is 0 and hence the ground state is $^5D_0$.

The ground state is obtained using the following three Hund rules:

(*i*) Choose the maximum value of *S* consistent with the Pauli principle.

(*ii*) Choose the maximum value of *L* consistent with the Pauli principle and rule 1.

(*iii*) If the shell is less than half full $J = L - S$, if it is more than half full $J = L + S$.

Let us apply these rules to a free iron atom whose electronic configuration is $1s^2\ 2s^2\ 2p^6$
$3d^6\ 4s^2$. The only electrons outside the closed shell are $3d^6$. According to Hund rules these sh
distributed as in Table 9.8.

Table 9.8 Distribution of 3d electrons in iron atom

m_l	2	1	0	−1	−2
m_s	↑↓	↑	↑	↑	↑

Now $L = \sum m_l = 2$, $S = \sum m_s = 2$. Since the shell is more than half full, $J = (L + S) = 2 + 2 = 4$. The state is denoted as ${}^5D_4$ where the letter D denotes $L = 2$, the subscript on left denotes the multiplicity, $2S + 1 = 5$, and the subscript on right denotes $J = 4$.

Crystal Field and Quenching of the Orbital Angular Momentum

The relation (9.52) fits well for many paramagnetic crystals including the materials containing ions of rare earth group. Deviations do occur, however, these are due to the fact that energy level system and states of an ion in a crystal are not necessarily the same as those for a free ion. The main reason for this is that in a crystal, a paramagnetic ion is surrounded by other ions with which it will interact. In particular, the neighbouring ions whether magnetic or not, will still be electrically charged and these create an inhomogeneous electric field in the neighbourhood of the paramagnetic ions which we are considering. This is often called *crystal field*. The interaction of the paramagnetic ions with the crystal field has two major consequences: The coupling **L** and **S** is largely broken up, so that the states are no longer specified by their **J** values; further, the (2*L* + 1) sublevels belonging to a given L which are degenerate in the free ion may now be spilt up by the crystal field. The splitting decreases the contribution of the orbital motion of the magnetic moment.

For ions of the iron transition group, the comparison of equation (9.52) with experiments far from satisfactory. The reason for this is that for the iron group, the ground state of the ions in a crystal is very different from that of the free ion. This is because, the partly filled electron shell, which is responsible for producing the magnetic moment, is the outer most (3*d*) shell of these ions. It is, therefore, very strongly influenced by the crystal field. The interaction is so strong that the orbital angular momentum of the electrons in the 3*d* shell is very often reduced to zero. This does not mean that electrons no longer encircle the nucleus, but rather that they will be travelling around it as often in one sense or in the other sense. This effect when *L* averages to zero is termed *quenching* of the orbital angular momentum and it means that when the ion is in the crystal, there is no orbital magnetic moment. In quenching, the crystal hardly interacts with the spin and hence, the spin magnetic moment still exists. Therefore, while calculating the susceptibility on the basis of equation (9.52), we must replace *J* by *S*.

Let us now consider Ni^{2+} ion. If we put $S = 1$, $L = 3$ and $J = 4$, g becomes

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

$$= 1 + \frac{4\times5+2-3\times4}{2\times4\times5}$$

$$= 1 + \frac{20+2-12}{40}$$

$$= 1 + \frac{10}{40} = 1.25$$

Now
$$\begin{aligned} C &= g^2 J(J+1)[N\mu_B^2/3k_B] \\ &= (1.25)^2 \times 4 \times 5 \\ &= 31.3 \text{ (in units of } N\mu_B^2/3k_B) \end{aligned}$$

If J is replaced by S,

then
$$J = S = 1, L = 0$$
$$g = 1 + \frac{1\times2+1\times2}{2\times2} = 1 + 1 = 2$$

Thus,
$$\boxed{\begin{aligned} C &= g^2 (J+1)[N\mu_B^2/3k_B] \\ &= 4(1+1) = 8 \text{ (in units of } N\mu_B^2/3k_B) \end{aligned}}$$

This value well agrees with the experimental value of 9.1.

XVIII. SUMMARY

(*i*) A paramagnetic substance has a non-vanishing angular momentum and so they possess permanent dipoles.

(*ii*) In the absence of an applied field, the dipoles are randomly oriented and so the net magnetisation in any given direction is zero.

(*iii*) At a finite temperature each atom has a thermal energy on the average equal to k_BT and the resulting thermal agitation tends to make the dipole observation random. To align the dipoles in a given direction, a field strong enough is needed to compete with the force due to thermal agitation. The field ordinarily available in the laboratory is far too small to turn the dipoles in the direction of the field. What the field does ? Is it to turn the dipoles slightly in the direction of the field so that on the average there are slightly more dipoles pointing in the direction of the applied field than in the opposite direction ? Since the applied field has to compete with thermal motion, paramagnetic susceptibility decreases with increasing temperature.

XIX. FERROMAGNETISM

When the average person speaks of a magnet, he is normally referring to a ferromagnet such as a piece of iron which has the ability to pick up other pieces of iron. Such a material is said to be a permanent magnet, since it exhibits magnetic properties even in the absence of an applied field; however it is found experimentally that the magnetisation is increased when an external magnetic field is applied to the specimen. Moreover, the [illegible] is non-linear i.e., ferromagnetic [illegible] and [illegible] Hysteresis [illegible]

Metal	M_s *(amp/metre)*	*Curie temperature K*
Fe	1.75×10^6	1043
Co	1.45×10^6	1393
Ni	0.51×10^6	631

XXI. QUANTUM THEORY OF FERROMAGNETISM

The modern theory of ferromagnetism, due to Heisenberg and Weiss, is an extension of that put forward by Ewing. These materials have their properties divided into two distinct and separate temperature ranges in such a way that the properties above a particular temperature are quite different from the properties below that temperature. This temperature is called the *ferromagnetic curie temperature* and is designated by θ_f. Among the materials, ferromagnetism occurs in Fe, Co, Ni, Gd and Dy. The important common characteristic of these elements is the existence of partly filled inner electron shells. The thermal motion of the lattices (atoms) affects ferromagnetic properties in different ways. The effect is most pronounced in the vicinity of the curie temperature, but it is also observable far below the curie temperature.

