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THE CHEMICAL EFFECTS OF
NUCLEAR TRANSFORMATIONS IN SOLIDS

ACKNOWLEDGEMENTS

I am deeply indebted to Dr. H.S. Mathur for suggesting the problem and for guidance during the course of the work.

I wish to gratefully acknowledge the cooperation of my colleagues, especially of Mr. H.P. Gupta and Dr. C.M. Jagannathan for their help during my Ph.D. studies. I would like to thank Mr. H.S. Mathur for his help in the preparation of the manuscript.

A THESIS

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for

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IN CHEMISTRY



by

R. JAGANNATHAN, M.Sc.

National Chemical Laboratory,
Poona-8, India.

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ACKNOWLEDGEMENTS

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Poona
July, 1968.

R. Jagannathan.

(R. JAGANNATHAN)

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STATEMENT OF THE PROBLEM

During the last two decades, a considerable amount of work has been done on the chemical effects of nuclear transformations in solids. Two of the characteristic features of these ^{irradiated} solids are : (1) the similar annealing kinetics in spite of the wide differences in the nature of these solids¹ and (2) a high degree of stereospecificity observed in the annealing reactions.² A number of models³⁻⁷ have been put forward to explain the post-irradiation annealing behaviour of the solids. Any model, suggested to explain the chemical effects of nuclear transformations in solids should be able to account for the observation of a high degree of stereospecificity in the concurrent and post-irradiation annealing reactions. The retention of configuration during the neutron irradiation and subsequent thermal annealing was found by Zuber *et al.*² in dextro - tris ethylenediamine-cobalt(III) nitrate and cis - and trans - dichloro-bis-ethylenediamine-cobalt(III) nitrate and by Maddock *et al.*⁸ in a number of neutron irradiated geometrical isomers of nitroamines cobalt complexes. However, a significant percentage activity in the forms isomeric to the parent was found by Saito *et al.*⁹ in cis- and trans- $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2](\text{NO}_3)$ and by Maddock *et al.*⁸ in cis- $[\text{Co}(\text{NO}_2)_2(\text{NH}_3)_4]$ trans- $[\text{Co}(\text{NO}_2)_4(\text{NH}_3)_2]$. All the earlier studies of the retention of configuration have so far been carried out only on stereoisomers of cobalt complexes.

In view of the conflicting results mentioned above it is desirable to find out whether the retention of the configuration is limited to a few cobalt complexes or can also be observed in the similar complexes of other metal ions. Part I of this thesis deals with a study of the degree of stereospecificity in the neutron irradiated cis- and trans-dichlorobis-ethylenediamine chromium chloride.

The analyses of the recoil species produced in the neutron irradiated solids have invariably been done by aqueous chemistry. The nature of the recoil species in the solid state need not necessarily be the same as found in the solution of the irradiated solid. Some of the metastable species which exist in the solid state may be unstable in solution and hence would be converted into stable forms by oxidation, reduction and hydration reactions.¹⁰ Consequently, different analytical techniques may not give the same results.^{11,12} The recently discovered technique of Mossbauer Spectroscopy^{13,14} can be utilized to throw light on the nature of the recoil nucleus and its environment in the solid state. In suitable cases, it is possible by means of the Mossbauer effect to detect different valency states of an element and also to observe the changes in its surroundings.¹⁵⁻¹⁷ Part II of this thesis deals with a study of the chemical states of ^{57}Fe formed due to the Auger effect following the electron capture decay of Co^{57} in some cobalt compounds of varying degree of covalency viz. KCoF_3 , CoCr_2O_4 , CoCr_2S_4 and $\text{Co}(1-10 \text{ phenanthroline})_3(\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}$.

PART - I : THE CHEMICAL EFFECTS OF NEUTRON CAPTURE
IN CIS- AND TRANS- $\text{Cr(en)}_2\text{Cl}_2$ Cl

CHAPTER - 1 : INTRODUCTION

INTRODUCTION

Several review articles,^{4,7,13,19} concerning the studies on the chemical effects of nuclear transformations in solids, have appeared during the last few years. The work done in this field has also been discussed at the two international conferences, the proceedings of which have already been published.^{20,21} No attempt has therefore been made by us to discuss in detail the earlier work on the chemical effects of nuclear transformations in solids. However, in order to facilitate a meaningful discussion of the results presented in this thesis, a brief review of the present state of our knowledge has been presented.

The chemical effects of nuclear transformations were first discovered by Szilard and Chalmers.²² They found that the neutron irradiation of liquid ethyl iodide brought about the rupture of the carbon-iodine bond. Fermi *et al.*²³ pointed out that the breaking of the C-I bond was due to the large recoil-energy imparted to the nucleus as a result of the (n,γ) reaction. In neutron capture reactions involving nuclei with masses ranging from 20 to 200 atomic mass units, the maximum energy the emitted gamma-ray can have, is approximately 6 to 8 Mev and hence, the recoil energy E_R would be of the order of 10^2 to 10^3 e.v. In nuclear reactions, followed by particle emission like (γ, n) , $(n, 2n)$ and (n, p) reactions,

E_R would be in the range of 10^5 e.v. These values of E_R far exceed the bonding energies (1-5 e.v.) in the chemical compounds and would invariably bring about the dissociation of the recoil-atom from the parent molecule. It has been found that a certain percentage of the radioactive atoms appear in the parent form, in spite of the fact that the recoil energies are much greater than the bond-energies. The percentage activity occurring in the parent form was defined by Libby³ as 'retention' (R). He suggested that it arose due to the secondary re-entry processes of the radioactive atoms. Williams et al.²⁴ first reported that the increase in the time of neutron irradiation of SbF_5 and NH_4SbF_6 also resulted in an increase in the retention. Soon after this observation Maddock et al.²⁵ found that an increase in the retention of neutron irradiated K_2CrO_4 could be brought about by heating the irradiated material. They called this behaviour thermal annealing of the radiation damage. Similar observations were made by Rieder et al.²⁶ in the case of $KMnO_4$. Cobble and Boyd²⁷ were the first investigators to make a detailed study of the post-irradiation thermal annealing in the course of their studies on potassium bromate. They also made the significant observation that the ionizing radiation like the gamma rays can also bring about annealing, in a manner similar to that of thermal annealing. Thermal and radiation annealing have since been observed in a number of systems. These developments triggered a renewed interest

in the studies on the chemical effects of nuclear transformations in solids, in several laboratories in the world. Mention may be made of some of the more active research groups, namely, Maddock et al at Cambridge, U.K., Shankar and coworkers at Bombay, Saito et al in Japan, Dodson and Harbottle at Brookhaven National Laboratory, U.S.A., and Heine and Herr in Germany. The numerous investigations made by a number of workers brought to light that the chemical effects of nuclear transformations in 'solids' exhibit certain features common to all systems viz.

- 1) Post-irradiation annealing can be induced thermally, photochemically or by ionizing radiations.
- 2) Most of the annealing reactions follow the same kinetic pattern in spite of the wide differences in the nature of these solids.
- 3) A high degree of stereo-specificity has been found in the concurrent and post-irradiation annealing studies of the irradiated stereoisomers.
- 4) The pre-irradiation treatment of the solids have a pronounced effect on the nature of the annealing reactions.

Any model put forward to explain the chemical effects of nuclear transformations in solids should be able to account for the above mentioned behaviour of the irradiated solids. Several models have indeed been suggested to explain the

chemical effects of nuclear transformations in solids. A brief and critical review of these models is given below:

The Fragmentation-recombination Model:

Libby³ proposed that the central atoms of the complex ions lose some of their ligands during the (n,γ) reaction. The removal of the ligand-ions from the complex-ions of the metal can lead to different metastable species. For example, in the neutron-irradiation of KMnO_4 , fragments such as $^*\text{MnO}_3^+$, $^*\text{MnO}_2^{3+}$, $^*\text{MnO}^{5+}$ and $^*\text{Mn}^{7+}$ are likely to be produced. The retention is then determined by the extent to which, the hydration or reduction of these fragments takes place. Hydration would lead to an increase in the retention, while reduction would have the opposite effect on the value of retention as shown below:



Maddock and coworkers²³ made use of Libby's hypothesis to explain the thermal-annealing behaviour of the neutron irradiated chromates. According to them, the irradiation of solid K_2CrO_4 produces metastable species such as $^*\text{CrO}_3$, $^*\text{CrO}_2^{2+}$, $^*\text{CrO}^{4+}$ and $^*\text{Cr}^{6+}$. On dissolving the irradiated crystals in water, the first two fragments hydrolyse to the chromate and lead to retention. The latter

two species get reduced (before hydrolysis can take place) and would give rise to the separable Cr^{3+} activity.

However, on the basis of the above mechanism Maddock *et al.*^{29,30} could not explain the results of the post-irradiation annealing behaviour of the irradiated potassium chromate. They, therefore, explained their results on the basis of a recombination process analogous to the growth of thin oxide film over metal substrate. Based on Mott's³¹ treatment of the growth of thin oxide films they derived an expression for the rate of increase of retention as a function of temperature, viz.

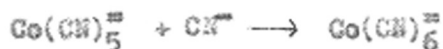
$$\frac{dR}{dt} = \exp (- u/kT) \exp (V/kTx) \quad (1)$$

where x is the separating distance of the fragments at time 't', T , the absolute temperature, k the Boltzman constant, V an electrostatic potential and u , the activation energy barrier opposing recombination. It was suggested that the annealing takes place through a primary reaction, such as



where the oxide ion is mobile. The product CrO_2^{2-} is hydrolysed to chromate on dissolution. It may be pointed out here, that according to this mechanism, the species CrO_4^{4-} which was originally assumed to be reduced to the trivalent chromium (page 6 in this thesis), now leads to an increase in the

retention. Maddock and deMaine also explained the results of Cobble and Boyd,²⁷ on irradiated bromate by means of this mechanism. The same model was used in explaining the results of (n, γ) reaction in a number of non-oxygenion systems e.g. ferrocene³² hexamine cobalt chloride,³³ potassium chlororhenite,³⁴ hexahalo complexes of Iridium and Osmium,¹² etc. Rauscher *et al.*³⁵ attributed thermal annealing to a recombination reaction of the type



and identified the different hydration and reduction steps leading to the retention.

Maddock and coworkers^{26,29} have in their detailed studies on the chemical effects of neutron irradiation of potassium chromate established the role of inherent crystal defects³⁶ and pretreatment of the target material on the post-irradiation thermal annealing. They showed that crushing, irradiation with ionizing radiations, doping with aliovalent cations or sudden quenching prior to neutron irradiation increased the susceptibility to thermal anneal. On the contrary, prior heat treatment brought about the opposite behaviour viz. little tendency to thermal anneal. Maddock *et al.*³⁶ therefore suggested that annealing required the participation of some defects such as a vacancy and that the defects diffuse preferentially towards the fragments close to them, and the interaction between them leads to an increase in the retention. The rapid annealing step corresponds to the annealing centers

situated near the defect; the extent of annealing increases with temperature and the process is of the first-order.

It may be pointed out that this model was put forward to explain the recoil effects in ionic compounds and the extension of this model to complex systems of metal chelates is difficult to visualise.

Interstitial-vacancy recombination model:

Based on the original work of Brown *et al.*³⁷ for simple monoatomic crystals, Harbottle and Sutin⁴ gave a more general description of the recombination model. They suggested that the annealing involved the recombination of an interstitial recoil-atom with a vacancy, controlled by a diffusion process. A vacancy in the complex crystal was defined as "a trap consisting of a fragment or any species capable of chemical combination with the interstitial atom". In the oxyanion systems like potassium chromate the recoil ^{51}Cr atom may come to rest at an interstitial position and the correlated vacancy would be the cluster of unbonded oxygen atoms or oxygen ions. The rate of recombination on this model is then given by

$$\ln(R_{\infty} - R_t) = \ln(R_{\infty} - R_0) - v_j t \quad (2)$$

where R_0 , R_t and R_{∞} represent initial retention, retention at time 't' and retention at infinite time of anneal, v_j , the jump-frequency of the vacancy or the interstitial. The quantity $R_{\infty} - R_t / R_{\infty} - R_0$ is the fraction of interstitial-vacancy pairs

still uncombined at time 't'. This expression gives rise to a change in retention as a function of the time of annealing similar to those observed experimentally. If the interstitial-vacancy pairs are spatially correlated it results in a unimolecular recombination reaction. An interstitial which does not bear such a correlation would give rise to a bimolecular recombination reaction. It may however be noted that a necessary condition of equation (1) is that the extrapolated resolved linear components of the annealing curves should give the same values of the intercepts at $t = 0$.³⁸

A similar model was also used earlier by Zuber³⁹ to explain his results on the neutron-irradiated dextro - tris - ethylenediamine cobalt(III) nitrate. In spite of the great complexity of the molecule and the high recoil energy expected for the (n, γ) reaction, the percentage activity in the present isomeric form was found to increase from 4.6 % to 69.2 % on post-irradiation isothermal annealing at 60°C. It was suggested that after the ejection of the cobalt atom due to recoil, the ligands in tris-ethylenediamine-Co(III) nitrate were preserved in their original position with a cavity in the place of the cobalt atom in the original molecule. The recoil-atoms which came to rest just outside the skeleton of the original molecule diffused on thermal treatment, back to the original molecule due to coulombic attraction giving rise to retention. As the distance of separation became greater, it became less likely for the recoil-atom to return to the original site. Its fate was then determined by a random

diffusion process. The fast and the slow components of an annealing curve were supposed to correspond to the quick re-entry of the recoil-atom which is in the proximity of the cavity and the slow diffusion process of the recoil-atom to the neighbourhood of the cavity-complex respectively.

Heine and Herr¹² explained their results on the neutron-irradiated hexahalo complexes of Iridium and Osmium using the above model. Apers and Capron⁴⁰ explained the isotopic effect in zinc phthalocyanine by means of vacancy-interstitial recombination model.

It may be mentioned here, that it is difficult to imagine how the ligand-skeleton would escape destruction concomitant to the recoil of the central metal atom, form a 'vacancy' and then subsequently recombine with the interstitial recoil-atom on thermal treatment to give back the reconstituted parent molecule. The definition of the 'vacancy' and the 'interstitial' presented for simple ionic crystals of oxysalts loses its significance, when applied to complex organometallic systems where the central metal atoms are very well shielded by the ligand molecules.

Hot zone model:

Harbottle and Sutin^{4,5} made use of the displacement spike concept, originally suggested by Seitz and Kohler⁴¹ for explaining radiation damage in monatomic solids and put forward the hot zone model to explain the chemical effects of nuclear

transformations in solids, the main features of which are given below:

According to the hot zone model the recoil-energy is dissipated in displacing atoms from their normal sites in the crystal lattice (displacement-spike) and through heating a small volume of the crystal (thermal-spikes). The 'thermal spike' comprising about a thousand atoms remains above the melting temperature of the crystal for about 10^{-11} sec. during which the chemical reactions such as free-radical reactions, charge transfer, ion molecule reactions and exchange reactions have reasonable chances of taking place. Due to the rapid fall of the temperature of the hot zone, the reactions which cannot be completed are quenched due to sudden cooling of the hot zone. Subsequent heating of the irradiated solids allows some of the quenched reactions to go to completion, giving rise to the experimentally observed annealing behaviour of the irradiated solids. This model has been used in explaining the results of a number of studies⁴²⁻⁴⁶ on the chemical effects of nuclear transformations in solids.

The increase in retention during irradiation and subsequent heating has been explained on this model as due to the chemical reactions in the 'hot zone'. Some of these reactions can also be expected to lead to a decrease in retention. However, no unambiguous example of a decrease in the retention due to annealing has been reported so far. This model cannot also explain the observed retention of configuration in some irradiated cobalt chelates. It should be borne

in mind that 'the displacement-spike concept' of Seitz and Kohler, originally used for the monoatomic solids, when applied to complex systems like those of the metal-chelates would lead to energy dissipation over a much larger volume. Hence the concept of 'hot zone' would lose its significance in such cases.

Recrystallisation of the recoil-site:

In order to explain the high degree of stereospecificity in the concurrent and post-irradiation annealing reactions of cobalt complexes, Zuber *et al.*⁹ compared the annealing behaviour to the recrystallisation process. According to them, the undisturbed crystalline phase around the recoil-site acts as a template from which, on heating, the recrystallisation starts leading to the reformation of the original complex in its former stereoisomeric form. This may be regarded as a transition from the disordered state to the ordered state. Aten *et al.*⁴⁷ had also suggested earlier that thermal annealing may involve, in addition to chemical recombination processes, a physical reconstitution of the disturbed parts of the crystal analogous to the recrystallisation process.

Processes distributed in activation energy (Vand-Primak's model)

Based on the suggestion of Vand⁴⁸ that the kinetics of annealing of metal films could be interpreted in terms of recombination of defects distributed in activation energy, Primak⁴⁹ gave a mathematical analysis on which the annealing kinetics can be treated viz.

$$p_0(E_0) = - \frac{1}{k(T)} \frac{dp}{d(\ln t)} \quad (3)$$

and

$$E_0 = kT \ln (Bt) \quad (4)$$

where p is fraction annealed at time t , T the absolute temperature, E_0 the activation energy, k , the Boltzmann constant and B is an arbitrarily chosen constant in frequency units. The property p_0 may then be taken to signify the initial distribution of the measured property, retention in the present case. By plotting p_0 against E_0 , one could get an idea of the distribution of the activation energy.

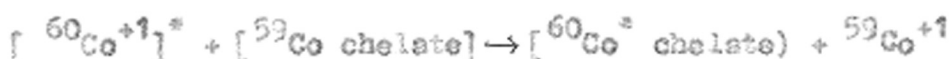
Herbottle and Sutin⁴ made use of this principle and analysed the results of DeMaine, Maddock and Taughbol³¹ on neutron irradiated potassium chromate. Shankar and Lal⁵⁰ used this concept to explain their results on neutron irradiated Co(III)-acetylacetonate diluted with aluminium and rhodium acetylacetonates. Costes⁵¹ made use of this model to analyse his data on hexamine cobalt nitrate.

Holmes⁵² originally employed the concepts of Vand and Prins for radiation damage in monostomic systems, and took into account the possible exaggeration of experimental error in taking the derivatives from experimental curves.⁵³ In the Szilard Chalmers studies, where the values are less accurate this method is not frequently used.

Variable depth electron trapping-isotopic exchange model:

It has been suggested from time to time that the electrons participate in the annealing of the metastable species to give rise to retention and that the isotopic exchange in the solid between the parent compound may partly be responsible for the observed thermal annealing of the irradiated solids.⁵⁴⁻⁶⁰ Amar Nath et al.⁶ have recently put forward a model which they call as "the variable depth electron trap isotopic exchange model" to explain the annealing behaviour of the irradiated solids. The salient features of this model are: electron traps of variable depths (energy) are formed in the irradiated solids as a result of the inherent crystal imperfections and impurities in the solids, as well as due to the concurrent gamma radiation and fast neutron flux in the nuclear reactor. Such traps can also be formed and populated by the electrons in the recoil-track as a result of fragmentation and the Auger-electrons emitted due to the internal conversion of the gamma-rays from the longer lived low energy nuclear excited states of the recoil-atom. These populated traps can act as donors during subsequent thermal annealing of the irradiated solids. The kinetics of thermal or radiation annealing of the irradiated solids is essentially controlled by the rate of release of electrons from these traps. The annealing provides the necessary energy for the release of the electrons from the populated traps. The released electrons are captured by the metastable recoil species (which is believed to be $^{60}\text{Co}^{2+}$ ion in cobalt chelates) to form $^{60}\text{Co}^+$ ion or ^{60}Co atom in the

excited state which reacts instantaneously with a neighbouring inactive chelate resulting in an isotopic exchange in the solid state thus:



The inactive $[{}^{59}\text{Co}^+]$ ion thus produced as a result of the second step can lodge itself in any interstitial position and would not be detected by any radiometric method of estimation. The observed multicomponent exponential annealing which is a function of temperature is due to the different rates of release of the electrons from the electron traps (donors) of different depths. In support of the postulates of this model, Amar Nath et al.^{6,61} have pointed out that the cobalt chelates which show considerable isotopic exchange in the solid state also give a high value of retention on thermal annealing after neutron irradiation, but chelates which show no isotopic exchange in the solid state exhibit little thermal annealing. The kinetics of the isotopic exchange reaction in solid state and thermal annealing of the irradiated solid cobalt chelates appear to be very similar. In addition, it has been shown that the rate and extent of annealing of the irradiated metal chelates is retarded in the presence of electron accepting ambient like oxygen (air), and hence the rate of annealing and the saturation annealing are higher in vacuum or inert atmosphere as compared to that

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in an ambient of oxygen (air). This model appears to explain the different aspects of post-irradiation annealing behaviour on a very simple and elegant picture. However, this has been put forward very recently and it has not yet been utilised by other groups of workers to explain their experimental results. It may be pointed out that it is necessary to establish that the recoil species in the cobalt chelates is Co^{+2} and that the Co^{+1} or Co^0 is formed as a result of interaction with the electrons.

The Disorder Model:

One of the more recent models put forward to explain the chemical effects of nuclear transformations in solids is the 'Disorder model' of Müller.⁷ The model has been derived on the basis of the general results obtained by Vineyard et al.^{63,64} on the computer calculations of radiation damage in copper. According to this model, in a (n,γ) reaction, the recoil atom of about 100 e.v. energy would lose its kinetic energy very quickly and come to rest within a few interatomic distances from its original site. There is an upper limit E_F , for the energy of the recoil atom below which the energy is dissipated by focussing collisions or 'focuseons'⁶⁵ along the crystal lattice-lines without any transport of material.^{65,66} The value of E_F depends upon the direction of recoil velocity and the nature of the matrix. For recoil energies greater than E_F , a vacancy is created due to the movement of each atom from its original position to the position of its nearest neighbour

forming a 'crowdion'⁶⁵ and thereby leads to transport of both material and energy, in contrast to a 'focuson' which involves only transport of energy. A focuson leads to retention since little transport of the material is involved. The general damage to the lattice in this model is very small. The rise of temperature in the reaction region is smaller and of shorter duration ($< 10^{-12}$ sec.) as compared to the hot zone model. The reaction region would therefore be much less disturbed. The disorder center is formed only when the recoil-atom is nearly at rest and hence the extent of disorder produced does not depend upon the initial energy of the recoil-atom giving rise to similar annealing behaviour of solids after (n, γ) , (γ, n) and $(n, 2n)$ reactions where the energies of the recoil are very different. The recoil atom in its new position after having lost its energy, may have the properties of a chemical compound and may remain intact on dissolution or may undergo a chemical reaction with the solvent. Alternatively the recoil atom may be in a metastable state which along with its neighbours may be considered as a disordered region. Such a disordered region may give rise to the separable activity on dissolution or lead to retention on annealing. In the disorder model, the defect controlled annealing behaviour is interpreted as being due to simple chemical transfer reactions. As the defect property such as abnormal charge, abnormal coordination etc. are not permanently associated with the primary recoil-species, they can be transferred to other atoms in the lattice. The greater the

ratio of the defect-associated radioactive atoms to the number of atoms taking part in the transfer reaction, the greater will be the retention.

Müller⁷ has tried to explain on the basis of this model, the various well-known features of the chemical effects of nuclear transformations in solids such as the isotope effect, the retention of configuration of stereoisomers, and the annealing behaviour in the mixed crystals. It should however be pointed out that a clear picture of the various steps leading to the formation of a disordered region is not yet available since simulation by computer calculations has not so far been possible. Maddock⁶⁷ has pointed out that the focussing collisions may not play any important role in the removal of energy from the recoil-site in complex crystals normally used in the studies of chemical effects of nuclear transformations in solids.

Review of the literature on the retention of configuration in the concurrent and post-irradiation annealing reactions:

Zuber and coworkers² were the first to report the retention of configuration of stereoisomers of cobalt chelates during the concurrent and the post-irradiation annealing reactions. They reported that the neutron irradiated dextro-tris-(ethylenediamine)-cobalt(III) nitrate gave an initial retention of 4.6 % of the dextro form. On annealing the irradiated chelate at 80°C for a time

corresponding to the plateau region, the percentage activity in the parent dextro form increased to 69.2 as compared to an increase to 3.1 of the levo isomer establishing that there was a high degree of retention of the original configuration. Costes et al.⁶⁸ also reported similar results. As a natural extension of these studies, Rauscher and coworkers^{69,70} determined the percentage activity in the cis and trans forms of the neutron irradiated geometrical isomers of dichloro-bis-(ethylenediamine)Co(III) nitrate. They reported that both ³⁸Cl and ⁶⁰Co activities were present only in the parent isomeric forms after neutron irradiation as well as at different stages of thermal annealing. The initial ³⁸Cl and ⁶⁰Co activities in the irradiated cis-isomer were found to be 12.5 % and 3.1 % respectively as compared to 0.4 % and 0.1 % in the trans isomer. On thermal annealing at 100°C to the plateau, the retention of ³⁸Cl and ⁶⁰Co rose to 65 % and 52 % respectively in the parent form but the percentage activities in the isomeric forms remained negligible as before. The neutron irradiated trans form gave similar results. Dimatokis and Paddock⁷¹ showed that the configurations of these isomers are also preserved during annealing with high energy electrons. On the other hand, Wolf⁷² reported that the cis- and the trans-[Co(en)₂Cl₂](NO₃) gave rise to significant percentage activities in the isomeric forms in a (n, 2n) reaction.

* en : ethylenediamine.

saeto et al.¹⁰ in their studies on cis- and trans-
 $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2](\text{NO}_3)$ also found that there was no significant degree of stereospecificity in the (n, γ) reaction. They observed 11.9 % and 6.7 % ^{60}Co activities in the isomeric forms as compared to the retentions of 20.5 % and 23.3 % in the cis- and the trans isomers respectively. They had, however, earlier reported⁷³ lower percentage activities in the isomeric forms. Maddock and coworkers¹¹ studied in more detail the behaviour of a number of neutron irradiated nitroammine-cobalt complexes viz.

1. $[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]$
2. trans- $[\text{Co}(\text{NO}_2)_2(\text{NH}_3)_4]^+ \text{trans-} [\text{Co}(\text{NO}_2)_4(\text{NH}_3)_2]^-$
3. cis- $[\text{Co}(\text{NO}_2)_2(\text{NH}_3)_4]^+ \text{trans-} [\text{Co}(\text{NO}_2)_4(\text{NH}_3)_2]^-$
4. trans- $[\text{Co}(\text{NO}_2)_2(\text{NH}_3)_4](\text{NO}_3)$
5. $(\text{NH}_4)^+ \text{trans-} [\text{Co}(\text{NO}_2)_4(\text{NH}_3)_2]^-$

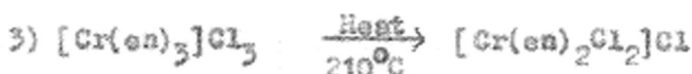
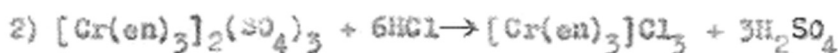
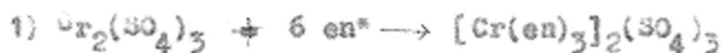
In all these complexes, except for compound No.3 they observed a high degree of stereospecificity in the reactions taking place during neutron irradiation and subsequent thermal and radiation annealing. However in cis- $[\text{Co}(\text{NO}_2)_2(\text{NH}_3)_4]^+ \text{trans-} [\text{Co}(\text{NO}_2)_4(\text{NH}_3)_2]^-$ they found 11.6 % to 39.1 % ^{60}Co activity in trans form $[\text{Co}(\text{NO}_2)_2(\text{NH}_3)_4]^+$, the isomeric form of the cation cis- $[\text{Co}(\text{NO}_2)_2(\text{NH}_3)_4]^+$ as compared to 1 to 4.5 % in the parent form depending upon the irradiation and annealing conditions. Very recently and after the completion of this work reported

in this thesis, Liu et al.⁷⁴ showed that the original isomeric configurations are preserved in cis- and trans- $[\text{Cr}(\text{en})_2\text{Cl}_2](\text{NO}_3)$ during a (n, γ) reaction.

CHAPTER - 2 : EXPERIMENTAL PROCEDURE

CHAPTER - IIa) Preparation and purification of cis- and trans-
 $[\text{Cr}(\text{en})_2\text{Cl}_2]\text{Cl}$ Cis- $[\text{Cr}(\text{en})_2\text{Cl}_2]\text{Cl}$

The preparation of cis- $[\text{Cr}(\text{en})_2\text{Cl}_2]\text{Cl}$, as described by Rollinson and Bailer⁷⁵ involves the following steps, viz.



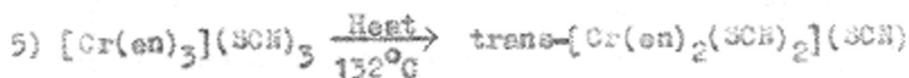
* en [ethylenediamine]

The last step is known to proceed only in the presence of ammonium chloride as catalyst. Several methods have been suggested⁷⁶ for contaminating $[\text{Cr}(\text{en})_3]\text{Cl}_3$ with ammonium chloride. It was found that a 1 % ammonium chloride solution used in step (2) gave the most satisfactory result. The impure product obtained, was purified by quickly dissolving in water, containing a few drops of concentrated hydrochloric acid, heating the solution to about 65°C and cooling the filtered solution in an ice-salt mixture, when the red-violet needles of cis- $[\text{Cr}(\text{en})_2\text{Cl}_2]\text{Cl} \cdot \text{H}_2\text{O}$ crystallised out. The product was separated by filtration and washed with alcohol and water.

The anhydrous product was obtained by dehydration in a vacuum oven at 90°C (yield 35 %).

Trans-[Cr(en)₂Cl₂]Cl

[Cr(en)₃]Cl₃ prepared by the method described earlier, was used as the starting material for the preparation of trans-[Cr(en)₂Cl₂]Cl according to the following procedure



The chlorination step (6) was carried out as described by Pfeiffer^{77,78}. The product obtained is impure and usually contains the sulphate ion. A saturated solution of this impure product was prepared in concentrated hydrochloric acid and by allowing the solution to evaporate in a desiccator over concentrated H₂SO₄, the bluish green acid chloride trans-[Cr(en)₂Cl₂]Cl.HCl.2H₂O was obtained. The acid chloride thus obtained was dissolved in 30 % hydrochloric acid solution and precipitated by the addition of alcohol and ether. The product was then dried at 100°C. Analysis of the compounds gave results corresponding to the molecular formula [Cr.(en)₂Cl₂]Cl.

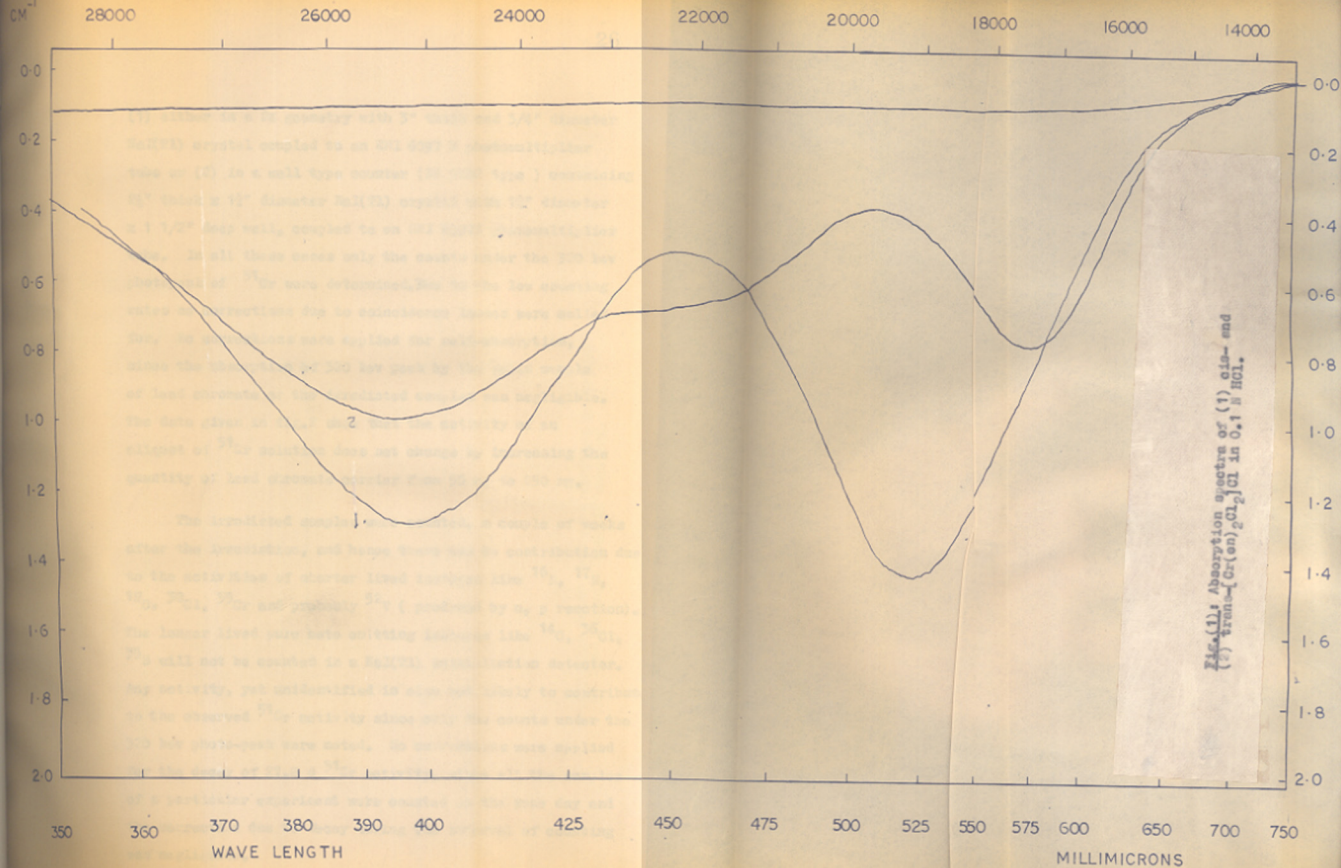
Analyses

	H	C	N	Cl	H ₂ O
<u>Cis-[Cr(en)₂Cl₂]Cl.H₂O</u>					
Theoretical	6.12	16.19	18.88	35.8	6.08
Experimental	6.5	17.5	19.0	34.3	6.4
<u>Trans-[Cr(en)₂Cl₂]Cl</u>					
Theoretical	5.7	17.3	20.1		
Experimental	5.7	17.8	19.4		

The chemical as well as the isomeric purity of the complexes were further confirmed from the position of the absorption maxima and molecular extinction coefficients, determined by taking their u.v. and visible absorption spectra in 0.1M HCl solution of these complexes in a Perkin-Elmer recording spectrophotometer. Solutions of cis- and trans-[Cr(en)₂Cl₂]Cl in 0.1M HCl had absorption maxima at 525 mμ and 396 mμ with molecular extinction coefficients of 71.5 M⁻¹ cm⁻¹ and 32.0 M⁻¹ cm⁻¹ in good agreement with those reported earlier.^{79,80} (Fig.1)

b) Counting Procedure

⁵¹Cr activity was counted by means of a gamma-ray single channel scintillation spectrometer of one micro-second resolution time, supplied by Nuclear Enterprises Ltd. U.K.. Counting was done in two different geometries,



(1) either in a 2 π geometry with 3" thick and 3/4" diameter NaI(Tl) crystal coupled to an EMI 6097 B photomultiplier tube or (2) in a well type counter (NE 5502 type) containing 2 1/2" thick x 1 1/2" diameter NaI(Tl) crystal with 1 1/2" diameter x 1 1/2" deep well, coupled to an EMI 6097A photomultiplier tube. In all these cases only the counts under the 320 kev photoppeak of ^{51}Cr were determined. Due to the low counting rates no corrections due to coincidence losses were called for. No corrections were applied for self-absorption, since the absorption of 320 kev peak by the solid sample of lead chromate or the irradiated complex was negligible. The data given in fig. 2 show that the activity of an aliquot of ^{51}Cr solution does not change by increasing the quantity of lead chromate carrier from 50 mg to 250 mg.

The irradiated samples were counted, a couple of weeks after the irradiation, and hence there was no contribution due to the activities of shorter lived isotopes like ^{16}N , ^{17}N , ^{13}O , ^{38}Cl , ^{55}Cr and probably ^{52}V (produced by n, p reaction). The longer lived pure beta emitting isotopes like ^{14}C , ^{36}Cl , ^{35}S will not be counted in a NaI(Tl) scintillation detector. Any activity, yet unidentified is also not likely to contribute to the observed ^{51}Cr activity since only the counts under the 320 kev photo-peak were noted. No corrections were applied for the decay of 27.8 d ^{51}Cr activity, since all the samples of a particular experiment were counted on the same day and the correction due to decay during the interval of counting was negligible.

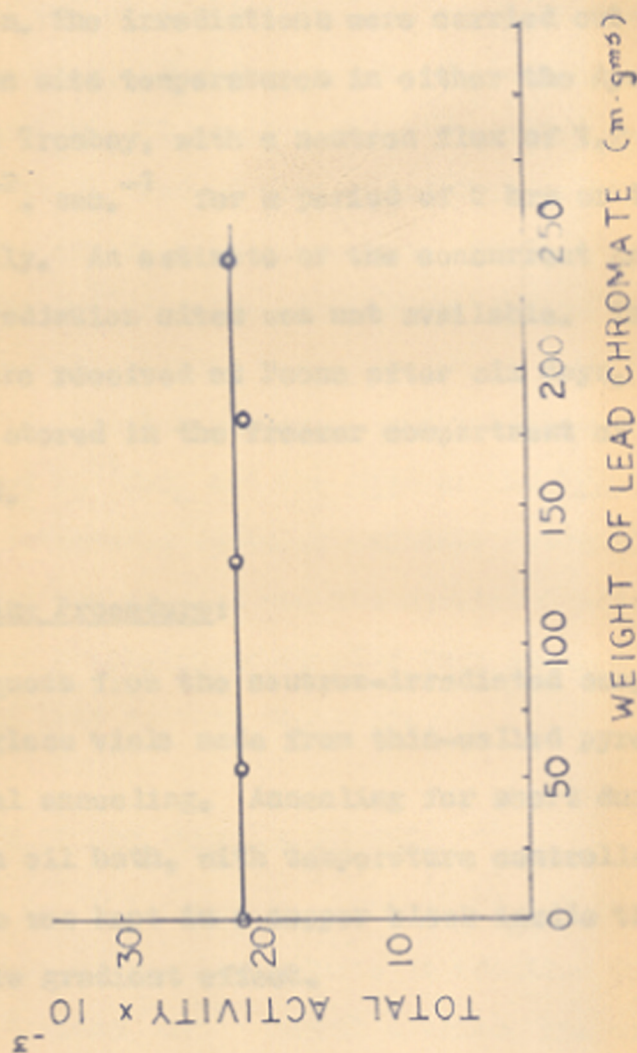


Fig. (2): Count rate as a function of weight of lead chromate used in counting.

c) Irradiations:

Aliquots of the samples, prepared in a single batch were used for neutron irradiations. The samples were sealed in quartz tubes in air, before being subjected to neutron irradiation. The irradiations were carried out at the reactor irradiation site temperatures in either the Apsara or Citrus reactor at Trombay, with a neutron flux of 1.2×10^{12} or 10^{13} n. cm⁻². sec.⁻¹ for a period of 2 hrs or 15 min. respectively. An estimate of the concurrent gamma-ray flux at the irradiation sites was not available. The irradiated samples were received at Poona after six days, and thereafter they were stored in the freezer compartment of the refrigerator until used.

d) Annealing Procedure:

Aliquots from the neutron-irradiated samples were taken in glass vials made from thin-walled pyrex glass tubes, for thermal annealing. Annealing for short durations were done in an oil bath, with temperature controlled to $\pm 1^\circ\text{C}$. The sample was kept in a copper block inside the oven to avoid temperature gradient effect.

e) Isotopic exchange in solutions:

The experiments to check the absence of isotopic exchange in solution were carried out, by dissolving 50 m.gms. of the complex in about 20 c.c. water, and by adding 10 λ of ^{51}Cr activity from an aqueous solution of $^{51}\text{CrCl}_3$. The activity

in the $^{51}\text{Cr}^{3+}$ form was then separated, by the addition of 4 m. gms of Cr^{3+} carrier and the precipitation of $\text{Cr}(\text{OH})_3$ by means of dilute ammonia. The solution was then centrifuged. The supernatant was further purified of any residual $^{51}\text{Cr}^{3+}$ activity by two more additions and precipitations of chromic chloride carrier. The supernatant containing the cis- or trans- $[\text{Cr}(\text{en})_2\text{Cl}_2]\text{Cl}$ complex and its aquated products were made up to 50 ml. and an aliquot of this solution counted for the activity of 320 kev. gamma-ray. No isotopic exchange between free Cr^{3+} and the cis- or the trans- $[\text{Cr}(\text{en})_2\text{Cl}_2]\text{Cl}$ and its aquated products was observed at room temperature (25-30°C). Similar exchange experiments with aqueous solutions of $\text{K}_2^{51}\text{CrO}_4$ and the cis- or the trans- $[\text{Cr}(\text{en})_2\text{Cl}_2]\text{Cl}$ showed no detectable isotopic exchange between hexavalent chromium and the complex and its aquated products. The chromate activity was precipitated at pH 2 to 3 as lead chromate by the addition of lead nitrate solution.

f) Analyses of the recoil products

In a (n, γ) reaction, $[\text{Cr}(\text{en})_2\text{Cl}_2]\text{Cl}$ is likely to give a number of recoil products in addition to the original complex. Besides $^{51}\text{Cr}^{3+}$ recoil species, one can also expect $^{51}\text{Cr}^{6+}$ and the aquated species of $[\text{Cr}(\text{en})_2\text{Cl}_2]\text{Cl}$.^{80,81} It has been reported that the separation of Cr^{3+} and Cr^{6+} in the presence of their carriers is beset with a number of difficulties. Maddock *et al.* have reported¹⁰ that it may be possible to effect the separation of Cr^{3+} and Cr^{6+} , if the precipitation

of Cr^{6+} as lead chromate is carried out in the first instance, since the precipitation of Cr^{3+} as $\text{Cr}(\text{OH})_3$ carries a major portion of the activity Cr^{6+} .

