CHAPTER - II

MOSSBAUER EFFECT, THERMAL DECOMPOSITION OF SOLIDS AND SUPERPARAMAGNETISM

This chapter briefly describes the study of hyperfine interaction through Mossbauer effect which is employed as fingerprint technique in analysing the products of thermal decomposition. The principle of thermal decomposition of solids along with a review of thermal decomposition of oxalates and mixed metal oxalates is discussed. The structure of ferrous oxalate and the Mossbauer effect studies of thermal decomposition of ferrous oxalate and mixed metal oxalates and their products of decomposition which are carried out till recently are reviewed. Also, Mossbauer effect study of superparamagnetism is discussed.

2.1 HYPERFINE INTERACTION THROUGH MOSSBAUER EFFECT STUDIES

Mossbauer effect produces monochromatic gamma radiation with a definition of the order of 1 part in $10^{12}$; this extremely high precision could be utilised to obtain chemical information. The key to the problem lies in the total interaction Hamiltonian for the atom, which contains terms relating to interactions between
the nucleus on the one hand and the electrons on the other, and hence the chemical environment. The Hamiltonian can be written as,

$$ H = H_0 + E_0 + M_1 + E_2 + $$

where $H_0$ represents all terms in the Hamiltonian for the atom except the hyperfine interactions being considered; $E_0$ refers to electric monopole i.e., Coulombic interaction between the nucleus and the electrons; $M_1$ refers to magnetic dipole hyperfine interactions; and $E_2$ refers to electric quadrupole interactions. Higher terms are usually negligible.

The Coulombic interaction term $E_0$ alters the energy separation between the ground state and the excited state of the nucleus, thereby causing a slight shift in the position of the observed resonance line. The shift will be different in various chemical compounds, and for this reason it is generally known as the chemical isomer shift. It is also frequently referred to as the isomer shift or chemical shift, but in view of the earlier use of these terms in optical spectroscopy, respectively, the expression, 'the chemical isomer shift' is preferred. A less frequently used synonym is centre shift.

The electric quadrupole and magnetic dipole interactions both generate multiple-line spectra, and
consequently can give a great deal of information. All three interactions can be expressed as the product of a nuclear term which is a constant for a given Mössbauer gamma-ray transition and an electronic term which can be varied and can be related to the chemistry of the resonant absorber being studied.

2.1.1 Chemical Isomer Shift

The nucleus in an atom is always surrounded and penetrated by the electronic charge with which it interacts electrostatically. One assumes that the nucleus is a uniformly charged sphere of radius \( R \) and that the electronic charge density \( \rho \) is uniformly distributed over the nucleus. The difference between the electrostatic interaction of a point nucleus and a nucleus with radius \( R \) is given by

\[
\delta E = -\int_0^R \rho (V - V_o) \, 4\pi r^2 \, dr
\]

where \( V_o = \frac{Ze}{r} \), for \( r > R \),

\[
V_o = \frac{Ze}{R} \left( \frac{3}{2} - \frac{r^2}{2R^2} \right) \text{ for } r \leq R, \text{ and}
\]

\( Ze = \text{nuclear charge.} \)

This yields

\[
\delta E = -\frac{2\pi}{5} Ze \rho R^2
\]

If \( -e/\psi(0)^2 \) is used for the electron charge density \( \rho \),
\[ \delta E = \frac{2\pi}{5} z e^2 R^2 / \psi (0)/^2 \]

For a transition from the excited state to the ground state,

\[ \delta E_{\text{ex}} - \delta E_{\text{g}} = \frac{2\pi}{5} z e^2 (R_{\text{ex}}^2 - R_{\text{g}}^2) / \psi (0)/^2 \]

\[ = \frac{2\pi}{5} z e^2 2R^2 \delta R / \psi (0)/^2 \]

where \( \delta R = R_{\text{ex}} - R_{\text{g}} \)

Thus the isomer shift observed in the Mössbauer effect is given by the difference between the shift in the source and the shift in the absorber. See Fig. 2-1. Kistner and Sunyar (1960), were the first to observe the isomer shift of the Mössbauer spectral lines.

This isomer shift may be used in nuclear physics to obtain information about the radius of the nucleus, while in solid state physics it provides information about the electron density at the nucleus. In chemistry the isomer shift is used in valence investigations.

2.1.2 Quadrupole Splitting

This splitting exists when the electrons and/or the neighbouring atoms produce an inhomogeneous electric field at the nucleus and when the nucleus possesses a quadrupole moment (Gruverman, 1967).
The interaction between the nuclear electric quadrupole moment $Q$ and the electric field gradient (EFG) is given by,

$$H = \frac{e^2 Q}{4I(2I-1)} - 3I_z^2 \left\{ - I(I+1) + \frac{\eta}{2} \left( I_+^2 + I_-^2 \right) \right\}$$

where $I_+$ and $I_-$ are the raising and lowering operators of the spin; the electric field is equal to

$$\epsilon_{ij} = \nabla^2 \rho = \frac{\partial^2 \rho}{\partial z^2} \quad (x, y, z \text{ are the principal axes of the field gradient tensor}),$$

$$\eta = \frac{\epsilon_{11} - \epsilon_{22}}{\epsilon_{22}}$$

is called the asymmetry parameter.

For the excited level of $^{57}\text{Fe}$, (Cohon, 1976)

$$E_Q = \pm \frac{1}{4} \frac{e^2 Q}{\epsilon} \left( 1 + \frac{\eta^2}{3} \right)^{1/2}$$

Fig. 2-2 illustrates the splitting due to quadrupole interaction.

Common iron compounds are either ferrous $[\text{A}]3d^6$ or ferric $[\text{A}]3d^5$, having different electronic configurations. This strongly affects the EFG observed in iron compounds. The degeneracy of the five $3d$ electron orbitals of an iron ion is removed in a crystalline field. In a cubic field the five orbitals split into two sets, a triplet $t_{2g}$ and a doublet $e_g$. The spin degeneracy remains. If the splitting between $t_{2g}$ and $e_g$ is small the electrons favour a configuration
with a maximum number of unpaired spins (Hund's rules), which is called a high-spin compound. When the difference between the $t_{2g}$ and $E_g$ states is large, a low spin configuration is attained. In a high spin ferric ion, $Fe^{3+}$, the EFG is caused by the external charges and not by the electrons of the ion, since $Fe^{3+}$ is an $s$-state ion, $6s$, having a spherically symmetric electronic distribution. By contrast the high-spin ferrous ion $Fe^{2+}$, has an additional $d$ electron and an $Fe^{3+}$ core. The EFG arises here from this electron and the external charges. In this case the temperature dependence of the quadrupole splitting is very pronounced. The absolute value of the quadrupole splitting depends on the degree of covalency of the compound. The EFG in low-spin compounds is more complicated and depends very strongly on the nature of the bonding to the ligands. In general, the crystal field affects the electrons of the atom, even those which possess spherical symmetry. These electrons are distorted and produce an electric field gradient at the nucleus which is frequently larger than the electric field gradient due to the crystal field. The electrons that do no possess spherical symmetry also produce a distortion of the closed electronic shells, and additional field gradient. The effective field gradient is given by
2.1.3 Magnetic Splitting (Nuclear Zeeman Effect)

Hanna et al (1960) have done the first correct measurements of the internal magnetic field in Fe metal. The magnetic splitting arises from the interaction of the nuclear magnetic dipole moment with a magnetic field, \( \vec{H} \), due to the atom’s own electrons. The Hamiltonian of the interaction is

\[
H = -g \mu_n \vec{I} \cdot \vec{H},
\]

where \( g \) is the gyromagnetic ratio, \( \mu_n \), the nuclear magneton, \( \vec{I} \), the nuclear spin, and \( \vec{H} \), the internal field. This interaction splits the degenerate \( I \) levels. For \( ^{57}\text{Fe} \), the first excited state \( (I = 3/2) \) is split into four sub-levels, and the ground state \( (I = \gamma 2) \) is split into two levels as shown in Fig. 2-3.

The gamma transition in \( ^{57}\text{Fe} \) from the excited to the ground state is of the magnetic dipole type and \( \Delta m = \pm 1,0 \). Due to this condition only six transitions are possible. The relative intensities of the transitions are given by,

\[
\left\{ \left( I_g m_g LM / I_e m_e \right) \right\}^2 F_L (\theta),
\]

where \( (I_g m_g LM / I_e m_e ) \) is the Clebsch-Gordon coefficient describing the vector coupling of \( I_e \) and \( I_g \) through the radiation.
pattern. $F_L^M(\theta)$ is given by

$$F_L^0(\theta) = \frac{3}{2} \sin^2\theta$$

and

$$F_L^{\pm 1}(\theta) = \frac{3}{4}(1 + \cos^2\theta)$$

for a magnetic dipole transition.