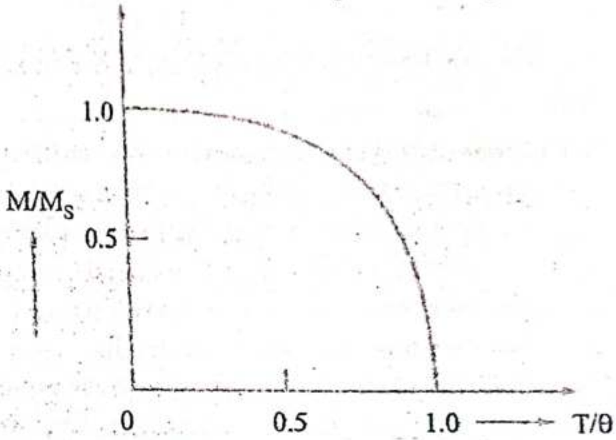

Fig. 9.30 Relative spontaneous magnetisation as a function of T/θ for iron, cobalt and nickel

We have already seen that the interaction between neighbouring atoms which tends to align their spin is the main cause for spontaneous magnetisation in ferromagnetic substances. When this effect is so strong that all adjacent spins are aligned, the magnetisation of the material has its maximum value. This long-range alignment results from both the strong nearest neighbour interactions and the continuity of the crystal. Thermal vibrations of atoms, however, tend to misalign the spins; hence we observe the maximum magnetisation only at the lowest possible temperature (0 K). At very high temperature the magnetisation has a lower value, until it becomes zero at the curie temperature. The magnetisation as a function of temperature is shown in Fig. 9.31. It decreases very slowly to start with and the curve drops more steeply at higher temperatures, until it finally falls precipitously to zero at the curie temperature.

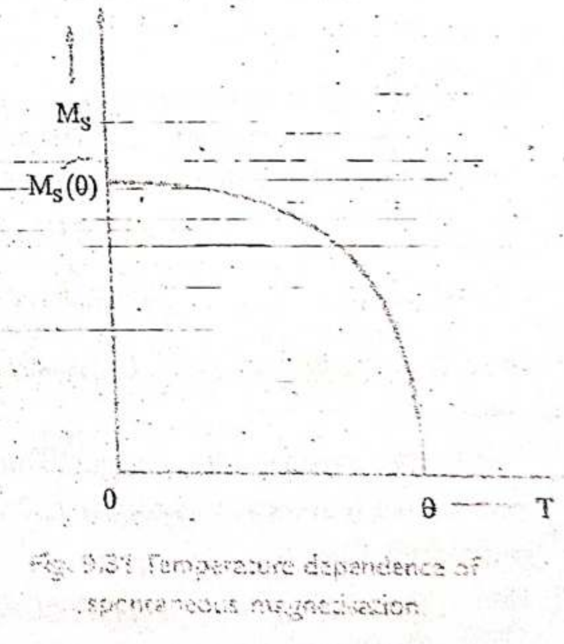

Fig. 9.31 Temperature dependence of spontaneous magnetisation

Well above the curie temperature, ferromagnetic materials behave like paramagnetic materials and have a well defined susceptibility given by *Curie-Weiss law*, namely,

$$\boxed{\chi = \frac{C}{T - \theta}}$$

where C is the *curie constant* and θ is called the *paramagnetic curie temperature.* θ is higher than the temperature θ_f (Fig. 9.27); but $(\theta - \theta_f)$ is small. It is now clear that these elements have a large susceptibi just above θ_f, but they do not obey Curie-Weiss law. Metals like Fe, Co, etc. obey Curie-Weiss law be but just above its curie temperature (θ_f), its susceptibility deviates somewhat from exact agreement wi this law *i.e.*, the behaviour of the metal just above θ_f has an interesting interpretation. It shows that although thermal motion of the atoms has destroyed long-range order of the spin moments, some ord of a much weaker character still persists. It is a kind of short-range spin order in which a given atom is surrounded by a small island in which the spins are more or less aligned. This phenomenon presumably exists for all ferromagnetic solids just above θ_f.

XXII. WEISS MOLECULAR FIELD

Spontaneous Magnetisation in Ferromagnetic Materials

Weiss, in 1907, postulated that in ferromagnetic materials, the internal field seen by a given dipole is equal to the applied field plus a contribution from the neighbouring dipoles which tend to align it in the same direction as it neighbours. Mathematically it may be written as

$$H_i = H + H_m \text{ with } H_m \propto M$$

i.e.,

$$\boxed{H_i = H + \gamma M} \tag{9.80}$$

where H_i is the *internal field*, H_m is the *internal molecular field* and γ is the Weiss *molecular field constant*.

Let us consider a ferromagnetic material with N atoms/m^3 each with an angular momentum J. We have already shown in [equation 9.57 (a)] that the total magnetic moment of these atoms in a field H is given by

$$M = Ng\mu_B J B_J(a) = M_s\, B_J(a) \tag{9.81}$$

where $a = \dfrac{J\mu_0\mu_B Hg}{k_B T}$

In the case of ferromagnetic solid materials,

$$\boxed{a = \frac{[g\mu_0\mu_B(H + \gamma M)J]}{k_B T}} \tag{9.82}$$

Thus
$$\frac{M}{M_s} = B_J(a)$$

When we deal with spontaneous magnetisation $H = 0$ and thus

$$a = \frac{g\mu_0\mu_B\gamma MJ}{k_B T}$$

and can rewrite

$$M = N g \mu_B (J+1)\, \alpha/3$$

with $\alpha = J g \mu_B (H + \lambda M)/K_B T$ (refer to subject matter between eq. 1 and eq. 2).

Because the effective field on an atom is now $(H + \lambda M)$ and not simply λM as considered in eq. (2) earlier. Thus

$$M = \frac{N g \mu_B (J+1)}{3} \cdot \frac{g \mu_B (H + \lambda M) J}{K_B T}$$

where $$\chi = \frac{M}{H} = \frac{N \mu_J^2 / 3 K_B T}{1 - N \mu_J^2 \lambda / 3 K_B T}$$

where $$\mu_J^2 = \mu_B^2 g^2 J^2$$

or $$\chi = \frac{C}{T - \theta}$$

where $$C = \frac{N \mu_J^2}{3 K_B} \text{ and } \theta = \frac{N \lambda \mu_J^2}{3 K_B} = \lambda C$$

This is Curie-Weiss law. Refer to fig. 8(c) in which $\left(\frac{1}{\chi}\right)$ is plotted as a function of temperature. It is observed that Curie-Weiss law predicts satisfactorily the variation of susceptibility in the paramagnetic region well above the Curie temperature, but not in the region close to the Curie temperatre. Accordingly, the temperature θ_f below which the ferromagnetic behaviour of these metals is observed, is not identical with temperature θ above which the paramagnetism sets in; θ is usually some degrees higher than θ_f:

	Fe	Co	Ni
θ_f (in K)	1043	1393	631
θ (in K)	1093	1428	650

Weiss-theory, however, does not distinguish between the ferromagnetic Curie temperature θ_f and the paramagnetic Curie temperature θ. We, on the basis of the discussion in this article, can say that Weiss-theory of ferromagnetism provides a comprehensive (although at times only qualitatively) description of the phenomenon of spontaneous magnetisation.