1) Determination of Cr^{6+} activity

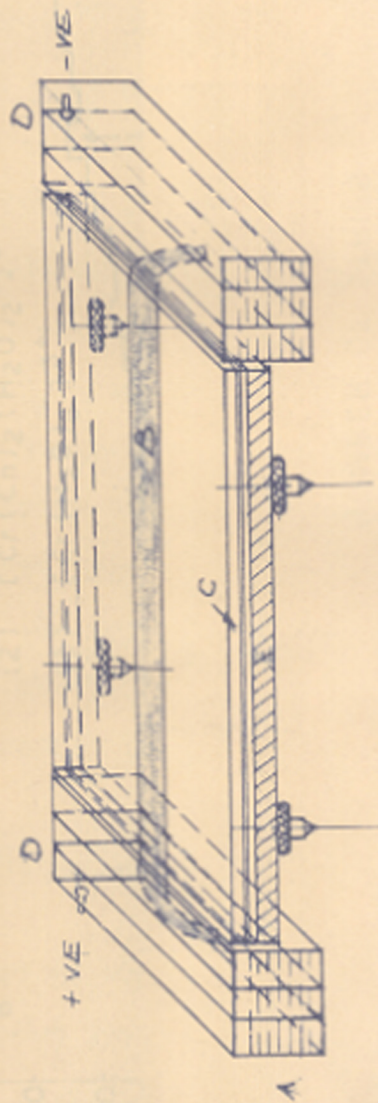
In order to determine the activity associated with any any possible Cr^{6+} species in the recoil products, about 100 m. gas of the irradiated cis or trans complex was taken on a thin aluminium planchet, and counted for its ^{51}Cr activity. It was then quantitatively transferred into a centrifuge tube, dissolved in an acetate buffer solution of pH 3.5, containing 10 m. gms of Cr^{6+} carrier as K_2CrO_4 and 20 m.gms of Cr^{3+} carrier as chromic nitrate. Lead chromate was precipitated by the addition of lead nitrate to the above solution and the pH of the resultant solution was adjusted to 2. The mixture was then centrifuged and the supernatant rejected. The precipitate was washed well with 30 cc acetate buffer, transferred into a filtration disc and washed thrice with hot water containing traces of nitric acid. The lead chromate was then transferred into a weighed aluminium planchet, dried, weighed and counted for its activity. After correction for the chemical yield, it was found that 12.5 % and 6.7 % ^{51}Cr activity was associated with the lead chromate precipitated from the solutions of irradiated cis- and trans- $[\text{Cr}(\text{en})_2\text{Cl}_2]\text{Cl}$ respectively.

11) High-voltage paper electrophoresis of the recoil products.

In order to confirm that the activity associated with lead chromate is indeed Cr^{6+} , high voltage electrophoresis

analysis at 0°C of the irradiated cis- and trans- $[\text{Cr}(\text{en})_2\text{Cl}_2]\text{Cl}$ were carried out. An electrophoresis equipment similar to that described by Shankar et al.⁸² was used and is shown schematically in fig.3. Electrophoresis was carried out on 56 cm. long and 2.5 cm. wide No.3 Whatman chromatograph paper which was sandwiched between two glass plates, smeared with silicone grease to keep their surface water-repellant. 100 μ of the solution of the irradiated complex was transferred to the center of the strip and the plates cooled to 0°C by placing an ice-cold tank over them. After an electrophoresis of three hours at 600 volts, the paper was dried, cut into strips one centimeter wide and counted in a well typed scintillation counter.

The electrophoresis of the irradiated complexes were carried out in 0.1 M NaClO_4 and 0.01 M HClO_4 as the supporting electrolyte since this medium was found to give the best separation of $^{51}\text{Cr}^{3+}$ and $^{51}\text{Cr}^{6+}$ activities. (Fig.3C). Experiments were also carried out in 0.1 M NaCl + 0.01 M HCl medium to see whether resolution of the different recoil products is possible in that medium. (Fig.3B). None of the experiments with the irradiated cis or trans $[\text{Cr}(\text{en})_2\text{Cl}_2]\text{Cl}$ indicated the presence of any anionic species in the solutions of the irradiated complexes. The results, as illustrated by the histograms, confirm that no Cr^{6+} activity was produced as a result of (n, γ) reaction in cis- or trans- $[\text{Cr}(\text{en})_2\text{Cl}_2]\text{Cl}$ and the ^{51}Cr activity associated with the PbCrO_4 is due to a cationic species co-precipitated with lead chromate.



A - PERSPEX TANKS, B - PAPER STRIP, C - GLASS PLATES,
D - ELECTRODES AND E - BENCH.

Fig. (3A): A schematic diagram of the electro-phoresis apparatus used.

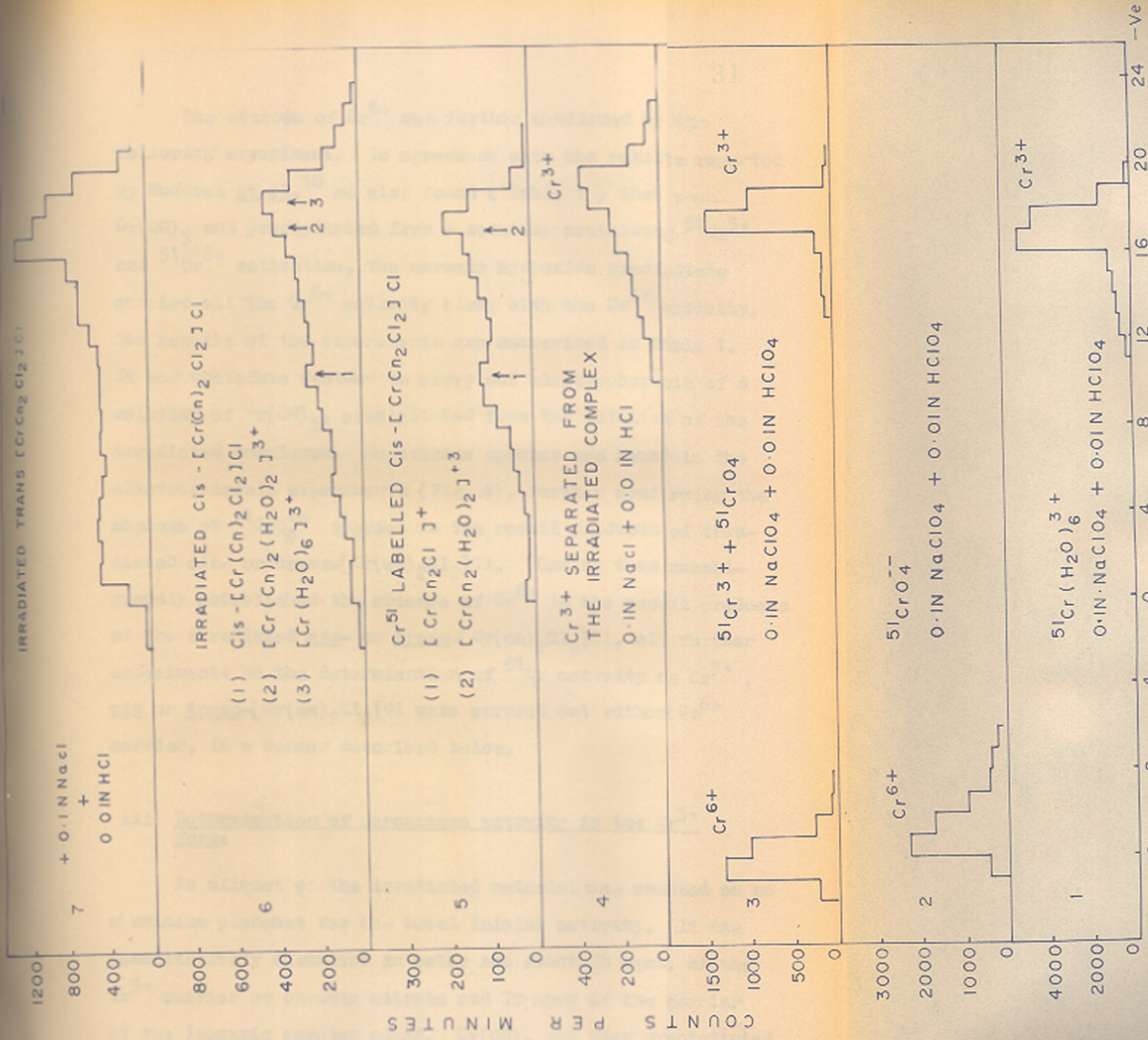


Fig. (3B). Electrophoresis histograms of different labelled compounds (Arrows indicate the positions of possible species).

The absence of Cr^{6+} was further confirmed by the following experiment. In agreement with the results reported by Maddock *et al.*¹⁰ we also found (Table 1) that when $\text{Cr}(\text{OH})_3$ was precipitated from a solution containing $^{51}\text{Cr}^{3+}$ and $^{51}\text{Cr}^{6+}$ activities, the chromic hydroxide precipitate carried all the Cr^{6+} activity along with the Cr^{3+} activity. The results of the experiments are summarised in table 1. It was therefore decided to carry out electrophoresis of a solution of $\text{Cr}(\text{OH})_3$ precipitated from the solution of the irradiated complexes. No anionic species was found in the electrophoresis experiments (Fig. 4), further confirming the absence of $^{51}\text{CrO}_4^-$ species in the recoil products of irradiated *cis*- or *trans*- $[\text{Cr}(\text{en})_2\text{Cl}_2]\text{Cl}$. Having thus unambiguously established the absence of Cr^{6+} in the recoil products of the irradiated *cis*- or *trans*- $[\text{Cr}(\text{en})_2\text{Cl}_2]\text{Cl}$, all further experiments on the determination of ^{51}Cr activity as Cr^{3+} , *cis* or *trans*- $[\text{Cr}(\text{en})_2\text{Cl}_2]\text{Cl}$ were carried out without Cr^{6+} carrier, in a manner described below.

iii) Determination of percentage activity in the Cr^{3+} form:

An aliquot of the irradiated material was counted on an aluminium planchet for the total initial activity. It was quantitatively dissolved in water and about 20 mgms. of the Cr^{3+} carrier as chromic nitrate and 70 mgms of the carrier of the isomeric complex added. $\text{Cr}(\text{OH})_3$ was then precipitated by addition of dilute ammonium hydroxide solution. The

TABLE No.1

Coprecipitation of $^{51}\text{CrO}_4^-$ with chromic hydroxide

No.	$^{51}\text{Cr}^{3+}$ taken (cpm)	$^{51}\text{Cr}^{6+}$ taken (cpm)	Total activity taken (cpm)	Activity associated with $\text{Cr}(\text{OH})_3$ (cpm)
1	28451	6911	35362	35626
2	25600	6229	31829	31742
3.	31296	7601	38897	38703

precipitate was dissolved in dilute nitric acid and reprecipitated by the addition of NH_4OH . This step was repeated three times and thereafter the $\text{Cr}(\text{OH})_3$ precipitate was dissolved in a dilute acid solution. This solution was neutralized by NaOH and then oxidised to chromate by potassium bromate. The chromium-51 activity was finally precipitated as lead chromate from an acidic solution (pH 2-3). The percentage activity in the Cr^{3+} form was calculated from the knowledge of the initial activity and the final activity corrected for the chemical yield.

iv) Determination of the percentage of ^{51}Cr activity in the parent and the isomeric forms of cis- and trans- $[\text{Cr}(\text{en})_2\text{Cl}_2]\text{Cl}$

After a trial of a number of possible methods, it was found that the separation of the geometrical isomers could be achieved by taking into account the differences in the solubilities of the chlorides, the nitrates and the perchlorates of the cis- and trans- $[\text{Cr}(\text{en})_2\text{Cl}_2]^+$ ion.

An accurately weighed quantity of the irradiated complex was taken on an aluminium planchet and counted. It was quantitatively transferred into a 50 c.c. beaker containing known amounts of carriers of Cr^{3+} , cis- $[\text{Cr}(\text{en})_2\text{Cl}_2]\text{Cl}$ and trans- $[\text{Cr}(\text{en})_2\text{Cl}_2]\text{Cl}$. The quantities of Cr^{3+} , cis- $[\text{Cr}(\text{en})_2\text{Cl}_2]\text{Cl}$ and trans- $[\text{Cr}(\text{en})_2\text{Cl}_2]\text{Cl}$ were approximately 20, 500 and 150 milligrams respectively, in a total volume of 10-15 c.c. of the solution. On adding 3.5 gas of

solid sodium chloride to the above solution, the reddish violet cis isomer salted out on standing, at room temperature. To the filtrate of the above solution was added 2 gms of solid sodium perchlorate to precipitate the trans-
 $[\text{Cr}(\text{en})_2\text{Cl}_2]\text{ClO}_4$. The salted out cis- $[\text{Cr}(\text{en})_2\text{Cl}_2]\text{Cl}$ after washing with alcohol and ether was dissolved in 12.c.c. water and reprecipitated by the addition of 4 gms. of ammonium nitrate, and cooling the solution in ice. The cis- $[\text{Cr}(\text{en})_2\text{Cl}_2]\text{NO}_3$ was redissolved and reprecipitated with ammonium nitrate and the procedure repeated until a constant specific activity was obtained. The precipitated trans- $[\text{Cr}(\text{en})_2\text{Cl}_2]\text{ClO}_4$ also was redissolved and reprecipitated a number of times as the perchlorate to a constant specific activity. The entire separation procedure was carried out in the minimum possible time to reduce the extent of aquation^{80,81} of the isomers and prevent the consequent decrease in the chemical yield of the isomers. A constant specific activity of the cis- or the trans- $[\text{Cr}(\text{en})_2\text{Cl}_2]\text{Cl}$ ensures its radioactive purity. The isomeric purity of the final separated cis and trans isomers was also confirmed from their visible and ultraviolet spectra which gave absorption maxima and the molecular extinction coefficients characteristic of pure specimens.^{78,80} (fig.4.)

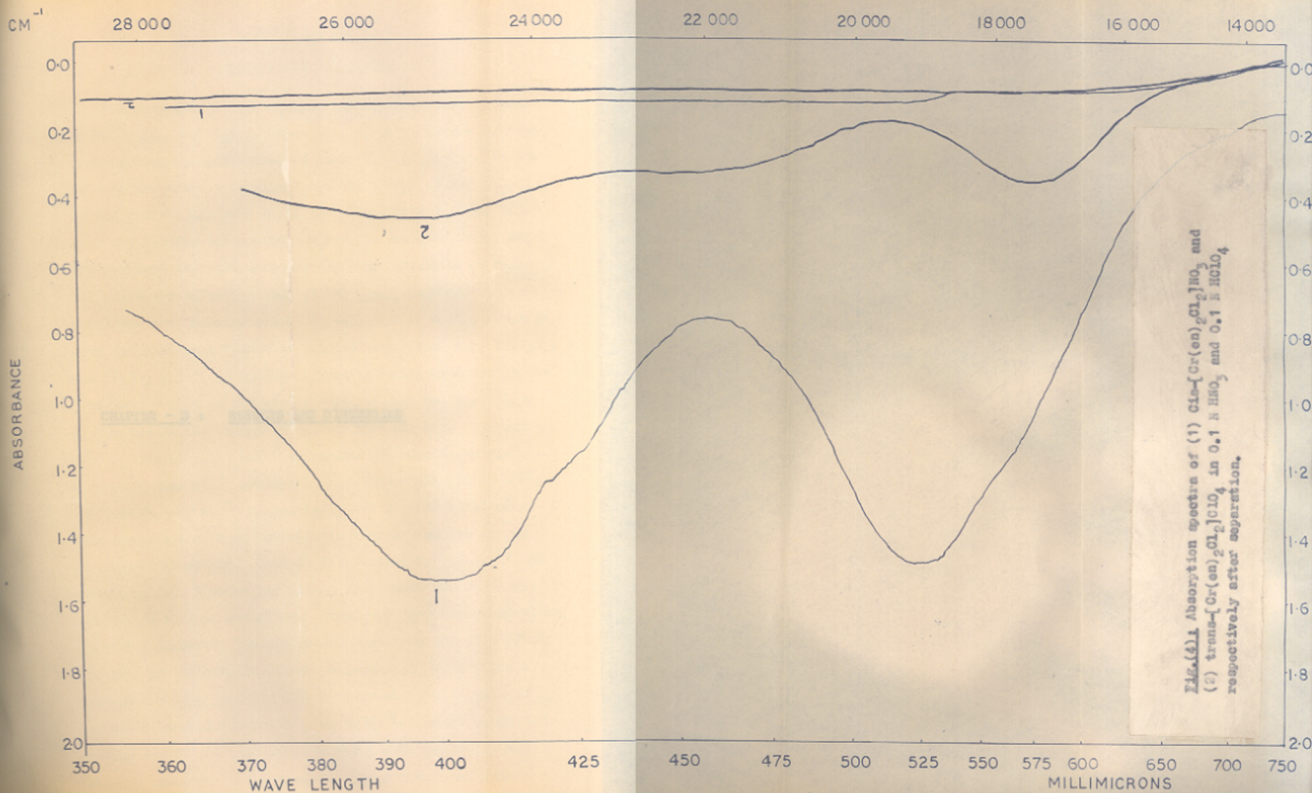


Fig. (4) Absorption spectra of (1) *cis*-[Cr(en)₂Cl₂]NO₃ and (2) *trans*-[Cr(en)₂Cl₂]ClO₄ in 0.1 N HNO₃ and 0.1 N HClO₄ respectively after separation.

CHAPTER - 3 : RESULTS AND DISCUSSION

CHAPTER - III

RESULTS AND DISCUSSION

The results of the analyses of the activities present as Cr^{3+} , cis- and trans- $[\text{Cr}(\text{en})_2\text{Cl}_2]\text{Cl}$ in different neutron irradiations are summarised in table 2. The initial retention in the neutron irradiated cis- or trans- $[\text{Cr}(\text{en})_2\text{Cl}_2]\text{Cl}$ varies from 19 per cent to 30 per cent (Table 2) depending upon the irradiation conditions and the interval after which the chemical analyses were carried out. It would be observed that in the irradiation No.3 of the trans complex, two chemical analyses carried out at an interval of twenty seven days gave two different values of initial retention, viz. 19.1 ± 0.4 and 26.3 ± 0.1 %. A similar effect was also observed in the irradiation No.4 of the cis complex, though the percentage difference in the values of initial retention is comparatively small. Tables 3,4,5 and 6 summarise the results of detailed isothermal annealing studies in cis- $[\text{Cr}(\text{en})_2\text{Cl}_2]\text{Cl}$ at 120° , 134° , 146° , and 160°C respectively and show that the retention increases with an increase in time or temperature of isothermal annealing. This is illustrated by the family of curves in fig. 5, where the values of percent retention are plotted vs time of annealing. During an isothermal annealing, retention increases rapidly at the beginning and thereafter the rate of increase in retention gradually falls until a temperature dependent plateau is reached. The results of isothermal annealing at 120° , 134° , 146° , and 160°C for the neutron irradiated cis- complex along with the percentage activity observed in the isomeric trans form have been

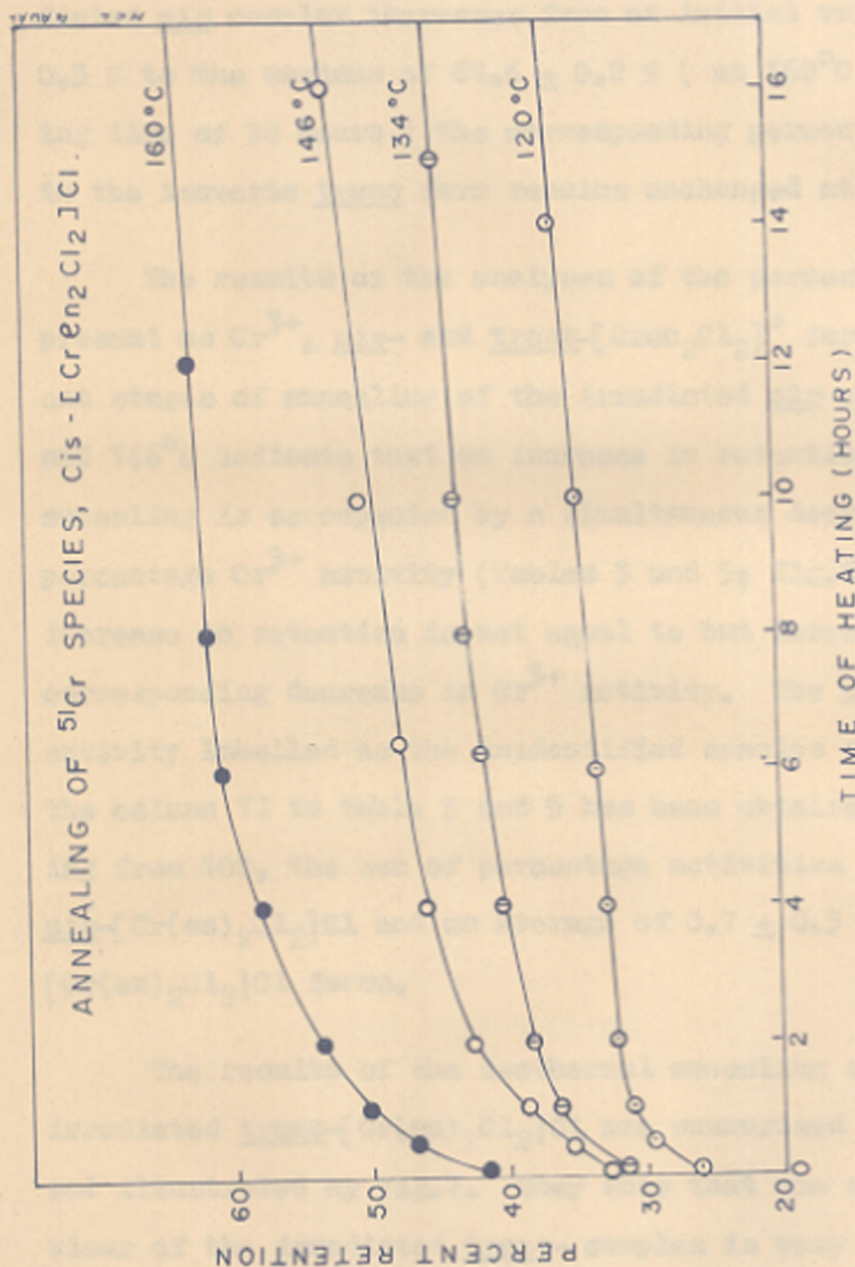
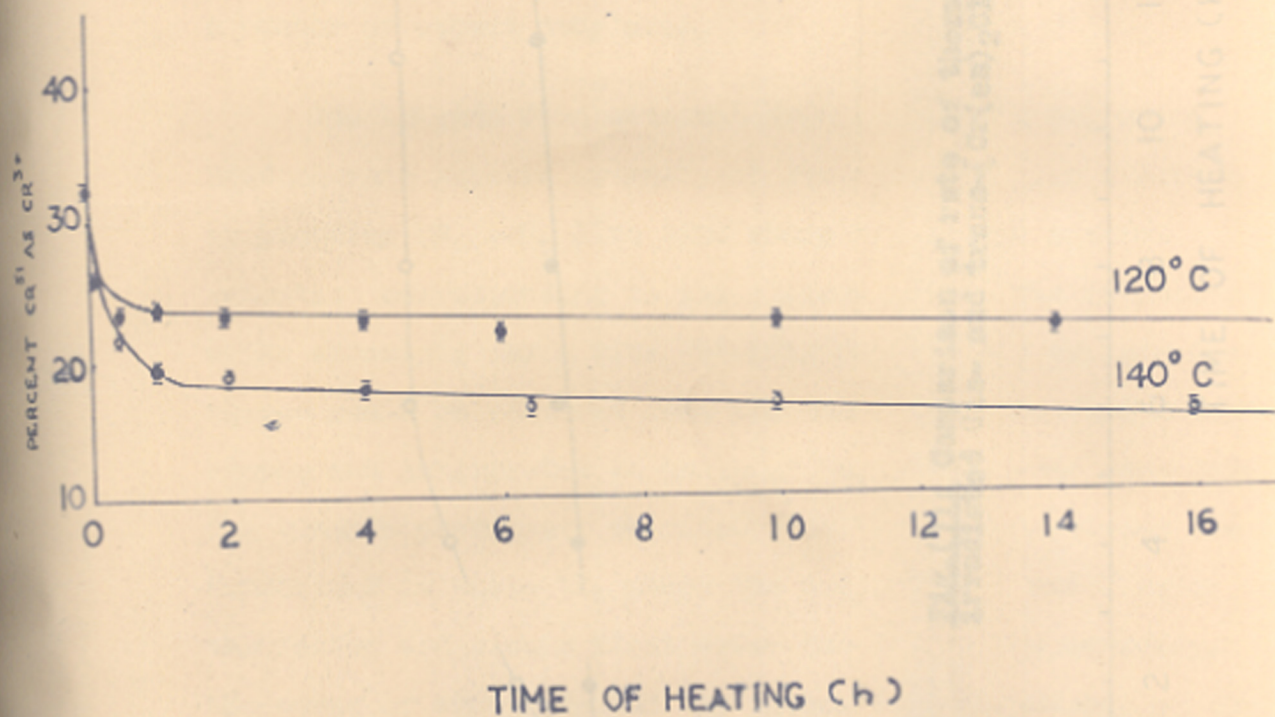


Fig. (5): Increase of retention in irradiated $\text{Cis}-[\text{Cr}(\text{en})_2\text{Cl}_2]\text{Cl}$ on heating at different temperatures.

compiled in table 7 for ready reference. It would be immediately apparent that though the retention in the irradiated cis complex increases from an initial value of $22.7 \pm 0.3 \%$ to the maximum of $62.6 \pm 0.2 \%$ (at 160°C for an annealing time of 98 hours) the corresponding percentage activity in the isomeric trans form remains unchanged at $0.7 \pm 0.3 \%$.

The results of the analyses of the percentage activity present as Cr^{3+} , cis- and trans- $[\text{Cr}(\text{en})_2\text{Cl}_2]^+$ forms at different stages of annealing of the irradiated cis complex at 120° and 146°C indicate that an increase in retention on isothermal annealing is accompanied by a simultaneous decrease in the percentage Cr^{3+} activity (Tables 3 and 5; Fig.6) though the increase in retention is not equal to but larger than the corresponding decrease in Cr^{3+} activity. The percentage activity labelled as the unidentified species and given in the column VI in table 3 and 5 has been obtained by subtracting from 100, the sum of percentage activities present as Cr^{3+} cis- $[\text{Cr}(\text{en})_2\text{Cl}_2]\text{Cl}$ and an average of $0.7 \pm 0.3 \%$ for the trans- $[\text{Cr}(\text{en})_2\text{Cl}_2]\text{Cl}$ forms.

The results of the isothermal annealing studies of the irradiated trans- $[\text{Cr}(\text{en})_2\text{Cl}_2]\text{Cl}$ are summarised in tables 8-11 and illustrated by fig.7. They show that the annealing behaviour of the irradiated trans- complex is very similar to that of the irradiated cis complex, viz. during isothermal annealing the retention increases, the Cr^{3+} activity decreases, (Table 10 and 11) but the percentage activity associated with the isomeric cis form does not change (Table 9) from an initial



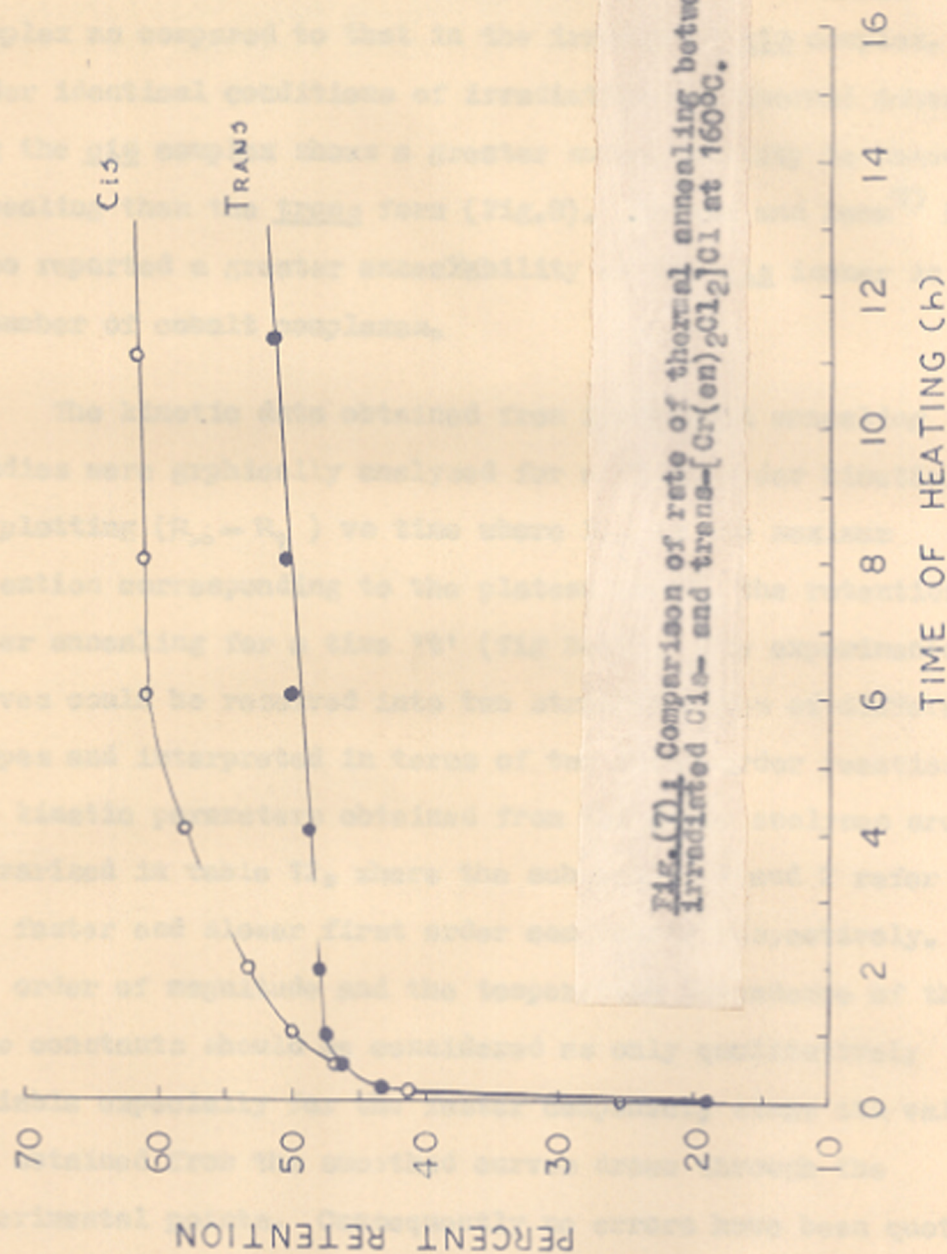
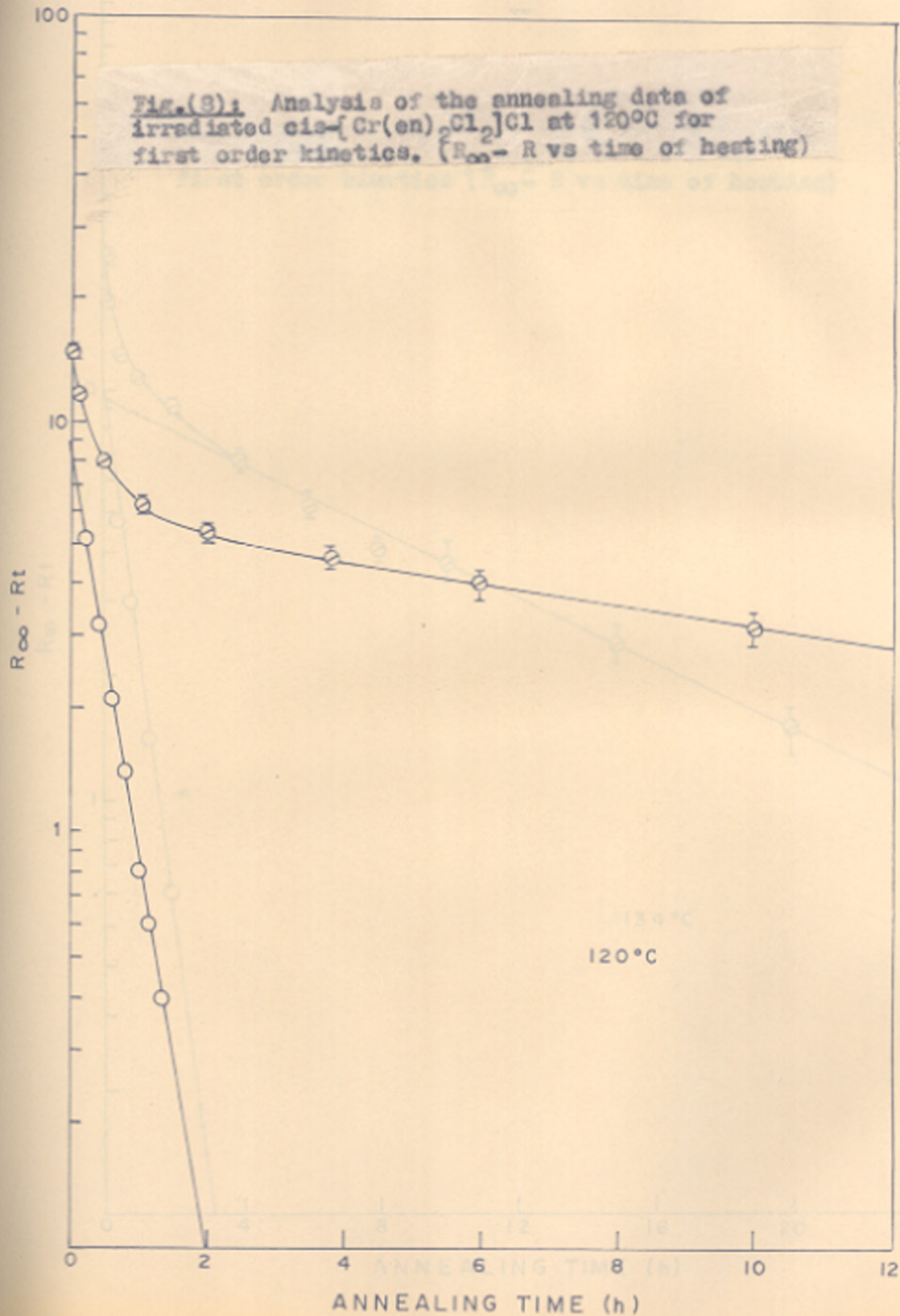


Fig. (7). Comparison of rate of thermal annealing between irradiated $\text{Cr(en)}_2\text{Cl}_2$ and $\text{trans-Cr(en)}_2\text{Cl}_2$ at 160°C .

value which in the present case is $2.8 \pm 0.6\%$. It may be pointed out here, that the activity associated with the isomeric form is slightly higher in the irradiated trans-complex as compared to that in the irradiated cis complex. Under identical conditions of irradiation and thermal annealing the cis complex shows a greater susceptibility to thermal annealing than the trans form (Fig.8). Costen and Denn⁸³ have also reported a greater annealability of the cis isomer in a number of cobalt complexes.

The kinetic data obtained from isothermal annealing studies were graphically analysed for a first-order kinetics by plotting $(R_{\infty} - R_t)$ vs time where R_{∞} is the maximum retention corresponding to the plateau and R_t the retention after annealing for a time 't' (fig 8-11). The experimental curves could be resolved into two straight lines of different slopes and interpreted in terms of two first-order reactions. The kinetic parameters obtained from the above analyses are summarised in table 12, where the subscripts 1 and 2 refer to the faster and slower first order components respectively. The order of magnitude and the temperature dependence of the rate constants should be considered as only qualitatively reliable especially for the faster component, since its values are obtained from the smoothed curves drawn through the experimental points. Consequently no errors have been quoted in the table or indicated in the figures. The activation energy E^* , for the slower component for which the rate constants (k) are quantitatively more reliable was determined from the slope of the straight-line (fig.13) obtained by

Fig.(9): Analysis of the annealing data of irradiated $\text{cis-[Cr(en)}_2\text{Cl}_2\text{)]Cl}$ at 120°C for first order kinetics. ($R_\infty - R$ vs time of heating)



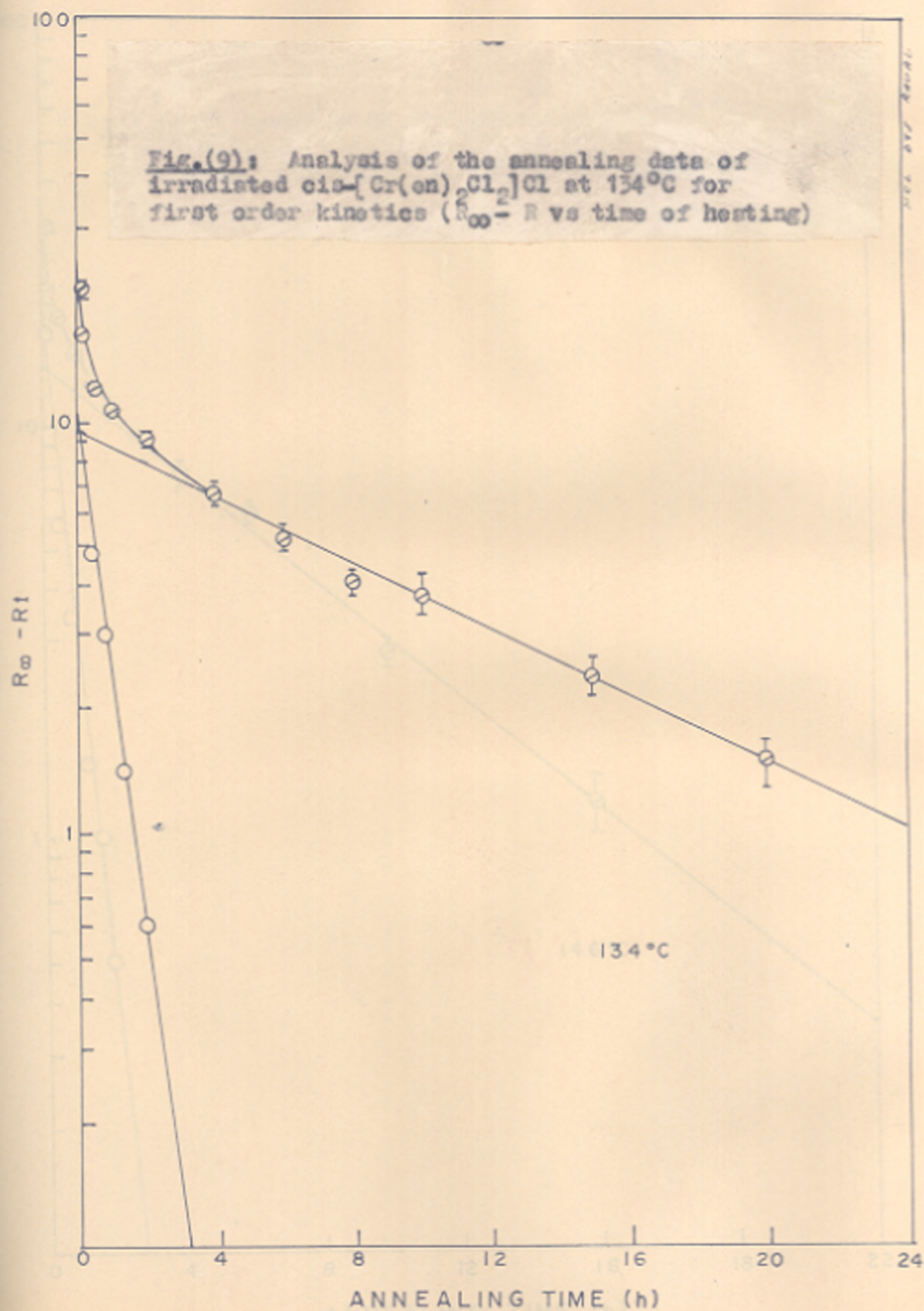
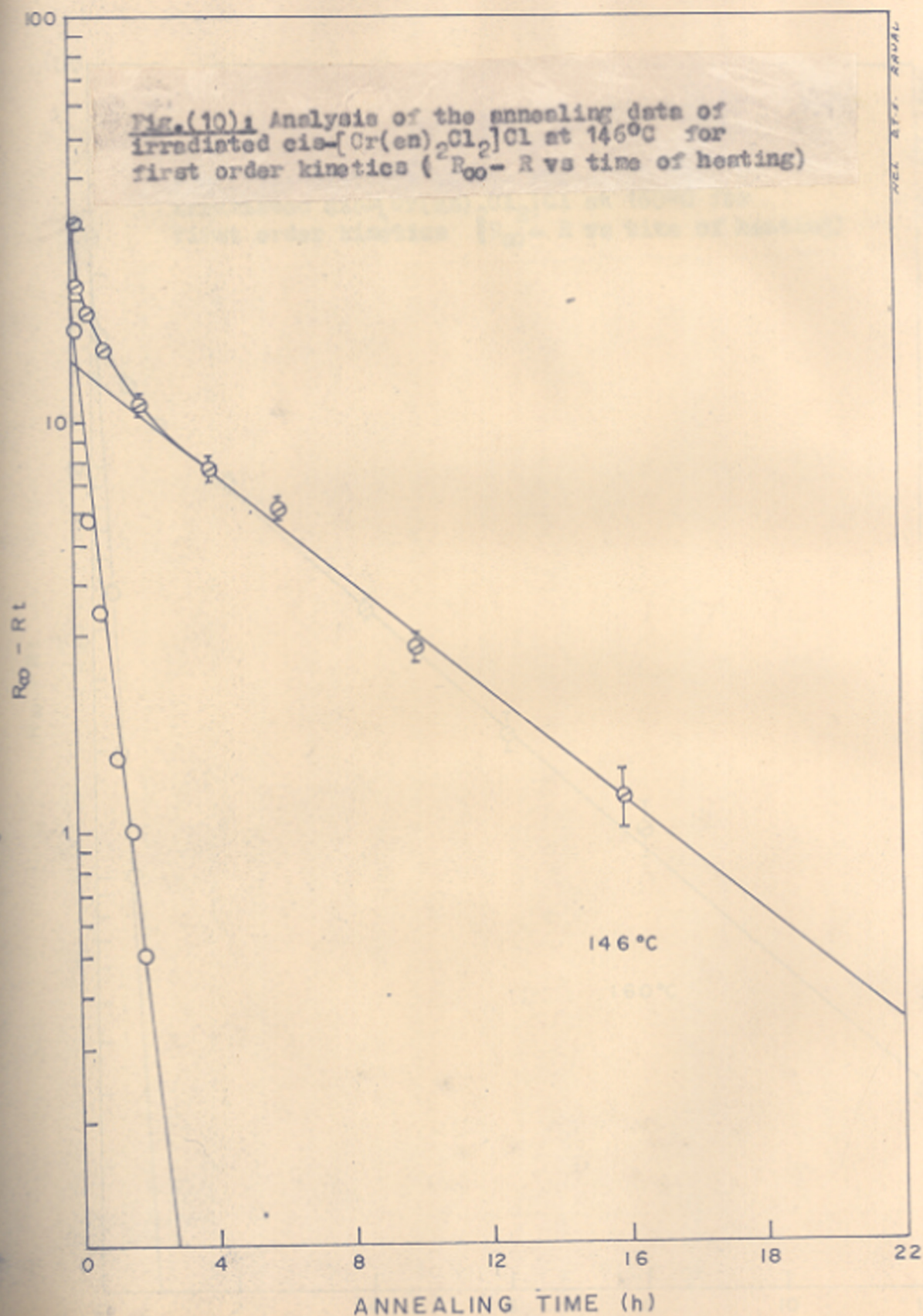
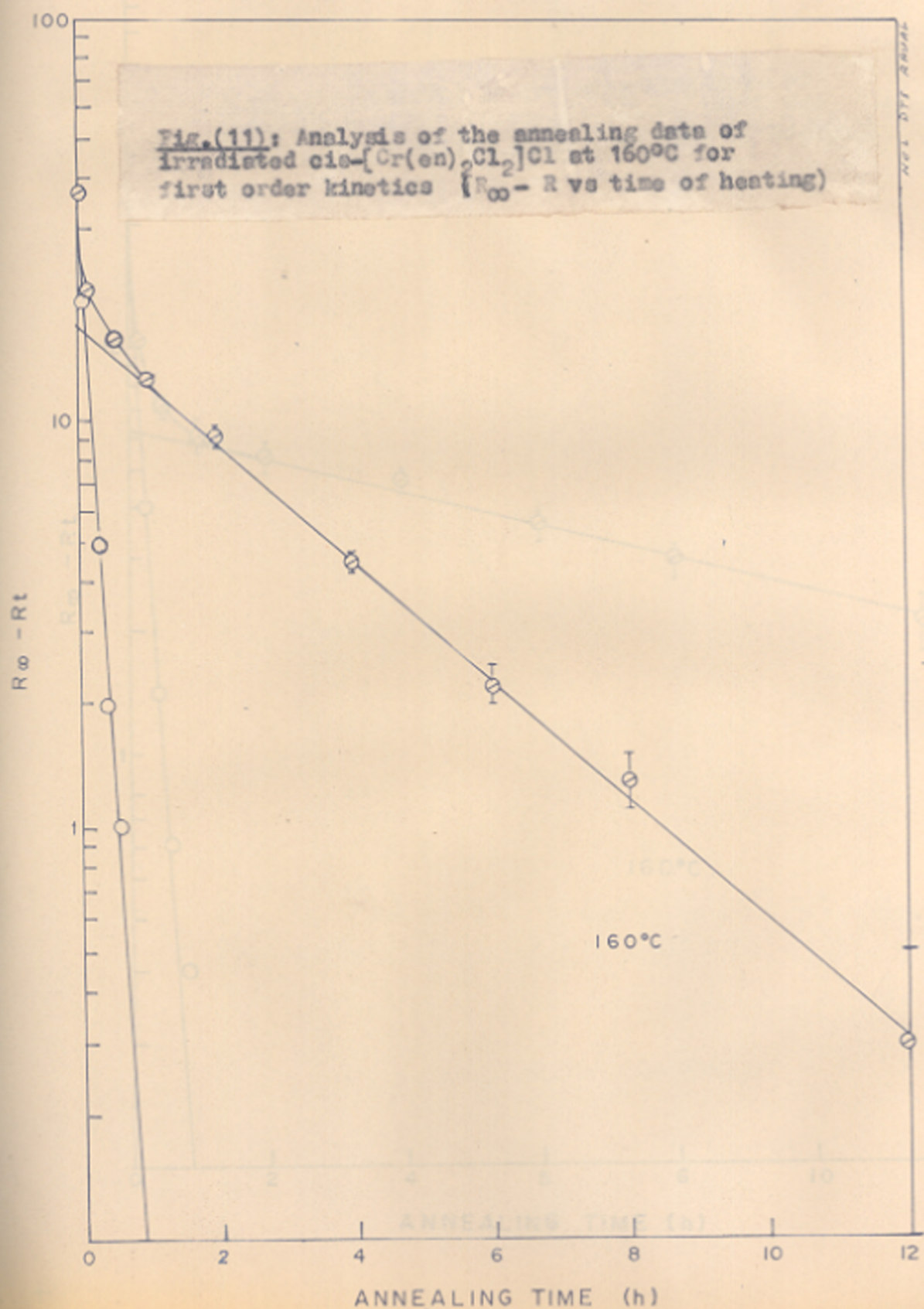