For an unmagnetized absorber and with a single line source the relative intensities have to be averaged over $\theta$ and the ratio of the transition is $3:2:1$, when the absorber is magnetized perpendicular to the gamma-ray direction the intensity ratio is $3:4:1$.

2.1.4 Combined Magnetic and Electric Quadrupole Interaction

If an EFG and an internal magnetic field $H$ are present at the nucleus, then the positions of the sublevels of Hfs will depend on the ratio of magnetic to electric interaction energy, on the symmetry of the EFG and on the angle $\phi$ between the $Z$-principal axis of the EFG tensor and $H$.

It is possible to write the Hamiltonian for this general case, but there is no general solution. There exists an approximation for the case where

$$\frac{e^2q\phi}{g\mu_nH} << 1,$$

which is the situation encountered in $\alpha$-Fe$_2$O$_3$. Then for an axially symmetric
EFG one obtains (Wertheim, 1964),

\[ \varepsilon = -g \mu_n H_m I + (-1)^m I + \gamma_2 \frac{e^2 q}{4} (3 \cos^2 \theta - 1) \]

From the experimental Mossbauer spectra the values of \( e^2 q \cdot Q \) and \( H \) may be determined. Fig. 2-4 illustrates the combined magnetic and electric quadrupole interaction.

The Mossbauer parameters described in the section above are used for

1) Fundamental studies of compounds with respect to
   a) electronic structure of the Mossbauer atom, e.g., oxidation state and spin state;
   b) bond properties, e.g., \( \sigma \) - and \( \pi \) - interaction between the Mossbauer atom and bonded ligands, influence of the electronegativity of the ligands;
   c) structural properties, e.g., molecular geometry, distortion from cubic symmetry, effect of polymerization;
   d) magnetic properties in 'diluted' systems (diamagnetism, paramagnetism and temperature-dependent spin change) and co-operative phenomena (ferro, ferri-, antiferromagnetism);
   e) dynamic processes, e.g., electron-hopping in spinels, spin-spin and spin-lattice relaxation.
EFG one obtains (Wertheim, 1964),

\[ E = -g \mu_n H_m I + (-1)^{(m_l)} + \frac{1}{4} \frac{e^2 q_{-} Q}{(3 \cos^2 \theta - 1)} \]

From the experimental Mössbauer spectra the values of \( e^2 q_{-} Q \) and \( H \) may be determined. Fig. 2-4 illustrates the combined magnetic and electric quadrupole interaction.

The Mössbauer parameters described in the section above are used for

1) Fundamental studies of compounds with respect to

a) electronic structure of the Mössbauer atom, e.g., oxidation state and spin state;

b) bond properties, e.g., \( \sigma \) and \( \pi \) interaction between the Mössbauer atom and bonded ligands, influence of the electronegativity of the ligands;

c) structural properties, e.g., molecular geometry, distortion from cubic symmetry, effect of polymerization;

d) magnetic properties in 'diluted' systems (diamagnetism, paramagnetism and temperature-dependent spin change) and co-operative phenomena (ferro, ferri-, antiferromagnetism);

e) dynamic processes, e.g., electron-hopping in spinels, spin-spin and spin-lattice relaxation.
2) Use of the Mossbauer effect as an analytical tool for identifying chemical species (qualitative and quantitative analysis) in various fields of chemistry, e.g.,

a) solid state reactions, e.g., ligand exchange in transition metal complexes, thermal and radiation induced decompositions, electron exchange reactions;

b) surface studies, e.g., corrosion on iron and steel surfaces, adsorption properties of ion exchange resins, surface reactions on catalysts;

c) phase transitions, e.g., magnetic ordering, change in crystal structure; and so on.

Before applying Mossbauer effect in the present study of thermal decomposition of ferrous oxalate and mixed metal oxalate in hydrogen atmosphere, the principle of solid state reaction, thermal decomposition and reaction mechanism, endothermic and exothermic, are described briefly in the following sections.

To start with, the thermal decomposition of a single solid substance is taken up and then the reaction between two or more substances are considered. The reaction types involved in such decomposition are also discussed.
2.2 THERMAL DECOMPOSITION OF SOLIDS

In view of the large applicability of various nitrates, perchlorates and oxalates, their decomposition kinetics have received considerable attention. Various concepts of thermal decomposition are discussed here as a background to the thermal processes described in this thesis. Excellent monographs and review articles have been written on the decomposition of solids (Garner, 1955, Jacobs and Tompkins, 1955, Young, 1966 and 1971 Jacobs, 1969, Levy and Frechtte, 1969 and Hannay, 1976).

2.2.1 General Principles

The decomposition of perchlorates, azides, nitrates, picrates and oxalates is exothermic and irreversible while hydrates and carbonates decompose reversibly. Most of the decomposition conform to the equation

\[ A(s) \rightarrow B(s) + C(g) \]  \hspace{1cm} (2.1)

The first stage of thermal decomposition of any compound is usually represented by means of a plot the fraction \( \alpha \) decomposed isothermally as a function of time \( \tau \) as shown in Fig. 2-5. The \( \alpha - \tau \) curve can be divided into four regions. The initial process, region(I), which involves typically \( 0.01 < \alpha < 0.05 \), may be due to desorption of physically absorbed gases or to a surface
decomposition. The region (II) is usually termed as induction period. At the end of the induction period, the decomposition rate increases rapidly, finally reaching maximum value at the point of inflexion \((x_i, t_i)\). The region (III) is called the acceleratory period. The region (IV) is the deceleratory period when the reaction rate decreases steadily and finally falls to zero. The fractional decomposition at this stage may or may not correspond to the complete decomposition of the starting material. A number of cases are known where the decomposition is partial - ammonium halates (Solymosi and Banasagi, 1969).

Typical \(\alpha-t\) curves obtained in the decomposition of solids are shown in Fig. 2-6. In general they are sigmoid indicating an autocatalytic reaction (a). Curve (b) is shown by substances decomposing with short initial acceleratory period and more pronounced final decay period resulting in a rather asymmetrical curve. Curve (c) is obtained for substances which show a small evolution of gases at the beginning of the reaction and later the curve is sigmoid.

In the decomposition reactions described by the equation (2,1) given above, the onset of the reaction involves the formation of the new phase B at special points in the lattice of A, when sufficient energy is available
due to local fluctuations in the crystal. Though in the initial period of reaction, the phase B is embedded in the lattice of A, the change in its molecular volume is negligible. As B grows in size, it forms a different type of lattice with a different molecular volume causing strain and deformation of the original crystal lattice.

The extra energy due to this deformation is called 'strain energy'.

It can be shown (Wischin, 1939) that the free energy change accompanying the formation of a fragment of B containing $m$ molecules is given by

$$
\Delta G = m \Delta G_B + \gamma (36\pi V_m^2)^{1/3} m^{2/3}
$$

Equation 2.2 shows that when $\gamma$ is positive $\Delta G_1$ must pass through a maximum at $m = m^*$, when a fragment has the critical size to be in equilibrium with its surroundings. The plot of $\Delta G_1$ as a function of $m$ is shown graphically in Fig. 2-7. As a result of strain produced by the formation of new phase, small fragments of B will be unstable and revert back to the original state whereas, those beyond a particular size can grow further resulting
in a decrease of the total free energy. These points where the reaction commences are generally known as 'nuclei'.

For nuclei with \( m > m^* \), \( \frac{dG}{dm} \) is -ve so that the nuclei grow freely. Nuclei with \( m < m^* \) tend to disappear unless statistical fluctuations in local energy are sufficiently favourable to produce successive additions to the nuclei until \( m > m^* \). Nuclei smaller than critical size are called 'germ nuclei', those with \( m > m^* \), 'growth nuclei'.