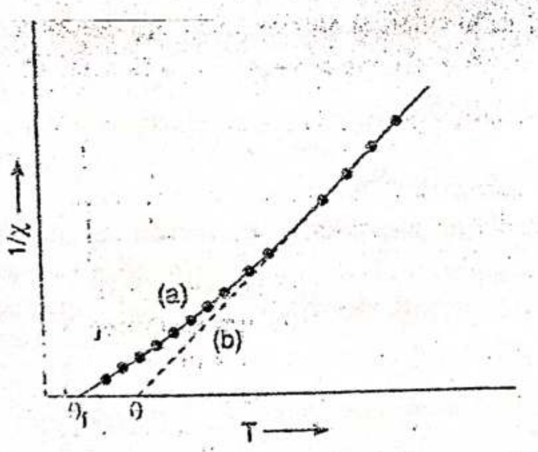

Fig. 8(c). Behaviour of the ferromagnetic metals above the Curie temperature :
(a) experimental behaviour (for Fe, Co, Ni)
(b) Weiss theory behaviour (plot of eq. 7)

12.4-3 HEISENBERG INTERPRETATION OF WEISS FIELD

In art. 12.4-1, we have pointed out clearly that it is not possible to explain an internal field of strength lying in the range $10^6 - 10^7$ oersted by classical dipole interaction which only amounts to 10^3 gauss. Heisenberg, in 1928, interpreted that such high value of internal fields can be explained in terms of *exchange interaction* between the electrons. An exchange force is essentially caused by a *static coulomb interaction (purely electrostatic)* and its magnitude can be much larger than that of the magnetic interaction. This exchange force appear the form of spin-spin interaction because orbital states of the electrons naturally impo limitation on the spin states according to Pauli principle : because of this principle, we can change the relative orientation of two spins without changing the spatial distributio charge. The strength of interaction depends upon the interatomic separation and it r change its sign as the separation is varied. It can be predicted that as the two approach e other, the electron spins of unpaired electrons in each atom assume parallel orientation interatomic separation decreases more and more, exchange force decreases until finally th pass through zero and an anti-parallel spin is favoured. The situation resembles with th which we found in Heitler-London model for a hydrogen molecule where the configuration parallel spins is very unfavourable compared to the configuration with anti-parallel spins

Following the Heitler-London theory of hydrogen atom, the interaction potenti between two atoms can be written as

$$V_{ab} = e^2\left(\frac{1}{r_{ab}} + \frac{1}{r_{12}} - \frac{1}{r_{b1}} - \frac{1}{r_{a2}}\right). \quad \ldots(1$$

where suffix a and b denote the two nuclei and 1, 2 the two electrons.

The energy of the system can be written as

$$E = K \pm J_e, \quad \ldots(2)$$

where K is the coulomb interaction energy and J_e the exchange integral given by

$$I = \int \psi_a(1)\, \psi_b^*(2)\, V_{ab}\, \psi_a(2)\, \psi_b(1)\, dv_1\, dv_2, \quad \ldots(3)$$

where ψ_b and ψ_a represent the atomic wave-functions of electrons 1 and 2 when in atoms a and b. The positive spin, in the expression for energy, stands for the state when the spins of the two electrons are anti-parallel *i.e.*, non-magnetic state, while negative sign is for the state when the spins of the two electrons are parallel *i.e.*, for magnetic state. Therefore for magnetic state

$$E = K - J_e,$$

which is stable only when J_e is positive because then

$$K - J_e < K + J_e.$$

Here we are concerned with the exchange energy and not with coulomb interaction energy K. Therefore considering the relative orientation of the two spins $\mathbf{S}_1$ and $\mathbf{S}_2$, we can write

$$E = \text{constant} - 2\, J_e\, \mathbf{S}_1 \,.\, \mathbf{S}_2,$$

predicting that exchange energy appears in the total energy as if there exists a direct coupling between the two spins and therefore exchange interactions between electron with spin vectors $\mathbf{s}_i$ and $\mathbf{s}_j$ will have the form

$$E = -J_e\, \mathbf{s}_i \,.\, \mathbf{s}_j. \quad \ldots(4)$$

For two atoms with total spin vectors $\mathbf{S}_i$ and $\mathbf{S}_j$ the total interaction energy can be written as

$$N = -2\, J_{ij} \sum_{ij} \mathbf{s}_i \, \mathbf{s}_j \quad \ldots(5)$$

$$= -2\, J_{ij}\, \mathbf{S}_i \,.\, \mathbf{S}_j,$$

and depends upon the relative orientation of the two total spin vectors $\mathbf{S}_i$ and $\mathbf{S}_j$. J_{ij} is the exchange integral for the two atoms. Behaviour of the exchange integral with ratio of interatomic distance r_{ab} to the orbital radius, r_0, of electrons (here r_{3d} is the radius of the unfilled 3*d*-shell) is shown in fig. 8(d). Bethe has shown that magnetic state is favoured, (*i.e.*, J_e is positive) if r_{ab} is sufficiently large compared with r_0, the orbital radius of electrons.

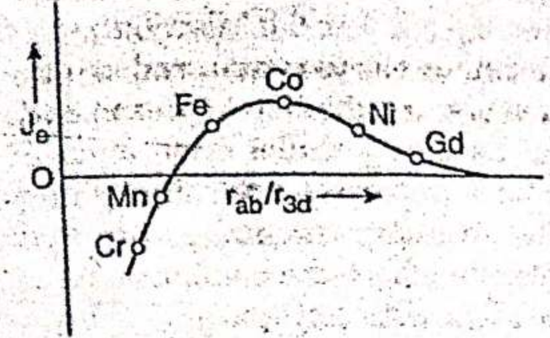

Fig. 8(d). **Behaviour of the exchange integral as function of the ratio of interatomic separation to the radius of the 3*d* orbit. Note that J_e is positive for Fe, Co, Ni and Gd and negative for Mn and Cr.**

Slater more specifically predicted that when $\frac{r_{ab}}{r_0}$ is slightly larger than 3, magnetic state is favoured. For Fe, Co, Ni and Gd this ratio has the value 3·26, 3·64, 3·94 and 3·1 respectively.

Note that for Cr and Mn, this ratio is 2·60 and 2·94 respectively, less than 3 and so a non-magnetic state is favoured. Exchange integral is negative for them–a negative value must be in fact more probable–the reason being that the attraction between the nuclei and the electrons is greater than the repulsion between the nuclei and between the electrons and hence the smaller interatomic spacings, r_{ab} (and so a smaller ratio of r_{ab}/r_0). Now the question arises whether an element with uncompensated spins, which itself is not ferromagnetic because the r_{ab}/r_0 value is not favourable, may be combined with another nonferromagnetic element to form a compound whose r_{ab}/r_0 value is suitable for ferromagnetism. This is possible. We find that both MnAs and MnSb are ferromagnetic; the lattice constants of these compounds are respectively 2·85Å and 2·89Å as compared with 2·58Å for pure Mn.

Relation between exchange integral J_e, Weiss constant, λ, and the ferromagnetic Curie temperature, θ_f.