Fig. (10): Analysis of the annealing data of irradiated $\text{cis-[Cr(en)}_2\text{Cl}_2\text{]Cl}$ at 146°C for first order kinetics ($R_\infty - R$ vs time of heating)





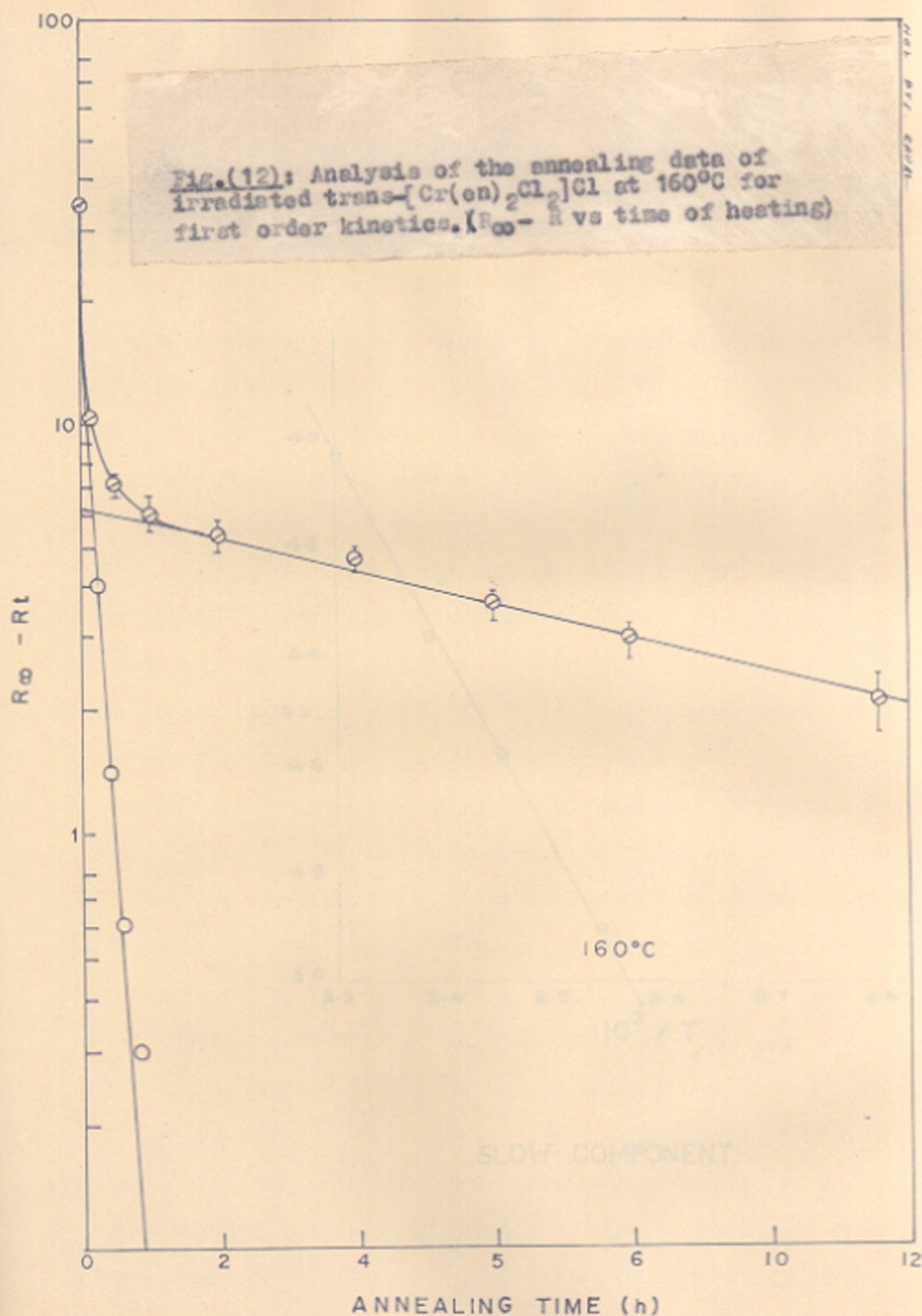
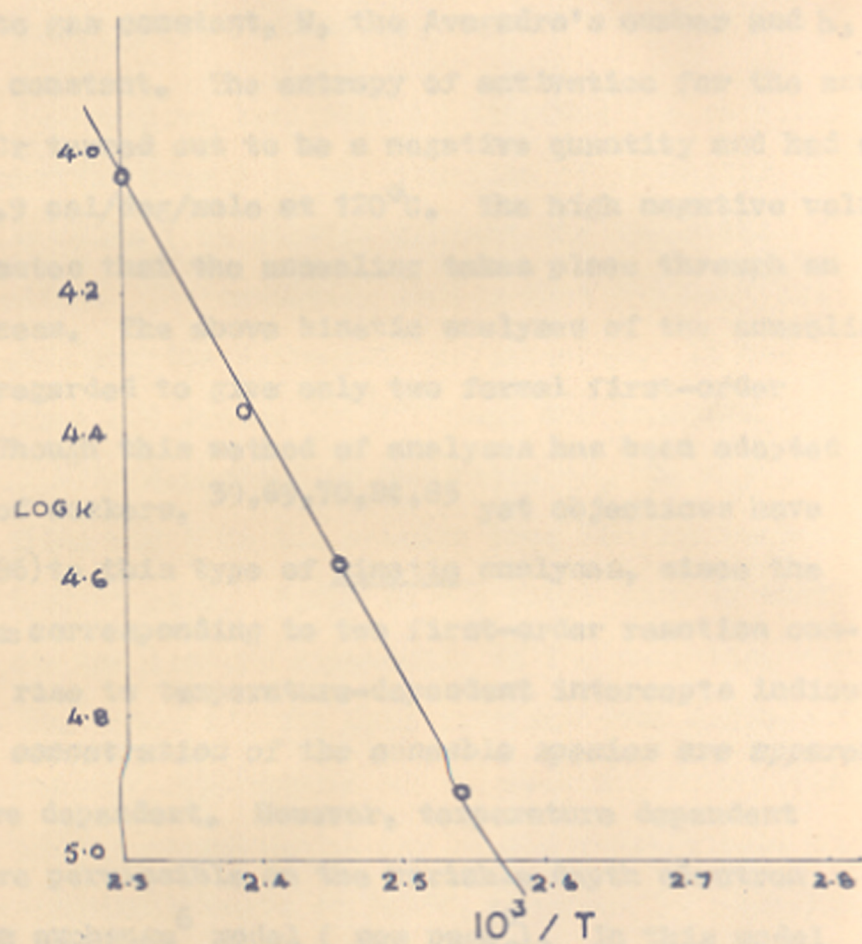


Fig. (13): Arrhenius plot for $\text{cis-}[\text{Cr(en)}_2\text{Cl}_2]\text{Cl}$ for the slow component.



SLOW COMPONENT

plotting $\log k$ vs $1/T$ (where T is the absolute temperature). It was found to be 13.4 kcal/mole. for the gig complex. The entropy of activation $\Delta S^\ddagger$ was calculated from the values of the rate constants using the following equation:

$$k = RT/Nh \exp(\Delta S^\ddagger / R) \exp(-E/RT + 1) \quad (5)$$

where R is the gas constant, N , the Avogadro's number and h , the planck's constant. The entropy of activation for the annealing of ^{51}Cr turned out to be a negative quantity and had a value of -48.9 cal/deg/mole at 120°C. The high negative value of $\Delta S^\ddagger$ indicates that the annealing takes place through an ordering process. The above kinetic analyses of the annealing data may be regarded to give only two formal first-order reactions. Though this method of analysis has been adopted by a number of workers, 39,69,70,84,85 yet objections have been raised (86) to this type of kinetic analyses, since the straight lines corresponding to two first-order reaction components give rise to temperature-dependent intercepts indicating that the concentration of the annealable species are apparently temperature dependent. However, temperature dependent intercepts are permissible on the variable depth electron trap-isotopic exchange⁶ model (see page¹⁵). In this model the two first-order reactions may be attributed to the rate determining step of the release of electrons from populated traps of variable depths. The released electrons are captured by the interstitial recoil metal ion (Co^{2+} for cobalt complexes or Cr^{3+} for chromium complexes) to form an excited metal ion of a lower charge which instantaneously exchanges with the inactive metal atom of an undisturbed chelate

molecule in the neighbourhood, giving rise to retention. The temperature dependence of the multicomponent exponential annealing may then ^{be} said to be due to the change in the rate of release of the electrons from the electron traps of variable depths which have been populated during irradiation by the fast neutron flux, concomitant gamma-ray fragmentation and the associated Auger processes.

In the alternative treatment of kinetics (also assuming discrete activation energy), the fraction of radiation damage annealed ($P = Rt - R_0$) is plotted against the logarithm of time of annealing. The annealing curves thus obtained are shown in fig.14. for the different temperatures. It has been shown by Fletcher and Brown, ^{4,37,87} that the fraction of damage annealed is dependent on the ratio t/τ where t is the time of annealing and τ is the average time for the vacancy to move to an adjacent site. Since in the final form of their expression, the temperature dependence of the annealing appears only through the ratio t/τ the data obtained from different isothermal annealing experiments can be combined into a single curve of equivalent annealing at any single temperature. Fig 15 shows such a composite curve at 146°C, obtained by adjusting the time scales of each isothermal annealing curve at 120, 134, 146 and 160°C. The composite curve can be duplicated by an expression involving three first order reaction components viz:

$$\begin{aligned}
 P = & 9(1 - e^{-t/72.28}) + 12(1 - e^{-t/5.454 \times 10^3}) \\
 & + 17(1 - e^{-t/5.771 \times 10^4})
 \end{aligned}
 \quad (6)$$

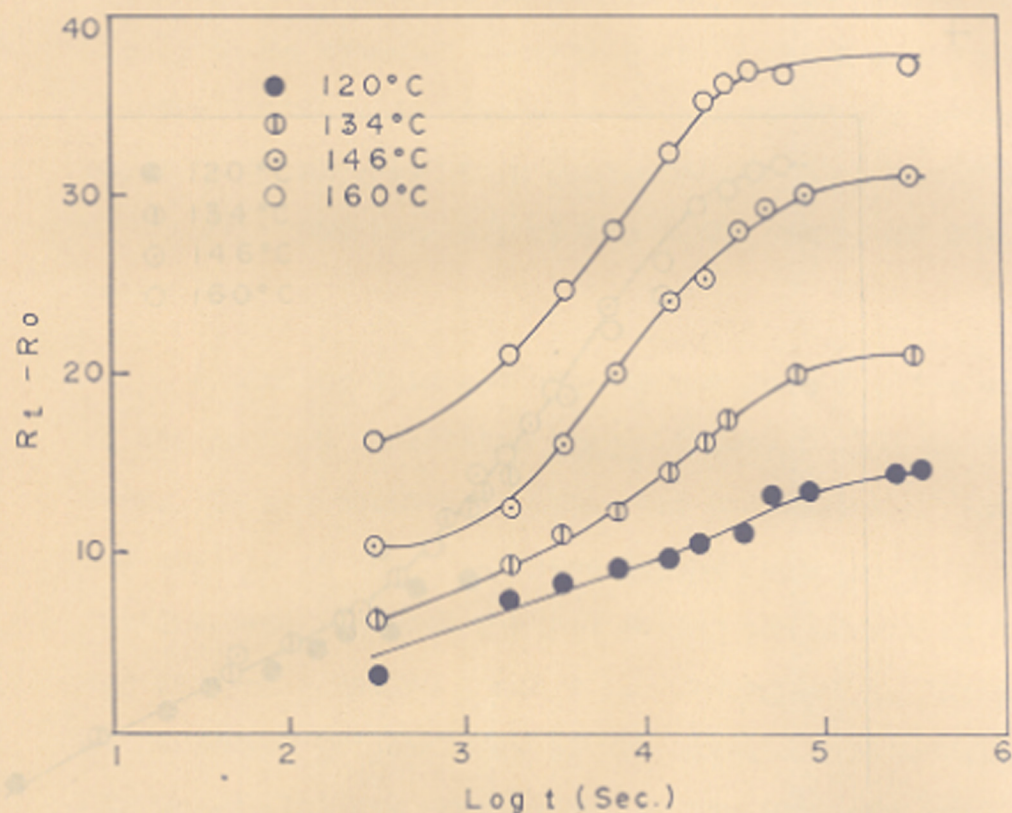


Fig. (14): Analysis of the annealing data for $\text{cis-[Cr(en)}_2\text{Cl}_2\text{]Cl}$ by the method of Fletcher and Brown; ($R_t - R_0$) vs time of heating.

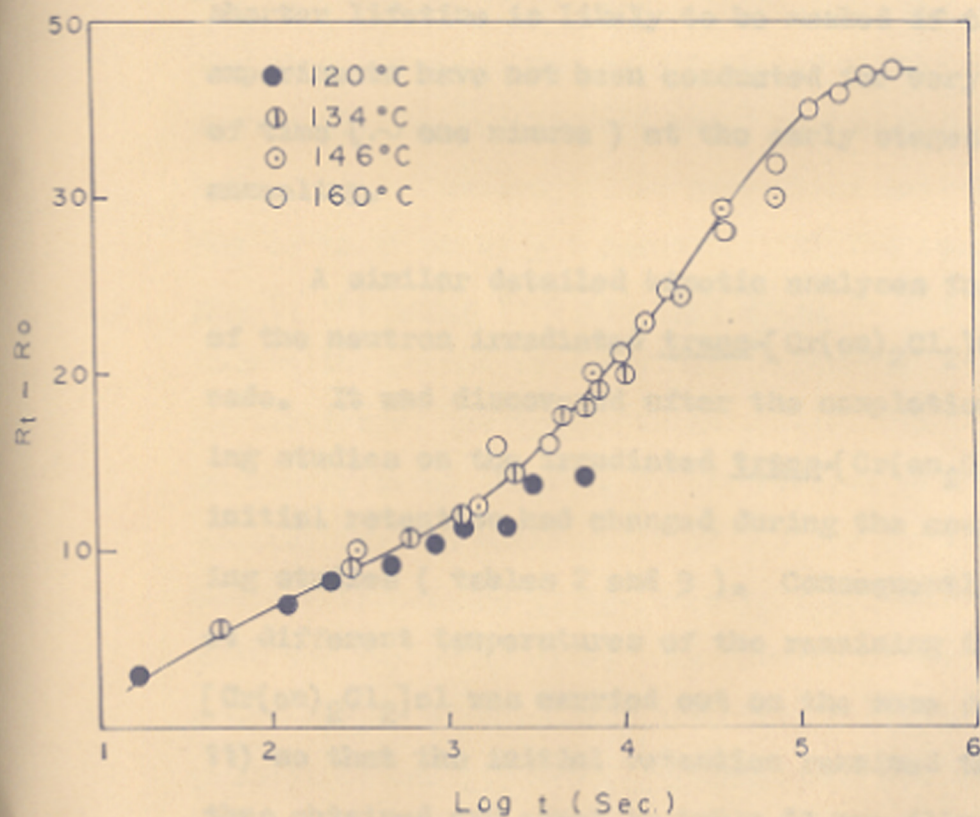


Fig. 15: Composite annealing curve obtained by adjusting the time scales for superposition of the curves of fig. (14) with respect to the curve at 146°C. The theoretical curve is shown by the solid line.

These may then be taken to represent the recombination reactions between three types of correlated pairs of fragments or three types of recoil sites. It may be remembered that in the earlier kinetic analyses (page 37) the experimental results could be explained on the basis of only two first-order reaction components. As pointed out earlier (p. 37) the graphical analyses particularly of the faster component is likely to be somewhat uncertain and a third component of much shorter lifetime is likely to be masked if the annealing experiments have not been conducted for very short intervals of time ($\sim$ one minute) at the early stages of isothermal annealing.

A similar detailed kinetic analyses for the annealing of the neutron irradiated trans-[Cr(en)₂Cl₂]Cl could not be made. It was discovered after the completion of the annealing studies on the irradiated trans-[Cr(en)₂Cl₂]Cl, that the initial retention had changed during the course of the annealing studies (tables 2 and 9). Consequently, the annealing at different temperatures of the remaining irradiated trans-[Cr(en)₂Cl₂]Cl was carried out on the same day (tables 10 and 11) so that the initial retention remained the same. The data thus obtained and given in table 11 are illustrated by plotting $R_{\infty} - R_t$ vs. time in fig. 12. This experimental curve can also be resolved into two first-order components as found for the irradiated cis-[Cr(en)₂Cl₂]Cl and hence the thermal annealing behaviours of both the irradiated geometrical isomers appear to be similar.

The results of our studies thus establish that there is a high degree of stereospecificity in the concurrent and postirradiation annealing reactions of the neutron-irradiated cis- and trans- $[\text{Cr}(\text{en})_2\text{Cl}_2]\text{Cl}$. The percentage activity associated with the isomeric form remains constant at $\sim 1\%$ for the cis (as compared to 62.6 % retention at the plateau) and $\sim 3\%$ for the trans complex (as compared to 53.5 % retention at the plateau) when annealed at temperatures upto 160°C . The observation of the small percentage of ^{51}Cr activity in the isomeric forms may be attributed to the following two causes (1) the results are based on low counting rates and hence the estimation of the percentage activity in these cases may be in error by ± 1 percent. (2) The isomerization of the cis to the trans form and vice versa in the aqueous solution during the period of analytical separation. The rate of isomerization of the trans- $[\text{Cr}(\text{en})_2\text{Cl}_2]\text{Cl}$ has been reported⁸¹ to be nearly twice the rate of the reverse reaction. This may account for the observation of ~ 3 per cent cis isomer in the neutron irradiated trans- $[\text{Cr}(\text{en})_2\text{Cl}_2]\text{Cl}$ as compared to ~ 1 per cent for the other case. The results of the analyses at different stages of annealing show that the percentage activity present as the cis and trans complexes and the Cr^{3+} does not remain constant and falls short of 100 indicating that some other unidentified species also take part in the reformation of the parent molecule. Hence the annealing does not involve a one step process. After the completion of the work presented in this thesis Garner and Coworkers⁷⁴ have reported the results of a similar study on the radiative neutron capture in cis and trans-dichloro-bis-ethylenediamine chromium(III) nitrates.

They have likewise observed that the original configuration of the stereoisomers is preserved during the annealing of the irradiated samples. The initial retention reported by them vary from 1.3 to 1.5 percent for both the geometric isomers. They attribute the low retention to a high nuclear efficiency for the rupture of the Cr-H and Cr-Cl bonds as compared to the Co-H and Co-Cl bonds. We have however observed initial retentions of 20 to 30 percent for both the cis and trans-[Cr(en)₂Cl₂]Cl. The significant differences between the values of the initial retentions found by us and those reported by Garner et al may be attributed to (1) the differences in the temperature of irradiation sites; their irradiations were done at -80° while our samples were exposed to neutrons at the reactor irradiation site temperature of ~ 40°C, (2) the differences in the quality of the irradiation beam viz. the concomitant fast neutron flux and the gamma-ray intensity which are known to bring about annealing during irradiation^{88,89}, (3) the effect of the ambient in which the irradiation is carried out.⁹⁰ Our irradiations were done in air, Garner et al⁷⁴ have irradiated their samples after sealing them in vacuum or nitrogen gas atmosphere, (4) the possible effect of the change in the nature of the anion, Saito et al.⁹¹ have studied in detail the effect of various anions on the radiative thermal neutron capture in Co(NH₃)₆³⁺ cation and have shown that the initial retentions varied from 3-5 % and 33-52 % when the anion was changed from chloride to nitrate. It is now generally agreed that unless irradiation conditions viz. temperature, cadmium ratio of the neutron beam, concomitant gamma-ray intensity etc are rigidly controlled any comparison of the initial retention in two

different irradiations has little significance.⁹² It has also been estimated that the inherent retentions may be as low as 2 per cent⁸⁵ and are unlikely to exceed 10 per cent.^{93,94} The initial retentions observed by us and many earlier workers, therefore include in addition to the inherent retention, contribution from the thermal and the radiation annealing during irradiation and thermal annealing during storage of the irradiated compounds. It is therefore not justified to speak of higher nuclear efficiency as indicated by Garner *et al*⁷⁴ unless the cobalt and chromium compounds are irradiated under identical conditions in the nuclear reactor. It may, here, be pointed out that Machado *et al*.⁹⁶ have recently reported equal retention (9.4 and 10.4 %) in neutron irradiated tris acetylacetonato cobalt (III) and chromium (III).

The stereospecific behaviour of the irradiated solids have been reported for only a few cobalt (III) complexes.^{2,8,9} The preservation of the original configuration of the stereoisomers in $^{50}\text{Cr}(n, \gamma) ^{51}\text{Cr}$ reaction (where the recoil energy is expected to be much higher than in the $^{59}\text{Co}(n, \gamma) ^{60}\text{Co}$ reaction⁹⁶) show that the phenomenon of stereospecificity may be common to compounds of different elements. Hence any model used to explain the chemical effects of nuclear transformations in solids should have provisions for explaining the observed isomeric specificity.

The earliest explanation for the stereospecific behaviour of the irradiated solids was given by Zuber³⁹ on the cavity complex model by assuming that in a (n, γ) reaction, the coordinated ligands preserve their original octahedral

skeleton structure with a cavity in the place of the metal atom ejected out due to the recoil. Maddock *et al.*⁸ have recently made use of the 'cavity complex' model to explain their results on the non-stereospecificity in radiative neutron capture reactions in cis-[Co(NH₃)₄(NO₂)₂]⁺ cation and attributed it to a low activation energy for the rearrangement of monodentate ligands to a more symmetric trans form. The higher activation energy required for the rearrangement involving polydentate ligands may lead to preservation of the original configuration.

The stereospecific behaviour of the irradiated solids cannot be explained on the hot zone model as originally put forward by Harbottle and Butin^{4,5} since it assumes a considerable amount of disorder in the hot zone, making it unlikely for a steric course of reaction to take place. However, if it is assumed that the process of recrystallisation as suggested by Zuber *et al.*² can take place during the cooling of the hot zone and subsequent annealing of the irradiated solids, then one can rationalise the observation of stereo-specificity on the hot zone model. The recrystallization into the original stereoisomeric form would be controlled by the configuration of undamaged crystalline matrix (around the hot zone) which acts as a template for the reformation of the parent isomeric form.

The 'variable-depth electron-trap isotopic-exchange model' recently put forward by Amar Nath *et al.*⁶ gives a very simple explanation for the stereospecific behaviour. On this model, the thermal annealing has been explained on the basis of

isotopic-exchange reactions in the solid state. It has been found^{6,97} that compounds which show a considerable isotopic exchange in the solid state, also give a high retention on thermal annealing and compounds which show no isotopic exchange in the solid state exhibit little thermal annealing. On the basis of this model, the stereospecificity in the Szilard-Chalmers reactions may be attributed to the absence of the isomeric form during irradiation or annealing. To test this assumption, the following two types of experiments were carried out: (1) Isotopic exchange in the solid state between $^{51}\text{Cr}^{3+}$ and the unirradiated cis- and trans- $[\text{Cr}(\text{en})_2\text{Cl}_2]\text{Cl}$. The complexes were doped with ^{51}Cr in two different ways, (a) A doping procedure similar to that used by Amar Nath et al.⁶ was adopted. 100 μCi of an aqueous solution of $^{51}\text{CrCl}_3$ (specific activity 88.8 C/g of Cr) was added to the solid unirradiated complex and the sample dried immediately in vacuum. It was then made homogeneous by grinding with an agate pestle and mortar, (b) 100 μCi of aqueous solution of $^{51}\text{CrCl}_3$ (specific activity 150 mc/g) was evaporated to dryness in an agate mortar and then mechanically mixed with the solid inactive complex to get a homogeneous mixture by grinding. The results of the experiments conducted according to the method of Amar Nath et al.⁶ are shown in table 13 and fig.16. It is apparent that both the cis- and trans- $[\text{Cr}(\text{en})_2\text{Cl}_2]\text{Cl}$ undergo considerable isotopic exchange in the solid state. The alternative doping method also gave similar results (Table 14.). The extent of isotopic exchange in this case was found to be comparatively smaller due to a lower specific activity of $^{51}\text{CrCl}_3$ used. (150 mc/g as compared to 88.8 C/g in the earlier method).

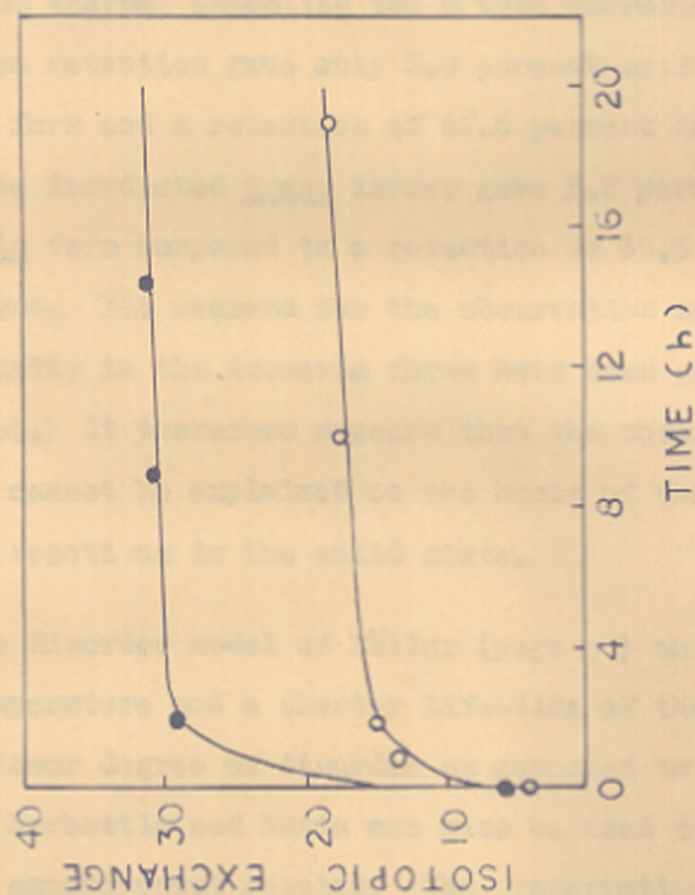


Fig. (16): Isotopic exchange of $\text{cis-[Cr(en)}_2\text{Cl}_2\text{]Cl}$ and of $\text{trans-[Cr(en)}_2\text{Cl}_2\text{]Cl}$ with $^{51}\text{Cr}^{3+}$ in the solid state at 160°C and 170°C respectively.

(2) Having thus established the occurrence of isotopic exchange in the solid state, annealing of a mixture of neutron irradiated cis-[Cr(en)₂Cl₂]Cl with the trans carrier in the ratio 5:3 and a mixture of irradiated trans-[Cr(en)₂Cl₂]Cl with the cis carrier in the ratio 1:2 were carried out. These mixtures were prepared mechanically by grinding as described in 1(b) above. The neutron irradiated cis-[Cr(en)₂Cl₂]Cl on subsequent thermal annealing for a time corresponding to the saturation retention gave only 2.0 percent activity in the isomeric form and a retention of 62.6 percent in the parent form. The irradiated trans isomer gave 3.2 percent activity in the cis form compared to a retention of 55.5 percent in the parent form. The reasons for the observation of 2-3 percent ⁵¹Cr activity in the isomeric forms have been given earlier (see page 44). It therefore appears that the observed stereospecificity cannot be explained on the basis of the isotopic exchange reactions in the solid state.

The disorder model of Müller (page 17) which assumes lower temperature and a shorter life-time of the hot-zone and hence a lower degree of disorder as compared to the hot-zone model of Harbottle and Sutin can also be used to explain the observed experimental results. The preservation of the original configuration may be attributed to a small disorder created at the recoil site in our compounds. Recently Wolf⁷² has reported significant ⁵⁸Co activity in the isomeric form in the (n, 2n) reaction in the cis- and trans-[Co(en)₂Cl₂](NO₃). The nonstereospecificity in this case may be attributed to a

higher degree of disorder on account of greater recoil energy of ^{58}Co in $\text{Co}^{59} (n, 2n) \text{Co}^{58}$ reaction as compared to that in $\text{Co}^{59} (n, \gamma) \text{Co}^{60}$ or $\text{Cr}^{50} (n, \gamma) \text{Cr}^{51}$ reactions.

APPENDIX

Table No. 2

The percentage activity present as Cr^{3+} , cis- and Trans- $[\text{Cr}(\text{en})_2\text{Cl}_2]\text{Cl}$ in different neutron irradiations of the geometric isomers of $[\text{Cr}(\text{en})_2\text{Cl}_2]\text{Cl}$.

Irradiation	Date of irradiation	Period of irradiation	Neutron flux Reactor	Compound irradiated	Date of analysis	Initial retention (parent form) (%)	Initial activity as the isomeric form (%)	Initial activity as Cr^{3+} (%)
1	18.11.65	15 min.	$10^{13} \text{ n/cm}^2/\text{sec}$	Cis- $[\text{Cr}(\text{en})_2\text{Cl}_2]\text{Cl}$	16-1-65	25.9 ± 0.4	1.0**	-
				Trans- $[\text{Cr}(\text{en})_2\text{Cl}_2]\text{Cl}$	18-11-65	30.2 ± 0.3	2.0	
2	24. 5.66	2 hrs	$1.2 \times 10^{12} \text{ n/cm}^2/\text{sec}$ Apsara	Cis- $[\text{Cr}(\text{en})_2\text{Cl}_2]\text{Cl}$	27- 6-66	29.5 ± 0.3	1.0	35.8 ± 0.3
				Trans- $[\text{Cr}(\text{en})_2\text{Cl}_2]\text{Cl}$	15- 6-66	30.6 ± 0.2	3.2 ± 0.3	37.4 ± 0.4
3	7.11.66	"	$1.2 \times 10^{12} \text{ n/cm}^2/\text{sec}$ Apsara	Cis- $[\text{Cr}(\text{en})_2\text{Cl}_2]\text{Cl}$	25- 1-67	28.2 ± 0.4	0.9 ± 0.2	-
				Trans- $[\text{Cr}(\text{en})_2\text{Cl}_2]\text{Cl}$	26-11-66	19.1 ± 0.4	5.2	32.6 ± 0.3
					23-12-66	26.3 ± 0.1	-	-
4	14. 3.67	"	"	Cis- $[\text{Cr}(\text{en})_2\text{Cl}_2]\text{Cl}$	24- 3-67	20.7 ± 0.3	0.5	32.3 ± 0.3
				Trans- $[\text{Cr}(\text{en})_2\text{Cl}_2]\text{Cl}$	27- 4-67	25.5 ± 0.1		
					21- 5-67	19.1 ± 0.2	2.9	27.2 ± 0.2

* Average of three analysis

** Average of two analysis.

Table No. 3

The effect of annealing at 120°C of neutron irradiated $\text{cis-}[\text{Cr(en)}_2\text{Cl}_2]\text{Cl}$ on the distribution of ^{51}Cr activity in different recoil products viz. Cr^{3+} , cis- and $\text{trans-}[\text{Cr(en)}_2\text{Cl}_2]\text{Cl}$.

Irradiation No. 4

Date of annealing	Duration of annealing	Activity as $\text{cis-}[\text{Cr(en)}_2\text{Cl}_2]\text{Cl}$ (Retention) (%) [*]	Activity as Cr^{3+} (%) [*]	Activity as $\text{trans-}[\text{Cr(en)}_2\text{Cl}_2]\text{Cl}$ (%)	Activity as unidentified species (%) ⁺⁺
24-3-67	-	22.7 ± 0.3	32.3 ± 0.3	0.5	44.3
24-3-67	5 min.	25.8 ± 0.2	25.1 ± 0.2	-	48.4
29-3-67	30 min.	29.4 ± 0.2	22.7 ± 0.1	0.7	47.2
3-4-67	1 hr.	31.0 ± 0.3	23.8 ± 0.4	-	44.5
27-3-67	2 hrs.	31.8 ± 0.2	23.5 ± 0.5	1.0	44.0
29-3-67	4 hrs.	32.5 ± 0.1	22.7 ± 0.2	-	44.1
29-3-67	6 hrs.	33.0 ± 0.1	21.9 ± 0.3	-	44.4
5-4-67	10 hrs.	33.9 ± 0.3	22.4 ± 0.3	0.5	43.0
3-4-67	14 hrs.	36.1 ± 0.2	22.2 ± 0.2	-	41.0
5-4-67	24 hrs.	36.3 ± 0.1	-	-	-
27-3-67	71 hrs. 20 min.	37.2 ± 0.2	20.9 ± 0.1	0.9	41.2
4-4-67	97 hrs.	37.1 ± 0.2	-	-	-
				Mean	0.7 ± 0.3

* Average of two analyses.

++ Obtained after subtracting from 100 the percentage activity in Cr^{3+} , $\text{cis-}[\text{Cr(en)}_2\text{Cl}_2]\text{Cl}$ and an average of 0.7% in trans isomer.

Table No.4

The effect of annealing at 134°C of the neutron irradiated $\text{Cis-[Cr(en)}_2\text{Cl}_2\text{]Cl}$ on the percentage activity in the parent and the isomeric forms of the complex.

Irradiation No.4

Date of annealing	Duration of annealing	Activity as $\text{Cis-[Cr(en)}_2\text{Cl}_2\text{]Cl}$ (Retention) % **	Activity as $\text{trans-[Cr(en)}_2\text{Cl}_2\text{]Cl}$ %
27-4-67	-	25.5 $\pm$ 0.1	0.5
"	5 min	31.6 $\pm$ 0.3	-
"	30 min	34.9 $\pm$ 0.2	0.6
"	1 hr	36.3 $\pm$ 0.3	-
"	2 hr	37.8 $\pm$ 0.1	0.7
"	4 hr	40.2 $\pm$ 0.1	-
"	6 hr 30 min.	41.7 $\pm$ 0.1	0.8
"	8 hr	42.9 $\pm$ 0.1	0.9
"	10 hr	43.2 $\pm$ 0.2	0.6
"	15 hr	44.5 $\pm$ 0.2	-
"	30 hr	45.4 $\pm$ 0.2	-
"	95 hr 30 min	46.9 $\pm$ 0.1	1.1
			Mean 0.7 $\pm$ 0.3

** Average of two analyses.

The effect of annealing at 146°C of neutron irradiated cis-Cr(en)₂Cl₂ Cl on the distribution of ⁵¹Cr activity in different recoil products viz. Cr³⁺, cis- and trans-Cr(en)₂Cl₂ Cl.

Irradiation No.4

Date of annealing	Duration of annealing	Activity as <u>cis</u> -Cr(en) ₂ Cl ₂ Cl (Retention) (%) [*]	Activity as Cr ³⁺ (%)	Activity as <u>trans</u> -Cr(en) ₂ Cl ₂ Cl (%)	Activity as unidentified species (%) ⁺⁺
24-3-67	-	22.7 ± 0.3	32.3 ± 0.3 [*]	0.5	44.3
22-4-67	-	24.7 ± 0.2	-	-	-
5-4-67	5 min.	32.2 ± 0.1	19.4	0.9	47.7
5-4-67	30 min.	35.2 ± 0.1	20.3	-	43.8
5-4-67	1 hr.	38.6 ± 0.6	19.0	0.8	41.7
5-4-67	2 hrs.	42.7 ± 0.2	19.2	-	37.4
5-4-67	4 hrs.	45.8 ± 0.1	17.6	-	35.9
5-4-67	6 hrs.	47.3 ± 0.2	16.3	0.9	35.7
5-4-67	23 min.				
5-4-67	10 hrs.	50.7 ± 0.2	16.3	0.5	32.3
5-4-67	16 hrs.	52.3 ± 0.5	15.9	-	31.1
5-4-67	7 min.				
5-4-67	24 hrs.	52.6 ± 1.1	-	-	-
5-4-67	45 min.				
5-4-67	87 hrs.	53.5 ± 0.1	14.0	0.8	32.5
5-4-67	15 min.				
				Mean	0.7 ± 0.3

* Average of two analyses.

++ Obtained after subtracting from 100 the percentage activity in Cr³⁺, cis-Cr(en)₂Cl₂ Cl and an average of 0.7 % in trans isomer.

Table No.6

The effect of annealing at 160°C of the neutron irradiated $\text{Cis-[Cr(en)}_2\text{Cl}_2\text{]Cl}$ on the percentage activity in the parent and the isomeric terms of the complex.

Irradiation No.4

Date of annealing	Duration of annealing	Activity as $\text{Cis-[Cr(en)}_2\text{Cl}_2\text{]Cl}$ (Retention) % **	Activity as $\text{trans-[Cr(en)}_2\text{Cl}_2\text{]Cl}$ %
27-4-67	-	25.5 $\pm$ 0.1	0.5
4-5-67	5 min	41.7 $\pm$ 0.3	-
"	30 min	46.6 $\pm$ 0.3	1.0
"	1 hr	50.2 $\pm$ 0.3	-
"	2 hr	53.5 $\pm$ 0.1	0.6
"	4 hr	58.1 $\pm$ 0.2	-
"	6 hr	60.8 $\pm$ 0.4	0.3
"	8 hr	61.3 $\pm$ 0.5	1.0
"	12 hr	62.3 $\pm$ 0.2	-
"	18 hr 8 min	62.0 $\pm$ 0.2	1.0
"	98 hr 8 min	62.6 $\pm$ 0.2	0.7
			Mean 0.7 $\pm$ 0.3

** Average of two analysis.

Table No.7

The effect of annealing of the neutron irradiated
 $\text{Cis}=[\text{Cr(en)}_2\text{Cl}_2]\text{Cl}$ on the retention and the
 percentage activity in the isomeric form.

Irradiation No.4

Date of annealing	Temp. (°C)	Duration of annealing	Retention Cis- [Cr(en) ₂ Cl ₂]Cl % **	Activity as trans- [Cr(en) ₂ Cl ₂]Cl %
24-3-67	-	-	22.7 ± 0.3 (Initial retention)	0.5
27-3-67	120	- 30 min	29.4 ± 0.2	0.7
5-4-67	120	2 hr -	31.8 ± 0.2	1.0
27-3-67	120	10 hr -	33.9 ± 0.3	0.5
27-4-67	134	- 30 min	34.9 ± 0.2	0.6
27-4-67	134	6 hr 10 min	41.7 ± 0.1	0.9
27-4-67	134	10 hr -	43.2 ± 0.2	0.6
5-4-67	146	6 hr 23 min	47.3 ± 0.2	0.9
6-4-67	146	10 hr -	50.7 ± 0.2	0.5
5-4-67	146	87 hr 15 min	53.5 ± 0.1	0.8
7-6-67	160	4 hr -	58.1 ± 0.2	0.6
21-5-67	160	6 hr -	60.8 ± 0.4	0.3
21-5-67	160	98 hr	62.6 ± 0.2	0.7
				Average 0.7 ± 0.3

** Average of two analyses.

Table No. 8

The effect of annealing of the neutron irradiated
trans-[Cr(en)₂Cl₂]Cl on the retention and the
percentage activity in the isomeric form.