The autocatalytic nature of the reaction may now be understood in terms of a general hypothesis. The reaction consists of the formation of nuclei at certain localized spots in the reactant followed by the relatively rapid growth of these nuclei. If the free energy of activation of the interface reaction is less than that for the formation of nuclei, growth of existing nuclei predominates over the formation of new ones and the product phase, therefore, assumes the form of compact individual nuclei, distributed in the matrix of A. Evidence for this has been obtained by Wischin (1939), in her observation of nucleus formation and growth in barium azide and by Bright and Garner (1934) and, Cooper and Garner (1936) in their work on the decomposition of hydrates. On the other hand if the free energy
of activation for nucleus formation ($\Delta G^*$) is not greatly different from that of the growth stage ($\Delta G^*_g$) then a large number of small nuclei will form, none of which grow to visible size. In this case the acceleratory period is reduced and, as an extreme case, may even be virtually removed if the formation of nuclei is facilitated by grinding or scratching the crystals (Garner and Tanner, 1935). See Fig. 2-6(b). Nuclei as formed during the decomposition of barium azide are called compact nuclei. Only such nuclei could be observed visually. Nuclei other than compact are called 'diffuse'. For reaction in which nucleation of the whole surface occurs rapidly the kinetics of the rest of the reaction is governed by the rate of progression of interface into the crystal (Fig. 2-6(c)). Curve of Fig. 2-6(d) is simply a combination of curves a and c and thus represents two phases to the reaction, one of which is initiated extremely rapidly. The general form of the decomposition curves (Fig. 2-6(a)-(b)) can thus be explained in terms of nucleus formation and growth.

2.2.2 Kinetics of Solid Decomposition

Nucleation, growth of the nucleus and the decay period are the basic kinetic characteristics of solid phase decomposition. Nucleation is favoured at definite localized spots where the activation energy is
least. The rate of nucleation depends upon the number of these potential nucleus-forming sites and the mean-activation energy for nucleus formation. Nucleation in certain decomposition reactions however, has been shown experimentally of silver oxalate to be a surface phenomenon associated with surface defects (Flynn, 1969).

Growth of the nucleus is the movement of reactant-product interface in a direction normal to its surface due to thermal decomposition reaction. The laws of the growth of nuclei have been discussed in detail by Jacobs and Tompkins (1955), Young (1966) and Gelway (1967). At the decay period, at later stages of solid decomposition, the contracting interface formed may collapse before the reaction is complete. This process leaves isolated blocks of material in which no nuclei are present.

2.2.3 Some Types of Reactions

In the present study of thermal decomposition both endothermic solid reaction and exothermic solid reaction are involved. In endothermic solid reactions, the dissociation and recombination processes occur simultaneously causing complications both in experimental techniques and in the theoretical interpretation of results. These reactions provide information about the mechanism of interface reactions and nucleation processes.
which are not readily obtainable by the exothermic processes alone. Investigations in this field have been almost restricted to the study of the dissociation of hydrates and carbonates. The loss of weight method is most suited for the study of such systems. Exothermic processes mostly fall into the class

$$A_{\text{Solid}} \rightarrow B_{\text{Solid}} + C_{\text{Gas}}$$

There are a small number of examples belonging to the classes

$$A_{\text{Solid}} \rightarrow B_{\text{Gas}} + C_{\text{Gas}}$$

and

$$A_{\text{Solid}} \rightarrow B_{\text{Solid}} + C_{\text{Solid}}.$$  

Solid-Solid Reaction

Solid state reactions usually occur between apparently regular crystal lattices in which motion of lattice units is very restricted and depends in a complex manner on the presence of lattice defects, interaction can occur only at points of intimate contact between the reacting phases. In solid-solid reactions a relatively immobile product layer usually builds up at the initial point of contact between reactants. If no appreciable ranges of solid solubility exist among the reactants and products of a solid-solid reaction, their thermodynamic activities remain constant throughout the course
of the process; the direction in which a solid-state reaction proceeds will clearly be that in which the standard free-energy change is negative. In a reaction involving solids only, the entropy change is small, and may for practical purposes be neglected. It is a useful generalization that solid-state reactions are exothermic.

Solid-Gas Reaction

This is concerned with a gas phase to form a new product rather than the evolution of a gas which is considered above. Obviously reversible decompositions involving a gas phase can be considered in either fashion. Gain or loss of oxygen giving rise to changing defect structures within a single composition is an important aspect of solid-gas reaction. The interaction between atmospheric oxygen and various oxides is of immense technological importance. The accompanying effects upon the semiconducting, magnetic, catalytic and other properties are enormous. Reaction of a solid phase with oxygen or hydrogen has been successfully employed in the formation of ultrafine particles. The present study in which the hydrogen gas has been employed for the thermal decomposition of ferrous oxalate and mixed metal oxalates falls under solid-gas reactions conveniently.
2.2.4 Thermal Decomposition of Some Typical Oxalates

Amongst the oxalates and formates (Bircumshaw and Edwards, 1950) the decomposition of silver oxalate has yielded results of the most general interest. Other oxalates such as those of nickel and uranyl illustrate special points.

Nickel Oxalate (NiC₂O₄·2H₂O)

Allen and Scaife (1954) decomposed nickel oxalate dihydrate between 280 and 320°C in an atmosphere of nitrogen and found that the kinetics could be divided into two regions termed,

(a) Initial reaction up to \( \alpha = 0.058 \) given by
\[
\alpha = k_1(t - t_0)^{1/2},
\]
k₁ gave the activation energy of 47.6 Kcal mole⁻¹

(b) Second stage given by \( \alpha = k_2t \) with the activation energy of 36.4 Kcal mole⁻¹.

The overall reaction produced nickel and carbon dioxide only. Metallic nickel was not detected during stage (a) by x-ray analysis though it was clearly present during stage (b). It was therefore suggested that the rate-determining step during the initial reaction is the diffusion of excess anion vacancies to the surface.
whereas stage (b) requires a charge transfer process from the oxalate ion to the nickel. Apart from the general criticism that decomposition in a nitrogen atmosphere retards the escape of water and carbon dioxide, Jacobs and Kureishy (1962) pointed out that the typical values for the electrical conductivity of oxalates \(10^{-9}\) to \(10^{-11}\) ohm\(^{-1}\) cm\(^{-1}\) are too small.

Danes and Ponec (1958), decomposed 100 mg samples of nickel oxalate in pressures of carbon dioxide between 100 and 800 mm in the temperature range 270-300°C. They considered that the acceleratory period could be fitted by the Prout-Tompkins equation i.e., exponential branching chains with overlap, with \(n = 2.4\) for \(0.04 < \alpha < 0.4\). It is clear from these results that the carbon dioxide had some inhibiting effect; indeed the surface reaction was absent. Jacobs and Kureishy (1962) therefore studied the thermal decomposition in vacuo, obtaining suitable reaction rates between 240 and 280°C. The initial reaction was well represented by the "contracting area" formula

\[1 - (1 - \frac{\alpha}{\alpha_0})^{1/2} = k_1 t\]

where \(\alpha_0 = 0.01\) for the particular preparation used.

The activation energy for this process was 32.9 Kcal mole\(^{-1}\) in disagreement with Allen and Scaife (1954). From the particle size of their preparation (0.6\(\mu\)) and
the value of $\alpha_0$, Jacobs and Kureishy (1962) calculated that about 3 monolayers of salt are involved in the initial reaction and they suggest that decomposition commences at surface defects immediately the salt reaches reaction temperature. The electron transfer step

$$\text{C}_2\text{O}_4^{2-} + \text{Ni}^{2+} \rightarrow \text{Ni} + \text{C}_2\text{O}_4$$

is rate-determining. After decomposition of the oxalate radicals the nickel atoms so formed aggregate, forming nuclei which become effective during the acceleratory period. Because the growth of linear nuclei is topochemically unsound, Jacobs and Kureishy (1962) reject nucleation at a constant rate and propose the growth of a constant number of nuclei, the volume of each nucleus depending on the square of the time. Such nuclei must either be plate like or cylindrical in form. The activation energies derived are equal for both hydrated and dehydrated oxalate. In view of the inhibiting effect of water, the nucleus forming sites for the main reaction are those which dehydrated most easily and that these product nuclei grow more slowly when small because the excitation energy for electron transfer is greater for macroscopic nuclei. The general form of these results has been confirmed by Jach (1964) and Dominey et al (1965).
Other Oxalates

Mercuric oxalate may be contrasted with nickel oxalate, for here the initial surface reaction is acceleratory and may be represented as the expansion of discs from a constant number of point nuclei which eventually cover the surface, giving rise to contracting envelope kinetics (Prout and Tompkins, 1947). After pre-irradiation with ultraviolet light, the acceleratory period, which normally extends up to $\alpha = 0.15$, is replaced by an initial burst of gas followed by a short constant rate period. The decay period is unaffected. The rate determining step is unknown, though it is probably concerned with the co-ordination of the oxalate ion because the activation energy for the surface process (25.6 Kcal mole$^{-1}$) is less than for interfacial penetration (37.1 Kcal mole$^{-1}$).