A simplified procedure to set up relation in J_e, λ and θ_f has been suggested by Stoner. It is assumed that exchange integral is negligible except for nearest neighbours and its value is J_e for all neighbouring pairs.

Therefore, following equation (5), exchange energy of a given atom *i* with its neighbours will be

$$V = -2J_e \sum_j \mathbf{S}_i \cdot \mathbf{S}_j \tag{6}$$

where the summation extends over the nearest neighbours of atom *i*. According to Stoner, the instantaneous values of the neighbouring spins may be replaced by their time averages. Thus, if there are *z* nearest neighbours, we have

$$V = -2zJ_e[S_{xi}\langle S_{xj}\rangle + S_{yi}\langle S_{yj}\rangle + S_{zi}\langle S_{zj}\rangle] \tag{7}$$

Assuming that the magnetisation *M* is along Z-direction, we can write

$$\left.\begin{aligned}\langle S_{xj}\rangle &= \langle S_{yi}\rangle = 0\\ \langle S_{zj}\rangle &= M/g\,\mu_B N\end{aligned}\right] \tag{8}$$

From equations (7) and (8), we have

$$V = -2zJ_e S_{zi} M/gN\mu_B. \tag{9}$$

which should be equal to the potential energy of spin *i* in the Weiss field λ*M*, *i.e.*,

$$\text{P.E.} = V = -g\,S_{zi}\,\mu_B\,\lambda M$$

Sindhuja

or

$$-\frac{2zJ_e S_{zi} M}{gN\mu_B} = -g\,S_{zi}\,\mu_B\,\lambda M$$

∴

$$\lambda = \frac{2zJ_e}{Ng^2\mu_B^2} \tag{10}$$

spin waves are called magnons. Each magnon lowers the total magnetisation by one unit of spin. Consequently, equation (26) represents the total decrease in magnetisation of the system. That is

$$\Delta M = M_S - M = \sum_k n_k = 0{\cdot}0587 \left(\frac{K_B T}{2 J_e S a^2} \right)^{3/2} \qquad ...(27)$$

Therefore, fractional decrease of magnetisation with temperature is given by

$$\frac{\Delta M}{M_S} = \frac{0{\cdot}0587}{n S} \left(\frac{K_B T}{2 J_a S a^2} \right)^{3/2} \qquad ...(28)$$

This result is due to Felix Bloch, known as the Bloch $T^{3/2}$ law and is found to hold good at low temperatures. At high temperatures, a high density of magnons is created and the assumed spin wave model breaks down, resulting in the invalidity of the law at such temperatures.

$$\frac{\Delta M}{M_S} = \frac{M_S - M}{M_S} = \frac{0{\cdot}0587}{n a^3 S} \left(\frac{K_B T}{2 J_e S} \right)^{3/2}$$

$$1 - \frac{M}{M_S} = \frac{0{\cdot}0587}{Q S} \left(\frac{K_B T}{2 J_e S} \right)^{3/2}$$

or

$$M = M_S \left[1 - \frac{0{\cdot}0587}{Q S} \left(\frac{K_B T}{2 J_e S} \right)^{3/2} \right] \qquad ...(29)$$

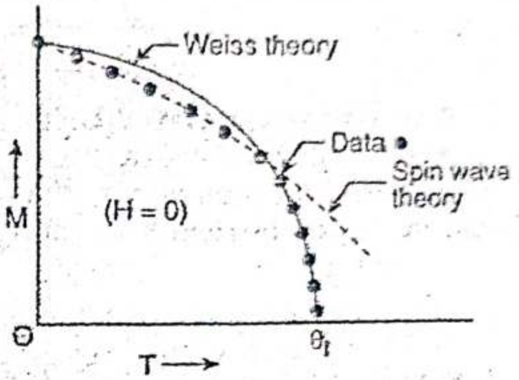

Fig. 10(b). **Comparison of experimental data with spin wave and Weiss theories of temperature dependence of M. θ is ferromagnetic Curie temperature beyond which spontaneous magnetisation vanishes.**

The result is famous Bloch $T^{3/2}$ law, after Felix Bloch. The temperature dependence of magnetisation predicted by this law is plotted in fig. 10(b) alongwith the results of experiments and of the independent spin model of Weiss. It is observed that the law holds with remarkable success at low temperatures but not at all at high temperatures (for *bcc* crystals $M = 0$ at $T = \theta$ experimentally but this law gives $M = 0$ at $T = 3\,\theta$). The reason is that, at high temperatures, a high density of magnons is created and the assumed spin wave model breaks down. From observation, of fig. 10(b), we find that Weiss theory (independent spin model) is in close agreement with the experimental data as compared to spin wave theory discussed in this article.

12.6 FERROMAGNETIC DOMAINS

12.6-1 INTRODUCTION

Weiss, in order to explain the fact that actual pieces of ferromagnetic materials are normally found in demagnetised state, assumed the existence of small domains within which the ferromagnetic material is magnetised to saturation. The direction of magnetisation, however, varies from domain to domain and thus the *net macroscopic magnetisation* may have value between zero and saturation (because over all magnetisation is given by the sum of domain magnetisation vectors and net magnetisation occurrs only when some of these vectors are caused to align themselves more or less parallel to an applied field).

In fig. 11(a) domain arrangement for zero resultant magnetic moment in a single crystal is shown. According to domain theory as suggested by R. Becker, when a magnetic field is applied then magnetisation of specimen or increase in the value of resultant magnetic moment of the specimen takes place by two independent processes :

(i) *By the motion of domain walls, i.e.*, by an increase in the volume of domains that are favourably oriented with respect to the magnetising field at the cost of those that are unfavourably oriented as shown in fig. 11(b).

(ii) *By rotation of domains, i.e.*, by the rotation of the direction of magnetisation towards the direction of the field as shown in fig. 11(c).

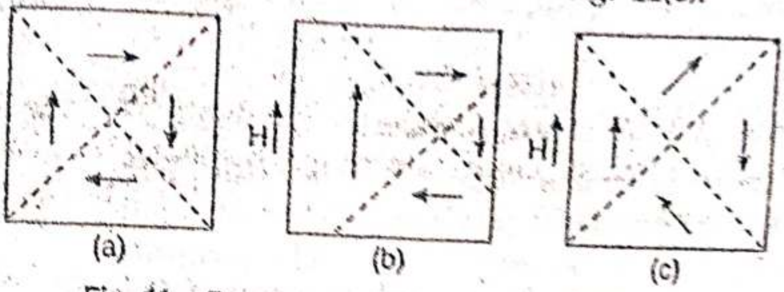

Fig. 11. Processes of domain magnetisation.

It is, however, inferred that in weak magnetising fields the first way is favoured that is domains change in size, *i.e.*, for the magnetic moment of the specimen to increase, boundary of the domains are displaced so as to change the domain volume. But in strong fields, the magnetisation changes by means of rotation of the direction of magnetisation.