Irradiation No. 3

Date of annealing	Temp. (°C)	Duration of annealing	Retention/ Trans- [Cr(en) ₂ Cl ₂]Cl % **	Activity as cis- [Cr(en) ₂ Cl ₂]Cl %
25-11-66	-	-	19.1 ± 0.4 (Initial retention)	3.0
29-11-66	100	10 hr	33.2 ± 0.1	2.6
29-11-66	100	20 hr	34.4 ± 0.1	3.2
8-12-66	140	2 hr	40.8 ± 0.1	2.2
9-12-66	140	11 hr	42.9 ± 0.6	2.2
26-12-66	170	20 min	47.5 ± 0.1	2.7
26-12-66	170	2 hr	52.8 ± 0.1	2.6
26-12-66	170	26 hr	53.2 ± 0.2	3.2

** Average of two analyses.

Table No. 9

Results of annealing studies on neutron irradiated
trans-[Cr(en)₂Cl₂]Cl at 100°C and 140°C

Irradiation No. 3

		Temperature of annealing			
		100°C	140°C		
Date of annealing	Duration of annealing	Activity as trans-[Cr(en) ₂ Cl ₂]Cl (Retention) (%) [*]	Date of annealing	Duration of annealing	Activity as trans-[Cr(en) ₂ Cl ₂]Cl (Retention) (%) [*]
25-11-66	-	19.1 ± 0.4	25-11-66	-	19.1 ± 0.4
6-12-66	30 min.	27.4 ± 0.1	23-12-66	10 min.	36.3 ± 0.1
5-12-66	2 hrs. 5 min.	32.8 ± 0.3	20-12-66	30 min.	38.0 ± 0.1
29-11-66	10 hrs.	33.2 ± 0.1	8-12-66	2 hrs.	40.8 ± 0.1
29-11-66	20 hrs.	34.4 ± 0.1	9-12-66	11 hrs.	42.9 ± 0.6
23-12-66	-	26.3 ± 0.1	15-12-66	20 hrs.	43.5 ± 0.4
			23-12-66	-	26.3 ± 0.1

* Average of two analyses.

Table No. 10

The effect of annealing at 170°C of neutron irradiated $\text{trans-[Cr(en)}_2\text{Cl}_2\text{]Cl}$ on the distribution of ^{51}Cr activity in different recoil products viz. Cr^{3+} , trans- and $\text{cis- Cr(en)}_2\text{Cl}_2$ Cl.

Irradiation No.3

Date of annealing	Duration of annealing	Activity as $\text{trans-[Cr(en)}_2\text{Cl}_2\text{]Cl}$ (Retention) (%) [*]	Activity as Cr^{3+} (%) [*]	Activity as $\text{cis-[Cr(en)}_2\text{Cl}_2\text{]Cl}$ (%)	Activity as unidentified species (%) ⁺⁺
26-12-66	-	26.3 ± 0.1	-	-	-
29-12-66	-	26.3 ± 0.1	32.6 ± 0.2	3.1	38.2
26-12-66	5 min.	43.4 ± 0.1	21.6 ± 0.1	-	32.1
26-12-66	10 min.	45.4 ± 0.4	19.9 ± 0.8	-	31.8
26-12-66	20 min.	47.5 ± 0.1	20.0 ± 0.3	2.7	29.6
26-12-66	45 min.	50.4 ± 0.1	18.3 ± 0.3	2.7	28.4
3-1-67	1 hr.	52.3 ± 0.3	18.8 ± 0.3	-	26.0
26-12-66	2 hrs.	52.8 ± 0.1	20.1 ± 0.1	2.6	24.2
26-12-66	26 hrs.	53.2 ± 0.2	17.7 ± 0.6	3.2	26.2
				Mean	2.9 ± 0.3

* Average of two analyses.

++ Obtained after subtracting from 100 the percentage activity in Cr^{3+} , $\text{trans- Cr(en)}_2\text{Cl}_2$ Cl and an average of 2.9 % in cis isomer.

Table No. 11

The effect of annealing at 160°C of neutron irradiated trans-[Cr(en)₂Cl₂]Cl on the distribution of ⁵¹Cr activity in different recoil products viz. Cr³⁺, trans- and cis- Cr(en)₂Cl₂ Cl.

Irradiation No.4

Date of annealing	Duration of annealing	Activity as <u>trans</u> -[Cr(en) ₂ Cl ₂]Cl (Retention) (%)	Activity as Cr ³⁺ (%)	Activity as <u>cis</u> -[Cr(en) ₂ Cl ₂]Cl (%)	Activity as unidentified species (%)++
21-5-67	-	19.1 ± 0.2*	27.2 ± 0.3*	2.9	50.8
"	5 min.	43.3 ± 0.3*	23.8	2.3	30.6
"	30 min.	46.4	22.2	2.7	28.7
"	1 hr.	47.4	21.2	2.7	28.7
"	2 hrs.	48.2	22.6	2.0	27.2
"	4 hrs.	48.7	22.8	2.2	26.3
"	6 hrs.	49.8	22.5	2.1	25.6
"	8 hrs.	50.5	22.2	2.2	25.1
"	11 hrs. 20 min.	51.4	21.5	2.1	25.0
"	43 hrs. 40 min.	52.8	-	2.4	-
"	96 hrs.	53.5 ± 0.2*	20.9	2.8	22.8
Mean				2.4 ± 0.5	

* Average of two analyses.

++ Obtained after subtracting from 100 the percentage activity in Cr³⁺, trans- and cis- Cr(en)₂Cl₂ Cl forms.

Table No. 12

Kinetic Analysis of the isothermal annealing curves of $\text{Cr(en)}_2\text{Cl}_2\text{Cl}$

Temp (°C)	Slow Component				Fast Component		
	R (%)	$(R_\infty - R_0)\%$	$(t_2)^{1/2}$	$k_2 \times 10^5$ sec ⁻¹	$(R_\infty - R_0)$	$(t_1)^{1/2}$	$k_1 \times 10^4$ sec ⁻¹
120	37.2	5.8	12.4 hr	1.55	8.7	22 min	5.17
134	46.9	9.6	7.4 hr	2.60	11.8	28 min	4.04
146	53.5	14.0	4.5 hr	4.24	16.8	21 min	5.50
160	62.6	17.0	2.0 hr	9.37	20.1	14 min	8.2

Table No.13

Isotopic exchange in solid state between $^{51}\text{Cr}^{3+}$
 and the $[\text{Cr}(\text{en})_2\text{Cl}_2]\text{Cl}$ complex.
 (Sp. activity used 88 c/gm)

Complex	Temp.	Time	Percent exchange

Cis- $[\text{Cr}(\text{en})_2\text{Cl}_2]\text{Cl}$	160°C	-	6.0
		2 h	29.4
		9 h	30.0
		14.5 h	31.0
Trans- $[\text{Cr}(\text{en})_2\text{Cl}_2]\text{Cl}$	170°C	-	5.4
		1 h	13.4
		2 h	15.2
		10 h	17.5
		19 h	18.0
		63 h	18.3

Table No.14

Isotopic exchange in solid state between Cr^{3+}
 and the $[\text{Cr}(\text{en})_2\text{Cl}_2]\text{Cl}$ complex
 (Sp. activity used : 150 mc/gm)

Complex	Temperature	Time	Percent exchange

Cis- $[\text{Cr}(\text{en})_2\text{Cl}_2]\text{Cl}$	160°C	-	1.8
		1 hr	4.7
		14 hr	6.9
Trans- $[\text{Cr}(\text{en})_2\text{Cl}_2]\text{Cl}$	170°C	-	2.0
		1 hr	4.0
		23 hr	5.4

REFERENCES

1. A.G.Maddock, Introductory Lecture, Chemical effects of nuclear transformations. (Proceedings series), 1, IAEA, Vienna, (1961).
2. A.V.Zuber, H.S.Rauscher, J.M.Miller and H.Sutin, Chemical effects of nuclear transformations (Proceedings series) 1, 358, IAEA, Vienna (1961).
3. W.F.Libby, J. Amer. Chem. Soc., 62, 1930 (1940).
4. G.Harbottle and H.Sutin, Advances in Inorganic Chemistry and Radiochemistry (Ed. Smeleus and Sharpe). Academic Press, 1, 267 (1959).
5. G.Harbottle and H.Sutin, J.Phys.Chem., 62, 1344 (1958).
6. Amer Rath, S.Zhorana, I.K.Mathur and S.Serup, Indian J. Chem., 4, 51, (1966).
7. H.Müller Angewandte Chemie, 6, 133 (1967).
8. A.G.Maddock, A.B.J.B.Todesco and (in part) D.Blaxell, Chemical Effects of nuclear transformations (Proceedings series), 2, 337, IAEA, Vienna (1965).
9. K.Saito, H.Seno, T.Tominaga, F.Ambe and T.Fujino, Bull. Chem. Soc. Japan, 35, 744 (1962).
10. J.H.Green, G.Harbottle and A.G.Maddock, Trans.Far.Soc., 49, 1413 (1953).
11. J.Shenker, V.G.Thomas and A.Rath, Chemical Effects of Nuclear Transformations (Proceedings series), 1, 383 IAEA, Vienna, (1961).
12. K.Heine and W.Herr, Chemical Effects of nuclear transformations (Proceedings series), 1, 343, IAEA, Vienna, (1961).

13. G.E.Wertheim, Mossbauer Effect, Principles and Applications, Academic Press, New York (1964).
14. V.I.Goldensky, The Mossbauer Effect and its application in Chemistry, Consultants Bureau, New York, (1964).
15. L.R.Walker, G.E.Wertheim, V.Jaccarino, Phys.Rev.Let., 6, 98 (1961).
16. J.Dannon, J.Chem.Phys., 39, 236(1963), Notas Fis. 10, 331(1963).
17. U.Gonser and H.Wiedersich, J.Phys.Soc. Japan, 18 (Supplement II) 47, (1963).
18. A.A.Murin, K.V.Bogdanov and S.N.Tomilov, Russian Chemical Reviews, (English translation) 33, 295 (1964).
19. G.Harbottle, Annual review of Nuclear Science (Ed.E.Segre), Annual Reviews, 15, 89 (1965).
20. Chemical Effect of Nuclear transformations, Proceedings of the symposium Prague, October 24-27, 1960 (IAEA, Vienna, 2 Vols, 1961).
21. Proceedings of the symposium on chemical effects of nuclear transformations, Vienna, December 7-11, 1964 (IAEA, 2 Vols. 1965).
22. L.Szilard and T.A.Chalmers, Nature, 134, 462 (1934).
23. E.Amaldi, O.D.Agastino, E.Fermi, B. Pontecorvo, F.Rosatti and E.Segre, Proc. Roy. Soc. (London), A149, 522 (1935).
24. R.R.Williams, J. Phys. and Colloid Chem., 52, 603, (1949).
25. J.H.Green and A.J.Maddock, Nature, 164, 788 (1949)
26. W.Rider, E.Broda and J.Erber, Monatsch Chem., 81, 657 (1950).
27. J.W.Cobble and G.E.Boyd, J.Am.Chem.Soc., 74, 1282 (1952)

28. J.H.Green, G.Harbottle and A.G.Maddock, Trans. Faraday Soc., 49, 1413 (1953).
29. M.M.deMaine, A.G.Maddock and K.Taugbol, Discussions Faraday Soc., 23, 211 (1957).
30. A.G.Maddock and M.M. deMaine, Can.J.Chem., 34, 275 (1956).
31. R.F.Mott, Trans. Faraday Soc., 43, 429 (1947).
32. A.Sutin and R.W.Dodson, J.Inorg. and Nuclear Chem., 6, 91 (1958).
33. H.Ikeda, K.Yoshihara and S.Yamagishi, Radiochim Acta, 2, 13 (1964)
34. D.J.Apers and A.J.Maddock, Trans. Faraday Soc., 56, 498 (1960)
35. H.Rauscher and G.Harbottle, J. Inorg. Nucl. Chem., 4, 155, (1957).
36. A.G.Maddock, F.S.Treloar and J.I.Vargas, Trans.Far.Soc., 59, 924 (1963).
37. R.L.Brown, R.C.Fletcher and S.Machlup, Phy. Rev., 90, 709, (1953).
38. Discussions, Chemical Effects of Nuclear Transformations (Proceedings series) 1, 373, IAEA, Vienna (1961)
39. A.V.Zuber, Dissertation, Ph.D., Columbia University (1954), USABC, Document NYO-6142 BNL.
40. D.J.Apers and P.C.Capron, Chemical Effects of Nuclear transformations (Proceedings series), 1, 429, IAEA, Vienna, (1961).
41. F.Seitz and J.S.Kohler, Solid State Physics, Vol.2, p.307-448 Academic Press, (1956).

42. J.Shanker, K.S.Venkateswarlu and Amar Nath, Chemical Effects of Nuclear Transformations (Proceedings Series), 1, 309, IAEA, Vienna, (1961).
43. J.Shanker, V.G.Thomas and A.Nath, Chemical Effects of Nuclear Transformations (Proceedings series) 1, 383 IAEA, Vienna, (1961).
44. Amar Nath, Chemical Effects of Nuclear transformations, (Proceedings series), 1, 335, IAEA, Vienna, (1961).
45. L.Lindner and G.Harbottle, Chemical Effects of Nuclear transformations (Proceedings series), 1, 485, IAEA, Vienna, (1961).
46. K.Yoshihara and H.Ebihara, J.Chem.Phys., 45, 896 (1966)
47. A.H.W.Aten Jr., G.K.Koch, G.A.Vessalink and A.M.De Roos, J. Amer. Chem. Soc., 79, 63 (1957).
48. V.Vand, Proc. Phys. Soc. (London), 55, 222 (1943).
49. W.Primak and H.Szymanski, Phys. Rev., 101, 1268 (1956).
50. J.Shanker and M.Lal., J.Inorg.Nucl.Chem., 27, 2507 (1965).
51. T.Costea, J.Inorg.Nucl.Chem., 19, 27 (1961).
52. D.K.Holmes, Chemical Effects of Nuclear transformations (Proceedings series), 1, 449, IAEA, Vienna, 1961.
53. Discussion F5, Chemical Effects of Nuclear Transformations, 1, 463, IAEA, Vienna, (1961).
54. A.G.Maddock and R.M.Mirsky, Chemical Effects of Nuclear Transformations (Proceedings series), 2, 41, IAEA, Vienna (1965).
55. R.Caillat and P.Sue, C.R.Acad.Sci., Paris, 230, 1666, (1950), 230, 1864 (1950).

56. K.Yoshihara and G.Harbottle, *Radiochimica Acta*, 1, 68 (1963)
57. D.J.Apers, K.E.Collins, C.H.Collins, Y.F.Ghoos and P.C.Gapron, *Radiochim. Acta*, 2, 18 (1964).
58. C.H.Collins, K.E.Collins, Y.F.Ghoos and D.J.Apers, *Radiochim. Acta*, 4, 211 (1965).
59. A.G.Maddock and T.Anderson, *Chemical Effects of Nuclear transformations (Proceedings series)*, 2, 277, IAEA, Vienna, (1965).
60. S.Kaucic and M.Vlatkovic, *Croet. Chem. Acta*, 32, 305 (1963).
61. J.Shankar, Amer Nath and S.P.Vaish, *Radiochimica Acta*, 4, 162 (1965).
62. Amer Nath, K.Annaji Rao and V.G.Thomas, *Indian J. Chem.*, 2, 331 (1964).
63. J.B.Gibson, A.H.Goland, M.Milgram and G.H.Vineyard, *Phys. Rev.*, 120, 1229 (1960)
64. G.H.Vineyard, *Discussions Faraday Soc.*, 31, 7 (1961)
65. R.H.Silsbee, *J.Appl. Phys.*, 28, 1246 (1957).
66. G.Liebfried, *J.Appl.Phys.*, 30, 1388 (1959).
67. *Chemical Effects of Nuclear Transformations (Proceedings Series)*, 2, 173, IAEA, Vienna, (1965).
68. T.Costea, I.Dema and A.Tiplinice, *Stud Cercet Chimie*, 9, 533 (1961).
69. H.E.Rauscher, Thesis, Faculty of Pure Science, Columbia University, New York (1960).
70. H.E.Rauscher, B.Sutin and N.Miller, *J.Inorg. & Nucl. Chem.*, 17, 31, (1961).
71. P.Dimitakis and A.G.Maddock, *Chemical Effects of Nuclear transformations (Proceedings series)*, 1, 365, IAEA, Vienna, (1961).

72. G.K. Wolf, *Radiochimica Acta*, 6, 39 (1966).
73. N. Saito, T. Teminaga and H. Sano, *Bull. Chem. Soc., Japan*
33, 1621 (1960)
74. Robert I-San Lin, A.S. Lefohn and C.S. Garner, *J. Inorg.*
and Nucl. Chem., 29, 1553 (1967).
75. G.L. Rollinson and J.C. Bailar Jr., *Inorganic Synthesis*,
(Ed. W.C. Fernelius). Vol. 2, p. 200, McGraw-Hill Book Co.
(1946).
76. G.L. Rollinson and J.C. Bailar, Jr., *J. Amer. Chem. Soc.*,
65, 250 (1943).
77. Pfeiffer, *Ber.*, 37, 4282 (1904).
78. Gert G. Schlesinger, *Inorganic Preparations*, p. 222,
Chemical Publishing Company, New York (1962).
79. Martin Linhard and Melitta Weigl., *Z. Phys. Chem.*, 5, 20 (1955).
80. C.S. Garner and J. McDonald, *J. Amer. Chem. Soc.*, 83, 4152 (1961).
81. Clifford S. Garner, 'Advances in the Chemistry of the
Coordination Compounds' Ed. S. Kirschner, p. 269,
Macmillan and Co., New York (1961).
82. J. Shankar and R. Shankar, *Journal of the University of Bombay*,
29, 63 (1961).
83. J. Costea and I. Dama, *Nature*, 189, 478 (1961).
84. A. Nath and S.B. Srivastava, *J. Inorg. Nucl. Chem.*, 7, 143 (1950).
85. J. Shankar, K.S. Venkateswarlu and M. Lal., *Chemical Effects*
of nuclear transformations (Proceedings series), 1, 417
IAEA, Vienna, (1961).
86. Discussion F2, *Chemical Effects of nuclear transformations*,
(*Proceedings series*), 1, 373, IAEA, Vienna (1961).

87. R.C.Fletcher and W.L.Brown, *Phys. Rev.*, 92, 585 (1953);
R.C.Fletcher, W.L.Brown and K.A.Wright, *ibid*, 92, 591 (1953).
88. A.Costea, *J. Inorg. Nucl. Chem.*, 17, 20 (1961).
89. T.Matzura, *J. Inorg. Nucl. Chem.*, 28, 313 (1966).
90. S.Sarup and Amar Nath, *J. Inorg. Nucl. Chem.*, 29, 299 (1967).
91. K.Saito, T.Tomonga and H.Sano, *Bull. Chem.Soc., Japan*,
35, 365 (1962).
92. N.Shankar, K.S.Venkateswarlu and M.Lal, *Radiochimica Acta*,
4, 52 (1965).
93. K.J.McCallum and A.G.Maddock, *Trans.Far.Soc.*, 49, 1150
(1953).
94. A.G.Maddock and J.I.Vargas, *Trans.Far.Soc.*, 57, 992 (1961).
95. J.C.Machado, R.M.Machado and J.I.Vargas, *Chemical Effects
of nuclear transformations (Proceedings series)*, 2, 195
IAEA, Vienna (1965).
96. Dag Brune, *Acta Chimica Scandinavica*, 21, 2087 (1967).
97. J.Shankar, Amar Nath and M.H.Rao, *Radiochimica Acta*, 2,
26, (1964).

PART - II: THE CHEMICAL EFFECTS OF ELECTRON CAPTURE
DECAY OF ^{57}Co IN DIFFERENT COBALT COMPOUNDS

CHAPTER - 1 : INTRODUCTION

C H A P T E R - II N T R O D U C T I O N

The discovery of recoil-free emission and absorption of gamma-rays by Mossbauer¹ has led to significant developments in different fields of investigation. The 'Mossbauer Effect' studies have been used for solving diverse problems, such as measurement of gravitational red-shift,² determination of isomeric life-times,³ estimation of nuclear moments,^{4,5} quadrupole and Zeeman splittings,^{6,7} studies on the nature of the chemical bonding⁸ and the chemical effects of nuclear transformations in solids.⁹⁻¹³ The present study pertains to some aspects of the last mentioned area of investigation. Earlier studies on the chemical effects of nuclear transformations in solids have invariably been done by solution chemistry^{14,15} and hence one cannot be sure of the nature of the metastable species originally present in the irradiated solids since they are likely to be converted into forms stable in solution by chemical reactions such as oxidation, reduction and hydration (page 6). With the aid of the Mossbauer Effect, one can in suitable systems, obtain information on the nature of the metastable species present for a time longer than the Mossbauer transition time (10^{-7} sec. for ^{57}Fe and 10^{-8} for ^{119}Sn). The present investigation deals with a study of the chemical states of iron formed as a result of Auger processes following the electron capture decay of 257-day cobalt-57 in several cobalt compounds,

viz. $K^{57}\text{CoF}_3$, $^{57}\text{CoCr}_2\text{O}_4$, $^{57}\text{CoCr}_2\text{S}_4$ and $^{57}\text{Co}(\text{1-10 phenanthroline})_3(\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}$. In order that the results reported in these investigations can be meaningfully discussed in brief description of the significance of the Mossbauer's discovery and the nature of information one can derive from the Mossbauer spectrum are given below. A detailed discussion of the theory of the Mossbauer effect and its applications has not been given since this information is now available in several recent reviews and publications.¹⁶⁻¹⁹

Although the phenomenon of resonance in acoustics, optics and electricity has been known for quite some time, for the electromagnetic radiations ^{like X-rays} it was observed for the first time by Moon²⁰ in 1950. But it was only after the work of Mossbauer in 1958 that the resonance emission and absorption of gamma rays could be demonstrated with a great ease and clarity.

Nuclear Recoil and Resonance

The excited state of a nucleus is characterized both by its excitation energy (E_T) and by its natural line-width (Γ). The line-width of the excited state is related to its life-time by the Heisenberg's uncertainty principle, viz.

$$\Gamma \cdot \tau = h / 2\pi = 1.05 \times 10^{-27} \text{ erg. sec.} \quad (1)$$

where h is the Planck's constant and τ is the average life-time of the excited state and is given by $t_{1/2} / \ln 2$ where $t_{1/2}$ is the half life of the excited state.

When an isolated nucleus of mass 'm' emits a gamma-ray of energy E' , the recoil-energy R is given by the relationship,

$$R = \frac{1}{2} mv^2 = \frac{p^2}{2m} = \frac{E'^2}{2mc^2} = \frac{E_T^2}{2mc^2} \quad (2)$$

where 'c' is the velocity of light and 'v' and 'p' are the recoil velocity and recoil momentum respectively, since $R \ll E$ and $E' \simeq E_T$. The computed values of the natural line-widths and the recoil energies for different energy transitions in the visible and low-energy gamma-ray region are compared in Table 1.

Since the recoil loss is involved both in the emission and the absorption processes, the maxima of the emitted and absorbed gamma-ray (E' and E'' respectively) are separated by twice the recoil energy (Fig. 1).

$$E_T = E' + R \quad (3)$$

$$E_T = E'' - R \quad (4)$$

$$E'' - E' = 2R \quad (5)$$

The nucleus like atoms and molecules is in constant thermal motion, which results in the broadening of the emission and absorption lines due to the Doppler Effect. The effective line-width at half maximum is given by Doppler line-width D instead of natural line-width, Γ . D is given by

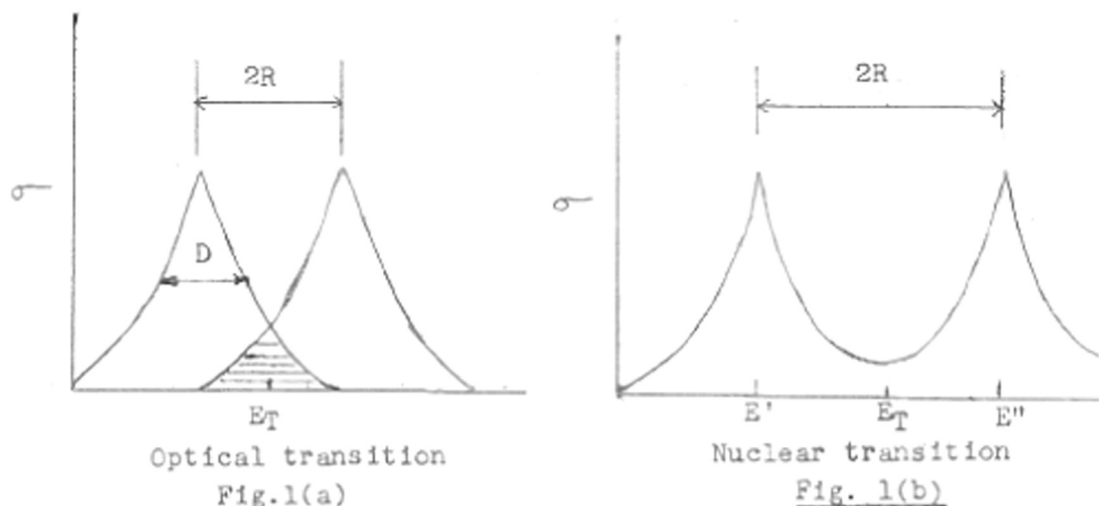
Table - 1

	Sodium D-line	Isomeric transition	Gamma ray emission
cm	5.89×10^{-5}	-	-
Energy (eV)	2.10	14.4×10^3	137×10^3
E_R (eV)	1.30×10^{-8}	1.9×10^{-3}	6.6×10^{-3}
(eV)	6.60×10^{-8}	4.5×10^{-9}	4.6×10^{-9}
R/	1.70×10^{-1}	4.2×10^6	1.4×10^6
$E_T/$	3.00×10^8	3.0×10^{12}	2.98×10^{13}

$$D = 1/C \sqrt{2kT/m} E_T \quad (6)$$

$$= 2\sqrt{E_T kT} \quad (7)$$

When $2R \leq D$ the maxima of the emission and absorption lines would overlap and hence resonance emission and absorption can occur as indeed happens in the optical transitions where $E_T \simeq 1$ e.v. In the case of gamma-ray transition of the order of 10 kev, the recoil energy is much larger than the Doppler line-width thus preventing an overlap of the emission and absorption lines and hence observation of nuclear resonance of the gamma rays as illustrated below (fig.1):



If the emitter and the absorber are bound in a crystal lattice then the equation (2) for the recoil-loss for an isolated nucleus is no longer valid. The mass ' m ' of the nucleus in equation (2) should be replaced by the mass of the crystal as a whole. The recoil energy would then be

reduced by the order of the value of Avagadro's number, viz. 10^{23} . This would bring about an overlap of the emission and the absorption lines and make it possible for nuclear resonance absorption to take place.

If the source is moved with respect to the absorber the energy of the recoil free emission peak is changed with respect to the recoil-free absorption peak due to Doppler Effect. The scattered or transmitted gamma-ray through the resonance absorber can be measured at a number of relative velocities so that the energy of the recoil-free emission peak is progressively changed from far off resonance to the position of exact resonance. The intensity of the transmitted/scattered radiation will then decrease in the region of resonance since a fraction of radiation will be removed on account of nuclear resonance absorption and the counting rate will drop. A plot of the intensity of the transmitted or scattered radiation as a function of the velocity of the source with respect to the absorber or vice versa is called the Mossbauer spectrum (fig. 2)

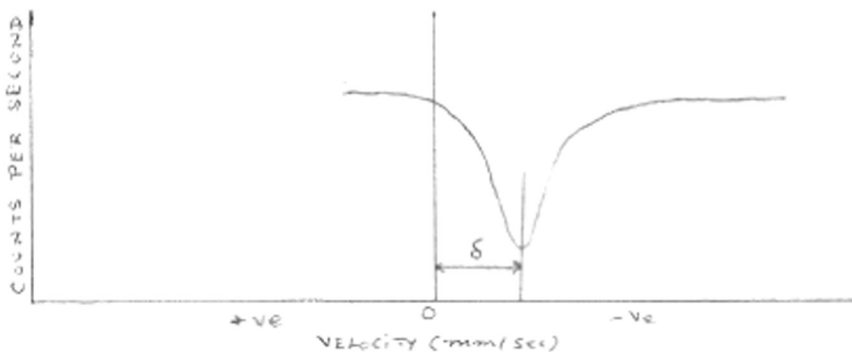


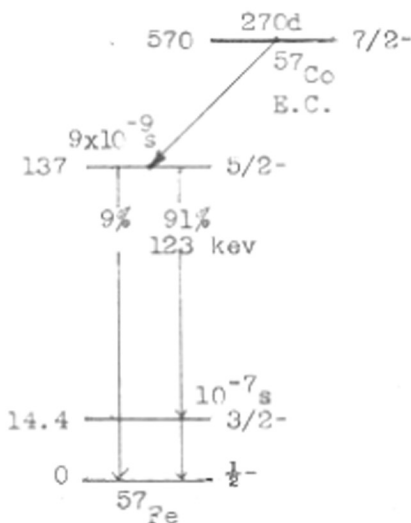
FIG. 2.

The profile of the resonance maximum can be described by a Lorentzian relationship¹⁷ viz.

$$\sigma_{\text{abs}}(E) = \sigma_0 \left[1 + 4 \left(\frac{E - E_T}{\Gamma} \right)^2 \right]^{-1} \quad (8)$$

where σ_0 is the maximum resonance absorption cross-section, $\sigma_{\text{abs}}(E)$ is the absorption cross-section at energy E , E_T the transition energy and Γ the full-width at half-maximum of the resonance line.

Although the resonance emission and absorption was first observed by Mossbauer¹ for the 129 kev. gamma ray in the decay of ^{191}Ir , there are at present nuclides of 32 elements for which the Mossbauer Effect has been observed. The work presented here deals with the use of the Mossbauer nucleus ^{57}Fe formed by electron-capture decay of ^{57}Co , the decay scheme of which is given below



The application of Mossbauer effect to chemistry can be traced to the hyperfine interaction between the nuclear levels in the Mossbauer nuclei and their extranuclear electrons, the disposition of which depends upon the nature of the chemical bonding of the atom to which the nucleus belongs. We briefly discuss below the significance of the parameters which can be obtained from a Mossbauer spectrum, viz., (a) the isomer shift, (b) the quadrupole splitting, (c) the magnetic hyperfine splitting, (d) the line-width, (e) the magnitude of the resonance effect.

(a) Isomer Shift

The shift of the resonance maximum from the zero velocity of an arbitrarily selected radiation source is called the isomer shift (Fig.2). It arises due to the fact that the energy of the nuclear levels and hence the nuclear transition energy can be modified as a result of Coulomb interaction with the extranuclear electrons and is therefore sensitively dependent on the environment of the nucleus. A change in the electron-density at the nucleus will alter the Coulomb interaction and hence would manifest itself as a shift in the energy of the nuclear levels and hence in the value of the isomer-shift.

The origin of the isomer shift was first pointed out by Kistner and Sunyar²¹ and its various applications have been discussed in detail by Shirley²² and others.^{23,24} The value of the isomer shift for a pair of resonant atoms denoted as the source (S) and the absorber (A) can be expressed by the equation,²⁵

$$\delta = \frac{2\pi}{5} Ze^2 (R_{\text{ex}}^2 - R_{\text{gd}}^2) \left[\underset{\text{nuclear}}{|\psi_A(0)|^2} - \underset{\text{atomic}}{|\psi_S(0)|^2} \right] \quad (9)$$

where R_{ex} and R_{gd} are the radii of the excited and ground states of the nucleus respectively. $|\psi_S(0)|^2$ and $|\psi_A(0)|^2$ represent the total electron densities at the nucleus of the source and absorber respectively, Z , the atomic number and e , the electronic charge. The above equation consists of two factors. The first one consists of only nuclear parameters while the second one in square brackets contains terms representing electronic charge density at the nucleus, which is basically a chemical parameter since it is affected by the valency of the atom.

A series of Mossbauer experiments carried out with high spin compounds of iron in different valency states revealed a systematic behaviour with respect to isomer shifts. Different oxidation states of iron have characteristic values of the isomer shifts as shown in table (2) and illustrated in fig. (4). As the d-electrons are removed in going from +1 to +6 state, the shielding of the s-electrons is decreased resulting in an increase in the total electron density at the nucleus. For ^{57}Fe , the expression $[R_{\text{ex}}^2 - R_{\text{gd}}^2]$ is negative and hence an increase in the electron density at the nucleus would bring about a lowering in the value of the isomer shift²⁶. For other Mossbauer nuclei like ^{119}Sn an increase in the s-electron density would bring about an increase in the isomer shift since the quantity $(R_{\text{ex}}^2 - R_{\text{gd}}^2)$ has a positive value.²⁷

Table - 2

Isomer shift values for high spin iron
compounds of different oxidation states

Valency state	Electronic configuration of the free metal ion	Isomer shift w.r.t. ^{57}Fe ss absorber (mm./sec.)	Ref.
Fe^{1+}	$3d^6 4s$	+2.1	28
Fe^{2+}	$3d^6$	+1.0 to +1.5	29, 30
Fe^{3+}	$3d^5$	+0.35 to +0.70	29, 30
Fe^{4+}	$3d^4$	+0.14 to +0.17	29, 85
Fe^{6+}	$3d^2$	-0.7 to -0.8	31, 32

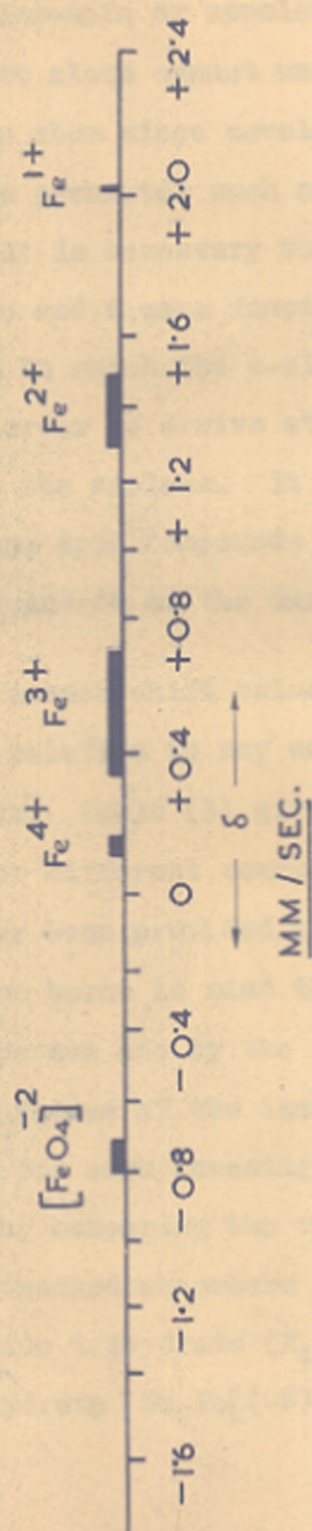


FIG. 4: ISOMER SHIFTS OF IRON COMPOUNDS WITH RESPECT TO ^{57}Co SOURCE IN STAINLESS STEEL 310

For low-spin or covalent compounds, the value of the isomer shift alone cannot unambiguously identify the oxidation state of an atom since covalency cannot be adequately described by a single parameter such as the 's' electron density at the nucleus. It is necessary to consider the relative importance of the s, p and d wave functions in the binding, as well as the extent to which the π -electrons are delocalized to the ligand in order to arrive at an estimate of the total electron density at the nucleus. It has been experimentally found that for low spin compounds of iron, the isomer shift tends to be independent of the oxidation state.

The isomer shift value obtained with any source can be converted relative to any another source by a suitable correction factor. Table (3) gives the values of the correction factors for different sources given by Herber.³³ Similar tables have been provided by other workers.³⁴ It should, however, be borne in mind that two sources prepared even by the same person and by the same method may give slightly different values of the isomer shift. It is therefore essential for each investigator to obtain his own correction factors, by comparing the values of isomer shifts obtained by him for standard absorbers like 310 stainless steel, potassium ferrocyanide trihydrate ($K_4Fe(CN)_6 \cdot 3H_2O$) and sodium nitroprusside dihydrate [$Na_2Fe[(CN)_5(NO)] \cdot 2H_2O$].

Table - 3

Isomer shifts of sodium nitroprusside with respect
to several ^{57}Co host matrices³³

^{57}Co source	Isomer shift mm./sec.
Pt	-0.607
Cu	-0.483
Pd	-0.442
Fe	-0.348 { -0.351 {
^{31}Oss , Vacromium	-0.182
^{302}ss	-0.175
Cr	-0.075

b) Quadrupole Splitting:

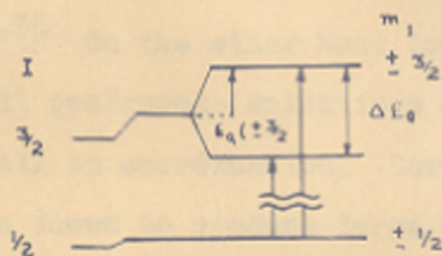
Any nucleus with a spin $I > 1/2$ would have a quadrupole moment Q and hence would align itself either along or across an electric field gradient (EFG) 'q'. In a nonspherically symmetric field, a nuclear level with spin I would split into $I+1/2$ sub-levels. The 14.4 keV energy level in ^{57}Fe with a spin of $3/2$ would split into two sub-levels (Fig.5) leading to a pair of lines in the Mossbauer spectrum (fig.6) in the place of a single line observed in the absence of an EFG. The separation between two such lines is called the quadrupole splitting because it arises due to the interaction of the quadrupole moment of the excited state with the electric field gradient. For an axially symmetric field gradient, the quadrupole splitting ΔE_Q is given by

$$\Delta E_Q = \frac{e^2 q \cdot Q}{4I(2I-1)} [3m_I^2 - I(I+1)] \quad (10)$$

where m_I is the magnetic quantum number and 'e' is the electronic charge.

In chemical compounds the electric field gradient at the nucleus can arise due to one or both of the following reasons. (1) asymmetric distribution of the charges on the ligand atoms, (2) nonspherical symmetry of the central metal orbitals (incompletely filled electronic shells). In compounds of spherically symmetric ions like Fe^{3+} the observed quadrupole splitting can arise only due to (1). On the other hand, the quadrupole splitting in the Ferrous compounds can arise due to both the factors (1) and (2). High spin ferric compounds have been

could be more quadrupole splittings from 0 to 0.5 cm/sec. at high spin currents depending upon the quadrupole splittings from 0 to 3.0 cm/sec. and similarly quadrupole splittings depending upon the presence of the quadrupole splittings and energy different levels in a crystal field at different temperatures.



ISOMER SHIFT QUADRUPOLE SPLITTING

FIG 5

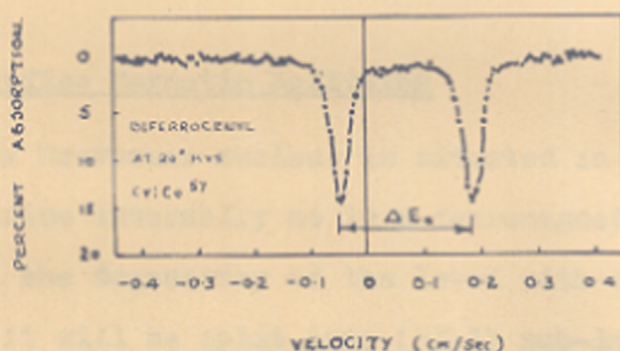


FIG 6

found to have quadrupole splittings from 0 to 0.6 mm/sec. but high spin ferrous compounds show large quadrupole splittings from 0 to 3.6 mm/sec. and exhibit relatively large temperature dependence due to the presence of the sixth d-electron which can occupy different levels in a crystal field at different temperatures.^{18,35,36} On the other hand low spin Fe(II) compounds show small quadrupole splittings due to the completion of the d^{10} shell on coordination. Low spin Fe(III) compounds have been found to produce large quadrupole splittings which are strongly temperature dependent due to the vacancy of one electron in the other-wise filled 3d shell. The range of quadrupole splittings observed for different types of iron compounds are illustrated in fig.(7)

(c) Hyperfine Magnetic Splitting

When a Mossbauer nucleus is situated in a magnetic field, which may arise internally as in a ferromagnet or be generated externally, the degeneracy of the level with spin I is further lifted and it will be split into $(2I+1)$ sub-levels. The 14.4 kev level in ^{57}Fe with a spin of $3/2$ will be split into four sub-levels and the ground state with spin of $1/2$ will be split into two sublevels as shown in fig.(8). Transitions between the split levels is governed by the appropriate selection rules. For a magnetic dipole (M1) transition $\Delta m = 0, \pm 1$ and hence there would be six possible transitions Fig 9 and a hyperfine split spectrum (HFS) of six absorption lines would be observed (Fig.13). It is thus possible to make use of Mossbauer effect studies in a study of paramagnetic-ferromagnetic or paramagnetic-antiferromagnetic transitions.^{38,39}

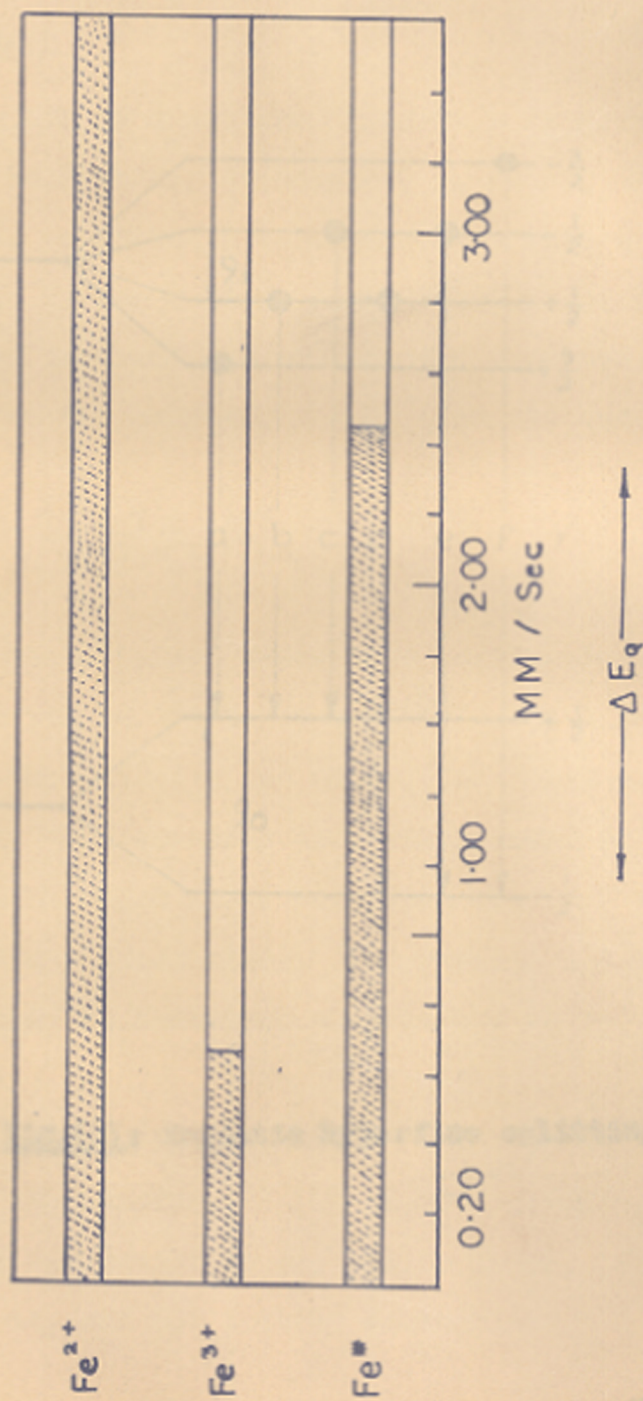


Fig. (7): Quadrupole splittings of iron compounds.
 Fe^{2+} indicates low spin $\text{Fe}(\text{II})$ and $\text{Fe}(\text{III})$ compounds.