Thorium, uranyl, lanthanum and lead oxalates are the lesser studied oxalates. Thorium oxalate is of technological interest (Beckett and Winfield, 1951). The decomposition of silver oxalate proceeds smoothly and completely between 100 and 160°C but the kinetics of the decomposition are subject to a variety of external influences (Macdonald and Sandison, 1938 and Haynes and Young, 1961).
2.2.5 Structure of Oxalate

Oxalates have been especially intriguing salts to chemists for many years. The complexing ability and the sensitivity towards oxidation have made them a fascinating and fruitful subject. As a consequence, many of the early applications of the Mossbauer effect to the study of chemical decompositions were directed toward the decomposition of simple and complex oxalates of iron induced by heat and radiation.

Because of the co-ordinating properties of the bidentate oxalate ion, most of the metals form complex oxalates in addition to simple oxalates. Many of the simple oxalates are crystalline solids or amorphous powders, white or coloured depending on the cation and are generally sparingly soluble in water. The metal oxalato complexes may be classified with respect to the number of oxalate groups co-ordinated to the metal ion. Evidence concerning the structure of the oxalato complexes has been obtained by means of many physico chemical methods, including electrical conductance, measurements, polarography, ion exchange, chromatography, electrophoresis, absorption spectroscopy, magnetic susceptibility measurements, x-ray crystallography, reaction kinetics and isotope exchange. A review on the 'Chemistry of the Metal Oxalato Complexes' is given by Krishnamurthy and Gordon (1961),
Fronaeus and Larsson (1960) have studied the solution equilibria of oxalato complexes in the 1500 - 1200 cm\(^{-1}\) region, where the CO stretching bands of the co-ordinated oxalato group appear. The infrared spectra of oxalato (\(\text{C}O\text{X}\)\(^2\)-) complexes have been made by using the results of normal co-ordinate analysis on the free oxalate ion (Murata and Kawai 1956 and 1960, Fujita et al 1957, Schumelz et al 1957). Fujita et al (1962), have carried out a normal co-ordinate analysis on the metal chelate ring of oxalato complexes. X-ray analysis indicates that the four C-O bonds in the free ion are equivalent, the bond distance being 1.27A. The C-O stretching force constant in this ion is 7.20 m dyn/A (Schmelz et al. 1957). It is suggested that the M-O bond becomes stronger, the C-O\(_I\) becomes weaker and the C-O\(_{II}\) and the C-C bonds become stronger. Thus a shift of the M-O stretching band to a higher frequency is expected to accompany a shift of the C-O\(_I\) stretching band to a lower frequency, together with a shift of the C-O\(_{II}\) stretching bond to a higher frequency. According to normal co-ordinate analysis both C-O\(_I\) and M-O stretching vibrations are coupled with other modes. Nevertheless linear relationship exists between the frequencies for the oxalate complexes of divalent metals.

In oxalato complexes of trivalent metals, strict linear relationship between the frequencies do not exist.
It is found however that there is an increase along the series Fe < V < Cr < Co < Al, for M-O stretching, which is the same order as that observed in a series of acetylacetylnato complexes.

The Raman spectra of metal oxalato complexes have also been examined to investigate the solution equilibria and the nature of the M-O bond (Hester and Plane, 1964 and Grwn and Plane, 1967).

**Iron Oxalate**

Although hydrated iron (II) oxalate is a well known complex, its crystal structure is unknown, it has been classified as possessing rhombic symmetry (Greenwood and Gibb, 1973). Mossbauer spectrum of low temperature antiferromagnetic phase (Ono and Ito, 1964 and Barros et al 1963) shows that the asymmetry parameter is approximately 0.7. The major axis of the electric field gradient tensor appears to be perpendicular to the magnetic axis, $e^2\eta Q$ is negative, but this cannot be confirmed by the magnetic perturbation technique because of the effect of the large asymmetry parameter (Nozik and Kaplan, 1967). Only two broad lines are seen at 20 k and presumably the Neel point is close to this temperature. The contributions to the internal field were estimated as were the excited-state electronic levels (Ingalls, 1964).
Spectroscopic data such as ultraviolet, visible and infrared regions are listed by Johnson (1935) and Krebs et al (1956). Studies on $\text{Fe(C}_2\text{O}_4\text{)}_3^{3-}$ prove conclusively that the resolution of this complex ion is not possible by conventional method. $\lambda_{\text{max}}$ for $\text{Fe(C}_2\text{O}_4\text{)}_3^{3-}$ is 650 m\(\mu\) (Bisikalova, 1951), in the visible absorption spectra. The infrared absorption spectra estimate for iron (III), that there is 50 percent covalent character (Schmelz et al 1957). Magnetic susceptibility experiments on $\text{Fe(C}_2\text{O}_4\text{)}_3^{3-}$ show that it is definitely ionic and the magnetic susceptibility is centered on the metal ion and not on the oxalate ion (Mota Prasad, 1950 and Ugai, 1954).

Using certain displacement reactions a method has been developed for obtaining the stability constants of $\text{FeC}_2\text{O}_4^+$, $\text{Fe(C}_2\text{O}_4\text{)}_2^-$ and $\text{Fe(C}_2\text{O}_4\text{)}_3^{3-}$ (Babko and Dubonenko, 1956 and 1958).

2.2.6 Thermal Decomposition of Ferrous Oxalate

There is an extensive literature on the thermal decomposition of what have been called the "simple" oxalates. The reactions are all relatively complicated and many products are reported including carbon, carbon monoxide, carbon dioxide, metal, metal oxides, metal peroxides and metal suboxides, metal formates, peroxyoxyxalates, carbonates and percarbonates.
Detailed kinetic studies have been made of only a few compounds: the oxalates of silver (I), mercury (I), mercury (II), nickel (II) and lead (II). See sec 2.2.3, for details. New techniques particularly, thermogravimetry have been applied and reports have appeared on many bivalent metal oxalates (Freeman and Carroll, 1958, Kornienko, 1957 and Venkateshwaralu and Sivaraman, 1957) of a few rare earth oxalates and two actinide oxalates, thorium IV, and americium (III).

Thermogravimetry studies are done by Kornienko (1956) on Iron (II) oxalate and also by Dosemienes and Boulte (1960). Gallagher (1965), has done TGA on iron oxalate and double oxalates of iron. Obviously much remains to be done in this area of the chemistry of complex oxalates. Gallagher (1965) has performed TGA, DTA and effluent gas analyses on \( \text{Ba}_3\left[\text{Fe(C}_2\text{O}_4)_3\right]_2\cdot\text{H}_2\text{O} \) and \( \text{Sr}_3\left[\text{Fe(C}_2\text{O}_4)_3\right]_2\cdot\text{H}_2\text{O} \). The results are compared with those of the individual oxalates and with a physical mixture having the same metallic ratio as the complex oxalates. The stoichiometry of the decomposition was found to be highly complex, involving at least four changes in the oxidation state of the iron. At an intermediate stage a considerable fraction of the total iron has the usual oxidation state of +4. Reagent grade oxalates are used without further purification. 0.1000g samples are arranged in a thin uniform layer which has
excellet contact with the furnace atmosphere. Samples of iron (III) oxalate and $\text{Ba}_3[\text{Fe}(\text{C}_2\text{O}_4)_3]_2\cdot8\text{H}_2\text{O}$ and $\text{Sr}_2[\text{Fe}(\text{C}_2\text{O}_4)_3]_2\cdot2\text{H}_2\text{O}$ are heated at a rate of 200°/hr in air. Small samples are removed at 100° intervals up to 1200°C and cooled rapidly.

The decomposition of iron (III) oxalate is more complex. Not much information is available for this compound. Dollimore et al (1963) have performed TGA experiments in air and although the total weight loss, initial temperature of decomposition, and end product are compatible with Gallagher's (1965) work, the shape of the weight loss curve is markedly different. The thermogram and the weight loss given in Table 2.1 distinctly show the two step loss of water with the additional loss of a molecule of carbon dioxide simultaneous with or immediately following the last three molecules of water. Dollimore et al (1963) indicate a single unresolved weight loss. Their use of a much larger sample (1.5 g) may have caused the reduced resolution. Table 2-1 gives the proposed scheme of decomposition of Iron (III) oxalate in air by Gallagher (1965). The formation of iron (II) oxalate is inferred from the separation of the carbon dioxide and monoxide peaks near 350°C. It is also consistent with the multi step appearance of the DTA and the results presented later for the complex oxalates. There is a much more apparent dependence of the temperature
upon atmosphere. The observed decomposition temperature of iron (II) oxalate is compatible with its immediate decomposition upon formation (Robin, 1953 and Gallagher and Schrey, 1964). This would further complicate any further resolution. Similar reductions have been shown to occur in the decomposition of europium (III) oxalate (Glassner et al, 1963) and in barium and strontium titanyl oxalates (Gallagher and Thomson, Jr., To be published). The small weight loss near 450°C probably arises from the decomposition of gas associated with the crystallization of the amorphous iron (III) oxide.