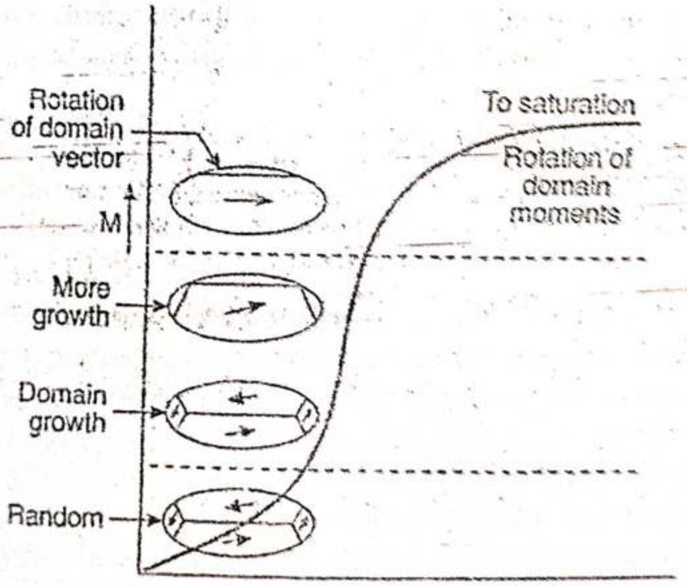

Fig. 12. The magnetisation curve.

Typical magnetisation curve of a virgin specimen is shown in fig. 12 that indicates the predominent process taking place in the different regions.

Evidence of domain existence : The direct evidence for the existence of domain structures is obtained from 'powder patterns'. In this technique a drop of colloidal suspension of finely divided ferromagnetic powder is allowed to spread over prepared surface of ferromagnetic material under investigation. The colloidal particles, as observed under microscope, collect along the domain boundaries since strong local magnetic fields exist near these domain boundaries.

12.6-2 ORIGIN OF DOMAINS

We know that according to thermodynamics the free energy of a solid tends to reach a minimum. Therefore, if we show that domain structure occurs in order to minimise the total energy of ferromagnetic solid then it should be sufficient to understand the existence of domains. The total energy comprises the sum of the exchange energy, anisotropic energy and the magnetic energy.

(a) The magnetic energy : We shall observe here that by dividing a crystal into two or more domains, the magnetic energy is reduced to minimum or even to zero for certain domain structures.

Fig. 13(a) represents a cross-section through ferromagnetic crystal having a single domain structure established by exchange energy and is saturated. Because of the free

As is obvious from the figure much greater fields are needed to produce magnetic saturation in [111] as compared to the field required in [100] direction. The difference in magnetic energy to produce saturation in an easy [100] direction and hard direction [111] is called crystal *anisotropic energy** and is important in determining the character of a domain boundary. For Fe, for example, the excess work done in magnetising to saturation a specimen in [111] direction compared with [100] direction is about 1.4×10^4 joule/m^2 and is thus anisotropic energy of Fe.

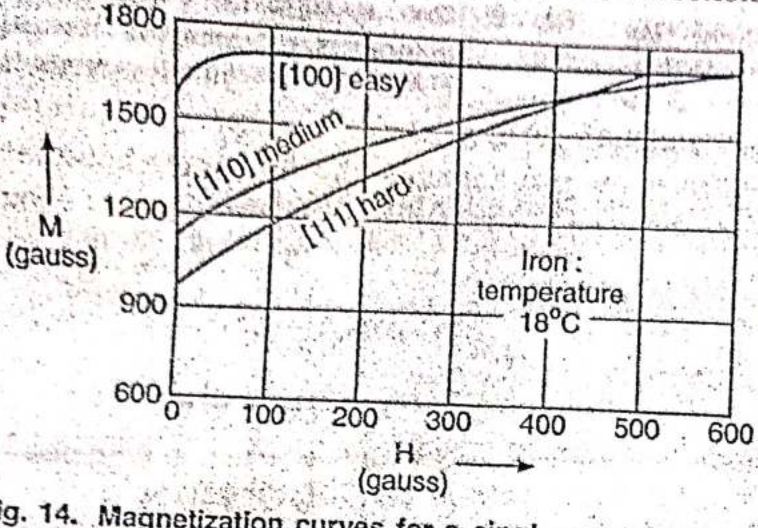

Fig. 14. Magnetization curves for a single crystal of iron for different directions of the field relative to the crystal axes.

In Fe crystal, which is cubic, the easy directions of magnetisation are cube edges whereas in nickel, which is also cubic, the easy directions are body diagonals. In cobalt there is only one preferred direction (easy direction)—the hexagonal axis of the crystal and is thus referred to as uniaxial.

We thus note that anisotropic energy makes the magnetisation of a domain to line up along certain crystallographic axes called preferred axes or easy directions. This anisotropy of the crystal determines the energy required to produce a closure domain.

Although number of domains and domain structure depend, to a large extent, upon the shape and size of the crystal under consideration but in a demagnetised material they are usually arranged in such a way as to make the magnetostatic energy small by ensuring that paths of flux closure exist within the solid for which the domains must have their magnetisation in a variety of directions.

Powder patterns reveal that domain structure always has its origin in the possibility of lowering the energy of a system by going from a saturated configuration with high magnetic energy to a domain configuration with lower energy.

12.6-3 THE DOMAIN WALL (BLOCH WALL)

The presence of domains requires the existence of the transition region in which the magnetisation goes smoothly from one direction to the other.

The energy of domain wall comes chiefly from two sources, the exchange energy and anisotropic energy as we note that :

(i) Spins must necessary change as M, the magnetisation, the changes from that of one domain to the adjacent one. Hence a certain number of spins must be misaligned in the boundary. The misalignment involves rotation of spins that associates with it a definite energy and is recognised as exchange energy which depends upon the degree of relative alignment of the spins.

(ii) Apart from the relative alignment of the spins, the spins also interact with the lattice atom. For if all the spins are completely aligned and this direction of alignment is rotated relative to crystal then we find that magnetisation in some directions (called easy directions) requires less strong magnetic field as compared to the fields required to produce the same saturation in other directions (called hard directions). This anisotropy of the crystal gives rise to anisotropic energy.

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[*] The magnetisation of a crystal in a certain direction always produces changes in atomic spacing and is called magnetostriction.