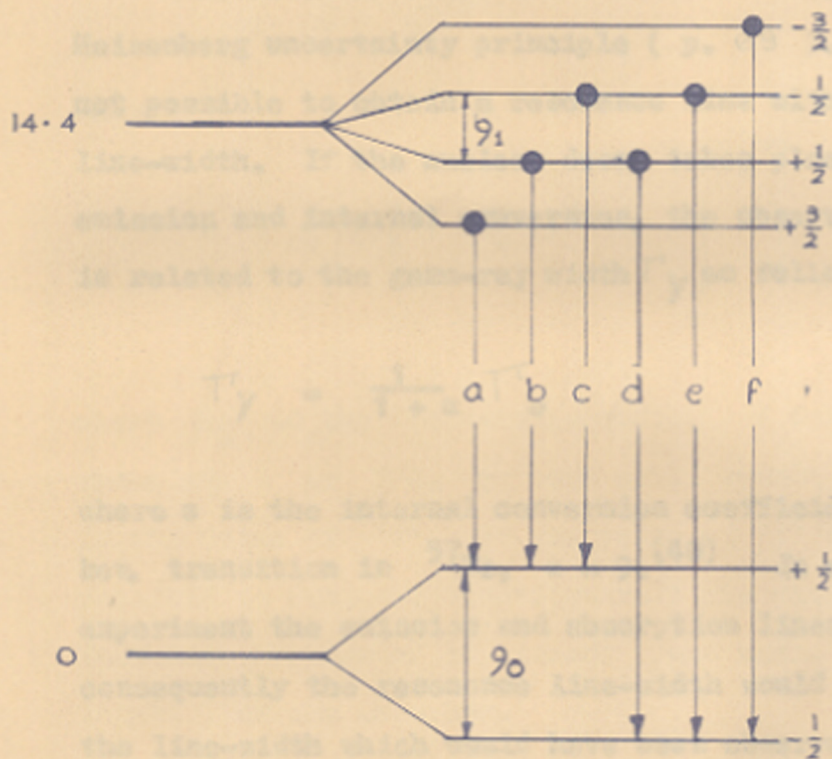


Fig.(8): Magnetic hyperfine splitting.

Many other applications of NPS have been discussed by Fraunfelder¹⁶ and Boyle and Hall.²⁵

d) Line-width

The width of a nuclear transition is governed by the Heisenberg uncertainty principle (p. 69). However, it is not possible to obtain a resonance line with the natural line-width. If the nuclear decay takes place both by gamma emission and internal conversion, the observed line-width Γ_0 is related to the gamma-ray width Γ_γ as follows:

$$\Gamma_\gamma = \frac{1}{1 + \alpha} \Gamma_0 \quad (11)$$

where α is the internal conversion coefficient. For the 14.4 kev. transition in ^{57}Fe , $\alpha = 9$.⁽⁴⁰⁾ In a Mossbauer experiment the emission and absorption lines are matched and consequently the resonance line-width would be equal to twice the line-width which would have been observed in an emission or absorption process alone. In practice the actual line-width observed in Mossbauer experiments is invariably greater than $2\Gamma_0$ due to the following factors which tend to broaden the resonance line, viz. (a) the finite thickness of the source and the absorber,⁴¹ (b) thermal effects, (c) the limits of velocity resolution of the motion drive, (d) the solid state defects, and (e) lattice distortions.

e) Magnitude of Resonance Effect

The fraction 'f' of the gamma-ray emitted or absorbed without recoil-loss can be theoretically calculated. In the Debye approximation of a solid, the value of 'f' is given by the Debye-Waller factor or the Lamb-Mossbauer factor.²⁵

$$f = e^{-2w} \quad (12)$$

where

$$w = 3 \frac{R}{h\theta_D} \left[\frac{1}{4} + \left(\frac{T}{\theta_D} \right)^2 \int_0^{\theta_D/T} \frac{x}{e^x - 1} dx \right] \quad (13)$$

where θ_D is the Debye-temperature. A decrease in the value of R or T/θ_D or both would result in an increase in the value of 'f'. If the value of 'f' is known it is possible to estimate quantitatively the concentration of the Mossbauer nucleus of an element (and hence of the element itself) in any absorber.

Review of the literature on the Mossbauer Effect studies on the chemical effects of electron-capture decay of ^{57}Co in solids.

In nuclear disintegration processes accompanied by electron capture or by isomeric transition, highly ionized states of the atom are likely to be produced due to the Auger Effect.⁴² Snell et al.⁴³ observed ionized states of xenon upto a charge of +23 in the isomeric transition of

12-day ^{131m}Xe and charge states of Bromine upto +13 in the electron-capture decay of 34 h ^{79}Kr . Pollak⁴⁴ has shown that in the electron-capture decay of the 270-day ^{57}Co , ionized states of iron upto +7 can be observed if the oxidation state of the cobalt parent is +2.

Wertheim^{10,45} was the first to make use of the Mossbauer effect studies for detecting the higher charged states of iron formed by the decay of ^{57}Co in CoO matrix. He observed two resonance lines of unequal intensities and interpreted them to be due to Fe^{3+} and Fe^{2+} states. This was further confirmed by the observation of two superimposed hyperfine split spectra of Fe^{3+} and Fe^{2+} at liquid nitrogen temperature, which is below the Neel temperature (291°K) of CoO.⁴⁰ It was suggested that the Fe^{3+} iron was non-equilibrium charge state with a life-time comparable to the mean life of 14.4 kev excited state of ^{57}Fe . On the basis of the results of Wertheim, Pollak⁴⁴ calculated the mean life-time of the $^{57}\text{Fe}^{3+}$ ions at cobalt sites in CoO to be 1.4×10^{-7} sec. It was also suggested that the ionized states higher than +3 are likely to have very short-life time ($< 10^{-9}$ sec) due to the presence of many free electrons in the CoO crystal. However, Bearden *et al.*⁴⁶ found no evidence of the Fe^{3+} state in the decay of ^{57}Co in CoO. Similar studies by Coston *et al.*⁴⁷ on the same system showed that their best samples of ^{57}CoO (based on X-ray analysis) showed 10 to 20 % of Fe^{3+} compared to 90 to 80 % of Fe^{2+} . They attributed the trivalent state to the presence

of Co_3O_4 impurity in CoO although their x-ray analyses showed no such impurity. Bhide and Shenoy¹¹ reinvestigated the ^{57}CoO system from 78° to 1000°K and obtained results similar to those of Wertheim. An increase in temperature was found to bring about an increase in the ratio of $I_{(3)}/I_{(2)}$ where $I_{(2)}$ and $I_{(3)}$ are the intensities of +2 and +3 states of iron. The increase in the ratio $I_{(3)}/I_{(2)}$ was interpreted in terms of an increase in the life-time of the +3 state at higher temperature. Their Mossbauer experiments on the $^{57}\text{Co}/\text{NiO}$ source gave very similar results.⁴⁸ On the other hand, Mullen and Ok⁴⁹ pointed out that the Mossbauer spectra of their sample of ^{57}CoO could be explained as due to two separate spectra of two different forms of CoO denoted by them as CoO(I) and CoO(II) , without invoking the Auger after effects. They attributed the difference between the two forms to a difference in the local lattice re-arrangement. CoO(II) was assumed to be a metastable state occurring at only low temperatures. The striking work of Craig and Triftshäuser⁵⁰ on the $^{57}\text{Co}/\text{CoO}$ and $^{57}\text{Co}/\text{NiO}$ systems set at rest the debate on the conflicting results reported by different workers. They conclusively showed by delayed coincidence Mossbauer-effect measurements that the ratio $I_{(3)}/I_{(2)}$ at a fixed temperature, remains constant for all delay times studied by them viz. 4 to 200 n. sec. It is therefore apparent that the change in the ratio of $I_{(3)}/I_{(2)}$ as a function of temperature in the same source of ^{57}Co or of different sources, reported by a number of

workers, cannot be due to a change in the life-time of the nonequilibrium Fe^{3+} state formed in the decay of ^{57}Co as a result of Auger effect.

Wertheim⁵¹ was also the first to study the chemical effects of electron capture decay of ^{57}Co in an organo-metallic compound. The Mossbauer spectrum of $^{57}\text{Co}(\text{III})$ Acetyl-acetonate source matched against an enriched $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ absorber was interpreted as being due to a mixture of high spin ferric and ferrous states. The observation of the Fe^{2+} state, which is lower than the oxidation state of cobalt (III) parent was surprising and thought to have been brought about on account of the rearrangement of the charge distribution to accommodate the presence of an imurity $\geq +4$ formed due to secondary Auger processes in the electron capture decay of $^{57}\text{Co}(\text{III})$. These investigators also reported the production of both divalent and trivalent states of iron in the decay of ^{57}Co in cobalticinium tetraphenyl borate.⁵²

Ingalls and Depasquali⁵³ in their studies by Mossbauer effect on $^{57}\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $^{57}\text{Co}[(\text{NH}_4)\text{SO}_4]_2 \cdot 6\text{H}_2\text{O}$ and $^{57}\text{CoSiF}_6 \cdot 6\text{H}_2\text{O}$ detected the presence of trivalent and divalent iron in addition to a very small percentage of +4 state in $^{57}\text{Co}(\text{NH}_4)_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}$. Their interpretation of +4 and +3 states as nonequilibrium states, is suspect for the following reasons: They show an unsplit line for the +4 state although they have shown marked quadrupole splitting for the +2 and +3 states of iron indicating the presence of an electric field

gradient (EFG). The absence of the quadrupole splitting for +4 state alone is therefore unconvincing. In addition, the line-width of the +4 state has been shown to be equal to the linewidth of the stable +2 state. The +4 state, supposed to be a nonequilibrium state should show a larger line-width. The results of their studies on $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ are similar to the results obtained by Mullen and Ok⁴⁹ and Friedt *et al.*⁵⁴ The Mossbauer spectrum of $^{57}\text{CoCl}_2 \cdot x\text{H}_2\text{O}$ was found to have two unequal resonance lines, tending to become equal as x decreases. Ingalls⁵³ and Friedt *et al.*⁵⁴ interpreted the spectrum to be due to +3 and +2 states of iron while Mullen and Ok⁴⁹ interpreted it as only due to Fe^{2+} state, the unequal intensity of the resonance lines being attributed ~~***~~ to the anisotropy due to local re-arrangement of the lattice during neutrino emission, which accompanies the K-capture. Friedt *et al.*⁵⁴ observed that $^{57}\text{CoF}_2$ used as a source also gave rise to +2 and +3 states of iron. Ingalls *et al.*⁵⁵ studied the Mossbauer spectra of $^{57}\text{CoSO}_4$ and $^{57}\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ and observed the presence of both Fe^{2+} and Fe^{3+} . On increasing the temperature or the pressure, the intensity ratio $I_{(2)}/I_{(3)}$ increased, a result opposite to that reported for $^{57}\text{Co}/\text{CoO}$ and $^{57}\text{Co}/\text{NiO}$ systems.^{11,48} They suggested that this may be due to the excitation of the electrons in the conduction band and/or the overlap between the orbitals of the metal ion and the ligands. Wertheim and Guggenheim⁵⁶ made use of ^{57}Co doped $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ (FAS) as a source as well as an absorber in their Mossbauer studies. The absorber spectrum showed only Fe^{2+} iron in contrast to the Mossbauer

spectrum of the source which in addition to +2 indicated a small percentage of trivalent iron interpreted as a non-equilibrium state. However, the recent work of Craig and Triftshauser,⁵⁰ making use of coincidence Mossbauer effect measurements with $^{57}\text{Co}/\text{FAS}$, $^{57}\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ and $^{57}\text{CoCl}_2 \cdot 4\text{H}_2\text{O}$ has unambiguously established that the temperature dependent proportion of different valency states observed in these cases is independent of delay times in the interval 4-200 nanoseconds. These states should not therefore be termed as non-equilibrium states.

Mallen^{28,57} prepared single crystals of NaCl with (a) diffused carrier-free $^{57}\text{CoCl}_2$ and (b) containing $^{57}\text{CoCl}_2$ with sufficient amount of carrier. The Mossbauer spectrum of the former showed three peaks which were interpreted as a doublet due to +2 or +3 state of iron associated with a positive ion vacancy and a singlet due to Fe^{1+} arising on account of the substitutional replacement of Na^+ ion. In the case of NaCl containing $^{57}\text{CoCl}_2$ with a considerable cobalt carrier, only the divalent iron was observed with a quadrupole splitting of 1.14 mm./sec. which was attributed to the partial alignment of $^{57}\text{Co}^{2+}$ within the NaCl lattice. Wertheim and Guggenheim⁵⁶ observed only +2 state of iron in the Mossbauer spectra of ^{57}Co doped ZnF_2 and +2 and +3 states of iron in ^{57}Co doped NaF. The origin of the trivalent iron was attributed to a divalent cobalt with oxygen ion charge compensation in a near neighbour site or possibly due to trivalent cobalt with proper charge compensation. $^{57}\text{Co}/\text{SrTiO}_3$ system⁵⁸ was however found to give a Mossbauer spectrum, that

could be analysed in terms of two resonance lines corresponding to a low spin Fe(III) and high spin Fe^{3+} states which were interpreted as due to Co^{2+} ion occupying a Ti^{4+} vacancy preferably in the ^{57}Co (III) state the decay of which results in low spin Fe(III) and high spin Fe^{3+} . Sano *et al.*⁵⁹ failed to observe the Fe^{3+} state in the Mossbauer spectrum of cobalt-57 labelled cobalt oxalate dihydrate and attributed it to the reducing property of the oxalate ion.

Very few studies on the chemical effects of nuclear transformation with the aid of Mossbauer spectroscopy involving isotopes other than ^{57}Co have been undertaken so far. Hannaford *et al.*⁹ showed that neutron irradiation of Mg_2SnO_4 partially reduces the oxidation state of tin from +4 to +2. Annealing of the irradiated Mg_2SnO_4 restored the valency to Sn^{4+} . Herber *et al.*⁶⁰ found the Mossbauer spectrum of ^{119}Sn labelled tetraphenyl-tin could be interpreted as composed of zero-valent parent and a monovalent species formed as a result of Auger cascade. Berger *et al.*⁶¹ irradiated anhydrous Ferrous sulphate with thermal neutrons and using it as a Mossbauer absorber showed that 40% of the divalent iron are converted to the trivalent state.

CHAPTER - 2 : EXPERIMENTAL PROCEDURE

CHAPTER - II

EXPERIMENTAL

(1) Mossbauer spectrometer

The main parts of the equipment needed for studies on Mossbauer Effect are (1) the source of gamma-ray, (2) the gamma ray detector, (3) the absorber containing the mossbauer nuclide (^{57}Fe in the present case), (4) a velocity drive for imparting a relative motion to the source with respect to the absorber or vice versa. (Fig.9.)



Fig. 9

Fig.10 shows the schematic diagram of the main parts of the Mossbauer spectrometer used. A 15-watt synchronous motor with a reduction gear system was mounted on a vibration-proof table. It was used to rotate a cam by means of a belt and pulley arrangement. The cam made out of the gun-metal to give a linear displacement of 3.6 mm was mounted on a separate vibration-proof table to eliminate any disturbance due to the motion of the motor and the friction of the gears. The source mounted on a perspex holder or the absorber made by sandwiching the material between two thin perspex discs

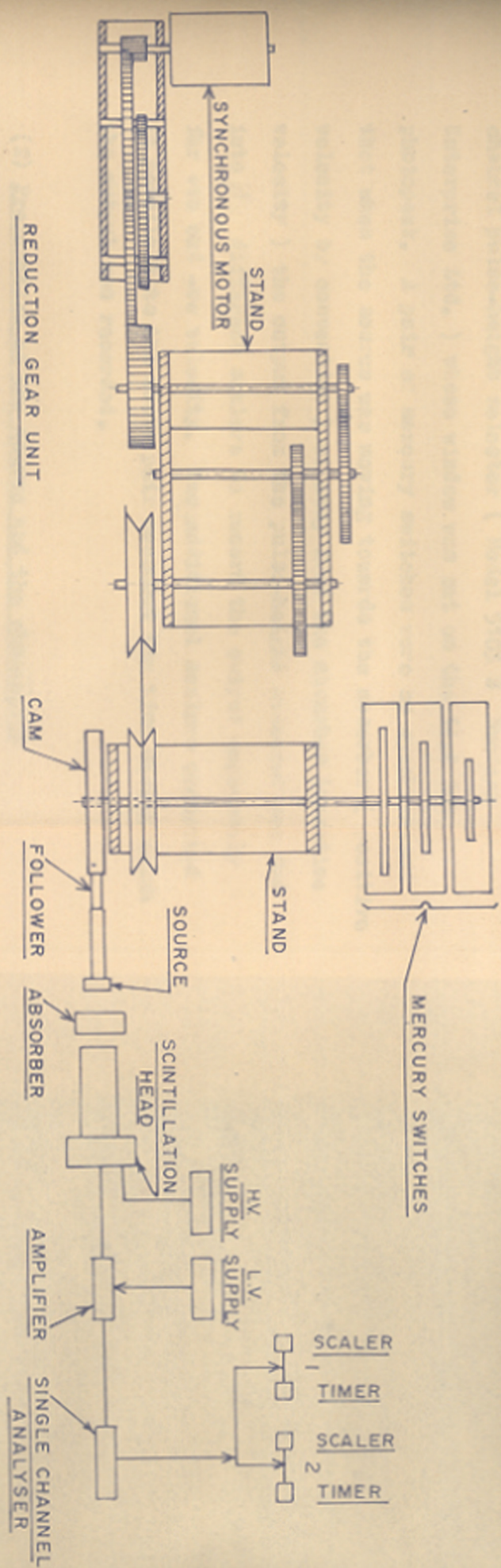


FIG. 10: SCHEMATIC DIAGRAM OF THE MÖSSBAUER APPARATUS

can be attached to cam-follower by screw and thread arrangement (See also Fig. 11). The source or the absorber could be given any linear velocity upto 3.6 c.m./sec. in steps of 0.0036 cm/sec. or its multiples by a suitable combination of gears.

The counting assembly consists of a 1 mm thick NaI (Tl) crystal coupled to a RCA - 6810A photomultiplier tube. The output from the scintillation detector was fed into a single-channel pulse-height selector (Model 5103 S Nuclear Enterprise Ltd.) whose window was set on the 14.4 Kev photopick. A pair of mercury switches were so synchronised that when the source was moving towards the absorber (positive velocity by convention) or away from the absorber (negative velocity) the output from the pulse-height selector was fed into two different scalars to record the output separately for +ve and -ve velocity. Two additional scalars connected in parallel to the above pair measured the time during which the output was recorded.

(2) Preparation of the source and the absorbers:

A ^{57}Co source on copper backing was prepared by electrodeposition from a solution of carrier free cobalt-57 on a 0.05 mm thick spectroscopically pure copper foil, which was subsequently annealed in hydrogen at 800°C for one hour and then in vacuum of 10^{-6} torr for another hour. The source was then mounted on a perspex holder. The methods of preparation of other sources in dielectrics are described separately (p. 98-102).

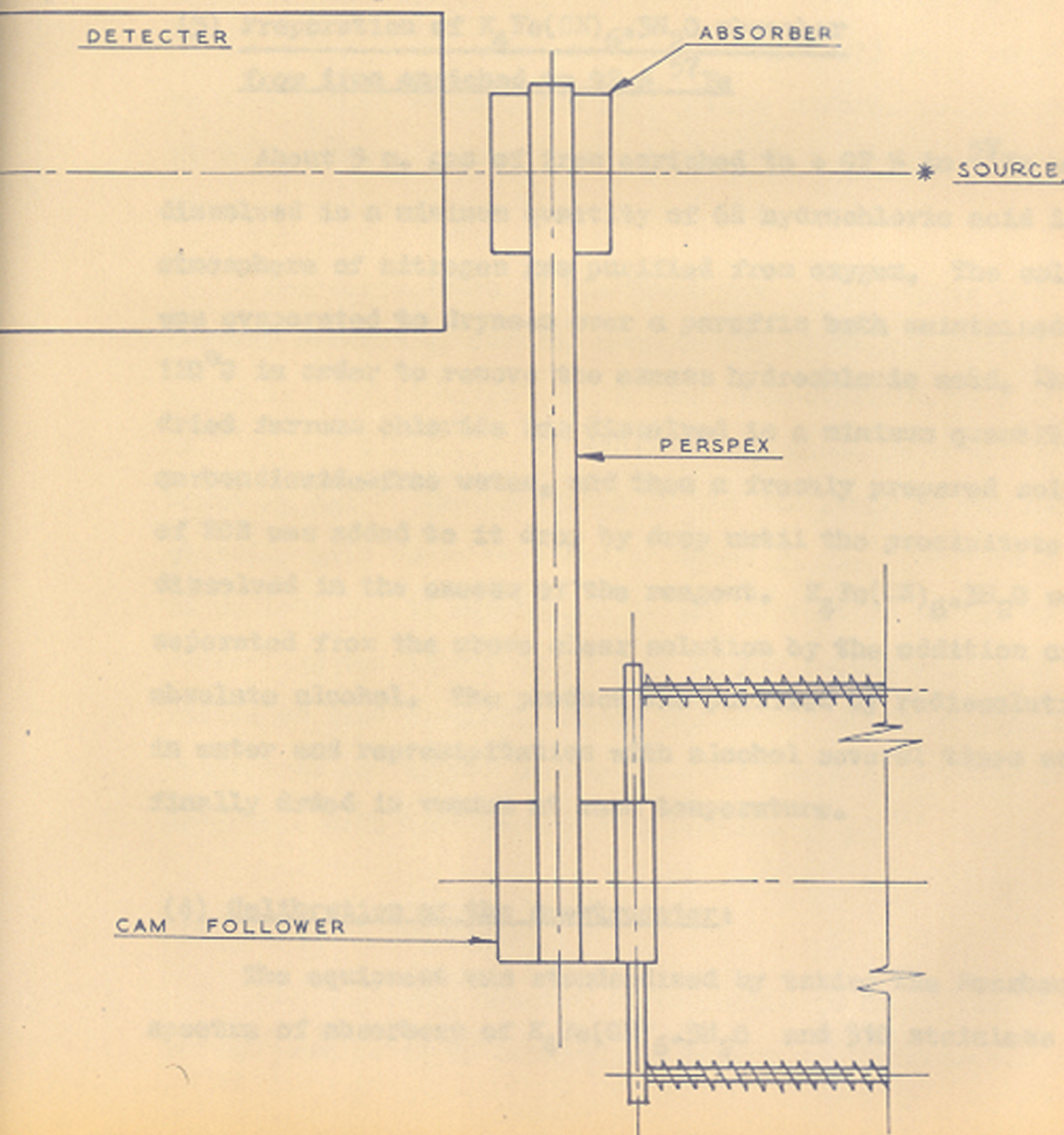


FIG. 11 DIAGRAM FOR THE MOVING ABSORBER

The absorbers under investigation were prepared by spreading the material in the powder form between two thin aluminium foils sandwiched between two brass or perspex rings. The quantity of the absorber material was adjusted to give an effective thickness of ~ 8 m. gms/cm² of natural iron or ~ 0.16 mg/cm² of ⁵⁷Fe.

(3) Preparation of $K_4Fe(CN)_6 \cdot 3H_2O$ absorber from iron enriched to 92 % ⁵⁷Fe

About 5 m. gms of iron enriched to + 92 % in ⁵⁷Fe was dissolved in a minimum quantity of 6N hydrochloric acid in an atmosphere of nitrogen gas purified from oxygen. The solution was evaporated to dryness over a paraffin bath maintained at 120°C in order to remove the excess hydrochloric acid. The dried ferrous chloride was dissolved in a minimum quantity of carbondioxide-free water, and then a freshly prepared solution of KCN was added to it drop by drop until the precipitate formed dissolved in the excess of the reagent. $K_4Fe(CN)_6 \cdot 3H_2O$ was separated from the above clear solution by the addition of absolute alcohol. The product was purified by redissolution in water and reprecipitation with alcohol several times and finally dried in vacuum at room temperature.

(4) Calibration of the spectrometer:

The equipment was standardized by taking the Mossbauer spectra of absorbers of $K_4Fe(CN)_6 \cdot 3H_2O$ and 310 stainless steel

foil. Single-line resonance spectra for $K_4Fe(CN)_6 \cdot 3H_2O$ and 310 stainless steel were obtained with their centroids shifted to -0.26 ± 0.04 mm/sec and -0.32 ± 0.04 mm/sec respectively from the zero velocity (fig. 12) and hence the isomer shifts obtained with our $^{57}Co_{Cu}$ source can be converted to that with respect to a ^{57}Co source on stainless steel backing by adding $+ 0.34$ mm/sec to our experimental results. The line-widths of 64 mg/cm^2 $K_4Fe(CN)_6 \cdot 3H_2O$ absorber [$\sim 7 \text{ mg/cm}^2$ of natural ^{57}Fe] and 0.02 mm thick stainless steel foil were found to be 0.36 ± 0.04 mm/sec. and 0.44 ± 0.04 mm/sec. respectively at $25^\circ C$. These values of the line-widths are comparable to those reported in the literature (Table 4).

The performance of the Mossbauer spectrometer was further checked by running a hyperfine split spectrum (HFS) (Fig.13) of 19 mg/cm^2 thick iron foil enriched to $+ 92\%$ in ^{57}Fe and comparing the results with those reported by Hanna et al.⁶⁶ The positions of the six lines in our HFS coincide with those reported by Hanna et al. (See Table 5), if we take $+ 0.17$ mm/sec. to be the correction factor for converting the isomer shift from copper backed source to a source on iron backing. Hence the isomer shift of iron with respect to our copper source is $- 0.17$ mm/sec. a value in agreement with that reported by Collins et al.⁶⁷

(5) Cryostat and heater

The Mossbauer spectra at temperatures below room temperature were taken by cooling the source or the absorber in a

Table - 4

Mossbauer data for potassium ferrocyanide absorber and 310 stainless steel foil
 $^{57}\text{Co}/\text{Cu}$ source at 25°C

Absorber at 25°C	Displacement of the centroid from zero velocity relative to copper backing mm./sec.		Displacement of the centroid from zero velocity relative to stainless steel mm./sec.		Line-width with respect to copper backing mm./sec.	
	Experi- mental	Litera- ture	Experi- mental	Litera- ture	Experi- mental	Litera- ture
Potassium ferrocyanide powder (64 mg./cm. ²)	-0.26 ± 0.04	-0.27^{62}	$+0.08 \pm 0.04$	$+0.083^{26,63}$	0.36 ± 0.04	0.29^{64}
310-Stainless steel foil (0.002")	-0.32 ± 0.04	-0.34^{65}	$+0.02 \pm 0.04$	-	0.44 ± 0.04	-

Table - 5

Comparison of the experimental values of the positions of the six lines in the hyperfine Mossbauer spectrum of iron with values reported by Hanna et al.⁶⁶

Source : $^{57}\text{Co/Cu}$ at 25°C

Absorber: Iron foil at 25°C (19 mg./cm.² thickness enriched to +92% in ^{57}Fe)

No.	Absorption maxima	Values calculated from the data of Hanna et al. (mm./sec.)	Experimental values
1	$1/2_+ \rightarrow 3/2_+$	-5.47	-5.46 ± 0.04
2	$1/2_+ \rightarrow 1/2_+$	-2.24	-3.26 ± 0.04
3	$1/2_+ \rightarrow 1/2_-$	-1.01	-1.06 ± 0.04
4	$1/2_- \rightarrow 1/2_+$	+0.67	$+0.64 \pm 0.04$
5	$1/2_- \rightarrow 1/2_-$	+2.90	$+2.90 \pm 0.04$
6	$1/2_- \rightarrow 3/2_-$	+5.13	$+5.14 \pm 0.04$

FIG. 12

COUNTS PER SECOND

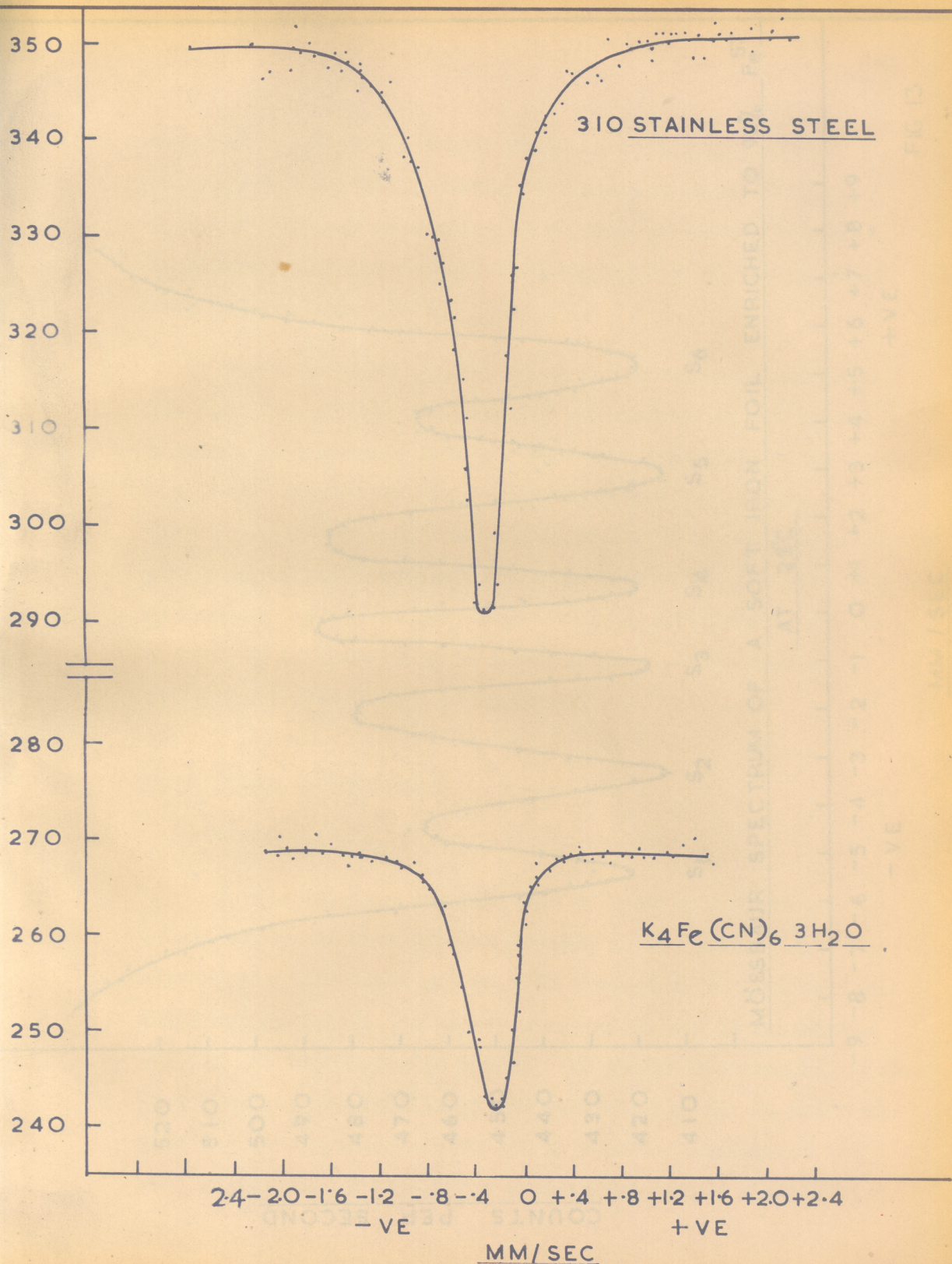
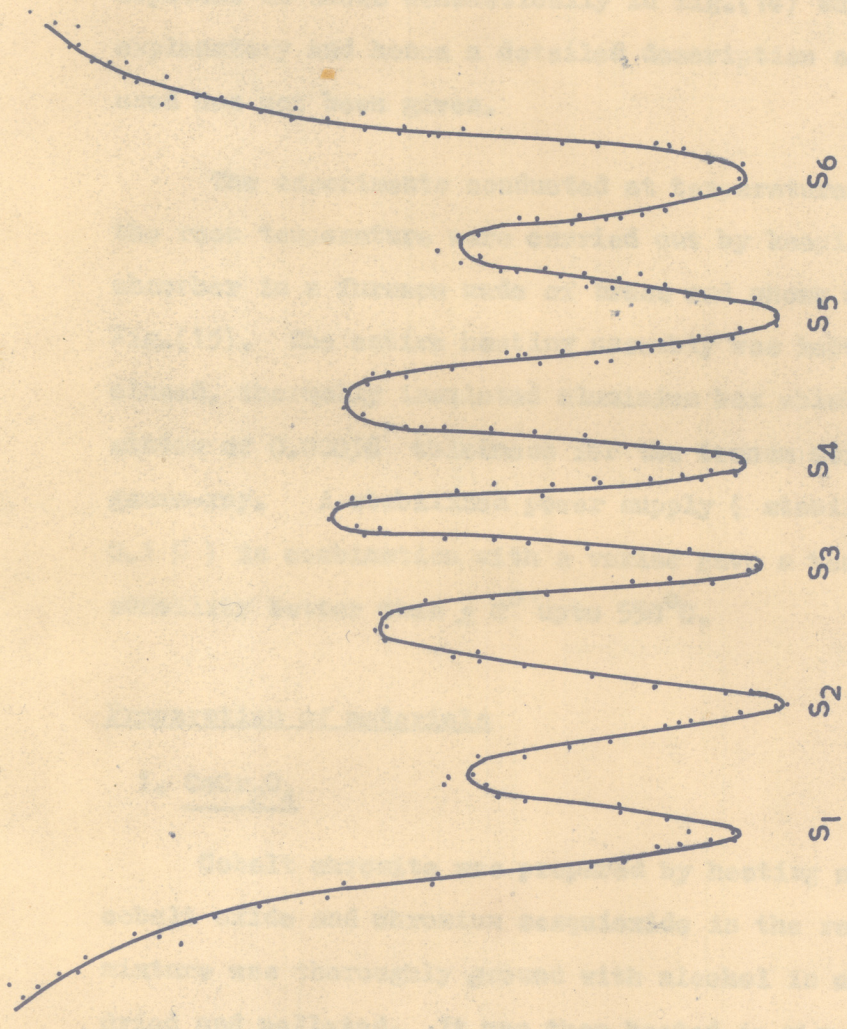

 MÖSSBAUER SPECTRA OF 310 STAINLESS STEEL FOIL AND $K_4Fe(CN)_6 \cdot 3H_2O$ ABSORBER AT 25°C

FIG.

COUNTS PER SECOND

520
510
500
490
480
470
460
450
440
430
420
410



MÖSSBAUR SPECTRUM OF A SOFT IRON FOIL ENRICHED TO 92% ^{57}Fe
AT 25°C

-9 -8 -7 -6 -5 -4 -3 -2 -1 0 +1 +2 +3 +4 +5 +6 +7 +8 +9

-VE +VE

MM / SEC

FIG 13

cryostat in which the sample could be cooled upto liquid nitrogen temperature by means of a glass to metal seal. The cryostat is shown schematically in fig.(14) which is self-explanatory and hence a detailed description of the cryostat used has not been given.

The experiments conducted at temperatures higher than the room temperature were carried out by keeping the source or absorber in a furnace made of brass and shown schematically in Fig.(15). The entire heating assembly was kept inside a closed, thermally insulated aluminium box which had two aluminium windows of 0.00036" thickness for the transmission of the 14.4 kev gamma-ray. A stabilised power supply (stability better than 0.1 %) in combination with a variac gave a temperature stability better than $\pm 2^\circ$ upto 550°C .

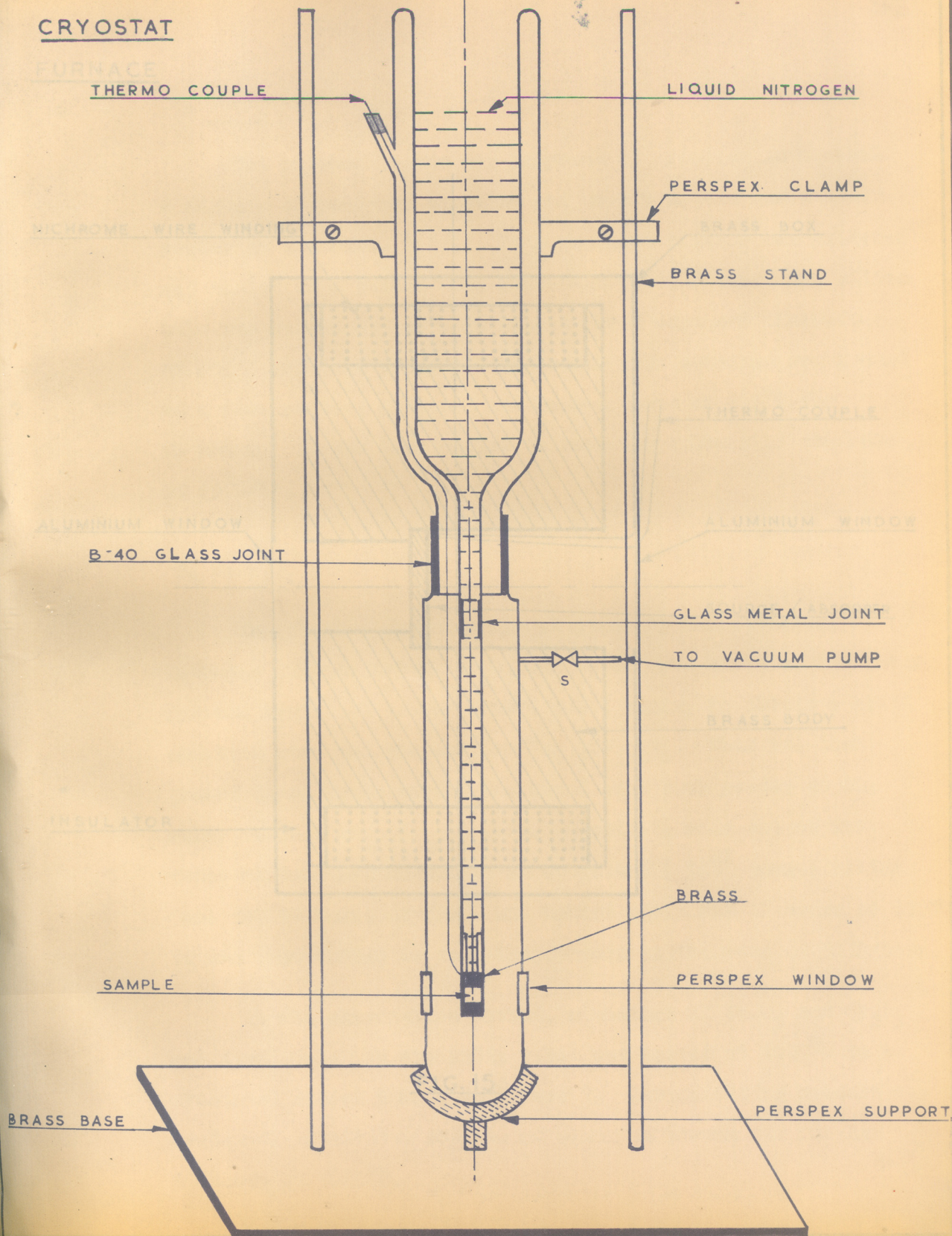
Preparation of materials

1. CoCr_2O_4

Cobalt chromite was prepared by heating a mixture of cobalt oxide and chromium sesquioxide in the ratio 1:1. The mixture was thoroughly ground with alcohol in a agate mortar, dried and pelleted. It was then heated in air in a platinum crucible at 1100°C for 12 hours. The pellet was crushed, ground to a fine powder, repelleted and heated again for 20 hours at 1280°C . This produce was cooled to room temperature at the rate of 40°C/hr to obtain the equilibrium cation distribution.

FIG. 14

CRYOSTAT



FURNACE

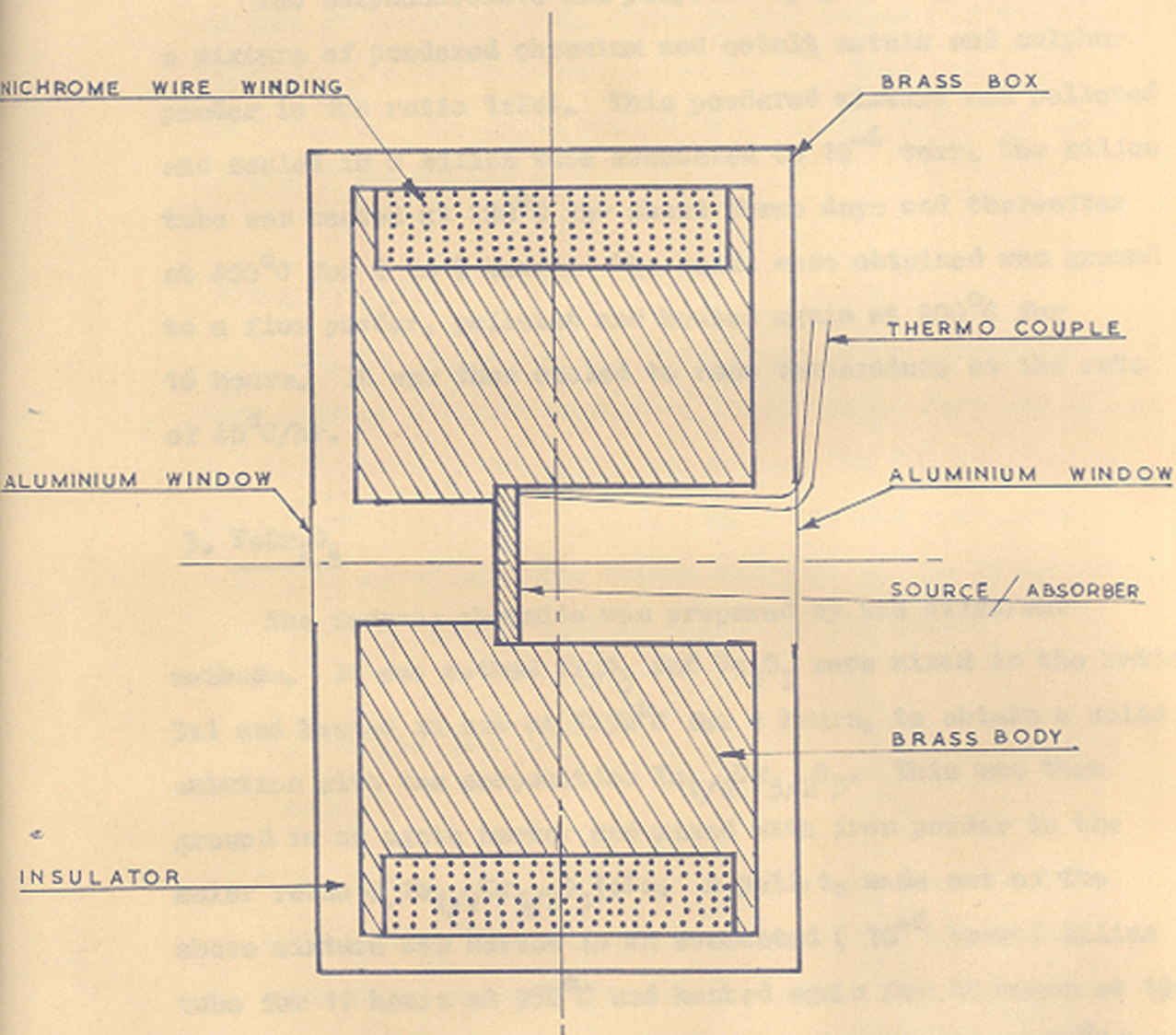


FIG. 15

2. CoCr₂S₄

The sulphochromite was prepared by grinding in alcohol a mixture of powdered chromium and cobalt metals and sulphur powder in the ratio 1:2:4. This powdered mixture was pelleted and sealed in a silica tube evacuated to 10^{-6} torr. The silica tube was heated at 200°C for about three days and thereafter at 400°C for 6 to 7 hours. The solid mass obtained was ground to a fine powder, pelleted and heated again at 900°C for 16 hours. It was then cooled to room temperature at the rate of 40°C/hr.