Although one of the first studies, the thermal decomposition of $\text{Ba}_3[\text{Fe(C}_2\text{O}_4)_3]_2$ and $\text{Sr}_3[\text{Fe(C}_2\text{O}_4)_3]_2$ is still highly informative and interesting due to the frequent changes in oxidation state that occur (Gallagher and Kurkjian, 1966). Fig. 2-8 displays selected spectra for samples of $\text{Sr}_3[\text{Fe(C}_2\text{O}_4)_3]_2\cdot2\text{H}_2\text{O}$ that had been heated in air to the indicated temperatures. These results are correlated well with previous thermoanalytical measurements (Gallagher, 1965).

The compound at room temperature (Fig. 2-8(a)) has an isomer shift indicative of trivalent iron. After having been heated to 300°C, the spectrum clearly indicates that the material has been reduced. Similar reduction was observed upon heating $\text{Fe}_2(\text{C}_2\text{O}_4)_3$ and $\text{Ba}_3[\text{Fe(C}_2\text{O}_4)_3]_2$. 
to 200°C. The parameters agree with the formation of FeC$_2$O$_4$ according to

$$3\text{Sr}_3[\text{Fe(C}_2\text{O}_4)_3]_2 \rightarrow 3\text{SrC}_2\text{O}_4 + 2\text{FeC}_2\text{O}_4 + 2\text{CO}_2$$

There is a hint of some trivalent remnant or product concealed within the lower energy peak. By 400°C in air (Fig. 2-8(c)), the oxalate has decomposed according to

$$2\text{FeC}_2\text{O}_4 + \frac{1}{2}\text{O}_2 \rightarrow \text{Fe}_2\text{O}_3 + 2\text{CO} + 2\text{CO}_2,$$

which undoubtedly represents the summation of several processes. In an inert atmosphere, Foerster et al. (1973) have shown that the decomposition proceeds to FeO and α-Fe. The FeO further disproportionates to Fe$_3$O$_4$ and α-Fe. In the presence of ample oxygen, these products are not evident. Because of the possible presence of Fe$_3$O$_4$, the initial Fe$_2$O$_3$ formed may be in the γ state (Krauth et al., 1967). Both Gallagher and Kurkjian (1966) and Krauth et al. (1967) agree that the initial Fe$_2$O$_3$ formed is so finely divided that it is superparamagnetic and gives rise to a quadrupole split doublet rather than the characteristic six-line patterns. Jach (1973 b) also observes a trivalent doublet upon the initial decomposition but assigns it to some unknown intermediate.

The solid products of the thermal decomposition of iron (II) oxalate dihydrate in an atmosphere of oxygen, free nitrogen at room temperature and at -195°C, have been
studied by Halsey et al (1968). Decomposition at 320°C has given magnetite but no trace of FeO is observed both by Mossbauer spectra and X-ray powder photographs. Decomposition above 365°C has yielded magnetite and $\gamma$-Fe$_2$O$_3$. Whereas in the presence of ample oxygen, the products indicated by Foerster (1973) are not evident. Zabarova et al (1967) have done Mossbauer and DTA studies of the decomposition of iron oxalate. Suzdalev et al (1966) investigated the thermal decomposition of iron oxalates by the methods of Nuclear Gamma Resonance and Derivatography. Thermal decomposition of iron (II) oxalate in an oxidizing atmosphere by Carie et al (1975), points to the formation of $\alpha$-Fe$_2$O$_3$ microcrystallites of grain size $\sim$80 Å.

2.2.7 Thermal Decomposition of Other Systems

The thermal decomposition of K$_3$Fe(C$_2$O$_4$)$_3$ is similar to the decomposition of the strontium and barium complexes described earlier, except that the ionic radii and charges are not suitable for the formation of perovskite structure. In the absence of this stabilizing influence, Fe(IV) is not formed. Bancroft et al (1970) have done an extensive investigation of this decomposition using the Mossbauer effect.
The effect of irradiation on oxalates have been extensively studied using the Mossbauer effect. Dharmawardena and Bancroft (1968), Bancroft et al (1969), and Temperley and Pumplin (1969) studied $K_3Fe(C_2O_4)_3$, and Saito et al (1965) studied $Fe_2(C_2O_4)_3$ by this technique. All the above studies indicated an initial reduction of iron with the release of $CO_2$.

Mossbauer effect has been used to follow the decomposition of solid solution of divalent oxalates to form $Ni_{0.6}Fe_{2.4}O_4$ spinel by Gallagher and Schrey (1969) or $Fe_{1-x}Mg_xO$ by Foerster et al (1973). The two groups agree, that substitution in solid solution by other divalent ions of comparable size does little to change the Mossbauer parameters of $FeC_2O_4.2H_2O$ and that the lines broaden somewhat upon dehydration. Brady and Duncan (1964) similarly found that iron absorbed on the surface of $CoC_2O_4.2H_2O$ did not appear chemically different from atoms in the bulk of $Fe_2C_2O_4.2H_2O$.

Gallagher and Schrey (1972) developed a synthetic technique based upon the precipitation and subsequent thermal decomposition of $BaSn(C_2O_4)_2.2.5H_2O$. This was in view to tackle the uncertainty in the stoichiometry of $BaSnO_3$ which forms a primary drawback in its use as a standard tin Mossbauer source.
Hang Nan and Moon Shik Han (1973) have studied the decomposition of oxalate in an hydrogen atmosphere. They have prepared fine particles of the 69 - 31 at % FeNi alloy, following the same method as Kachi et al (1962), but these people have used enriched iron. The oxalates are heated at 500°C for 2 hours in hydrogen atmosphere. They indicate that the central peak obtained by Mossbauer studies on this sample is from the superparamagnetic behaviour of fine particles of the alloy. They heat the oxalate to 800°C at a rate of 20°C/min and then maintain it at 800°C for 1 hour. The Mossbauer studies on this sample show that the central line in the first case is absent. They conclude that the central line is thus not due to the paramagnetic regions but is due to the superparamagnetic fine particles of FeNi alloy. The studies of Kachi et al (1962) are on the equilibrium diagram and characteristics of phase transformation of Fe-Ni alloy in fine particles through x-ray diffraction and specific heat measurements. The specimens were prepared by the reduction of the solid solution Fe$_x$Ni$_{1-x}$C$_2$O$_4$ in hydrogen at various temperatures below 800°C. The fine particles reduced at temperatures below 600°C did not undergo a martensitic transformation even when they were cooled to room temperature. The diagram determined by the reduction method is in close agreement with those obtained by annealing of bulk alloys for very long periods.
Therefore the diagram was easily determined because of the absence of martensitic transformation and because of the acceleration effects during the reduction upon the diffusion rate. The existence and superstructure Fe$_3$Ni was suggested by the specific heat measurements.

2.3 MOSSBAUER EFFECT STUDIES OF SUPERPARAMAGNETISM

Superparamagnetism is the process of collective reorientation of the magnetic moment direction in fine particles. It is commonly encountered in iron-containing clay minerals, pigments, chemical precipitation reaction products, and catalysts. A few biological systems containing large number of iron atoms in a single molecule like iron dithiocarbamate and gastroferrin are also similar to this category. Superparamagnetism arises in the following way: if a magnetic material is cooled below the magnetic ordering temperature, the spins of the magnetic ions will tend to lock together, producing magnetic ordering. In a large crystallite, once a particular spin orientation is established below the magnetic ordering temperature, it will not change except under the influence of external magnetic fields. If there are only some tens or hundreds of magnetic ions in the particle, however, thermal excitation energy may be enough to invert all of the spins simultaneously, thereby reversing the magnetisation of all the sublattices. For the normal
situation of no applied field, the overall energy of the two spin states is equal, and the mean time between spin flips is proportional to \( \exp \left( \frac{KV}{kT} \right) \), where \( K \) is the anistropy energy of the material, \( V \) is the particle volume, \( k \) is the Boltzmann constant, and \( T \) is the temperature. This formula has been extensively used to analyse superparamagnetic hf structure by Kundig et al (1966) and Afanas'ev et al (1970).