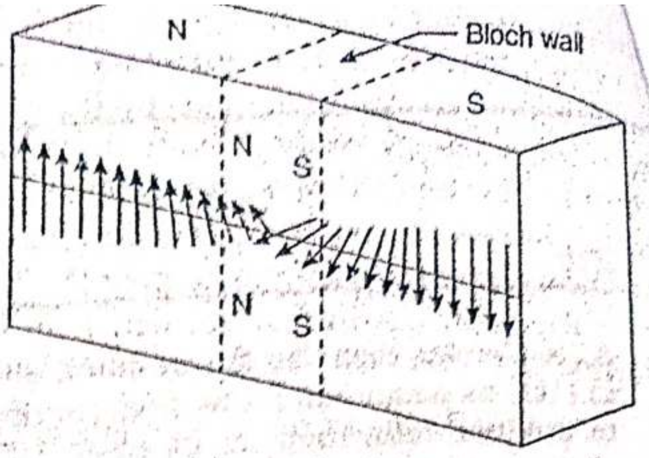

Fig. 15. The structure of a 180°-Bloch wall separating two domains : the gradual change of spin direction is obvious.

change in spin direction magnetised in different direction takes place in one atomic spacing or it might spread out over a number of atomic planes. We find, as discussed below, that for a given total change of spin direction, the exchange energy is lower when the change is distributed over many spins than when the change occurrs abruptly and since the idea of domain structure lies in the principle of minimum energy, this change should occurr not abruptly but gradually over many atomic spacings.

The exchange energy depends upon the spins of the interacting atoms and their relative orientation. We shall write it as

$$E_{ex} = -2\,\mathbf{S}_1 \cdot \mathbf{S}_2\, J_e\,.$$

Here J_e is the exchange integral and S is the spin quantum number.

If the two spin vectors $\mathbf{S}_1$ and $\mathbf{S}_2$ make a small angle θ with each other, then

$$E_{ex} = -2\,J_e\,S^2 \cos\theta,$$

$$= -2\,J_e\,S^2\left(1 - \frac{\theta^2}{2}\right),$$

which shows that due to rotation through an angle θ, exchange energy is increased by $J_e\,S^2\,\theta^2$ as compared to the case when $\mathbf{S}_1$ and $\mathbf{S}_2$ are parallel, (*i.e.*, θ is zero).

Suppose this change of θ in spins is brought in N equal steps then change in angle between neighbouring spins is θ/N and the exchange energy between each pair of neighbouring atoms is

$$= J_e\,S^2\left(\frac{\theta}{N}\right)^2$$

$$= \frac{J_e\,S^2\,\theta^2}{N^2}$$

Therefore total exchange energy of the row of $(N+1)^*$ atoms is thus

$$(E_{ex})_{\text{row}} = N \cdot \frac{J_e\,S^2\,\theta^2}{N^2},$$

$$= \frac{J_e\,S^2\,\theta^2}{N}. \qquad \text{...(I)}$$

The equation shows that exchange energy decreases as N increases. Thus with the increase in the thickness (more pairs of atoms) of the wall, the exchange energy decreases. It means in the formation of domains there should necessarily be a transition region in which

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* For N pairs, there should be $(N+1)$ atoms.

spins change gradually over finite domain spacing. As the domain configuration favours the minimisation of energy, we should except the Bloch wall to be infinitely thick which can not be the case because anisotropic energy limits the thickness. The reason being that if the spin direction undergoes a complete change in a number of steps, some of the individual magnetic moments must be in hard directions [111]. Obviously, the moments in hard directions will have higher energy than they would have in easy directions and consequent increase in anisotropic energy results. Since the anisotropic energy is proportional to the thickness of the wall, this tends to make the domain wall as thin as possible (for anisotropic energy should be minimised to favour domain formation). The domain wall assumes a thickness which balances these two energies to give the lowest total energy which is calculated below :

The total energy per sq. cm. may be written as a sum of exchange and anisotropic energy, *i.e.*,

$$E = E_{ex} + E_{an} \qquad \text{...(2)}$$

If we consider a wall of unit area, thickness being $N a$, where a is lattice constant, then

$$E_{an} = K \cdot N a, \qquad \text{...(3)}$$

where K is called anisotropic constant.

Further the exchange energy $\mathbf{F}_{ex}$ will be obtained on multiplying equation (1) by the number of row of spins per cm^2, *i.e.*, by $1/a^2$. Thus :

$$E_{ex} = \frac{1}{a^2} \frac{J_e S^2 \theta^2}{N} \qquad \text{...(4)}$$

Therefore,

$$E = \frac{J_e S^2 \theta^2}{N a^2} + K N a. \qquad \text{...(5)}$$

We know that the value of N, the number of pairs, which will keep E minimum will be compromising one for which we put

$$\frac{dE}{dN} = 0$$

or

$$\frac{dE}{dN} = 0 = -\frac{J_e S^2 \theta^2}{N^2 a^2} + K a$$

$$N = \left[\frac{J_e S^2 \theta^2}{K a^3}\right]^{1/2} \qquad \text{...(6)}$$

Putting this value of N in equation (5), the total energy per cm^3 of a Bloch wall is

$$E = \frac{J_e S^2 \theta^2}{a^2}\left[\frac{K a^3}{J_e S^2 \theta^2}\right]^{1/2} + K a \left[\frac{J_e S^2 \theta^2}{K a^3}\right]^{1/2}$$

$$= S \theta \left[\frac{J_e K}{a}\right]^{1/2} + S \theta \left[\frac{J_e K}{a}\right]^{1/2}$$

$$= 2 S \theta \left[\frac{J_e \cdot K}{a}\right]^{1/2} \qquad \text{...(7)}$$

5

which for iron having

$$J_e^* = \frac{K\,\theta_f^*}{3}, \qquad \theta_f = \pi$$

$$K = 10^5\ \text{erg/cm}^3, \qquad S = \frac{1}{2},$$

turns out to be of the order of 1 erg/cm^2. Putting these data in equation (6), we obtain

$$N = 300$$

or

$$t = 1000\ \text{Å},$$

where t is the thickness of the wall.

The above treatment is rather crude because due to anisotropy, the angle betwee successive spins is not constant throughout the Bloch wall, *i.e.*, it is improper to take which implies that total spin is shared equally by each of the pair of atoms on a line throug the wall.

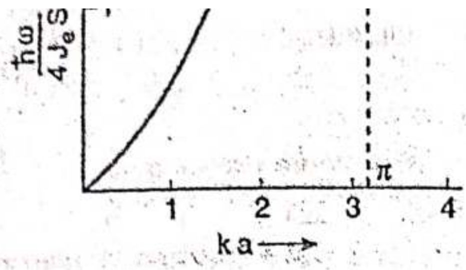


Fig. 9(b). Dispersion curve according to eq. (10).

representing their circular precession about z-axis. ...(12)

Quantisation of Spin Waves : In the ferromagnetic ground state, the spin waves are not excited and therefore all spins are parallel. The total spin quantum number of a system of N-spins, each S, in this state, has the value NS. The excitation of a spin wave lowers the total spin because the spins do not remain parallel. Thus total spin value is reduced below the value NS. We shall develop first a relation between the amplitude of the spin wave and the reduction in the z-component of the total spin quantum number and then find the expression for energy E_k when a spin wave k is excited.