3. FeCr₂O₄

The ferrous chromite was prepared by two different methods. In one method Cr₂O₃ and Fe₂O₃ were mixed in the ratio 3:1 and heated in air at 1250°C for 4 hours, to obtain a solid solution with the composition Fe_{1/2}Cr_{3/2}O₃. This was then ground in an agate mortar and mixed with iron powder in the molar ratio 4[Fe_{1/2}Cr_{3/2}O₃]:Fe. A pellet, made out of the above mixture was heated in an evacuated (10^{-6} torr) silica tube for 12 hours at 950°C and heated again for 12 hours at 1000°C. It was then cooled to room temperature at the rate of 30°C/hour.

In the alternative method, a mixture of Fe₂O₃ and Cr₂O₃ and iron powder in the ratio 1:3:1 was heated at 1000°C in an evacuated silica tube (10^{-6} torr). The resulting product was powdered, repelleted and heated again in vacuum for further 12 hours at 1000°C.

(4) FeCr₂S₄

The thiochromite FeCr₂S₄ was prepared by heating a mixture of powdered iron, chromium and sulphur in the ratio 1:2:4 in a silica tube evacuated to 10⁻⁶ torr. at 400°C for 6 hours. The solid was powdered again, pelleted and heated at 1000°C for 48 hours.

X-ray analyses

All the above samples were examined by taking their x-ray powder patterns with Mo-K_α radiation. They all showed a single phase cubic spinel structure. The 'a' parameters calculated for the x-ray diffraction pattern are given in Table (6) along with the values reported in the literature⁶⁸ with which there was good agreement in all cases.

Method of doping ⁵⁷Coa) CoCr₂O₄

200 microcurie carrier-free ⁵⁷Co as cobalt chloride was pipetted out on the surface of the pellet of cobalt chromite and evaporated by an infra-red lamp. The sample was then heated at 950°C in a platinum boat for one hour. It was then quenched to room temperature. The doped sample was then mounted in a brass source holder.

b) CoCr₂S₄

CoCrS₄ was in the form of a fine, light green powder. About 200 μc of carrier-free cobalt chloride was added to the

Table - 6

X-ray analyses of the materials used in the Mossbauer studies

No.	Compound	Structure	'a' values obtained (Å)	'a' values reported (Å)	References
1	CoCr_2O_4	Spinel	8.314	8.332	68
2	CoCr_2S_4	Spinel	9.89	9.91	68
3	FeCr_2O_4	Spinel	8.366	8.37	69
4	FeCr_2S_4	Spinel	9.983	9.98	70
5	KCoF_3	Perovskite	4.04	4.069	72

cobalt thiochromite powder in a platinum planchet and the solution evaporated by infra-red lamp. The sample was then sealed in an evacuated silica tube and heated at 950°C for about an hour and quenched to room temperature. The doped sample was then mounted in a brass source-holder and covered with thin aluminium foil.

(5) Preparation of ^{57}Co labelled KCoF_3

Both dry and wet methods have been described in the literature^{71,72} for the preparation of KCoF_3 . The later method which is considered more suitable since it eliminates non-stoichiometry and oxidation, was adopted. 0.40365 gms of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 10 ml water in a platinum crucible and 0.25 mc. carrier free $^{57}\text{CoCl}_2$ was added to the solution. To this solution was then added 0.1988 gms of A.R. Potassium hydrogen fluoride and the solution was concentrated on a water bath to about 2 cc. The solution was then transferred into a centrifuge tube and the supernatant was rejected after centrifugation. The supernatant was found to be acidic and any oxidation of divalent cobalt can therefore be ruled out. The pink product was washed thrice with 5-10 ml. hot water to remove any excess potassium chloride or hydrogen fluoride. The resultant product was dried in vacuum at 200°C for one hour.

A parallel preparation was carried out without radioactive cobalt and subjected to chemical and x-ray analysis. The x-ray powder pattern gave an 'a' value in agreement with those

reported by earlier workers (See table 6). Analysis of the pink compound gave the following results. Found : Co = 38.01 %; K = 25.8 %; calculated for KCoF_3 : Co = 38.02 %, K = 25.3 %. A differential thermal analysis of the parallel inactive preparation of KCoF_3 was carried out to confirm the absence of water of hydration and determine the temperature range of stability where the Mossbauer studies could be made without any possibility of decomposition. (Fig. 16).

75 mg of the radioactive compound was packed into a circular cavity 2.5 mm diameter and 1.5 mm depth in a brass source holder and covered with thin aluminium foil.

(6) Preparation of ^{57}Co labelled cobalt (III)
(1-10 phenanthroline) $_3(\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}$

$^{57}\text{Co}(1-10 \text{ phenanthroline})_3 \cdot 2\text{H}_2\text{O}$ was prepared according to the method described by Schilt and Taylor.⁷³ About 250 μc of carrier-free ^{57}Co in the chloride form was added to 10 c.c. of a solution containing a mixture of 32.5 mgms $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and 82 mgms 1-10 phenanthroline monohydrate. To this solution was added 0.3 ml 30 % H_2O_2 and 0.3 ml conc. HCl and then concentrated to a few ml over a water bath. The insoluble perchlorate was precipitated as a golden yellow precipitate by adding about 20 ml water followed by about 0.2 ml 60% HClO_4 . The compound was recrystallised thrice from hot water containing a few drops of hydrogen peroxide. The final product was dried in a vacuum desiccator at room

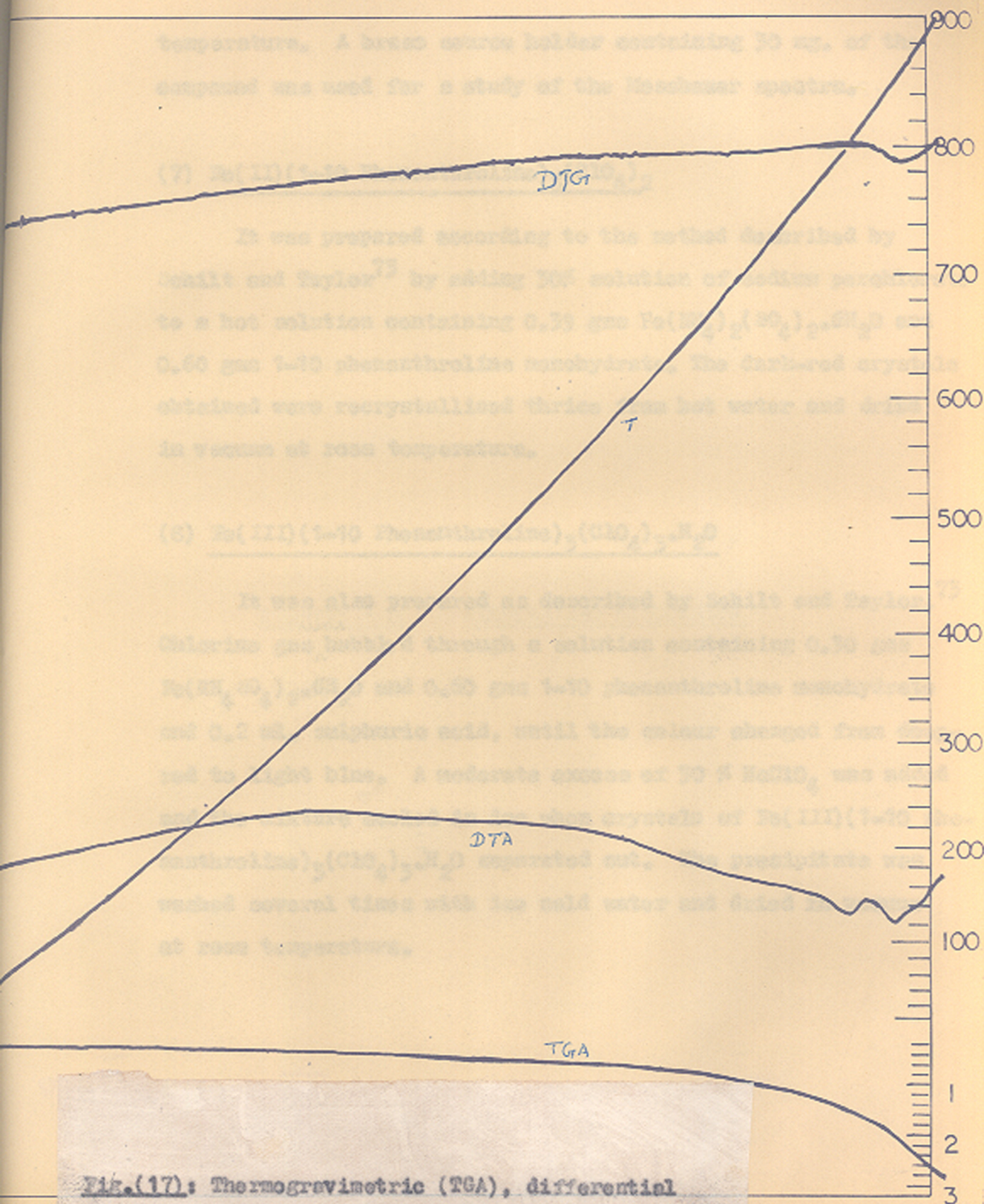


Fig.(17): Thermogravimetric (TGA), differential thermal (DTA) and differential thermogravimetric (DTG) analysis of KCoF_3 ; T represents temperature.

temperature. A brass source holder containing 30 mg. of the compound was used for a study of the Mossbauer spectra.

(7) $\text{Fe(II)(1-10 Phenanthroline)}_3(\text{ClO}_4)_2$

It was prepared according to the method described by Schilt and Taylor⁷³ by adding 30% solution of sodium perchlorate to a hot solution containing 0.39 gms $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ and 0.60 gms 1-10 phenanthroline monohydrate. The dark-red crystals obtained were recrystallised thrice from hot water and dried in vacuum at room temperature.

(8) $\text{Fe(III)(1-10 Phenanthroline)}_3(\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$

It was also prepared as described by Schilt and Taylor.⁷³ Chlorine gas ^{was} bubbled through a solution containing 0.30 gms $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ and 0.60 gms 1-10 phenanthroline monohydrate and 0.2 ml. sulphuric acid, until the colour changed from deep-red to light blue. A moderate excess of 30 % NaClO_4 was added and the mixture cooled in ice when crystals of $\text{Fe(III)(1-10 phenanthroline)}_3(\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$ separated out. The precipitate was washed several times with ice cold water and dried in vacuum at room temperature.

CHAPTER - IIIRESULTS AND DISCUSSION

Significant changes can be created in the distribution of electrons in the valency shells of an atom as a result of the disintegration of the unstable nucleus of the atom in question, especially in the electron capture decay or the isomeric transition. In the electron capture decay, the unstable nucleus absorbs an electron from one of the nearest electronic shells e.g. K shell. The vacancy in the K-shell would be filled up by an electron from one of the next outer shells e.g. L shell and the excess energy liberated by the emission of an x-ray or alternatively the x-ray may transfer its energy to one of the electrons in the outer electronic shells causing the formation of an additional vacancy in the electronic shell by the emission of a second electron. Such an electron is called the Auger electron, and the fraction of the number of primary vacancies of a certain shell leading to the emission of x-rays is called the fluorescence yield. The two vacancies (the primary vacancy plus the vacancy due to Auger effect) thus created may be filled in a similar manner by electrons from the outer shells and produce temporarily a quadruply charged ion. This outward movement of the vacancies proceeds through the remaining shells and as a result of the Auger cascade, one obtains a highly charged ion in a time interval of $\sim 10^{-15}$ sec. after the nuclear decay. Such highly charged ions have been observed in the case of the free atoms.⁴³

In solids, however, these highly ionized atoms would be converted to their stable valency states in a very short time (10^{-13} to 10^{-15} second) by the capture of electrons from the neighbouring atoms, as indeed happens in metallic lattices. In a dielectric lattice, the highly ionized, non-equilibrium states would take a longer time to relax to their stable states. Theoretical calculations by Pollak⁴⁴ indicated that in the electron capture decay of $^{57}\text{Co}^{2+}$ charge states upto +7 can be produced by the Auger cascade. The results of his calculations are shown in fig. (17) and given in table (7). If cobalt is initially triply ionized all the oxidation states given in table (7) would be ionized once more.

About two years ago, when the present work was planned, a number of reports had already appeared reporting the presence of +3 nonequilibrium state of iron in addition to expected +2 stable state formed in the decay of $^{57}\text{Co}^{2+}$ in various crystal lattices.^{11,48,51-53} However, the results reported by different groups of workers on the Mossbauer spectra of ^{57}CoO were interpreted differently, not necessarily involving contribution from the after-effects of the Auger cascade^{11,49,46}. (See p. 34 + 35). The mean life-time of the so-called non-equilibrium state observed are expected to be smaller, the greater the degree of covalency in the bonding of the source lattice due to greater overlap between the orbitals of the metal atom and the ligands and thereby increasing the availability of the electrons for charge relaxation. A study of the relative percentage of the non-equilibrium states as a

Table - 7

Percentage intensities $I_0(n)$ of various ionized states 'n' resulting at the end of the Auger cascades following the electron capture decay of $^{57}\text{Co}^{2+44}$

Ionized state of iron n	Percentage intensity $I_0(n)$ %
2	5.0
3	21.5
4	25.3
5	29.5
6	14.2
7	4.1

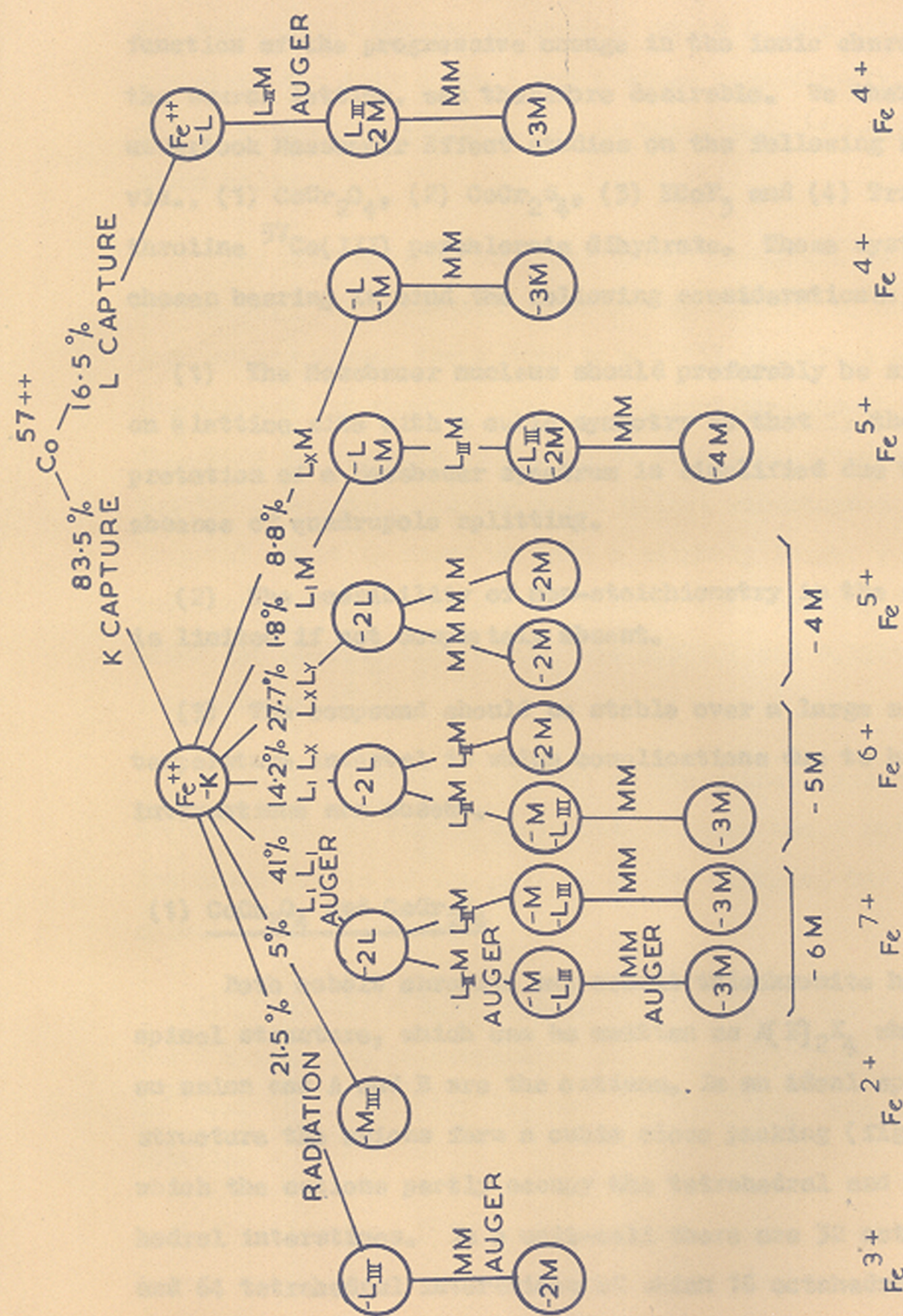


FIG 17 THE AUGER CASCADE SCHEME OF Co⁵⁷

function of the progressive change in the ionic character of the source lattice, was therefore desirable. We therefore, undertook Mossbauer Effect studies on the following systems, viz., (1) CoCr_2O_4 , (2) CoCr_2S_4 , (3) KCoF_3 and (4) Tris Phenanthroline $^{57}\text{Co(III)}$ perchlorate dihydrate. These systems were chosen bearing in mind the following considerations:

- (1) The Mossbauer nucleus should preferably be situated on a lattice site with a cubic symmetry so that the interpretation of a Mossbauer spectrum is simplified due to the absence of quadrupole splitting.
- (2) The possibility of non-stoichiometry in the compound is limited if not completely absent.
- (3) The compound should be stable over a large accessible temperature interval in which complications due to hyperfine interactions are absent.

(1) CoCr_2O_4 and CoCr_2S_4

Both cobalt chromite and cobalt thiochromite have a spinel structure, which can be written as $\text{A}[\text{B}]_2\text{X}_4$ where X is an anion and A and B are the cations. In an ideal spinel structure the anions form a cubic close packing (fig.18) in which the cations partly occupy the tetrahedral and the octahedral interstices. In a unit-cell there are 32 octahedral and 64 tetrahedral interstices of which 16 octahedral and 8 tetrahedral interstices are occupied by the metal ions.

The tetrahedral and the octahedral sites in the spinel structure are called the A and B sites respectively. Some of the characteristic features of the spinel structure are given below.

The unit cell of an ideal spinel structure is shown in Fig.18. The non-ideal structure is derived by moving the four anions around the A site in a $[111]$ direction away from the nearest tetrahedral ion. The deviation from the ideal structure is measured by the value of anion parameter called the 'u' parameter. In the ideal spinel structure $u = 0.375$. In practice it is found to have a slightly larger value, indicating larger A sites and smaller B-sites. The 'u' parameter for CoCr_2O_4 and CoCr_2S_4 are 0.38707 and 0.3821 respectively.^{74,75}

A characteristic property of the spinel type compounds is the nature of cation distribution among the A and B sites. The distribution of the cation, as for example, for a 2-3 spinel $\text{A}[\text{B}]_2\text{X}_4$ may be

(I) 'Normal' $\text{A}[\text{B}_2]\text{X}_4$ i.e. one A ion is in the tetrahedral and 2 B ions are in octahedral sites e.g. $\text{Co}^{2+}[\text{Cr}_2^{3+}]\text{O}_4$. $\text{Co}^{2+}[\text{Cr}_2^{3+}]\text{S}_4$, $\text{Fe}^{2+}[\text{Cr}_2^{3+}]\text{O}_4$ and $\text{Fe}^{2+}[\text{Cr}_2^{3+}]\text{S}_4$ are normal spinels.

(II) 'Inverse' $\text{B}[\text{AB}]\text{X}_4$ i.e. one B ion is in the octahedral position and one another in the tetrahedral position e.g. NiFe_2O_4 is an inverse spinel with the cation distribution $\text{Fe}^{3+}[\text{Ni}^{2+}\text{Fe}^{3+}]\text{O}_4$.

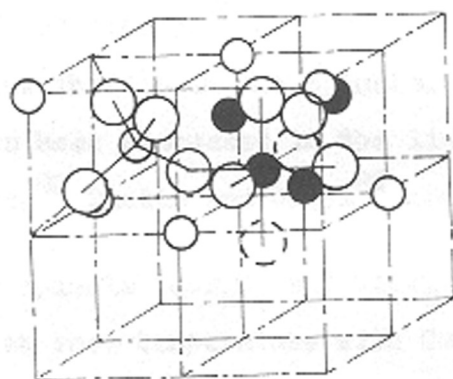


FIG. 18 UNIT CELL OF AN IDEAL SPINEL
SHOWING ONLY TWO OCTANTS.



(III) 'Intermediate', the distribution of the cations is between normal and inverse, which may be denoted by the general formula $B_{1-x}A_x[A_{4-x}B_{1+x}]X_4$. For example the cation distribution in $FeAl_2O_4$ is intermediate $Fe_{0.75}^{2+}Al_{1.25}^{3+}[Fe_{0.25}^{2+}Al_{0.75}^{3+}]O_4$.⁷⁶

It is known that some cations have a pronounced preference for certain coordination numbers and this influences the cation distribution in the spinel structure. Verwey⁷⁷ Heilmann⁷⁸ and Romeijn⁷⁹ have made a systematic study of the cation distribution in the spinels. The nature of the distribution has been discussed in the light of crystal field theory by McClure,⁸⁰ Dunitz and Orgel⁸¹ and Miller.⁸²

The spinels $CoCr_2O_4$ and $CoCr_2S_4$ studied by us are paramagnetic at room temperature with Curie points of 100° and $240^\circ K$ below which they undergo a ferrimagnetic transition.⁶⁸ Since there is a unique cobalt +2 site viz. tetrahedral A-site in these spinels, carrier-free $^{57}Co^{++}$ diffused into these spinels (p. 93) will occupy only the A-sites and one can rule out the possibility of $^{57}Co^{2+}$ in an interstitial or the octahedral B sites.

Cobalt is known to have also valency +3 and chromium can exist in +2 oxidation state. Hence there is a possibility that some of the Co^{2+} ions may be oxidised to +3 state with a concomitant reduction of Cr^{3+} to Cr^{2+} , so that the charge neutrality is still preserved. This will lead to the presence of +2 and +3 chromium ions at the octahedral sites and hence

would markedly increase the conductivity. High room temperature resistivities of $\text{Co}[\text{Cr}_2]\text{O}_4$ and $\text{Co}[\text{Cr}_2]\text{S}_4$ viz 10^6 and 5×10^3 ($83, 84$) ohm-cm respectively rule out the above possibility in $\text{Co}[\text{Cr}_2]\text{O}_4$ and $\text{Co}[\text{Cr}_2]\text{S}_4$. The cobalt ions are therefore in +2 oxidation state and are at the A sites.

a) The Mossbauer spectra of $^{57}\text{CoCr}_2\text{O}_4$

The Mossbauer spectra of $^{57}\text{Co}[\text{Cr}_2]\text{O}_4$ matched against 92% ^{57}Fe enriched $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ absorber (0.24 mg/cm^2 in ^{57}Fe) taken at -80° , 25° , 200° and 362°C are shown in figs. 19-22. A perusal of the spectrum at -80°C (Fig. 19a) shows that there are three absorption peaks of unequal intensities at approximately 0.20, 0.52 and 1.0 mm/sec. The nature of the spectrum at room temperature (fig. 20a) is very similar except for a change in the ratio of the intensities of the three resonance peaks. With an increase in the temperature of the $^{57}\text{CoCr}_2\text{O}_4$ source, the resolution between the three lines become poorer and at 200°C only two maxima appear, the third peak being indicated only by an asymmetry of the spectrum (fig. 21a). At 362°C only a single broad asymmetric peak is observed (Fig. 22a).

After a consideration of a number of possibilities with and without quadrupole splitting, the experimental data were finally analysed by synthesizing each observed spectrum as a sum of three single separate absorption lines of Lorentzian shape by making use of the equation given by Shirane *et al.*²³ viz.

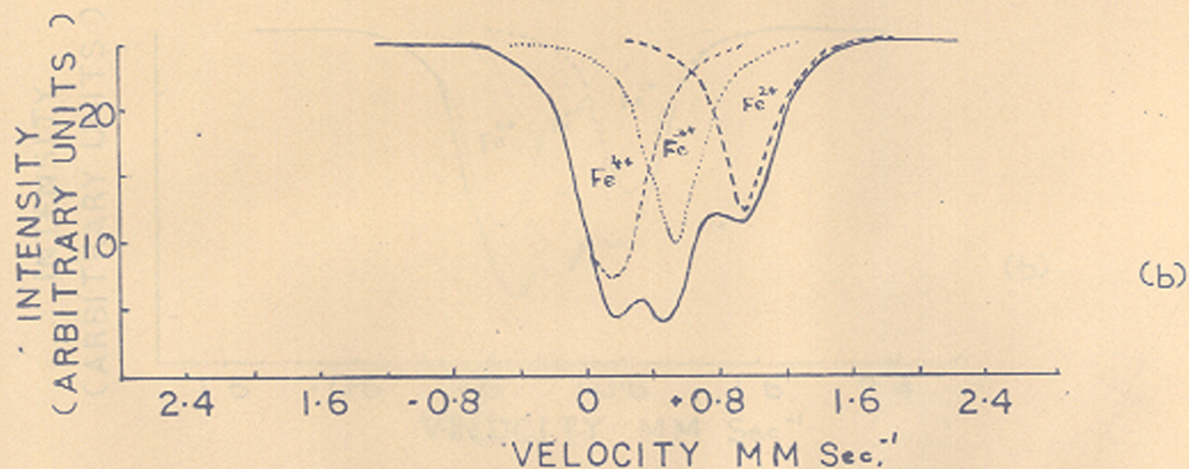
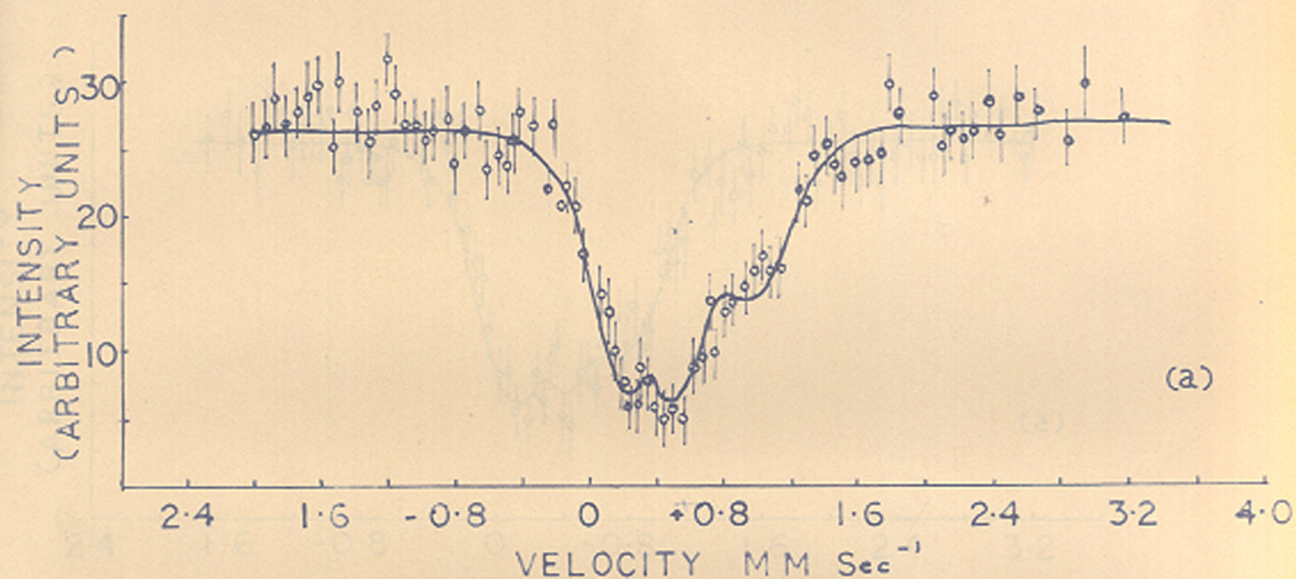


Fig.(19): (a) The Mössbauer spectrum of $^{57}\text{CoCr}_2\text{O}_4$ at -30°C . Solid curve is the synthetic curve superposed on experimental points. (b) Synthetic curve composed of three components viz. +4, +3, +2 states of iron (+ve velocity corresponds to absorber moving away from the source)

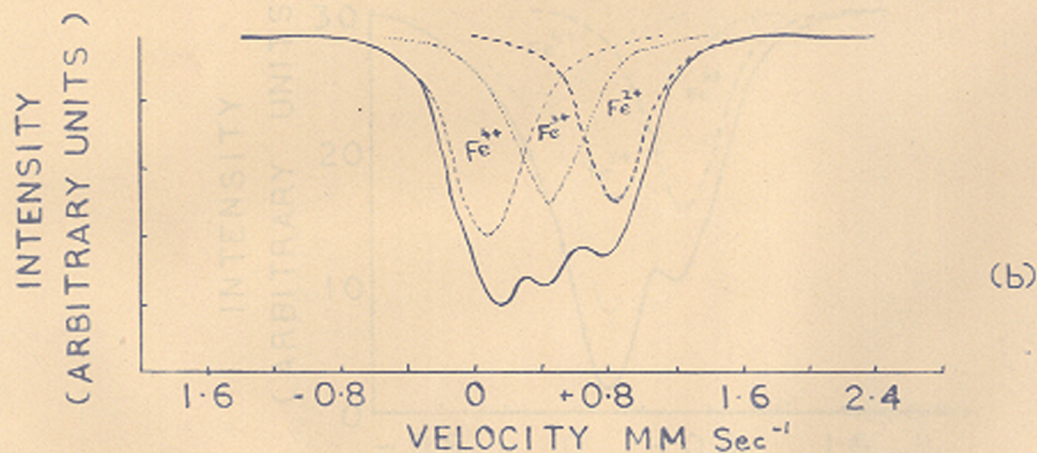
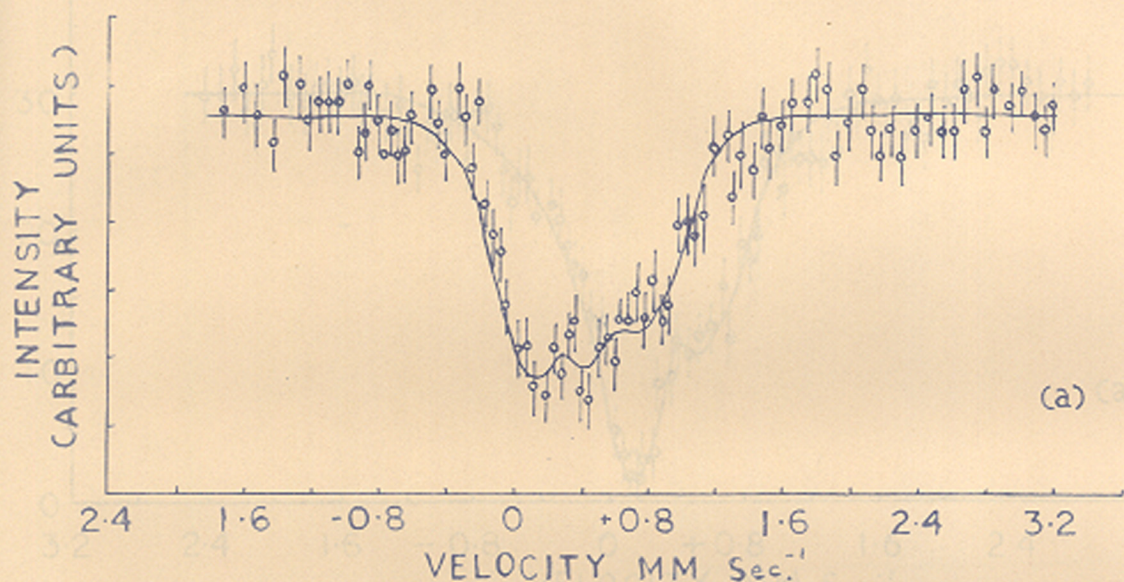


Fig.(20): (a) The Mössbauer spectrum of $^{57}\text{CoCr}_2\text{O}_4$ at 25°C . Synthetic curve superposed on experimental points.
 (b) Synthetic curve composed of Fe^{4+} , Fe^{3+} and Fe^{2+}
 (+ve velocity: absorber moving away from the source).

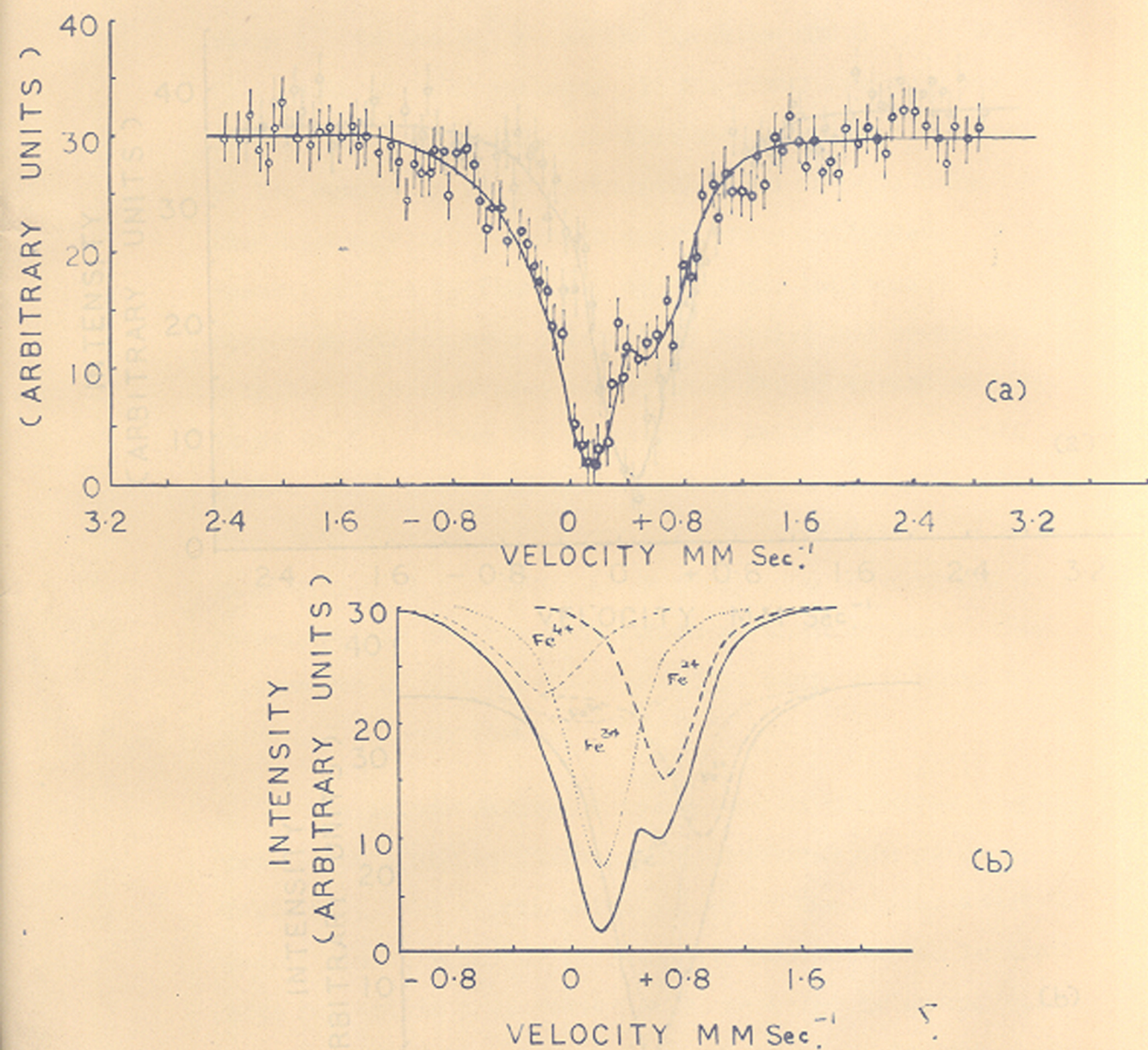
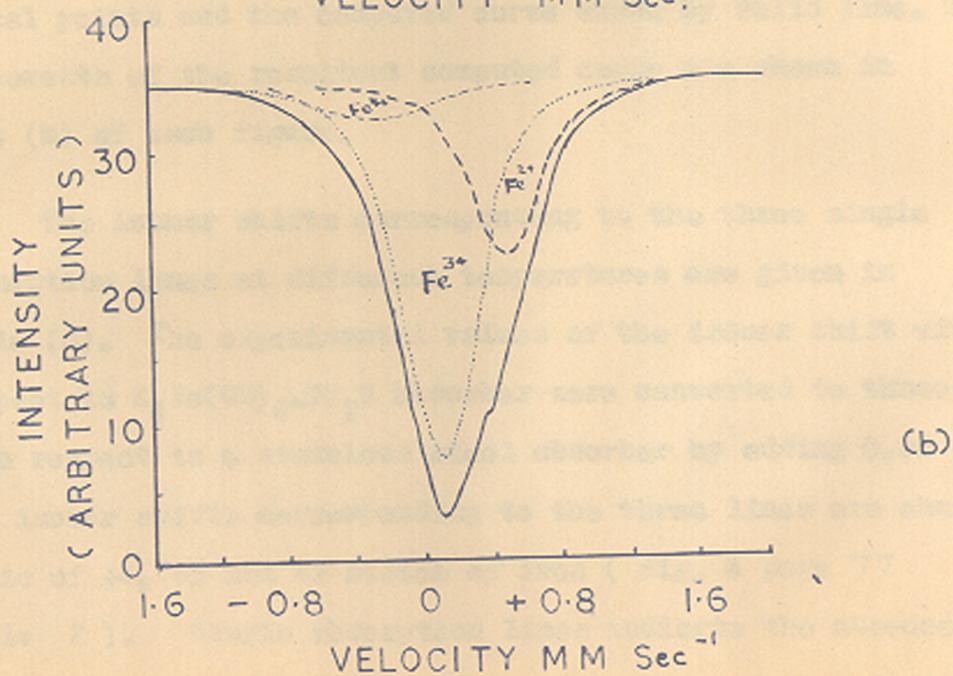
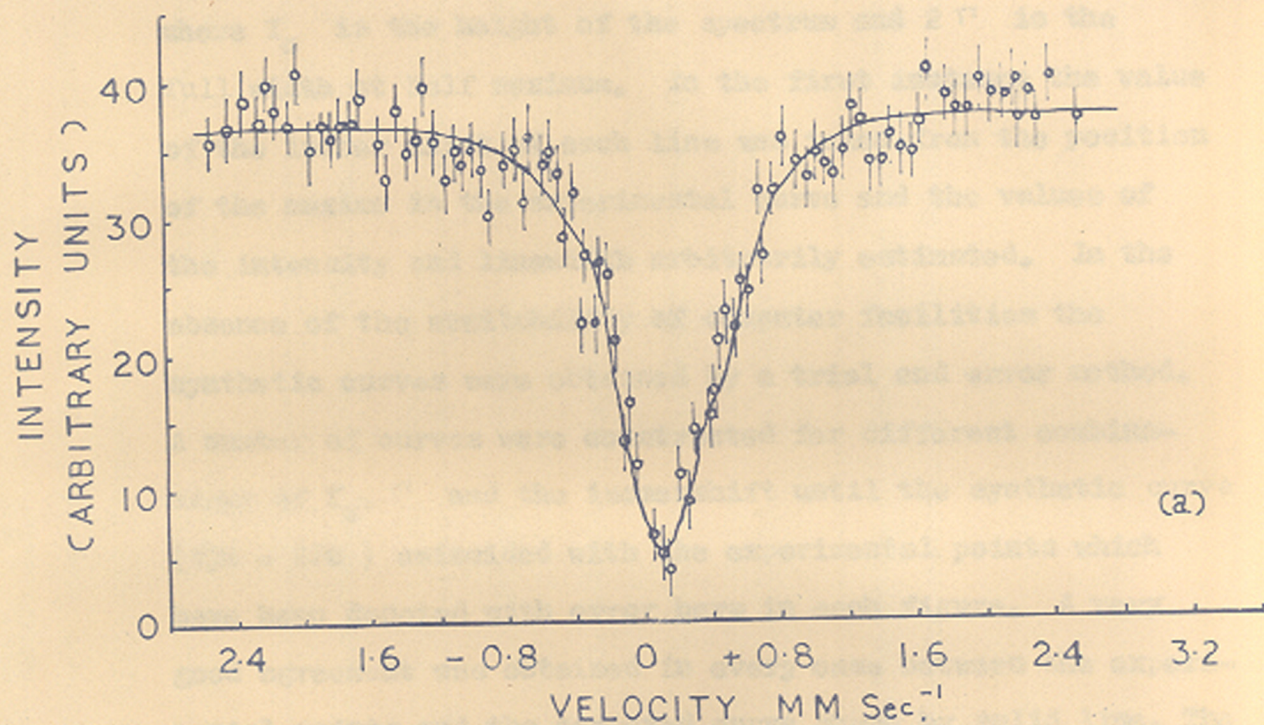


Fig.(21): (a) The Mossbauer spectrum of $^{57}\text{CoCr}_2\text{O}_4$ at 200°C . Synthetic curve superposed on experimental points.
 (b) Synthetic curve composed of Fe^{4+} , Fe^{3+} and Fe^{2+}
 (+ve velocity: absorber moving away from the source).