The hf field seen by the nucleus is aligned with the ion's spin moment, and when the spin is inverted by the superparamagnetic relaxation, the hf field inverts also. All spins in the particle flip simultaneously in contrast to the case of paramagnetic relaxation, where spin flips of different ions occur independently.

There are three ways in which hf structure in the Mossbauer spectra of fine particles can be useful. First, the observation of relaxation spectra below the magnetic ordering temperature may be evidence that very fine particles are involved. Second, the temperature dependence of the relaxation time may be determined from the spectra and used to determine the particle size. Third, at very low temperatures, \( \tau \) will be very long, and the spectrum will be that obtained in the static case. If the hf parameters are the same as those obtained for
the bulk material, that is good evidence that the micro-
structure of the particles is similar to that of the bulk.

A review of Mossbauer effect studies of super-
paramagnetic fine particles is given below along with a brief note on the bulk sample of each specimen.

**Metallic Iron**

Iron in bulk form (natural foil) as a standard is used to calibrate all Mossbauer spectrometers, for $^{57}$Fe Mossbauer work. Iron has an internal field of 330 kG and gives a six line hf spectrum. The earliest work done on metallic iron is by Preston et al (1962).

Petrov et al (1974) have studied magnetic properties of small spherical iron particles in the temperature range 4.2 to 300 K. Particles of size 140 to 1000 Å were suspended in paraffin. Magnetic fields upto 25 kG were applied. They have studied the dependence of the coercive force and saturation magnetisation on particle dimensions and temperature. The critical diameter of sample and the effective magnetic anisotropy constant were also determined. They found that the saturation magnetisation decreased, when the particle diameter was reduced. Their spectra have not shown any oxidation of particles. The decrease in coercive force has been
attributed to the superparamagnetic behaviour of the particles. They have discussed their result with current models.

Amulyavichus and Suzdalen (1973) have investigated the ultrafine particles of iron. Magnetic relaxation properties on particles of size of the order of 100Å have been investigated in an external field.

Iron Oxide Particles

An oxide may be considered as a close packed lattice of oxygen anions containing sufficient metal cations in the largest interstices to get electrical neutrality. Here the anion determines the basic structural type. The ability of the anion lattice to accommodate widely differing cations results not only in a wide range of different stoichiometric oxides but also in the very important property of non stoichiometry.

In iron oxides the iron cation almost invariably has either the high-spin iron (II) or high-spin iron (III) electronic configuration although a few examples of iron (IV) compounds are known. Disorder phenomena, in which two or more different cations can distribute themselves statistically on a given lattice site, are also frequently found.
Both Fe\(^{2+}\) and Fe\(^{3+}\) cations possess a large spin moment which frequently results in co-operative magnetic ordering processes. Because of this, much of the interpretation of the internal magnetic fields in iron (II) and iron (III) compounds like iron(II) halides, chlorides is also applicable to the oxides. Here the complications are that there may be more than one distinct type of cation site and that there may be effects due to order-disorder phenomena in the next nearest-neighbour co-ordination sphere of cations. Sometimes it is also found that the site occupancy in a disordered oxide is a function of the conditions of preparation and this causes sometimes confusion when comparing results from different laboratories.

Mossbauer spectrum can give a great deal of information about individual sites. Bulk magnetisation properties are averaged functions of the whole material. So, an antiferromagnetic oxide has a small magnetisation. This averaging process does not occur in the Mossbauer spectrum since each resonant atom is unique and the result is a statistical summation of all possible spectra. An antiferromagnetic oxide would therefore give a single hf 6 line spectrum because each iron atom is identical as regards the resonant process. So, because of this, the Mossbauer spectrum provides a means of studying micro-structural properties of these systems in a way which
x-ray diffraction and magnetic susceptibility measurements cannot, and it is therefore particularly valuable in the study of order-disorder and other cooperative phenomena.

The chemical isomer shift is only of limited diagnostic use because of its relative lack of sensitivity to environment in these systems. However the shift of a tetrahedrally coordinated cation is generally noticeably less than that of an octahedrally co-ordinated cation because of increased covalency in the former and this can sometimes be used to differentiate site symmetries.

Interest in the present study mainly centres around binary oxide systems. Even the hydroxides do not have a direct bearing on the work but they have superparamagnetic properties. Table 2.2 gives details of the properties of bulk iron oxides.

Haematite (α-Fe₂O₃)

Historically, α-Fe₂O₃ has attracted the attention of chemists and physicists alike for many years. The crystal structure is that of corundum (α-Al₂O₃) with a close packed oxygen ion lattice and Fe³⁺ cations in octahedral sites. Magnetically it is usually complex being antiferromagnetic at low temperature, then undergoing a transition above the so called Morin temperature
to a weak ferrimagnetic state as a result of spin canting, before finally becoming paramagnetic at high temperatures. The impurities on bulk magnetic measurements makes them difficult to interpret but Mossbauer spectroscopy gives much clearer indications of the ordering processes involved.

The first reported Mossbauer spectrum of $\alpha$-$\text{Fe}_2\text{O}_3$ was by Kistner and Snyar (1960), who recorded the chemical shift $\delta$ and electric quadrupole hyperfine interactions to be observed by this technique. With a single line source the room temperature spectrum comprises of six lines due to a hyperfine filed of 515 kG, $\delta = + 0.38 \text{ mm/sec}$ (rel to Fe) and there is a small quadrupole interaction of $+ 0.12 \text{ mm/sec}$.

Vander Woude (1966) showed that the spins directed in the [111] plane of the crystal at room temperature, rearrange below 260 K along the [111] trigonal direction. This gives rise to a change in the sign of

$$E = \left\{ \frac{1}{2} \left( \frac{e^2q}{h} - \frac{3}{2} \right) (1 - 3 \cos^2\theta) \right\} = -0.22 \text{ mm/sec}$$

at low temperatures. Ono and Ito (1962) have studied the $E$ sign change between 200 to 280 K - it reaches to zero at 260 K - which is called the Morin temperature. The definitive work by Vander Woude (1966) on powdered $\alpha$-$\text{Fe}_2\text{O}_3$ gives the temperature dependence of Mossbauer parameters very accurately. Neel temperature was
determined to be equal to 956 K. The value of $H_{\text{eff}}(T=0)$ is equal to 544 kG. The magnetic field data approximately follow that for an $S = 5/2$ Brillouin function. Blum et al (1965) showed that spin-flip process can also be induced by an externally applied field.

Ultrafine particles of $\alpha -$Fe$_2$O$_3$ exhibit superparamagnetism due to a decreasing relaxation time with decreasing particle size. Nakamura et al (1964) have studied $\alpha -$Fe$_2$O$_3$ ultrafine particles of size 50Å. At 300°C they obtain only quadrupole doublet and at 120°C a hf spectrum was obtained.

Kundig et al (1966) have studied fine particles of $\alpha -$Fe$_2$O$_3$ as a function of average particle size ranging from <10 nm to bulk oxide. This work has given a detailed description of the phenomenon. Fig. 2.9(a and b) give the Mossbauer spectra of $\alpha -$Fe$_2$O$_3$ (1) as a function of average particle size (2) as a function of temperature for 135Å size particles. For small particles with diameter less than 100Å, asymmetric quadrupole spectra were observed. As the particle size increased, the hf spectra gradually developed at the cost of central quadrupole doublet, and finally for samples with size greater than 150Å, a well resolved Zeeman-split spectra were observed. These authors also investigated the temperature dependence of the Mossbauer spectra for various particle
size clusters. It is seen at low temperatures, one observes a well-defined Zeeman spectrum where as, as the temperature is increased, the Zeeman-split spectrum decreases in the hf field, but with an increase in the intensity of central quadrupole doublet. Finally at higher temperatures, the hf splitting is hardly detectable.