According to equation (12), the z-component of a spin is

$$S_z = (S^2 - u^2)^{1/2}$$

$$= S - \frac{u^2}{2S} \text{ for small amplitudes } \frac{u}{S} \ll 1 \quad ...(13)$$

or

$$NS - NS_z = \frac{Nu^2}{2S} \longrightarrow ③ \quad ...(14)$$

Quantum theory allows only integral values for $(S - S_z)$. If N is the total number of spins and $NS - n_k$ is the z-component of the total spin when a spin wave **k** is excited, then by eq. (14),

$$n_k = \frac{N u_k^2}{2S}$$

or

$$u_k^2 = \frac{2 S n_k}{N} \quad ...(15)$$

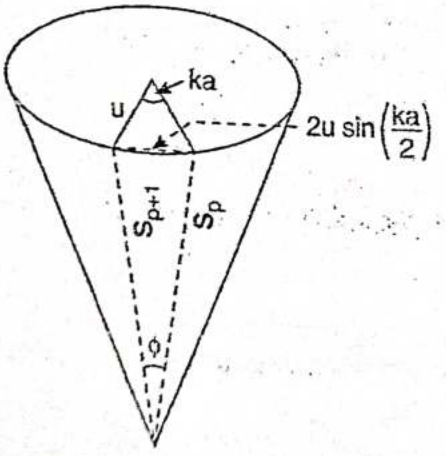


Fig. 10(a). Sketch relating the angle φ between two successive spin vectors to the spin wave amplitude u and the phase angle ka.

which represents quantisation condition for spin wave amplitude u_k, n_k is an integer equal to the number of *magnons* of wave vector **k** that are excited. Each magnon lowers the z-component of the total spin by one.

To find the energy E_k when a spin wave k is excited, we consider the interaction energy between two spins $\mathbf{S}_p$ and $\mathbf{S}_{p+1}$. From ~~eq. (6) art. 12.4-3, we have~~

$$E_e = 2 J_e \mathbf{S}_p \cdot \mathbf{S}_{p+1} \qquad E_e = -2 J_e \vec{S}_p \cdot \vec{S}_{p+1}$$

$$= 2 J_e S^2 \cos\phi \qquad = -2 J_e S^2 \cos(\phi)$$

where φ is the angle between $\mathbf{S}_p$ and $\mathbf{S}_{p+1}$, and S is the magnitude of their spin. From fig. 10(a) it is obvious that

$$2u \sin\left(\frac{ka}{2}\right) = S \sin\frac{\phi}{2} + S \sin\frac{\phi}{2}$$

where S is the length of a spin.

Therefore,

$$\sin\frac{\phi}{2} = \left(\frac{u}{S}\right)\sin\left(\frac{ka}{2}\right)$$

For $\frac{u}{S} \ll 1$, we have

$$\cos\phi = 1 - 2\sin^2\frac{\phi}{2}$$

$$= 1 - 2\left(\frac{u}{S}\right)^2 \sin^2\left(\frac{ka}{2}\right)$$

$$= 1 - 2\left(\frac{u}{S}\right)^2 \left(\frac{1-\cos ka}{2}\right) \qquad \ldots(17)$$

(5) (4)

Putting eq. (17) in equation (16), we get

$$E_0 = -2J_e S^2\left[1 - 2\left(\frac{u}{S}\right)^2 (1-\cos ka)\right].$$

The total interaction energy of the spin system of N spins will be

$$E_0 = -2J_e N S^2\left[1 - 2\left(\frac{u}{S}\right)^2 (1-\cos ka)\right]$$

$$= -2J_e N S^2 + 2J_e N u^2 (1-\cos ka) \qquad (6) \qquad \ldots(18)$$

and the excitation energy of a spin wave of amplitude u_k and wave vector k is

$$E_k = 2J_e N u_k^2 (1-\cos ka) \qquad (7) \qquad \ldots(19)$$

With quantisation condition (15), Eq. (19) becomes

$$E_k = 4J_e S(1-\cos ka)\, n_k$$

$$= n_k \hbar\,\omega_k \qquad (8) \qquad \ldots(20)$$

on using eq. (10). Thus we observe that energy E_k satisfies the same quantum condition as for phonons.

Thermal Excitation of Magnons : As already stated each magnon lowers the z-component of the total spin by one or in other words each magnon lowers the total magnetisation by one unit of spin. We shall now proceed to calculate total number of magnons $\sum_k n_k$ in all the states excited in the system at a temperature T. It is given by

$$\sum_k n_k = \int d\omega\, Z(\omega)\, \bar{n}_k \qquad \ldots(21)$$

where $Z(\omega)$ is the number of states k per unit frequency range and $\bar{n}_k$ is the average number of magnons in the state k. The integral is taken over the allowed range of k, which is first Brillouin zone. At sufficiently low temperatures, we may carry the integral between 0 and ∞ because $\bar{n}_k \to 0$ exponentially as $\omega \to \infty$.

Magnons have only a single polarisation for each value of k. In three dimensions the number of modes of wave vector less than k is[*]

$$\left(\frac{1}{2\pi}\right)^3\left(\frac{4\pi k^3}{3}\right)$$

---

[*] *Refer to Chap. 6—Calculation of modes of vibration in frequency range ν and ν + dν.*

Magnons:

A magnon is a quantised spin wave the concept of a magnon was introduced in 1930 by, Felix Block, in order to explain the reduction of the spontaneous magnetisation in a ferromagnet.

Magnon behaviour can be studies with a variety of scattering techniques we can find the magnon dispersion relation for 'ω' Vs 'k'.

Then quantised the magnon energy and interpret the quantisation interms of time reversal. At absolute zero temperature (0K) a Heisenberg ferromagnet reaches the states of lowest energy (so called ground state) in which all the atomic spin (& hence magnetic moments) point in the same direction

As the temperature increases more and more spins deviate randomly from the alignment, increasing the internal energy & reducing the net magnetisation.

If one views the perfectly magnetised state at zero temperature, the low temperature state with a few mis-align spins can be viewed as a gas of quasi particles in magnons.

The ground state and the excited state of the ferro magnet is shown is fig below.

↑ ↑ ↑ ↑ ↑ ↑

fig (a) classical picture of the ground state of a simple ferromagnet.

↑↑↓↑↑↑

fig (b) A possible excitation one spin reversed.

The elementary excitation of a spin system have a wave like form and are called magnons.

These are analogous to lattice vibrations or phonons spin waves are oscillations in the relative orientation of spins on a lattice.

Lattice vibrations are oscillations in the relative positions of atoms on a lattice.

fig (a)

fig (b)

A spin wave on a line of spins

(a) The spin viewed in perspective

(b) spin viewed from above showing one wavelength. the wave is drawn through the ends of the spin vectors

Quantum theory of paramagnetism:

The magnetic moment of an electron atom or ion in free space is given by

$$\vec{\mu} = \gamma \hbar J$$

$$= -g\mu_B J \quad — ①$$

Hence, total angular momentum $\hbar J$ = orbital angular momentum $\hbar L$ + spin angular momentum $\hbar S$.