Fig.(22): (a) The Mossbauer spectrum of $^{57}\text{CoCr}_2\text{O}_4$ at 362°C . Synthetic curve superposed on experimental points.
 (b) Synthetic curve composed of Fe^{4+} , Fe^{3+} and Fe^{2+}
 (+ve velocity: absorber moving away from the source).



$$Y = \frac{Y_0}{1 + 0.75 \left(\frac{X}{\Gamma} \right)^2 + 0.25 \left(\frac{X}{\Gamma} \right)^4} \quad (14)$$

where Y_0 is the height of the spectrum and 2Γ is the full width at half maximum. In the first instance the value of the isomer shift of each line was taken from the position of the maxima in the experimental curve and the values of the intensity and linewidth arbitrarily estimated. In the absence of the availability of computer facilities the synthetic curves were obtained by a trial and error method. A number of curves were constructed for different combinations of Y_0 , Γ and the isomer shift until the synthetic curve (19b - 22b) coincided with the experimental points which have been denoted with error bars in each figure. A very good agreement was obtained in every case between the experimental points and the computed curve shown by solid line. The components of the resultant computed curve are shown in part (b) of each figure.

The isomer shifts corresponding to the three single absorption lines at different temperatures are given in table (8). The experimental values of the isomer shift with respect to $K_4Fe(CN)_6 \cdot 3H_2O$ absorber were converted to those with respect to a stainless steel absorber by adding 0.08 mm/sec. The isomer shifts corresponding to the three lines are characteristic of +4, +3 and +2 states of iron (fig. 4 page 77 table 2). Single absorption lines indicate the absence of

Table - 3

Mossbauer parameters of different components in the Mossbauer spectrum
 $^{57}\text{CoCr}_2\text{O}_4$ at different temperatures*

Temp.	Fe^{2+}		Fe^{3+}		Fe^{4+}		Percentage of each component		
	Isomer shift w.r.t. 310ss absorber† mm./sec.	Line-width mm./sec.	Isomer shift w.r.t. 310ss absorber† mm./sec.	Line-width mm./sec.	Isomer shift w.r.t. 310ss absorber† mm./sec.	Line-width mm./sec.	Fe^{2+}	Fe^{3+}	Fe^{4+}
- 80°C	1.04±0.04	0.36±0.04	0.60±0.04	0.40±0.04	0.24±0.04	0.49±0.04	25±2	31±2	44±2
25°C	0.92±0.04	0.44±0.04	0.52±0.04	0.48±0.04	0.16±0.04	0.52±0.04	26±2	32±2	42±2
202°C	0.74±0.04	0.48±0.04	0.28±0.04	0.52±0.04	-0.12±0.04	0.64±0.04	28±2	51±2	21±2
362°C	0.60±0.04	0.52±0.04	0.20±0.04	0.56±0.04	-0.16±0.04	0.72±0.04	27±2	65±2	8±1

* Absorber: $\text{K}_2\text{Fe}(\text{CN})_6\cdot 3\text{H}_2\text{O}$ at 25°C containing 0.24 mg. $^{57}\text{Fe}/\text{cm}^2$ (enriched to +92% in ^{57}Fe)

† Converted to values relative to 310ss absorber by adding 0.03 mm./sec. to the experimentally observed values.

an EFG at the iron site, a result in agreement with the cubic point symmetry of the A site in the spinel structure. The isomer shift of the +2 state is equal to that for the spinel $\text{Fe}^{2+}[\text{Cr}_2^{3+}]_4\text{O}_4$ (& fig. 23a, table 9). The isomer shift for Fe^{4+} is in good agreement with the experimental value for the tetravalent iron reported by earlier workers.^{29,85} The experimental value of the isomer shift for the +4 state is much less negative than expected from the theoretically predicted values²⁶ for a purely ionic $3d^4$ configuration. This may be explained as due to an increase in the covalency of a cation with a higher charge. A higher charge brings about the reduction in the size of the cation and the consequent greater polarization of the surrounding anions. The d^3s bonding instead of the sp^3 bonding of the cation at the octahedral (B) sites, would bring about a decrease in electron density at the nucleus, and hence an increase in the isomer shift, due to a greater shielding effect of the d-electrons.

The temperature coefficients of the isomer shifts for the +4, +3 and +2 states of iron were found to be -3.0×10^{-15} , -3.0×10^{-15} and -3.3×10^{-15} / deg. respectively. These values are of the same order of magnitude as the limiting value of the second order Doppler effect arising from the lattice vibrations, viz.⁸⁷

$$\frac{d}{dT} \left(\frac{\delta E}{E} \right) = -\frac{3kT}{2Mc^2} = -\frac{3}{2} \frac{C_2}{Mc^2} = -2.44 \times 10^{-15} / \text{deg.} \quad (15)$$

Table - 9

Mossbauer parameters for FeCr_2O_4 and FeCr_2S_4
at room temperature

Spinel	Isomer shift relative to stainless steel mm./sec.	Line-width mm./sec.	Ref.
FeCr_2O_4	0.92 ± 0.04	1.04 ± 0.04	Present work.
	0.96 ± 0.04	1.04 ± 0.04	86
FeCr_2S_4	0.72 ± 0.04	0.48 ± 0.04	Present work
	0.72 ± 0.04	0.48 ± 0.04	101

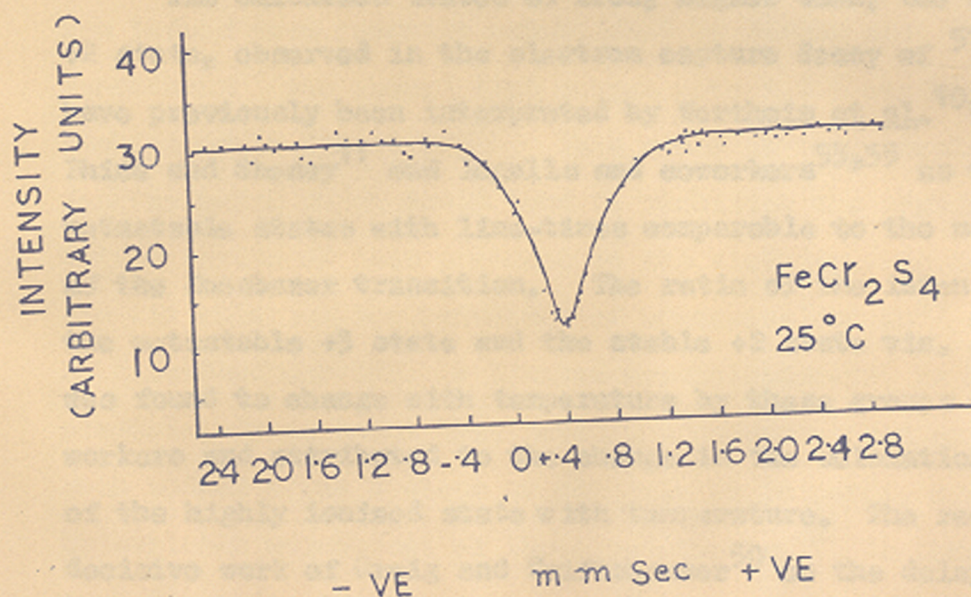
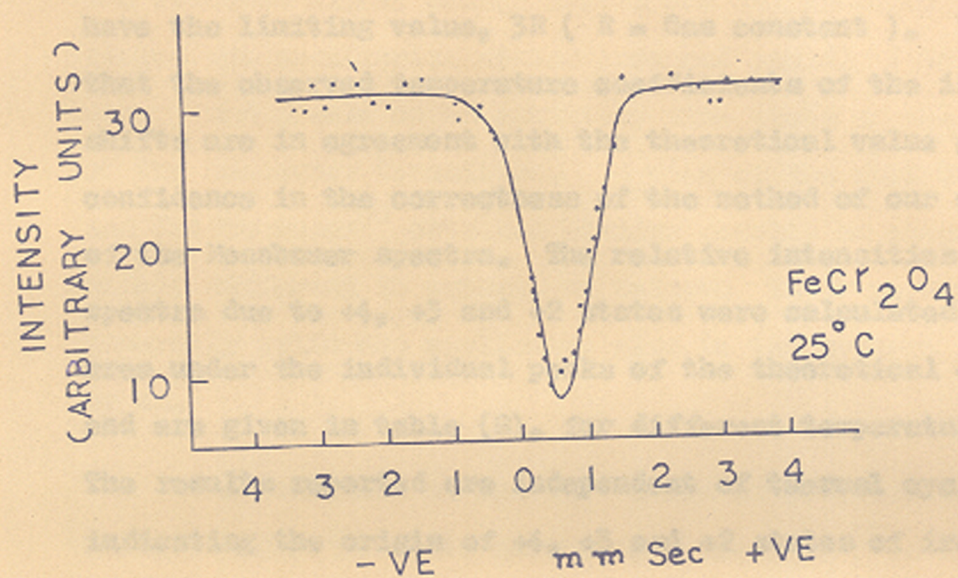


Fig.(23): The Mossbauer spectra of (a) FeCr₂O₄ and (b) FeCr₂S₄ at 25°C (Source : ⁵⁷Co/Cu at 25°C)

where C_v the specific heat at constant volume is taken to have the limiting value, $3R$ (R = Gas constant). The fact that the observed temperature coefficients of the isomer shifts are in agreement with the theoretical value gives confidence in the correctness of the method of our analyses of the Mossbauer spectra. The relative intensities of the spectra due to +4, +3 and +2 states were calculated from the area under the individual peaks of the theoretical curves and are given in table (3), for different temperatures. The results reported are independent of thermal cycling indicating the origin of +4, +3 and +2 states of iron to be reversible.

The oxidation states of iron, higher than, the expected +2 state, observed in the electron capture decay of $^{57}\text{Co}^{+2}$ have previously been interpreted by Wertheim *et al.*^{10,51,52} Rhide and Shenoy¹¹ and Ingalls and coworkers^{53,55} as the metastable states with time-times comparable to the mean-life of the Mossbauer transition. The ratio of the intensity of the metastable +3 state and the stable +2 state viz. $I_{(3)}/I_{(2)}$ was found to change with temperature by these groups of workers and attributed to the change in the relaxation time of the highly ionized state with temperature. The recent decisive work of Craig and Triftshauser⁵⁰ on the delayed coincidence Mossbauer effect measurements on ^{57}CoO , ^{57}Co doped Ferrous Ammonium sulphate and NiO , $^{57}\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ and $^{57}\text{CoCl}_2$ established that the ratio $I_{(3)}/I_{(2)}$ though dependent on the temperature remains constant at a fixed temperature for

delay times 4 to 200 n.secs. It is therefore evident that the observed higher charge states are not non-equilibrium states but equilibrium states produced rapidly (10^{-15} - 10^{-9} sec.) and stable on an arbitrary time scale of the mean life of the Mossbauer transition. In view of the fact that Craig and Triftshauser⁵⁰ obtained similar results on compounds widely differing in nature, we believe their results to be generally valid and applicable also to the systems studied by us.

The formation of the Fe^{3+} state in addition to the anticipated Fe^{2+} state in the E.C. decay of ^{57}Co in CoO was attributed to nonstoichiometry of CoO or to a mixture of two types of CoO .⁵⁰ The existence of nonstoichiometry in CoO has indeed been recently established by Fisher and Tannenbaum⁸⁸ who showed that oxygen upto 1.2 % can be stabilised in CoO at 900°C . This would in turn create metal ion vacancies which would tend to stabilise the higher oxidation states of iron produced in its vicinity. In CoCr_2O_4 one can rule out the existence of nonequivalent Co^{2+} sites as discussed earlier. A limited nonstoichiometry is however possible. It is known that metal ion vacancies can exist in such spinel type systems or can even be purposely created by suitable adjustment of the constituents.⁸⁹ We shall denote such vacancies as 'intrinsic' vacancies. In addition to the intrinsic vacancies in cation deficient systems, vacancies will also be produced by thermal energies. A close relationship has been reported between the cation vacancy density and the

disaccommodation phenomena in ferrites with spinel structure.⁹⁰⁻⁹² The vacancy density can be estimated from the value of diffusion coefficient of a cation since the former varies with the cation vacancy density. The activation energy of diffusion is however independent of vacancy density.⁸⁹ According to the vacancy diffusion mechanism,⁹³ the activation energy for diffusion (E_d) is the sum of the activation energy for the formation of the vacancy (E_f) and the activation energy for the migration of vacancy (E_m).

$$E_d = E_f + E_m \quad (16)$$

If a system already has "intrinsic vacancies" the term E_f would vanish and the value E_d would be equal to E_m .

Lindner⁹⁴ has tabulated the values of activation energies for the cation self-diffusion in spinel lattices of different types, viz. aluminates, ferrites, chromites etc. (table - 10). The values of E_d lie between 70 and 85 k.cal./mole (3.46 e.v.). Markel and Schmalzried⁹⁵ have reported the activation energy for diffusion of $^{60}\text{Co}^{2+}$ in CoCr_2O_4 to be 80 k.cals./mole (3.46 e.v.). However, Sun⁹⁶ has reported a value of 51 k.cal./mole (2.2 e.v.) for the same system. He prepared CoCr_2O_4 in a strongly oxidising atmosphere. His sample of $\text{Co}[\text{Cr}_2]\text{O}_4$ may therefore be expected to contain an excess of oxygen and hence intrinsic cation vacancies. The smaller value of E_d reported by Sun may therefore be attributed to the absence of contribution due to E_f in equation (16). Confirmatory evidence for cation vacancies

Table - 10

Activation energies for self-diffusion of different cations in different spinels given by Lindner⁹⁴

Systems	Q (K.cals./mole)
<u>Aluminates</u>	
Mg in MgAl_2O_4	86
Zn in ZnAl_2O_4	78
Ni in NiAl_2O_4	53.3
<u>Ferrites</u>	
Zn in ZnFe_2O_4	86
Fe in ZnFe_2O_4	82
Fe in FeFe_2O_4	55
<u>Chromites</u>	
Zn in ZnCr_2O_4	85
Cr in ZnCr_2O_4	81
Co in CoCr_2O_4	51
Cr in CoCr_2O_4	70
Ni in NiCr_2O_4	61.4
Cr in NiCr_2O_4	73.0

is available from the work of Bradburn and Rigby⁸³ who have found CoCr_2O_4 to be positive hole conductor. It is therefore reasonable to assume that cation vacancies can exist in CoCr_2O_4 and this probably is true for our sample of CoCr_2O_4 also. One vacancy at the A site would tend to stabilize in its vicinity two Fe^{3+} ions produced as a result of Auger effect following electron capture decay of $^{57}\text{Co}^{2+}$. It is known that vacancies can exist in clusters.⁹⁷ A pair of vacancies can therefore bring about the stabilisation of Fe^{4+} state. It is not necessary that the vacancies be present in the immediate vicinity. For example isolated Fe^{2+} ions with charge compensation at large distances are stable in NaF lattices.⁹⁸ On the other hand EPR spectrum of Cr^{3+} in ZnF_2 indicates the presence of a nearby defect for charge compensation.⁹⁷ The observation of +4 and +3 oxidation states of iron in addition to the +2 state formed in the decay of ^{57}Co in CoCr_2O_4 matrix may therefore be explained as due to the following sequence of events.

As a result of Auger effects following $^{57}\text{Co}^{2+}$ E.C. decay, ionized states of iron upto +7 are produced in a time interval 10^{-15} sec. The charge states higher than +4 relax to the lower charge states rapidly. Due to the presence of the cation vacancies in the $\text{Co}[\text{Cr}_2]\text{O}_4$ lattice the +4 and +3 oxidation states of iron are stabilised for a period which is very long compared to the arbitrary time scale of 10^{-7} sec. the mean

life of the 14.4 keV excited state of ^{57}Fe . These higher charge states would ultimately relax to the +2 stable state of iron and may not exist for a period long enough to be observed by conventional analytical methods. As for example, due to the short electron-spin relaxation time, static magnetic measurement shows NiFe_2O_4 (163 Å) to be paramagnetic (super paramagnetism). Mossbauer measurements indicate the same material to possess stable ferromagnetism.¹⁰⁰ The apparent 'contradiction' is due to the difference in the measurement time in the two techniques.

A characteristic feature of the measurements on the Mossbauer spectra at different temperatures is the greater line-width associated with +4 and +3 states as compared to +2 state of iron. The line-width of +2 state at 25°C is 0.44 mm./sec. and is nearly equal to the value of the line-width (0.36 mm./sec.) obtained on our apparatus by matching the ferrocyanide absorber against ^{57}Co source on copper backing. The line-width for +4 and +3 states were found to be 0.48 and 0.52 mm./sec. respectively at 25°C. The larger line-widths of the higher charge states have been explained as due to a decrease in the time of charge relaxation of the ionized states,^{11,56} which brings about an increase in the linewidth due to the uncertainty principle. However, the intrinsic vacancy model offers a simple explanation of the line-broadening in terms of the inhomogeneous local environment of the +4 and +3 oxidation states of iron, due to the associated vacancies. The random distribution of the vacancies

around the Fe^{4+} and Fe^{3+} sites would produce unequal metal to vacancy distances and hence would give rise to a distribution of small quadrupole splittings due to local inhomogeneities thus leading to the broadening of +4 and +3 resonance lines. The line-width for Fe^{2+} would remain unaffected as it is present at its lattice site unaffected by the vacancies.

Yet another result of significance is the variation of the percentage of +4, +3 and +2 states of iron with temperature (table (8) column V). It may be observed that (1) the area under Fe^{4+} , Fe^{3+} and Fe^{2+} peaks remains constant in the interval -80°C to 25°C within the limits of the estimated error in our analysis, (2) the percentage of Fe^{3+} remains constant in the temperature range -80°C to 25°C and thereafter it increases, (3) the percentage of Fe^{4+} also remains constant in the -80°C to 25°C range and thereafter it decreases sharply, (4) the percentage of Fe^{2+} shows no significant change in the temperature range studied. The vacancies which can exist in pairs at low temperature dissociate into single isolated vacancies at a higher temperature. Consequently the Fe^{4+} state can no longer be stabilised and would be converted to Fe^{3+} . Since the vacancies are bound with a very small amount of energy, a temperature of 200°C is quite sufficient to dissociate the vacancy pairs and it is at this temperature the percentage of Fe^{4+} has been found to decrease sharply.

An alternative explanation for the increase of Fe^{3+} percentage can be found in the increase in the number of cation vacancies due to the stabilisation of additional oxygen in CoCr_2O_4 lattice at these temperatures. The phase diagram of CoCr_2O_4 in equilibrium with oxygen has not been studied so far but it is highly unlikely that CoCr_2O_4 would take up additional oxygen at the low temperature of 362°C .

b) The Mossbauer spectra of $^{57}\text{CoCr}_2\text{S}_4$

The Mossbauer spectra of ^{57}Co doped CoCr_2S_4 matched against a 92 % ^{57}Fe enriched $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ absorber (thickness, $0.24 \text{ mgm } ^{57}\text{Fe} / \text{cm}^2$) at room temperature and 200°C are shown in figs. (24) and (25). The spectrum at -80°C and below were not studied on account of the complication arising due to hyperfine splitting in ferrimagnetic state and at higher temperatures due to possible thermal decomposition of the compound. The spectra were analysed as described before as the sum of two single line Mossbauer spectra of Fe^{3+} and Fe^{2+} states. There is very good agreement between the theoretical curve shown by the continuous line and the experimental points within the limits of statistical error. The values of the isomer shift, line-width and the relative intensities of $\text{Fe}^{3+} [I_{(3)}]$ and $\text{Fe}^{2+} [I_{(2)}]$ are summarised in table (11). The isomer-shift corresponding to the two absorption lines are characteristic of slightly covalent Fe^{3+} and Fe^{2+} states of iron. These values are lower than the

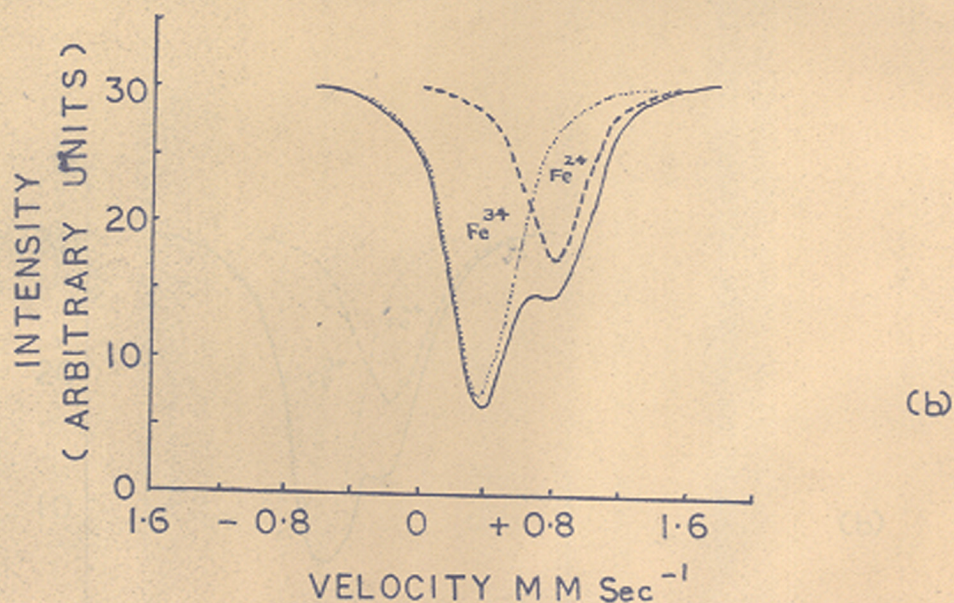
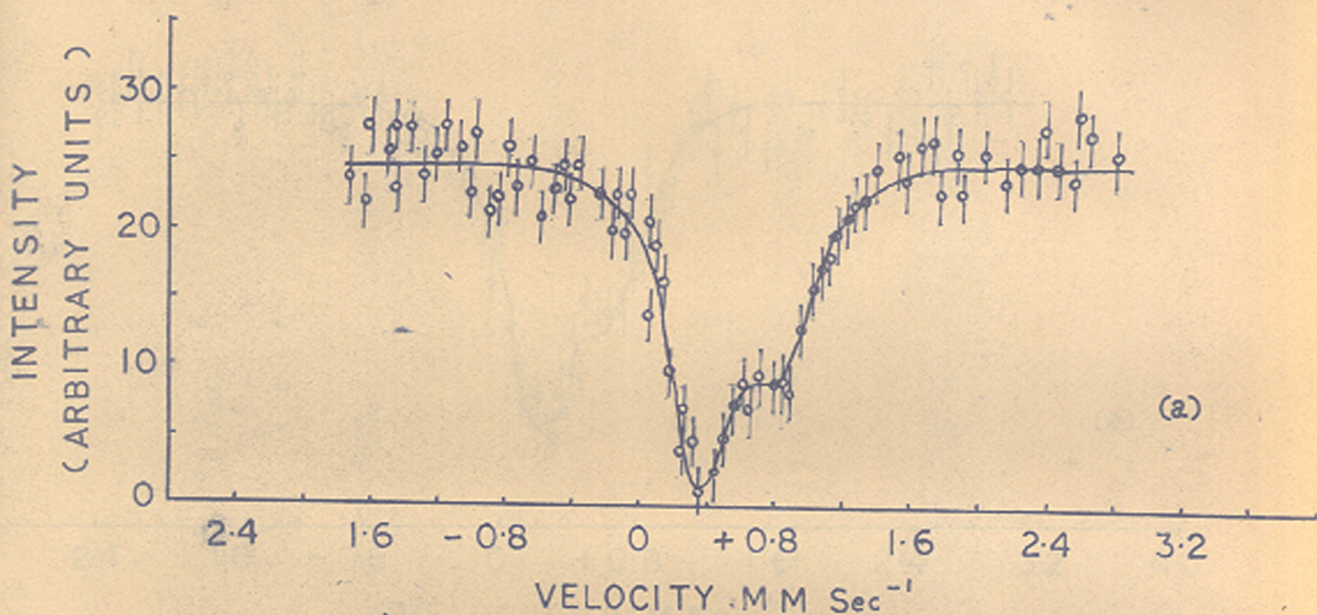


Fig.(24): (a) The Mössbauer spectra of $^{57}\text{CoCr}_2\text{S}_4$ at 25°C . Synthetic curve superposed on experimental points.
 (b) Synthetic curve composed of Fe^{3+} and Fe^{2+} (+ve velocity: absorber moving away from the source).

Fig.(25): (a) The Mossbauer spectrum of $^{57}\text{CoCr}_2\text{S}_4$ at 200°C .

FIG 25

Synthetic curve superposed on experimental points.

(b) Synthetic curve composed of Fe^{3+} and Fe^{2+} (+ve velocity: absorber moving away from the source).

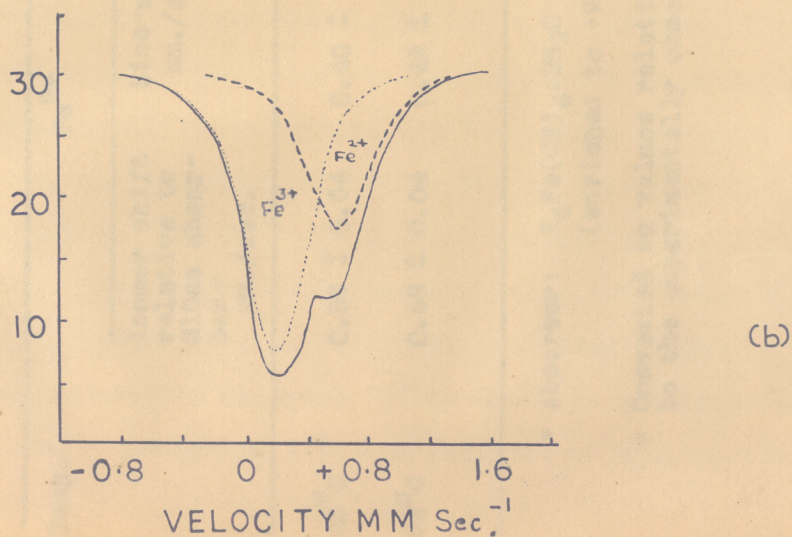
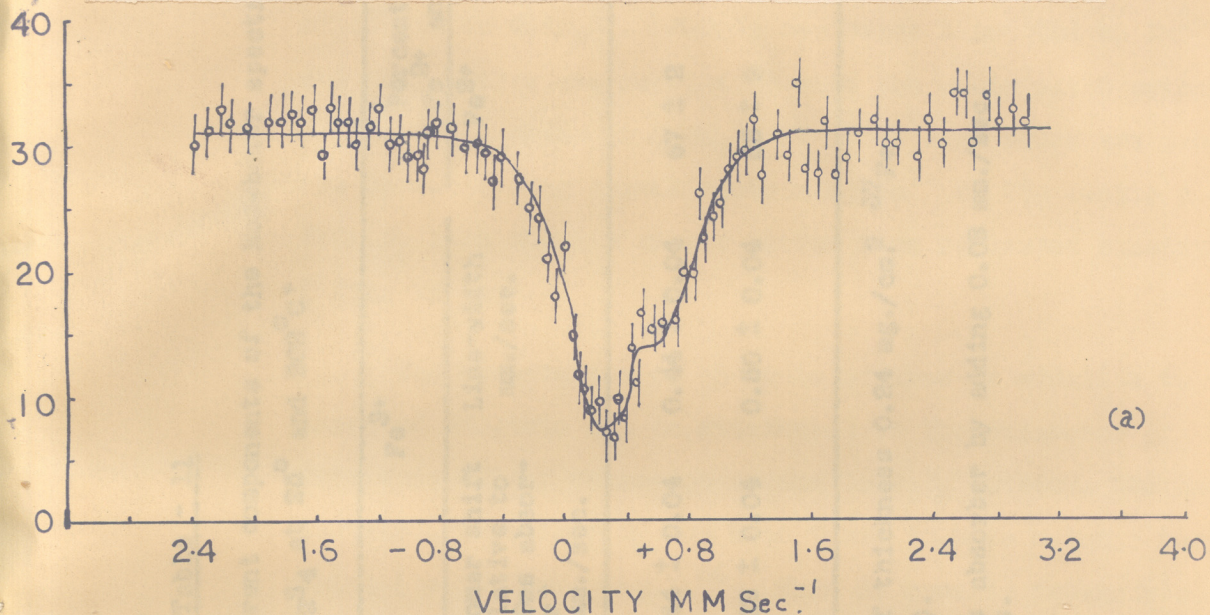


Table - 11

Mossbauer parameters of different components of the Mossbauer spectrum
of $^{57}\text{CoCr}_2\text{S}_4$ at 25° and 202°C^*

Temp.	Fe^{2+}		Fe^{3+}		Percentage of Fe^{2+} and Fe^{3+}	
	Isomer shift relative to 310ss absor- ber + mm./sec.	Line-width mm./sec.	Isomer shift relative to 310ss absor- ber + mm./sec.	Line-width mm./sec.	Fe^{2+}	Fe^{3+}
25°C	0.38 ± 0.04	0.40 ± 0.04	0.44 ± 0.04	0.44 ± 0.04	67 ± 2	33 ± 2
202°C	0.68 ± 0.04	0.42 ± 0.04	0.28 ± 0.04	0.50 ± 0.04	65 ± 2	35 ± 2

* Absorber: $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ at 25°C , of thickness 0.24 mg./cm.^2 ^{57}Fe
(enriched to +92% in ^{57}Fe).

+ Converted to values relative to 310ss absorber by adding 0.08 mm./sec.
to the experimentally observed values.

isomer shifts corresponding to the +3 and +2 states of iron in CoCr_2O_4 due to the greater polarizability or covalency of S^{2-} ion in CoCr_2S_4 . Single resonance lines due to Fe^{3+} and Fe^{2+} state are consistent with the cubic point symmetry of the Co^{2+} sites in CoCr_2S_4 at which iron atoms are produced. The corresponding spinel containing Fe^{2+} at the A-site i.e. FeCr_2S_4 also shows a single narrow line resonance spectrum (Fig. 23).

The observation of +3 state of iron in addition to the expected +2 state may be attributed to the existence of intrinsic cation vacancies in the CoCr_2S_4 lattice. The Seebeck coefficient of CoCr_2S_4 has been found to have a large positive value (+ 852 $\mu\text{V} / \text{deg}$).⁸⁴ This is usually interpreted as characteristic of the p-type semiconductivity.¹⁰² The p-type semiconductivity can arise either due to (a) positive holes or cation vacancies, or (b) anion excess i.e. S^{2-} occupying interstitial positions in the $\text{Co}[\text{Cr}_2]\text{S}_4$ lattice. Due to the large size of the sulphide ion, it cannot be accommodated in the interstitial positions and ^{hence} the p-type semiconductivity of the spinel $\text{Co}[\text{Cr}_2]\text{S}_4$ indicates the existence of the cation vacancies. The Fe^{3+} state can therefore be stabilised by these vacancies as explained earlier. The ratio $I_{(3)}/I_{(2)}$ of the intensities of +3 and +2 oxidation states of iron, in the temperature interval 25° to 200°C is constant within the limits of uncertainty in the analysis of the spectra. The larger linewidth of the higher valency state arises due to the

inhomogeneous local environment of the iron atom stabilised in the trivalent state due to the associated vacancy as described earlier (p. 119). The increase in linewidths of the Fe^{3+} and Fe^{2+} states with an increase in the temperature may be attributed to the Doppler broadening.

2) The Mossbauer Spectra of $\text{K}^{57}\text{CoF}_3$

KCoF_3 belongs to the family of isomorphous transition metal compounds of the general formula $\text{K}^+\text{Me}^{2+}\text{F}_3$ [$\text{Me}^{2+} = \text{Mn}^{2+}, \text{Fe}^{2+}, \text{Co}^{2+}$ and Ni^{2+}] with perovskite structure.¹⁰³ It is known to be highly ionic in nature and it is expected that the relaxation time of a highly charged ion in such a matrix would be longer enough to be detected by Mossbauer Effect studies. It can be prepared by a wet method in an acid solution where oxidation of Co^{2+} to Co^{3+} can be ruled out. Besides, it is unlikely that the compound prepared by wet method would have a nonstoichiometric composition. It has a Neel temperature of 114°K below which it is antiferromagnetic.⁷¹ The corresponding iron compound, KFeF_3 is known to give a single line resonance spectrum with an isomer shift of 1.40 mm/sec. , characteristic of a highly ionic Fe^{2+} state in cubic surrounding.^{26,104} Differential thermal analysis and thermogravimetric analysis of a freshly prepared sample of KCoF_3 (fig. 16) showed that it is thermally stable upto 210°C beyond which it melts and evaporates slowly.

The Mossbauer spectra of $K^{57}CoF_3$ source at -80° , 25° and $190^\circ C$ matched against an enriched potassium ferrocyanide absorber (0.24 mgm/cm^2 ^{57}Fe thick) are shown in figures (26-28). Two partially resolved broad resonances of unequal intensity with their maxima at ~ 0.4 and 1.3 mm/sec. were observed at all the three temperatures. The spectrum at any single temperature may be considered as (1) a single quadrupole split spectrum of a high spin Fe^{2+} ion, the unequal intensities of the two wings of the quadrupole split spectrum arising due to (a) a preferential orientation of the crystallites or (b) the anisotropy in the recoil fraction as explained by Goldanskii¹⁰⁵, (2) a superposed spectrum of two-component spectra due to high spin Fe^{2+} and Fe^{3+} states. In analysing the spectra by Shirane's method (page 110) the first possibility can be ruled out for the following reasons

(a) The $K^{57}CoF_3$ source, rotated by 180° through its diameter gave an identical spectrum eliminating the possibility of 1(a).

(2) $^{57}Co^{2+}$ on electron capture would be ultimately converted to Fe^{2+} which would occupy a Co^{2+} site octahedrally surrounded by 6 F^- ions in $KCoF_3$. Such a cubic symmetry is unlikely to be responsible for the observed large quadrupole splitting of the spectrum & if it is interpreted according to the alternative (1) indicated above.

(3) If the spectrum is analysed in terms of two-component spectra as mentioned in the second alternative, then one of the single line components is typical of the Mossbauer

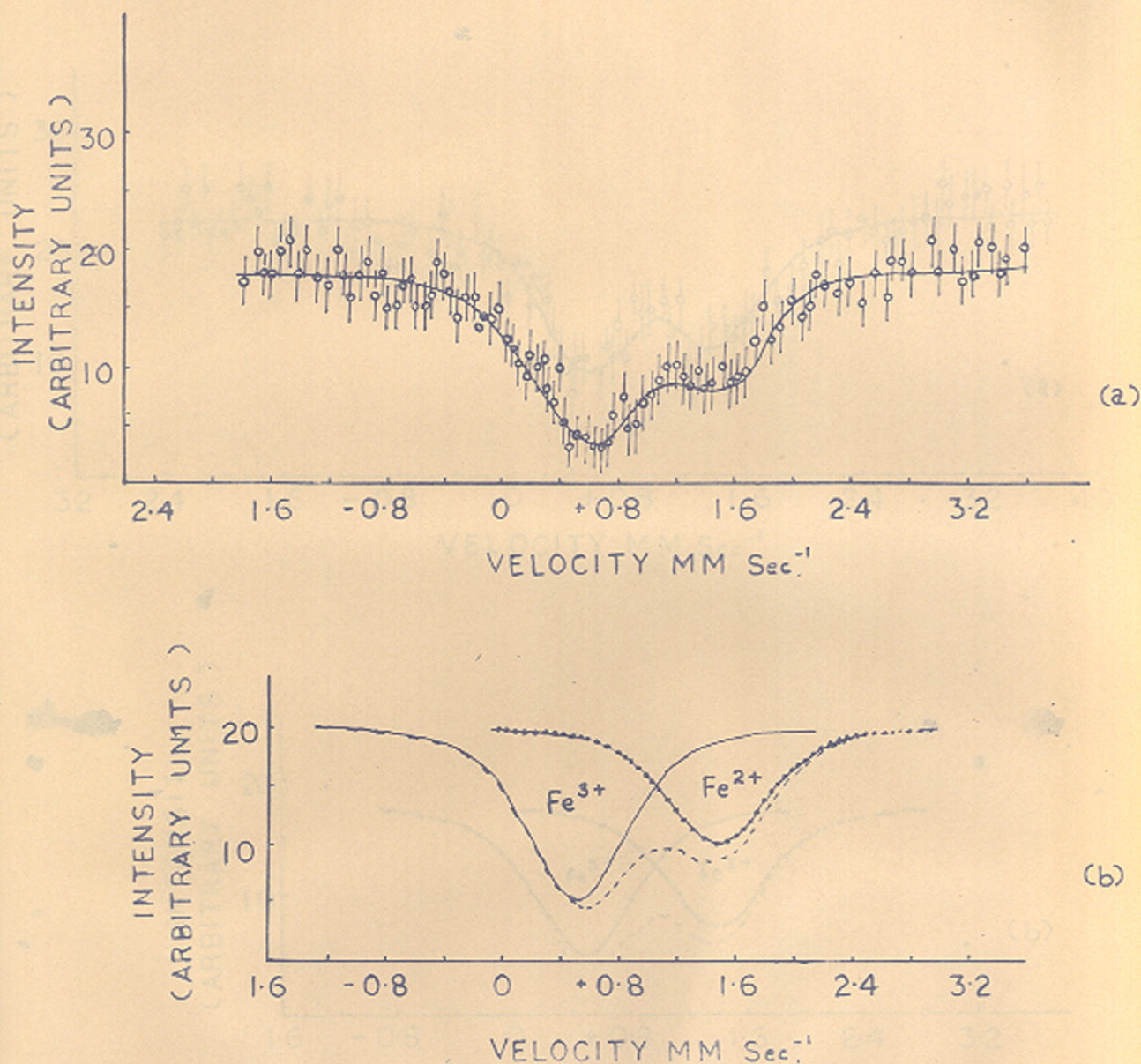


Fig. (26): (a) The Mossbauer spectrum of $\text{K}^{57}\text{CoF}_3$ at -80°C . Synthetic curve superposed on experimental points.
 (b) Synthetic curve composed of Fe^{3+} and Fe^{2+} (+ve velocity: absorber moving away from the source).

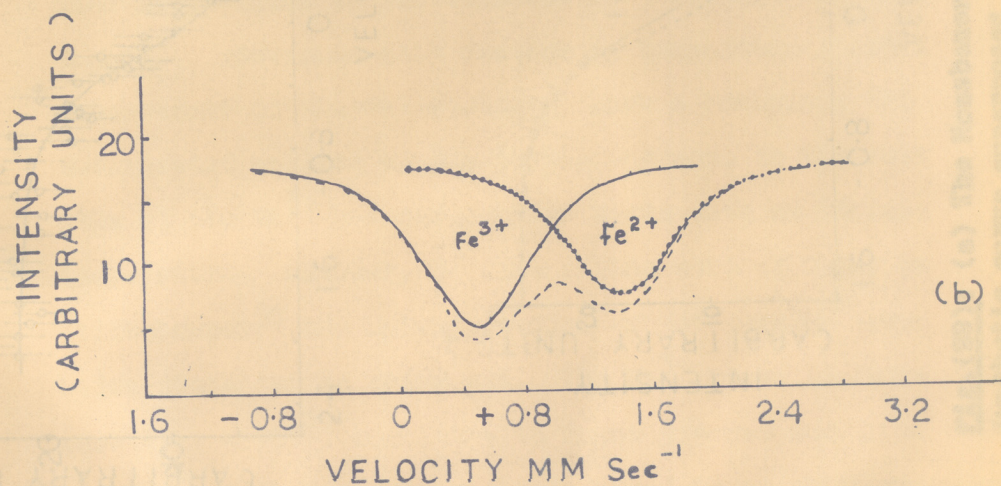
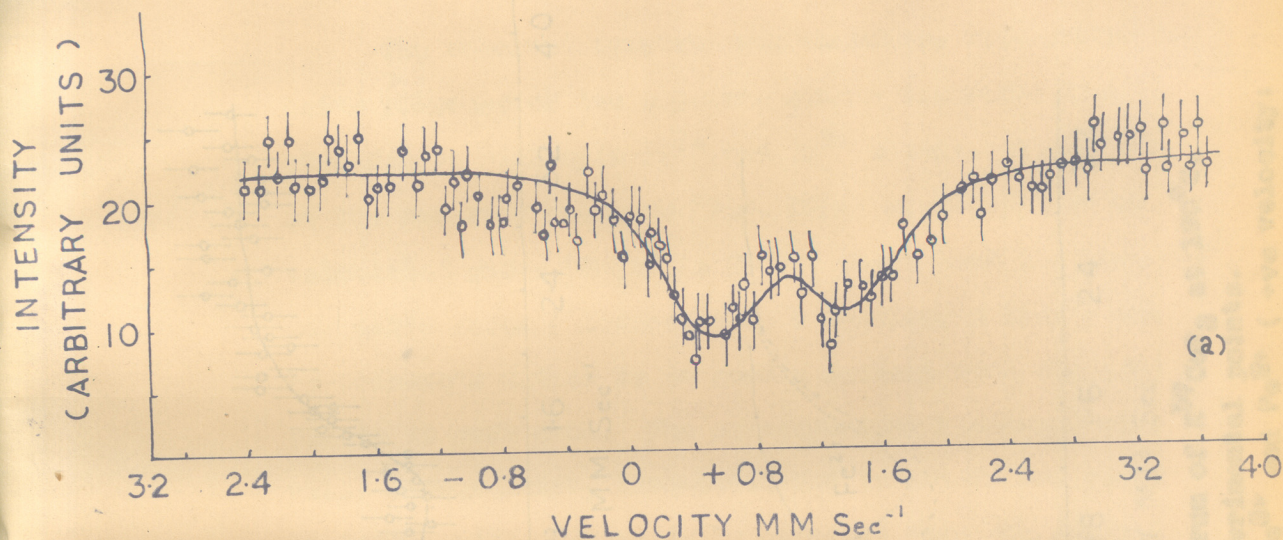


Fig.(27): (a) The Mossbauer spectrum of $K^{57}CoF_3$ at $25^\circ C$. Synthetic curve superposed on experimental points.
 (b) Synthetic curve composed of Fe^{3+} and Fe^{2+} (+ve velocity: absorber moving away from the source).