Single-domain ferro or antiferromagnetic particles are normally spontaneously magnetized in one of the easy directions. If $K$ is the crystalline anisotropy and $V$ is the volume of the particle, then the energy required to change the direction of magnetization from one easy direction to another is $KV$. At any finite temperature, a magnetization vector undergoes a kind of Brownian motion around the easy direction. The relaxation time for such random changes in the direction of magnetization from one easy direction to another is given by

$$\tau = (af)^{-1} \exp \left(\frac{KV}{kT}\right)$$

where $a$ is the geometrical factor, $f$ is the Larmor frequency of the magnetization vector $M$ in an effective field, $H_{\text{eff}} = KV/M$. Applying relaxation theory, the Mossbauer spectra for various relaxation times can be understood as follows: (1) if $Z_{\text{obs}} \lesssim \tau$, the particle will show ferromagnetic or antiferromagnetic behaviour (2) if $Z_{\text{obs}} \geq \tau$, the particle will appear to be superparamagnetic and the Zeeman splitting will disappear.
Krauth et al (1967) have found in the Mössbauer spectrum the superimposition of the spectra for 70Å particles of $\alpha$-Fe$_2$O$_3$ with $\gamma$-Fe$_2$O$_3$ during the thermal breakdown of FeC$_2$O$_4$.2H$_2$O. Suzdalev (1967) has studied in ultramicrosized $\alpha$-Fe$_2$O$_3$ the existence of a critical volume, depending linearly on $T$, below which the material is magnetically disordered and above it, it is magnetically ordered. Vander Kraan (1971) also has found SPM in small $\alpha$-Fe$_2$O$_3$ crystallites through Mössbauer effect.

$\alpha$-Fe$_2$O$_3$ microcrystals supported on (with H$_2$S and H$_2$O) were treated with H$_2$O, methanol and ammonia and $E$ dependence on chemical environment was studied by Gager et al (1972 and 1974). Vander Kraan (1973) studied the surface ions of ultrafine $\alpha$-Fe$_2$O$_3$ particles. Krupyanskii and Suzdalev (1975) have studied ultrafine oxide between 10 - 1000 Å and oxide particles supported on silica gel.

**Mag Haematite ($\gamma$-Fe$_2$O$_3$)**

This has a AB$_2$O$_4$ structure in which the A-cations have regular tetrahedral co-ordination by oxygen and the B-cations are octahedrally co-ordinated by oxygen. There are insufficient Fe$^{3+}$ cations to fill all the A and B sites so that the stoichiometry corresponds to Fe$_{8/3}$ $\sqsubset$ $1/3^0$ where $\sqsubset$ represents a cation vacancy. Antiparallel alignment
of the A and B sublattices makes \( \gamma-\text{Fe}_2\text{O}_3 \) ferrimagnetic. The Mössbauer spectrum shows apparently only one hyperfine pattern below the Neel temperature as if the A and B site cations are indistinguishable (Bauminger et al, 1961 and Kelly et al, 1961). This is not untypical of iron (III) oxides because the \( 6S \) state \( \text{Fe}^{3+} \) ion is not sensitive to environment. However, it is possible to separate the two sublattice contributions slightly by application of an external field (Armstrong et al, 1966). In this way it was shown that the A and B site fields align parallel and antiparallel to the applied field respectively so that the two resultant fields are now dissimilar and have internal fields of 488 and 499 kG at room temperature. The field values given by Khalaffalla and Morrish (1972) are 502 & 503 kG for A and B sites at 300°K.

Constabaris et al (1965) have studied very finely divided \( \gamma-\text{Fe}_2\text{O}_3 \) on different supports. In all cases, they get quadrupole-split spectra showing no effect of supports. Krauth et al (1967) indicates that during the thermal breakdown of \( \text{FeC}_2\text{O}_4\cdot2\text{H}_2\text{O} \), \( \gamma-\text{Fe}_2\text{O}_3 \) is formed till the particle size is 70A°. Above 100A° all the particles formed are \( \alpha-\text{Fe}_2\text{O}_3 \), a stable form. Coey (1971) and Coey and Khalaffalla (1972) have studied 60A° particles of \( \gamma-\text{Fe}_2\text{O}_3 \) and find non-collinear spin-arrangement. Coey et al (1972) have studied 65A°, \( \gamma-\text{Fe}_2\text{O}_3 \)
at 5°K with 50 kG field and studied A and B sites showing a cation distribution of 1:1.71 ± 0.05 for them and a non-collinear spin arrangement. Clark and Morrish (1973) studied relative magnetisation of γ-Fe₂O₃ at 4.2°K with 50 - 90 kG field.

Magnetite (Fe₃O₄)

Magnetite is a spinel ferrite which can be written as Fe³⁺[Fe²⁺Fe³⁺]O₄. Unlike γ-Fe₂O₃, it has no cation vacancies on the octahedral sites, but these sites contain equal numbers of Fe²⁺ and Fe³⁺ ions. A transition in many of the physical properties takes place between 110 and 120°K and Verwey postulated a fast electron-transfer process called, electron hopping, between the Fe²⁺ and Fe³⁺ ions on the octahedral B sites above this temperature. The low temperature form has discrete valence states and orthorhombic symmetry. Bauminger et al (1961), Ito et al (1963) and Banerjee et al (1967) have confirmed that this hopping process takes place, although the exact interpretations of the spectra differ considerably. At 77K where the Fe²⁺ and Fe³⁺ states are discrete, two partially resolved hyperfine patterns with field of 503 and 480 kG are obtained. The 503 kG field corresponds to the Fe³⁺ ions on A and B sites and 480 kG field is due to the B site Fe²⁺ ions. At 300K, above the transition temperature, there are fields of
491 and 543 kG corresponding to the A site Fe$^{3+}$ ions and to the B site (Fe$^{2+}$ + Fe$^{3+}$) cations respectively. The fast electron hopping process produces a completely averaged spectrum from these latter ions which does not show a quadrupole effect.

The temperature dependence of the A and B sites magnetic fields have been recorded from 300 to 800 K and show good agreement with the sublattice curves from neutron diffraction data (Van der Woude et al, 1969). An application of external field of 12 kG gives a better resolution of the two patterns at room temperature and establishes that the tetrahedral A-site spins align antiparallel and the B-site spins align parallel to the applied field (Kundig and Hargrove, 1969). Single crystal of Fe$_3$O$_4$ have been studied around the Verwey transition with external fields and low temperature by Hargrove and Kundig, (1970) and Romanov et al (1969). Debye temperature estimates are done for A and B sites by Sawatzky et al (1969). The results were $\Theta_A = (334 \pm 10)K$ and $\Theta_B = (314 \pm 10)K$ with ratio of the recoil free fraction at room temperature $f_B/f_A = 0.04$.

Ahroni and Morton (1971) have studied the superparamagnetism and exchange anisotropy in microparticles of magnetite embedded in an inert carbonaceous matrix. Particle sizes of 35Å were studied at liquid
N\textsubscript{2} and liquid He temperatures, (Fig. 2-10). They have discussed electron hopping within Fe\textsubscript{3}O\textsubscript{4}. Roggwiller and Kundig (1973) studied the SPM-Fe\textsubscript{3}O\textsubscript{4}. They find that hf field disappears with increasing T in zero applied field. With the application of external field, hyperfine splitting redevelops. The particles of 100Å diameter were used. Size effects in small particles of Fe\textsubscript{3}O\textsubscript{4} were investigated by Krupyanskii and Suzdalev, (1974). By means of Mossbauer measurements on Fe\textsubscript{3}O\textsubscript{4} particles with decrease in specimen dimension upto 200Å was studied. For T = 300 K and H = 0, 200Å is the dimension of the particles at which the transition occurs.

**Superparamagnetic Alloy (FeNi)**

The transition-metal alloys present several new features. Many of them have a spin moment on both the iron and solute atoms, and the simple non-magnetic impurity hole model as applied to aluminium will no longer be necessarily valid. The magnetic moment on the solute atom will affect the spin density at the iron nuclei and hence may also change the magnetic moment on the iron. The saturation magnetic moment is an average over the two components. It is dependent on the total electron concentration in the alloy, and is approximately related to the saturation magnetic field at the iron.
However, this hyperfine field is generally intermediate between that predicted from the local moment on the iron atom and that from the saturation moment, although it is difficult to decide whether the anomaly is due to changes in core polarisation or in conduction polarisation. The variation in the hyperfine field with electron concentration is shown in Fig. 2-11. The values plotted often represent an average field because of fluctuations in the nearest-neighbour environment.

The body-centred cubic alloys of nickel (0 - 24 at % Ni) show a slight rise in the hyperfine field with increasing nickel content. Several investigations of $\gamma$-FeNi 'Invar' type alloys (20 - 34 at % Ni) have reported the coexistence of paramagnetic and ferromagnetic contributions in the spectra (Asano, 1968 and 1969, Nakamura et al, 1968 and 1964, Tino and Maeda, 1968 and Dekhtias et al, 1967). A considerable difference is found between ordered and disordered alloys containing 50 at % Ni (Gros and Pebay-Peyroula, 1964). The ordered alloy shows much narrower resonance lines because of the more uniform site environments.