The ratio of the magnetic of $\vec{\mu}$ to that of J is called gyromagnetic ratio (γ) or magnetogyric ratio.

μ_B is the Bohr magneton

It is defined as $e\hbar/2m$

For a free atom the g factor is given by the Lande equation

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

for an electron spin $g = 2.00$

The energy levels of the system in a magnetic field are

$$U = -\mu, B = m_J g \mu_B B \quad -3$$

Here m_J is the azimuthal quantum no.

$$m_J = J., (J-1), \ldots -(J-1), -J$$

For a single spin with no orbital moment, we have,

$$m_J = \pm\frac{1}{2} \text{ and } g = 2$$

$$U = \pm \mu_B B \quad — ④$$

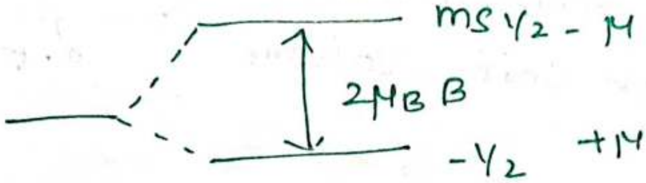
Thus an energy difference exists b/w spin magnetic dipole moments ||el and anti-||el to the field.

$U = m_J g \mu_B B$

$\pm \frac{1}{2} \times 2 \mu_B B$

The magnitude of energy difference is $2\mu_B B$

This splitting is shown in fig



Let us suppose that in unit volume of the paramagnetic material there is a total of N atoms. The spin moments of N_1 atoms are ||el to the fields and N_2 spin moments are anti-||el.

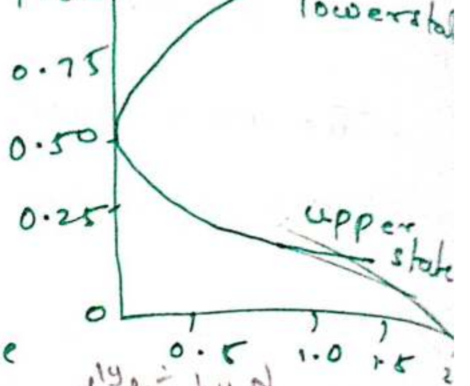
If a system has only two levels the equilibrium populations are with $\tau = k_B T$.

$$\frac{N_1}{N} = \frac{\exp(\mu B/\tau)}{\exp(\mu B/\tau) + \exp(-\mu B/\tau)} \quad \text{–⑤}$$

$$\frac{N_2}{N} = \frac{\exp(-\mu B/\tau)}{\exp(\mu B/\tau) + \exp(-\mu B/\tau)} \quad \text{– 6}$$

Here, N_1 and N_2 are the populations of the lower and upper levels and $N = N_1 + N_2$ is the total number of atoms.

The fractional populations are ~~pa~~ plotted in fig.



The projection of the magnetic moment of the upper state along the field direction is $-\mu$ and of the lowerstate is μ. The resultant magnetization for N atoms per unit volume is

$x^{1y}2 \div$ by N

$\mu(N_1-N_2)\frac{N}{N}$

$= N\mu\left(\frac{e^x}{e^x+e^{-x}} \times \frac{e^{-1}}{e^x+e^{-1}}\right)$

$$M = (N_1 - N_2)\mu$$

$$= N\mu \cdot \frac{e^x \cdot e^{-x}}{e^x + e^{-x}}$$

$$M = N\mu \tanh x \quad -⑦$$

$$\text{Here, } x = \mu B/k_BT \quad -⑧$$

For $x \ll 1$ $\tanh x \simeq x$ we have

$$M = N\mu(\mu B/k_BT) \quad -⑨$$

$= N\mu_B(\mu_B B/k_BT)$

$\mu = \mu_B$

$B = \mu_0 H$

Sindhu

In a magnetic field an atom with angular momentum quantum number J has $(2J+1)$ equally spaced energy levels,

The magnetization is given by

$$M = NgJ\mu_B B_J(x) \quad -⑩$$

$$x = gJ\mu_B B/k_BT \quad -⑪$$

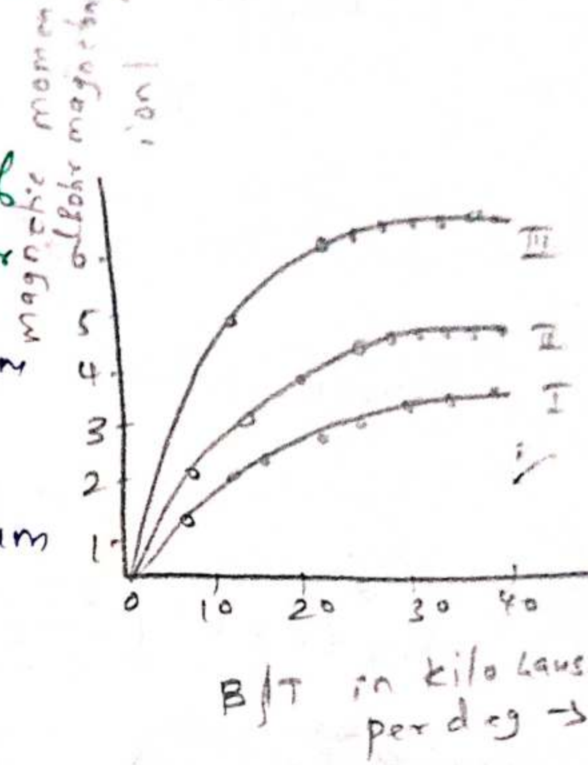
Here, Eq ⑩ called the curie - Brillouin law

$B_J(x)$ is called the Brillouin function defined

$$B_J(x) = \frac{2J+1}{2J}\coth\left(\frac{(2J+1)x}{2J}\right) - \frac{1}{2J}\coth\left(\frac{x}{2J}\right) \quad -(12)$$

Eg ⊕ is a special case of eqn ⑫ for $J = 1/2$

The fig. shows the plot of magnetic moment verses B/T for spherical samples of (I) potassium chromium atom, II ferric ammonium alum, and III gadolinium sulphate octahydrate.



for $x << 1$, we have

$$\coth x = \frac{1}{x} + \frac{x}{3} - \frac{x^3}{45} + \ldots \quad -(13)$$

The susceptibility per unit volume is

$$\chi = \frac{M}{B} = \frac{NJ(J+1)g^2\mu_B^2}{3K_BT} = \frac{Np^2\mu_B^2}{3K_BT} = \frac{C}{T} \quad -(14)$$

Here p is called the effective no. of Bohr Magnetons.

It is defined as $p = g\left[J(J+1)\right]^{1/2}$