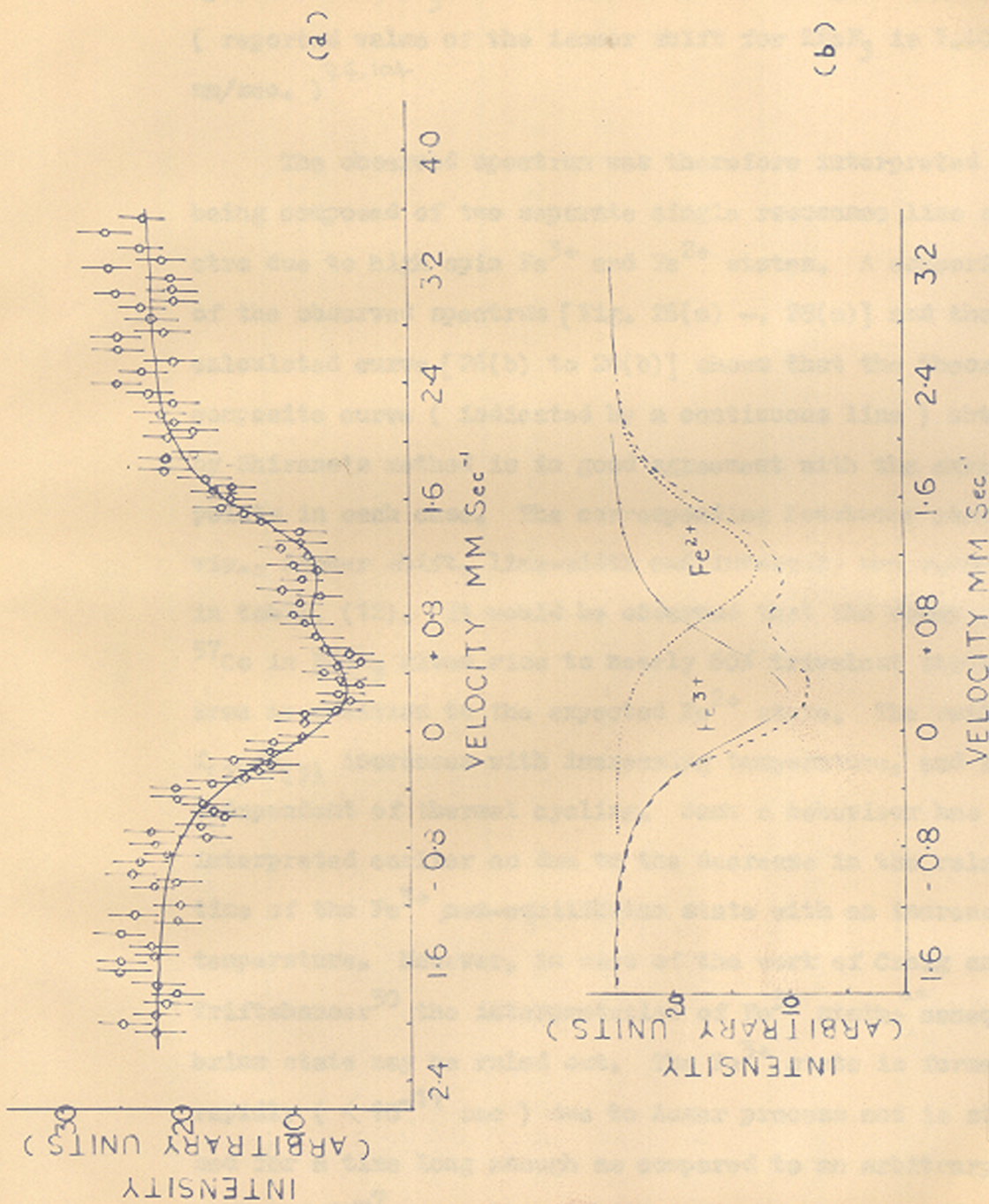


Fig. (23): (a) The Mossbauer spectrum of $K^{0.7}CoF_3$ at $190^\circ C$. Synthetic curve superposed on experimental points. (b) Synthetic curve composed of Fe^{3+} and Fe^{2+} (+ve velocity: absorber moving away from the curve).

spectrum of $KFeF_3$ with an isomer shift of 1.48 mm/sec. (reported value of the isomer shift for $KFeF_3$ is 1.40 mm/sec.)^{26, 104}

The observed spectrum was therefore interpreted as being composed of two separate single resonance line spectra due to high spin Fe^{3+} and Fe^{2+} states. A comparison of the observed spectrum [Fig. 26(a) -, 28(a)] and the calculated curve [26(b) to 28(b)] shows that the theoretical composite curve (indicated by a continuous line) obtained by Shirane's method is in good agreement with the experimental points in each case. The corresponding Mossbauer parameters viz., isomer shift, line-width and intensity are summarised in table. (12). It would be observed that the decay of ^{57}Co in $KCoF_3$ gives rise to nearly 60% trivalent state of iron in addition to the expected Fe^{2+} state. The ratio $I_{(2)}/I_{(3)}$ increases with increasing temperature, and is independent of thermal cycling. Such a behaviour has been interpreted earlier as due to the decrease in the relaxation time of the Fe^{3+} non-equilibrium state with an increase in temperature. However, in view of the work of Craig and Triftshauser⁵⁰ the interpretation of Fe^{3+} state as nonequilibrium state may be ruled out. The Fe^{3+} state is formed rapidly ($< 10^{-11}$ sec) due to Auger process and is stabilised for a time long enough as compared to an arbitrary time scale of 10^{-7} sec. The stabilisation may be brought about by the crystal defects and impurities such as metal ion vacancies or substitution of F^- ions by higher charged anions such as O^{2-} ions. The Goldschmidt radius of the Fe^{3+} ion ($0.67 \text{ \AA}$) is smaller than the radius of the Fe^{2+} ion ($0.75 \text{ \AA}$).

Table - 12

Mossbauer parameters of different components in the Mossbauer spectrum of $^{57}\text{CoF}_3$ at different temperatures*

Temp. of the source	Fe^{3+}		Fe^{2+}		Percentage of each component		I_2/I_3
	Isomer shift relative to ^{57}Fe absorber ⁺ mm./sec.	Line-width mm./sec.	Isomer shift relative to ^{57}Fe absorber ⁺ mm./sec.	Line-width mm./sec.	$\text{Fe}^{2+} (I_2)$	$\text{Fe}^{3+} (I_3)$	
- 80°C	0.62 ± 0.04	0.80 ± 0.04	1.56 ± 0.04	0.80 ± 0.04	40 ± 2	60 ± 2	0.666
25°C	0.54 ± 0.04	0.84 ± 0.04	1.49 ± 0.04	0.82 ± 0.04	45 ± 2	55 ± 2	0.818
190°C	0.32 ± 0.04	0.88 ± 0.04	1.16 ± 0.04	0.86 ± 0.04	49 ± 2	51 ± 2	0.960

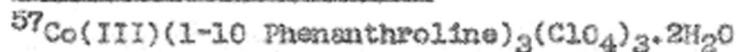
* Absorber: $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ at 25°C, of thickness 0.24 mg./cm.² ^{57}Fe (enriched to +92% in ^{57}Fe).

+ Converted to values relative to ^{57}Fe absorber by adding 0.03 mm./sec. to the experimentally observed values.

($0.83 \text{ \AA}$) and Co^{2+} ion ($0.82 \text{ \AA}$)¹⁰⁶ and hence it may tend to get stabilised strictly due to a volume effect in a Co^{2+} site in cobalt compounds with appropriate charge compensation.⁴⁴

The decrease in the ratio I_3/I_2 with increasing temperatures appears to be intimately related to the state of equilibrium of the crystal lattice at any temperature since it is independent of thermal cycling. The possible excitation of the electrons into the conduction band at high temperature would cause the reduction of the Ferric to Ferrous state by absorption of an electron.

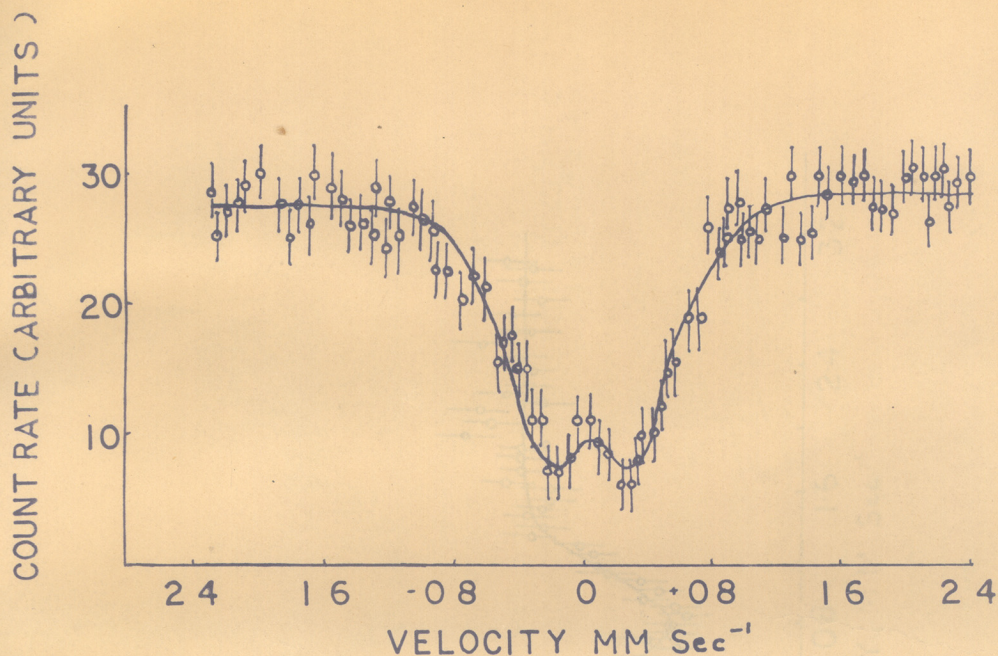
3) The Mossbauer Spectrum of



Soon after the discovery of the resonant absorption of gamma rays, Mossbauer experiments indicated the presence of nonequilibrium states of iron formed in the electron capture decay of $^{57}\text{Co}^{2+}$ due to the Auger process. If the reported results on the observation of Fe^{3+} state, in addition to the expected Fe^{2+} state were really due to long relaxation times of the highly ionised states of iron, then the decay of ^{57}Co in a predominantly covalent matrix should not give rise to any appreciable percentage of the nonequilibrium higher charge states, due to easier availability of electrons on account of a greater overlap of the ligand orbitals with the metal ion orbitals. In order to interpret the results unambiguously one should be able to eliminate

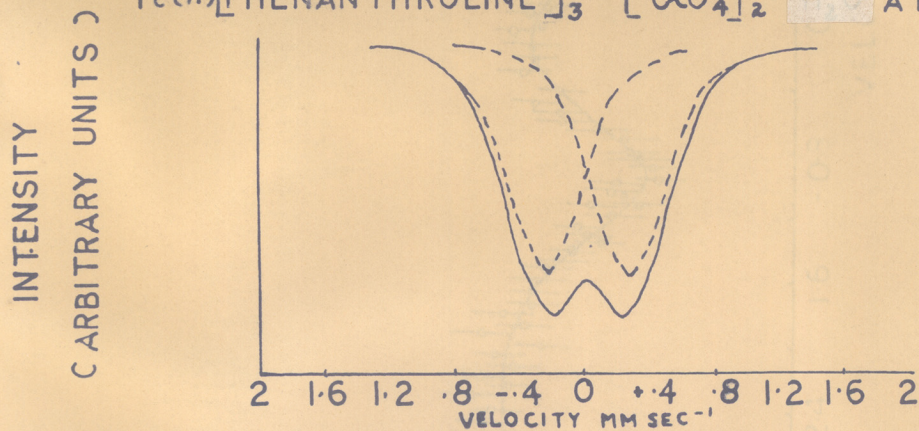
nonstoichiometry as well as correctly identify the valency and the environment of the parent nucleus. It would also be useful to have information on the Mossbauer spectra of the corresponding iron compounds in different oxidation states. A molecular complex of the type Tris (1-10 phenanthroline) Co(III) perchlorate dihydrate appears to meet these above requirements.

The Mossbauer spectra at liquid nitrogen temperature of ^{57}Co labelled Tris (1-10 phenanthroline) Co(III) perchlorate dihydrate matched against ^{57}Fe enriched $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ absorber (containing $0.8 \text{ mgm } ^{57}\text{Fe}/\text{cm}^2$), of $\text{Fe}(\text{II})(1-10 \text{ phenanthroline})_3(\text{ClO}_4)_2$ and $\text{Fe}(\text{III})(1-10 \text{ phenanthroline})_3\text{H}_2\text{O}$ with $^{57}\text{Co}/\text{Cu}$ source are shown in figs. (29, 30, 31) respectively. The Mossbauer parameters of these spectra are given in tables (13 and 14). The $\text{Fe}(\text{II})(1-10 \text{ phenanthroline})_3(\text{ClO}_4)_2$ spectrum shows a quadrupole splitting of $0.4 \pm 0.08 \text{ mm/sec.}$ with an isomer shift of $+ 0.06 \text{ mm/sec.}$ with respect to $^{57}\text{Co}/\text{Cu}$ source or $0.40 \pm 0.04 \text{ mm/sec.}$ with respect to $^{57}\text{Co}/\text{SS}$ source (fig. 29) characteristic of covalently bound $\text{Fe}(\text{II})$ ion. The existence of a small quadrupole splitting indicates that the EFG at the $\text{Fe}(\text{II})$ nucleus arises due to a slight distortion of the octahedral symmetry of the compound. There will not be any electronic contribution to the EFG due to the fact that the ferrous ion in this complex has a $(t_{2g})^6 (e_g)^0$ configuration. These results are in agreement with those reported by Epstein¹⁰⁷ and Collins *et al.*⁶⁷ with



(a)

FIG THE MOSSBAUER SPECTRUM OF
 $\text{Fe(II)[PHENANTHROLINE]}_3 [\text{ClO}_4]_2$ AT -194°C



(b)

CURVE FITTING BY SHIRANE'S METHOD FOR
 $\text{Fe(II)[PHENANTHROLINE]}_3 [\text{ClO}_4]_2$ AT -194°C

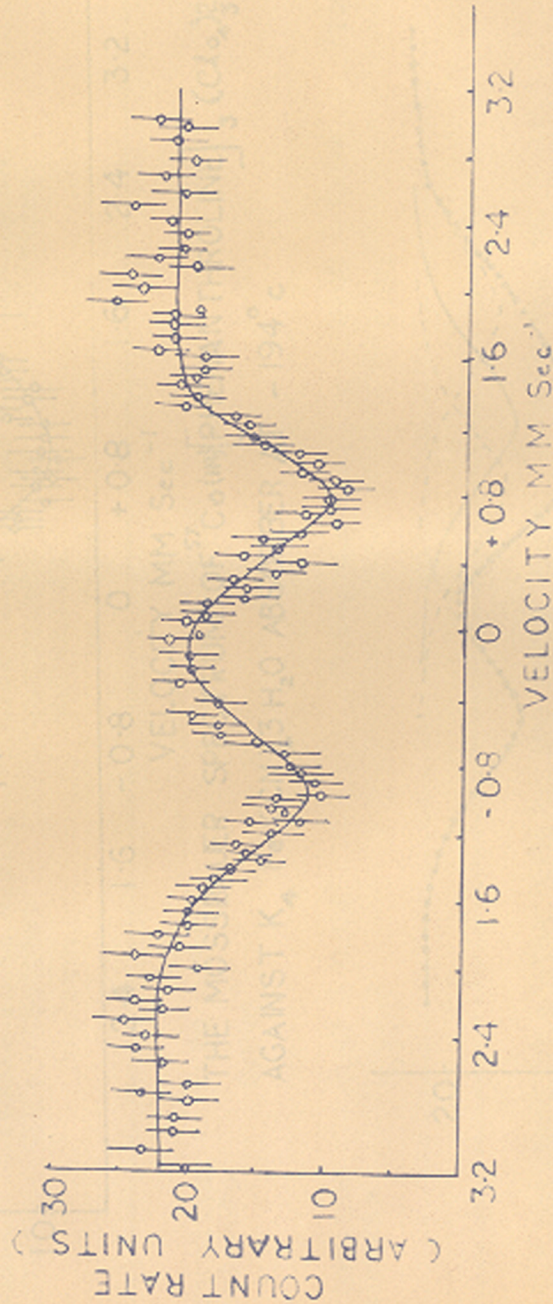


Fig. (20): The Mössbauer spectrum of $\text{Fe(III)}(1-10 \text{ phenanthroline})_3(\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$ at -190°C (source: $^{57}\text{Co/Cu}$ at 25°C)

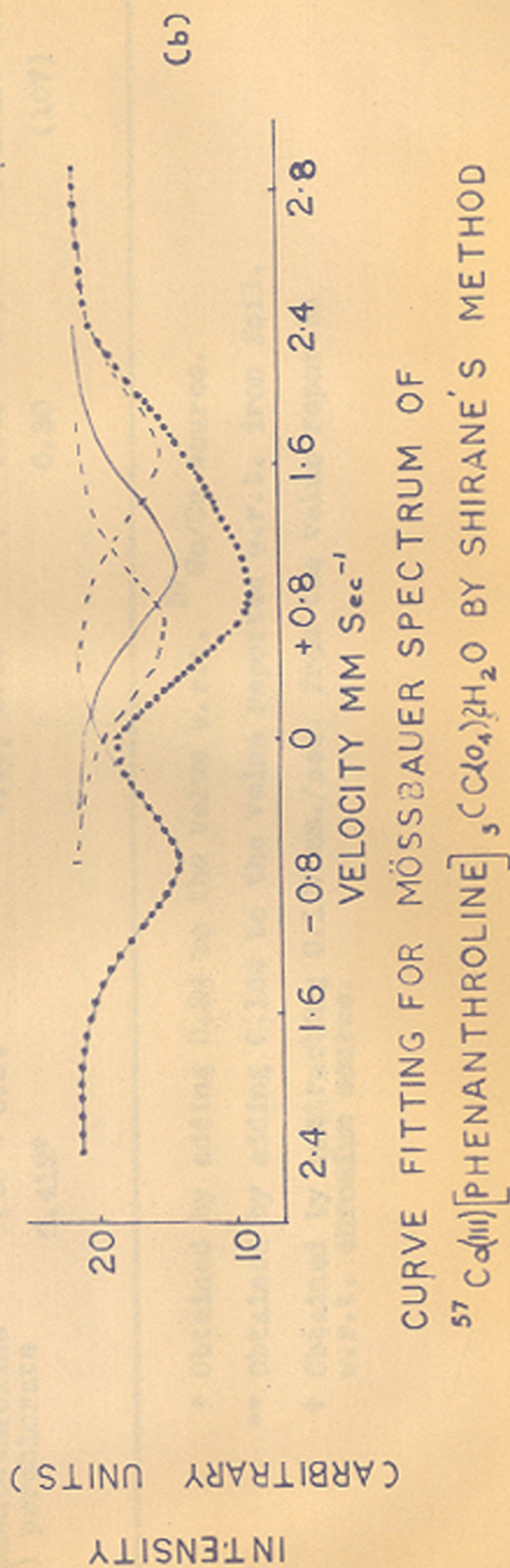
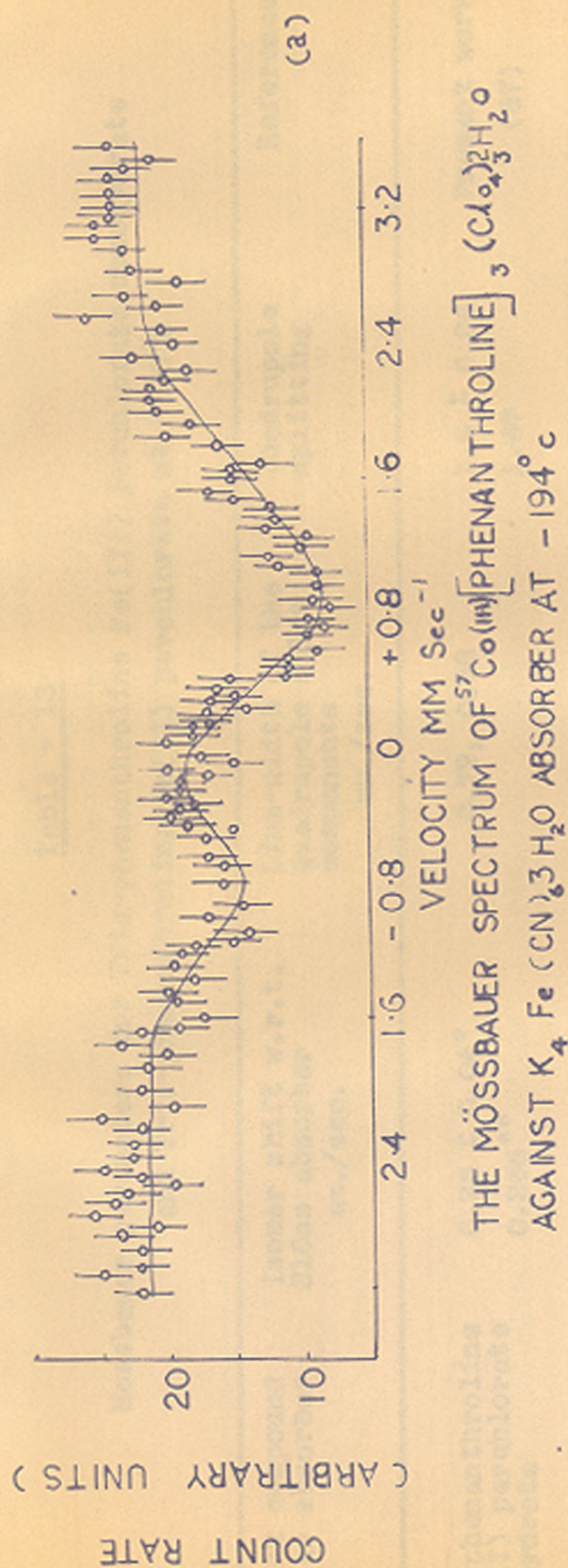


FIG. 31

Table - 13

Mossbauer parameters for Tris-phenanthroline Fe(III) perchlorate monohydrate
and Tris-phenanthroline Fe(II) perchlorate at -190°C

Complex compound used as absorber	Isomer shift w.r.t. 31055 absorber mm./sec.	Line-width of the quadrupole split components mm./sec.	Quadrupole splitting	Reference
Tris-phenanthroline Fe(III) perchlorate monohydrate	0.26 ± 0.04* 0.266**	0.72, 0.80	1.6 ± 0.04 1.67	Present work (67)
Tris-phenanthroline Fe(II) perchlorate	0.40 ± 0.04* 0.412†	0.68, 0.68	0.40 ± 0.04 0.30	Present work (107)

* Obtained by adding 0.34 to the value w.r.t. ⁵⁷Co/Cu source.

** Obtained by adding 0.166 to the value reported w.r.t. iron foil.

† Obtained by subtracting 0.107 mm./sec. from the value reported w.r.t. chromium source.

Table - 14

Mossbauer parameters of different components of the Mossbauer spectrum of

 $^{57}\text{Co(III)(1-10 Phenanthroline)}_3(\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}$ at -190°C^*

Fe(III)			Fe ²⁺			Percentage of each component	
Isomer shift w.r.t. ^{57}Fe absorber [†] mm./sec.	Line-width mm./sec.	Quadrupole splitting mm./sec.	Isomer shift w.r.t. ^{57}Fe absorber mm./sec.	Line-width mm./sec.	Quadrupole splitting mm./sec.	Fe(III)	Fe ²⁺
0.22±0.04	0.96±0.04	1.72±0.04	1.22±0.04	0.96±0.04	1.0±0.04	54.4±2	45.6±2

* Absorber: $\text{K}_4\text{Fe(CN)}_6 \cdot 3\text{H}_2\text{O}$ at 25°C , of thickness 0.24 mg./cm^2 ^{57}Fe (enriched to +92% in ^{57}Fe).

† Converted to values relative to ^{57}Fe absorber by adding 0.08 mm./sec. to the experimentally observed values.

the exception that our Mossbauer spectrum shows a distinct doublet while the above mentioned investigators have reported only single broad resonance line which may be attributed to a finite thickness of their source and/or absorber.

The $\text{Fe(III)(1-10 phenanthroline)}_3(\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$ spectrum on the other hand shows an isomer shift of -0.08 mm/sec with respect to $^{57}\text{Co/Cu}$ source or 0.26 mm/sec with respect to $^{57}\text{Co/SS}$ source, characteristic of low spin Fe(III) compounds and a large quadrupole splitting of 1.6 mm/sec . (Fig.30) which may be attributed mainly to the SFG arising due to a vacancy of one electron in the otherwise completed d-shell. There may also be a small additional contribution to the SFG due to the distortion of the octahedral symmetry. The Mossbauer parameters found by us are in agreement with those found by Collins *et al.*⁶⁷

The Mossbauer spectrum at 25°C of $^{57}\text{Co(1-10 phenanthroline)}_3(\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}$ matched against the ferrocyanide absorber with shows a small resonant absorption and since its analysis was rather indefinite, it is not shown here. The spectrum obtained by keeping the source at liquid nitrogen temperature is shown in fig. (31). It shows two resonance maxima at $\sim -0.8 \text{ mm/sec}$. and $\sim +0.8 \text{ mm/sec}$. with a large difference in their intensities. It may be interpreted as (i) a single Mossbauer spectrum with asymmetrically split quadrupole splitting which may arise due to a preferential orientation of the crystallites or due to Goldanskii Effect.¹⁰⁵

The former was ruled out by taking a second Mossbauer spectrum after rotating the source through the diameter by 180° when an identical spectrum was obtained, (ii) a composite Mossbauer spectrum consisting of contribution from the separate spectra of the following states of iron viz. (a) low spin Fe(III), (b) low spin Fe(II), (c) high spin Fe^{2+} , (d) high spin Fe^{3+} . A comparison of the Mossbauer spectra of $\text{Fe(II)(1-10 phenanthroline)}_3(\text{ClO}_4)_3$ absorber and the $^{57}\text{Co(III)(1-10 phenanthroline)}_3(\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}$ source against Ferrocyanide absorber clearly shows that there is little contribution due to low spin Fe(II) compound. It was found that the experimental results could be reproduced by a combination of the Mossbauer spectra due to a quadrupole split spectrum of low spin Fe(III) and a quadrupole split spectrum of high spin Fe^{2+} . The curve was analysed by the trial and error method according to the Shirane's procedure as already described (See page 110). A perusal of fig.(31) would show that there is a very good agreement between the theoretical curve shown by a continuous line drawn matched against the experimental points. The isomer shift, line-width and the percentage absorption for the two states are summarised in table (14). The four resonance maxima at - 0.72 and 1.0 mm/sec. and 0.64 and 1.64 mm/sec. correspond to an isomer shift of 0.14 mm and 1.14 mm/sec. respectively with respect to Ferrocyanide absorber or 0.22 and 1.22 mm/sec. with respect to stainless steel absorber, and quadrupole splittings of 1.72 and 1.04 mm/sec. respectively. The former is characteristic of low spin Fe(III)(1-10 phenanthroline)₃(ClO₄)₃·H₂O and the latter of high spin Fe^{2+} compounds.

The observation of the low spin Fe(III) state in the Mossbauer spectrum of $^{57}\text{Co(III)(1-10Phenanthroline)}_3(\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}$ is consistent with the conversion of the $^{57}\text{Co(III)}$ to $^{57}\text{Fe(III)}$. As expected, no charge state higher than +3 have been observed. The observation of the high spin Fe^{2+} is however unexpected. Wertheim *et al.*⁵¹ have also observed a +2 ionic state of iron in the Mossbauer spectrum of $^{57}\text{Co(III)(Acetyl acetate)}_3$ and interpreted it as due to a rearrangement of charge distribution among the near neighbour atoms to accommodate the presence of ions of charge $\geq +4$. This seems to be unlikely since there is no evidence for +4 state in the spectrum. In the case of multiple charge atoms produced in a solid, two charge states of the same element with charges n and $n+2$ can exchange an electron both becoming $n+1$. However, such exchange processes are more likely at high temperatures than at 4°K (the temperature of Wertheim's experiment) and hence one should be able to observe the +4 state as well. Therefore, we believe the explanation given by Wertheim cannot account for the existence of +2 state. The explanation for the valency state lower than that of the parent atom should therefore be sought for, in the fragmentation of the metal complex due to Coulombic repulsion¹⁰⁸ arising out of the Auger process, following the electron capture decay of ^{57}Co .

As discussed earlier (see pp. 103 & 104) the electron capture decay of an unstable nucleus produces a highly charged central metal ion due to the 'vacancy cascade'

process, which has been estimated to take place in a very short time interval of 10^{-15} sec.¹⁰⁸ The highly charged metal ion produced as a result of Auger cascade would distribute its excess charge to other atoms of the molecule since the time of Auger cascade is much less than the period of vibration of atoms in the molecule. The distribution of positive charges throughout the molecule produces strong coulombic repulsion between different atoms of the molecule leading to its virtual decomposition. One would therefore obtain a new chemical species consisting essentially of ionic ferric state. The Fe^{3+} state can easily acquire an electron and get reduced to Fe^{2+} since a large number of electrons would be produced in the fragmentation of the molecule as explained above. It is significant that the value of the isomer shift and the quadrupole splitting of the Fe^{2+} component in our case are comparable to those reported by Wertheim for the Fe^{2+} component in the Mossbauer spectrum of $^{57}\text{Co(III)(Acetylacetonate)}_3$. Mossbauer studies by Saito *et al.*¹⁰⁹ have shown that Fe^{3+} ions in ferric oxalate can be reduced to Fe^{2+} ions by the gamma irradiation.

Recently Amar Nath *et al.*¹¹⁰ have reported the results of the Mossbauer studies on a similar system viz. Tris-dipyridyl $^{57}\text{Co(III)}$ perchlorate. They have claimed the absence of the above fragmentation process. Their Mossbauer spectrum has a distinct asymmetry in the quadrupole split spectrum, which has not been explained. We believe that the asymmetry is indicative of the fragmentation process with the exception that the percentage fragmentation in their case is

somewhat smaller than in our system. The results of Wertheim *et al.*⁵² on the Mossbauer spectrum of cobaltincinium tetraphenyl borate can also be interpreted in terms of a fragmentation process. Their spectrum was found to consist of a singlet and doublet the former being identified as due to a ferricinium ion resulting from the cobaltincinium ion while the latter being due to a decomposition product of the fragmented parent molecule.

REFERENCES:

1. R.L. Mossbauer
 - (a) Z.Physik., 151, 124 (1958).
 - (b) Naturwissenschaften, 45, 538 (1958).
 - (c) Z. Naturf., 142, 211 (1959).
2. H.J.Hay, Peoc. Second Int. Conf on the Mossbauer effect
P. 225, (John Wiley & Sons, New York, (1962).
3. D.A. Shirley, M.Kaplan, R.W. Grant and D.A. Keller,
Univ. of California, Lawrence Radiation Laboratory
Report, UCRL-10168, April, 1962.
4. R.W. Grant, M.Kaplan, D.A. Keller and D.A. Shirley,
Phys. Rev., 133, 1062 (1964).
5. C.E. Johnson, M.S. Ridout, T.E. Crenshaw and P.E. Madsen,
Phys. Rev. Letters 6, 450 (1961).
6. A.J.T. Boyle, D. St. P. Bunbury and C. Edwards, Proc.
Phys. Soc., 77, 1062 (1961b).
7. H.M. Delyagin, V.S. Shpinel, V.A. Bryukhanov and B. Zhvenglinskii, Soviet, Phy. JETP, 12, 619 (1961).
8. J.F. Duncan and R.M. Golding, Quarterly Review, 19
(1), 36-56 (1965).
9. P. Hennafoord, C.J. Howard and J.W.G. Wignall, Phys.
Letters 19, 257 (1965).
10. G.K. Wertheim, Phys. Rev., 124, 764 (1961).
11. V.G. Bhide and G.K. Shenoy, Phys. Rev., 147, 306, (1966).
12. W. Triftshauser and P.P. Craig, Phys. Rev., 162, 274 (1967).
13. G.K. Wertheim, W.R. Kingston and R.H. Herber, J. Chem.
Phys., 37, 687 (1962).

14. Chemical effects of Nuclear Transformations, Proceedings of the Symposium, Prague, October 24-27, 1960 (IASA, Vienna Vol. 1, 1965).
15. Chemical Effects of Nuclear Transformations, Proceedings of the Symposium, Vienna, December 7-11, 1964 (IASA, Vol. 2, 1965).
16. H. Frauenfelder, "The Mossbauer Effect", W.A. Benjamin, Inc., Publishers, New York. (1962).
17. G.K. Wertheim, Mossbauer Effect, 'Principles And Applications', Academic Press, New York and London (1964).
18. E. Fluck, Advances in Inorganic Chemistry and Radiochemistry, Vol. 6 P 433, Academic Press (1964).
19. V.I. Goldanskii, The Mossbauer Effect and its Application in Chemistry, Consultants Bureau, New York (1964).
20. P.B. Moon, Proc. Phys. Soc., 63A, 1189 (1950); ibid 64A, 76 (1951).
21. O.G. Kistner and A.W. Sunyar, Phys. Rev. Letters 4, 412 (1960).
22. D.A. Shirley, Proceedings of the Third International Conference on the Mossbauer Effect P. 339 (1963) (Ed. A. J. Bearden.) Rev Mod. Phys. 36, 339 (1964).
23. J. Dannon, J. Chem. Phys., 39, 236 (1963).
24. V.G. Bhide, G.K. Shenoy and M.S. Multani, Solid State Comm 2, 221 (1964).
25. A.J.F. Boyle and H.S. Hall, 'The Mossbauer Effect', Reports on Progress in Physics, 25, 441-524 (1962).
26. L.R. Walker, G.K. Wertheim, and V. Jaccarino, Phys. Rev. Letters, 6, 98 (1961).
27. T.C. Gible and N.M. Greenwood, J. Chem. Soc., A43, (1966).
28. J.G. Mullen, Phy. Rev., 131, 1415 (1963).

29. G. Shirane, D.E. Cox and S.L. Ruby, Phys. Rev., 125,
1158 (1962).
30. U. Shimony and J.M. Knaudson, Phys. Rev., 144, 361 (1966).
31. G.K. Wertheim and R.H. Herber, J. Chem. Phys., 36,
2497 (1962).
32. W. Kerler, W. Neuwirth and E. Fluck, Z. Physik., 173,
321 (1963).
33. R.H. Herber, "Mossbauer Effect Methodology", P. 1-12,
Ed. I.J. Gruverman, Plenum Press (New York) 1965.
34. J.J. Spijkerman, F.C. Ruegg and J.R. Devoe, "Mossbauer
Effect Methodology", P. 115-120, Ed. I.J. Gruverman,
Plenum Press, (New York), 1965.
35. E. Fluck, W. Kerler and W. Neuwirth, Angewandte Chemie,
75, 461 (1963).
36. W. Kerler and W. Neuwirth, Zeit Physik., 167, 176 (1962).
37. C.E. Johnson, W. Marshall and G.J. Ferlow, Phys. Rev.,
126, 1503 (1962).
38. D.E. Nagle, H. Frauenfelder, R.D. Taylor, D.R.F. Cochran
and B.T. Mathias, Phys. Rev. Letters 5, 364 (1960).
39. D.H.E. Buchanan and G.K. Wertheim, Bull. Am. Phys. Soc.
[2], 7, 227 (1962).
40. O.C. Kistner and A.W. Sunyar, Phys. Rev., 139B, 295 (1965).
41. S. Margulies and J.R. Ehrman, Nuclear Instruments and
Methods, 12, 131 (1961).
42. I. Bergstrom in "Beta and Gamma-ray spectroscopy" Ed.
K. Siegbahn (North Holland Publishing Company, Amsterdam)
P. 624 (1955).
43. A.H. Snell, F. Plessanton and J.L. Need, Phys. Rev., 116,
1548 (1959); ibid., 107, 740 (1957); ibid. 100, 1396 (1955).
44. H. Pollak, Phys. Status Solidi, 2, 720 (1962).

45. G.K. Wertheim, and D.N.S. Buchanan, 'The Mossbauer Effect' P. 130, Ed. D.M.J. Compton and A.H. Schoen, John Wiley & Sons. (New York), 1962.
46. A.J. Bearden, P.L. Mattern and T.R. Hart, Rev. Mod. Phys. 36, 470 (1964).
47. C.J. Coston, R. Ingalls and H.G. Drickamer, Phys. Rev., 145, 409 (1966).
48. V. G. Bhide and G.K. Shenoy, Phys. Rev., 143, 309 (1966).
49. J.G. Mullen and H.N. Oke, Phys. Rev. Letters, 17, 287 (1966).
50. W. Triftshauser and P.P. Craig, Phys. Rev., 162, 274 (1967).
51. G.K. Wertheim, W.R. Kingston and R.H. Herber, J. Chem. Phys., 37, 687 (1962).
52. G.K. Wertheim and R.H. Herber, J. Chem. Phys., 38, 2106 (1963).
53. R. Ingalls and G. Depasquali, Phys. Letters, 15, 262 (1965).
54. Jean Marie Friedt and Jean Pierre Adloff, C.R. Acad. Sc. Paris, 264, 1356 (1967).
55. R. Ingalls, C.J. Coston, G. Depasquali, H.G. Drickamer, and J.J. Pinajian, J. Chem. Phys., 45, 1057 (1966).
56. G.K. Wertheim and H.J. Guggenheim, 42, 3873 (1965).
57. J.G. Mullen, Phys. Rev., 131, 1410 (1963).
58. V.G. Bhide and H.C. Bhasin, Phys. Rev., 159, 586 (1967).
59. H. Sano and T. Hashimoto, Bull. Chem. Soc. Japan, 38, 1565 (1965).
60. R.H. Herber and H.A. Stockler, "Chemical Effects of Nuclear Transformations" P. 403, Vol. 2 (IASA) 1965.

61. W.G. Berger, J. Fink and F.E. Obenshain, *Phys. Letters*, 25A, 466 (1967).
62. W. Karger and B. Bunsenges, *Physik. Chem.*, 68, 793 (1964).
63. R.L. Coster, J. Danon and R.M. Xavieur, *J. Phys. Chem. Solids*, 23, 1733 (1962).
64. R.D. Taylor, T.A. Kitchens, D.B. Nagle, W.A. Steyert and W.E. Millet, *Solid State Communications*, 2, 209 (1964).
65. T. Mizoguchi and M. Tanaka, *J. Phys. Soc. Japan* 18, 1301 (1963).
66. R.S. Preston, S.S. Hanna and S. Heberle, *Phys. Rev.* 128, 2207 (1962).
67. R.L. Collins, R. Pettit and W.A. Baker, *J. Inorg. Nuc. Chem.*, 28, 1001, (1966).
68. F.K. Lotgering, *Philips Research Reports*, 11, 190 (1956).
69. R.H. Francoise, *J. Phys. Chem. Solids*, 2, 37 (1957).
70. C.B. Colominas, M.R. Ballastracci and G. Roult, *J. Physique. Radium*, 25, 526 (1964).
71. K. Knox, *Acta Cryst.* 14, 583 (1961).
72. K. Hirakawa, K. Hirakawa and T. Hashimoto, *J. Phys. Soc. Japan*, 15, 2063 (1960).
73. A.A. Schilt and R.C. Taylor, *J. Inorg. Nuc. Chem.*, 9, 211 (1959).
74. H. Menyuk, K. Dwight and A. Wold, *J. De. Physique, Radium*, 25, 528 (1964).
75. P.M. Raccach, R.J. Bouchard and A. Wold, *J. Appl. Phys.*, 37, 1436 (1966).

76. H.B. Mathur and C. M. Yagnik, J. Phys 'C' (Proc. Phys. Soc.) 1, 469 (1968).
77. E.J.W. Verwey, Z. Krist. 91A, 65 (1935).
78. E.J.W. Verwey and B.L. Heijman, J. Chem. Phys., 15, 174 (1947).
79. F.C. Romeijn, Philips. Res. Repts., 8, 304 (1953).
80. D.S. McClure, J. Phys. Chem. Solids, 2, 311 (1957).
81. J.D. Dunitz and L.E. Orgel, J. Phys. Chem. Solids, 2, 318 (1957).
82. A. Miller, J. Appl. Phys., 30, 248 (1959).
83. T.S. Bradburn and G.R. Rigby, Trans. Brit. Ceramic. Soc., 52, 417 (1953).
84. R.J. Bouchard, P.A. Russo and A. Wold, Inorg. Chem. 4, 685 (1965).
85. P.K. Gallagher, J.B. Macchesney and D.N.B. Buchanan, J. Chem. Physics, 41 2429 (1964).
86. H.B. Mathur, A.P.B. Sinha and C.M. Yagnik, Solid State Communications, 2, 401 (1965).
87. R.V. Pound and G.A. Rebka, Jr., Phys. Rev. Letters, 4, 274 (1966).
88. B. Fisher and D.S. Tannhauser, J. Chem. Phys., 44, 1663 (1966).
89. S. Ogawa and Y. Nakagawa, J. Phys. Soc. Japan, 23, 179 (1967).
90. K. Ohta, J. Phys. Soc. Japan, 16, 250 (1961).
91. A. Yanase, J. Phys. Soc. Japan, 17, 1005 (1962).
92. S. Lida and T. Inoue, J. Phys. Soc. Japan. 17, Supp. B-1, 231 (1962).
93. W. Jost, Diffusion in Solids, Liquids Gases, Academic Press. (New York) 1952.

94. R. Lindner in Peaceful uses of Atomic Energy, Vol. 20,
P. 106 (1958).
95. A. Morkel and H. Schmalzried, Zeit, Physik. Chemie,
32, 76 (1962).
96. R. Sun, J. Chem. Phys., 28, 290 (1958).
97. J.S. Kolhler, F. Seitz and J. Bauerle, Phys. Rev.,
107, 1499 (1957).
98. G.D. Watkins, Phys. Rev., 113, 79 (1959) ibid, P. 91
and references quoted therein.
99. H. Tinkham, Proc. Roy. Soc. (London), A 236, 549 (1956).
100. W.J. Schuele, S. Shtrikman and T. Treves, J. appl.
Phys., 36, 1010 (1965).
101. C.M. Yagnik and H.B. Mathur, Solid State Communications.
5, 841 (1967).
102. U.R. Evans, "The Corrosion and oxidation of metals",
Edward Arnold (publishers) Ltd., (London) 1961.
103. A. Oksaki, Y. Suemune and T. Fuchikami, J. Phys. Soc.
Japan, 14, 1823 (1959).
104. R. Fathallah, G.K. Shenoy, N.P. Sastry and R. Nagarajan,
Phys. Letters, 25A, 453 (1967).
105. V.I. Goldanskii, S.F. Makarov and V.V. Kharapov, Phys.
Letters, 3, 344 (1963).
106. S.E. Gorter, Philips Res. Repts., 9, 295 (1954).
107. L.H. Epstein, J. Chem. Phys., 40, 435 (1964).
108. T.A. Carlson and R. Milford White, P. 23, Chemical
Effects of Nuclear Transformations. Vol. 1, (IASA)
Vienna, 1965.

109. N. Sato, H. Sano, T. Tominaga and F. Ambe, "Applications of the Mossbauer Effect in chemistry of solid state Physics", Technical Reports Series No. 50, P. 251-253, IAEA, Vienna (1966).
110. Amer Nath, R.D. Agarwal and P.K. Mathur, Inorg. Nuc. Chem. Letters, 4, 161 (1968).