An investigation by Afanas'ev et al (1970) of particles of ferromagnetic alloy FeNi (37% Ni) with a FCC lattice by Mossbauer spectroscopy revealed a pronounced anomaly in the hf structure of 190 and 120 Å particle
spectra. Hang Nan Ok and Moon Shik Han (1973) used the Mossbauer effect to study the superparamagnetic behaviour of fine particles of 69 - 31 at % FeNi alloy. FeNi alloy were prepared by heating the oxalate in a H₂ atmosphere at 500°C for 2 hours following the method reported by Kachi et al (1962). The Mossbauer spectra of the alloy consists of a central single and a six-line magnetic hyperfine pattern for fine particles. The single line disappears for large particles, indicating that it is due to the superparamagnetic FeNi particles and not due to paramagnetic FeNi.

Intermetallic Compound (Fe₃C)

There are several elements which do not readily form alloy phases with iron, but which give one or more compounds which are metallic in character, and have a closely defined composition corresponding to a simple stoichiometric formula. Such intermetallic compounds are important in enabling the magnetic environment of metallic iron to be modified without introducing the statistical complications of alloys. They also give some insight into the way in which chemical bonding modifies the magnetic properties of the sublattices.

Cementite, Fe₃C, is an interstitial solid solution of carbon in iron which is frequently found in steels
and cast iron containing carbon. It is ferromagnetic below $T_c$ nearly equal to 210°C, the magnetic field being 208 kG at room temperature; the chemical isomer shift is $+0.19\text{mm/s}\text{sec}$ above that of $\alpha$-Fe (Shinjo et al 1964 and Ron et al, 1966). This corresponds to a 3d-band population of iron of $3d \sim 8$. The presence of a precipitate of Fe$_3$C in cast iron is readily detected by Mossbauer spectroscopy. The separate cementite obtained by dissolving the steel in hydrochloric acid shows a central paramagnetic doublet in addition to the six-line magnetic spectrum, and it has proved possible to prepare from carbon steel a paramagnetic form of Fe$_3$C which appears from x-ray measurements to have a slightly modified structure in the lattice (Ron et al 1966).

Caer et al (1971) have reported Mossbauer spectra of well identified $\varepsilon$-carbide. They show the SPM of small particles of $\varepsilon$-carbide allowing its detection where x-ray diffraction method is useless. The hf fields are coarsened by adding Si and are very close to the fields observed in Fe$_5$C$_2$ showing that they mainly depend upon the number of carbon nearest neighbours of Fe-C distance.

The Mossbauer effect is particularly suitable for microcrystal studies because it directly samples the microscopic surroundings of the emitting or absorbing
nucleus. This is in contrast to the other techniques which are dependent on gross effects, such as x-ray scattering, with its broadening in microcrystals, or sensitivity measurements, which are hampered by the many interfaces in microcrystal samples. Using Mössbauer spectra a particle size distribution can be derived in SPM specimen. A typical particle-size distribution is shown in Fig. 2-12.

Each microcrystal of a ferro or antiferromagnetic material constitutes a single domain, in which the hf field fluctuates randomly with a characteristic relaxation time $\tau = \tau_0 \exp \left\{ - \frac{KV}{kT} \right\}$ where $1/\tau_0$ is the relaxation frequency in the absence of anisotropy. $K$ is the anisotropy constant, $V$ is the volume of the microcrystal and $kT$ is the thermal energy. $KV$ is the energy barrier which the magnetisation must overcome in going from one easy direction to another. If $kT \ll KV$ then there is magnetic hf spectrum and if $kT \gg KV$ the hf spectrum collapses to one line and for $kT \approx KV$ partially relaxed magnetic hyperfine spectrum is obtained. The relaxation temperature yields the value of the anisotropy energy density $K$. From the particular temperature dependence of the ratio of the single line to hf structure in the spectra one can extract the particle size distribution as in Fig. 2-12 and from the spectrum shape one can get information about the relaxation time involved (Lindquist et al 1968).
Proposed scheme of decomposition of iron-III oxalate

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temp</th>
<th>Products</th>
<th>% Wt loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Fe}_2(\text{C}_2\text{O}_4)_3 \cdot 6\text{H}_2\text{O}$</td>
<td>50-125</td>
<td>$\text{Fe}_2(\text{C}_2\text{O}_4)_3 \cdot 3\text{H}_2\text{O}$</td>
<td>3H$_2$O</td>
</tr>
<tr>
<td></td>
<td>125-170</td>
<td>$\text{Fe}_2(\text{C}_2\text{O}_4)_3$</td>
<td>3H$_2$O</td>
</tr>
<tr>
<td></td>
<td>150-350</td>
<td>2FeC$_2$O$_4$</td>
<td>2CO$_2$ [57.2]</td>
</tr>
<tr>
<td></td>
<td>225-350</td>
<td>Fe$_2$O$_3$</td>
<td>2C$_2$O, 2CO</td>
</tr>
</tbody>
</table>

* A part of the Table I of Gallagher (1965).
### Table 2.2

**Mossbauer parameters of iron and iron oxides**

<table>
<thead>
<tr>
<th>Compound</th>
<th>T/K</th>
<th>$\Delta E$ mm/sec</th>
<th>H/kG</th>
<th>$\delta$ mm/sec w.r.t Fe</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>296</td>
<td>-</td>
<td>330</td>
<td>-</td>
<td>Preston et al (1962)</td>
</tr>
<tr>
<td>Fe$_{0.93}$O</td>
<td>297</td>
<td>0.46</td>
<td>0</td>
<td>0.91</td>
<td>Johnson (1969)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.78</td>
<td>0</td>
<td>0.86</td>
<td></td>
</tr>
<tr>
<td>$\chi$-Fe$_2$O$_3$</td>
<td>298</td>
<td>0.12</td>
<td>515</td>
<td>0.38</td>
<td>Kister &amp; Sunyar (1960)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(0)</td>
<td>515 (544)</td>
<td>Gastebois &amp; Quidort (1966)</td>
</tr>
<tr>
<td>$\gamma$-Fe$_2$O$_3$</td>
<td>RT</td>
<td>-</td>
<td>488</td>
<td>0.27</td>
<td>Armstrong et al (1966)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>499</td>
<td>0.41</td>
<td></td>
</tr>
<tr>
<td>Fe$_3$O$_4$</td>
<td>300</td>
<td>-</td>
<td>491</td>
<td>A site</td>
<td>Banerjee et al (1967)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>453</td>
<td>B site</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-0.05</td>
<td>511</td>
<td>0.37</td>
<td></td>
<td>Hargrove</td>
</tr>
<tr>
<td></td>
<td>0.50</td>
<td>533</td>
<td>0.77</td>
<td></td>
<td>and</td>
</tr>
<tr>
<td></td>
<td>82</td>
<td>516</td>
<td>0.59</td>
<td></td>
<td>Kundig</td>
</tr>
<tr>
<td></td>
<td>0.95</td>
<td>473</td>
<td>0.77</td>
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<tr>
<td></td>
<td>-2.62</td>
<td>374</td>
<td>1.20</td>
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</tr>
</tbody>
</table>
FERROUS OXALATE VS $^{57}\text{Co}(\text{Pd})$

- COMPUTER FIT DATA
- EXPERIMENTAL DATA

**Fig. 2-2. QUADRUPOLE SPLITTING IN $^{57}\text{Fe}$**
Fig. 2-5. Typical $\alpha$-t plot in the thermal decomposition of a solid.
Fig.2-6. GENERAL TYPES OF $\alpha$-t CURVES OBTAINED IN THE ISOTHERMAL DECOMPOSITION OF SOLIDS.
Fig. 2-7. $\Delta G$ as a function of $m$. 
Fig. 2-8. MOSSBAUER SPECTRA MEASURED AT ROOM TEMPERATURE RELATIVE TO $^{57}$Co(Cu)$_2$ of Sr$_3$[Fe(C$_2$O$_4$)$_3$]$_2$ 2H$_2$O
(CALCINED IN AIR)
MOSSBAUER SPECTRA OF $\alpha$-Fe$_2$O$_3$ a) as a function of average particle size b) as a function of temperature with average particle size of 13.5±1 nm
Fig. 2-10. MÖSSBAUER SPECTRA OF Fe₃O₄ AT THREE DIFFERENT TEMPERATURES
Fig. 2-11. VARIATION IN THE HYPERFINE FIELD WITH ELECTRON CONCENTRATION.
Fig. 2-12. A TYPICAL PARTICLE SIZE DISTRIBUTION