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UHV MOSSBAUER EMISSION SPECTRA IN THIN IRON FILMS

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UHV MÖSSBAUER EMISSION SPECTRA IN THIN IRON FILMS

by

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Submitted in partial fulfillment of the requirements
for the Degree of Doctor of Philosophy

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ABSTRACT

by

MATESH NARAYAN VARMA

Mössbauer spectra of thin iron films in the thickness range $1 \text{ \AA}$ to $42 \text{ \AA}$ at temperatures from 15° K to 350° K have been studied. The films are condensed and analyzed in ultra high vacuum. One observes that the films are magnetically stable when the particle size is about $90 \text{ \AA}$ at room temperature and show a transitional behavior for particle size of the order of $85 \text{ \AA}$ at room temperature corresponding to the superparamagnetic fluctuation frequency of 1.2×10^8 radian/sec. The films having particle size of about $70 \text{ \AA}$ show a doublet spectrum at room temperature; this spectrum is interpreted in terms of superparamagnetic fluctuations and is explained as arising from magnetic hyperfine interaction and not from electric quadrupole interaction. The large separation of the doublet in the $0.4 \text{ \AA}$ film is explained in terms of an electric field gradient experienced by the iron nuclei due to the glass substrate or some contamination present on the surface of the substrate. A value of 6.7×10^{17} volts/cm² is estimated for the electric field gradient. Since the intensities of the two lines and the widths are nearly equal it is concluded that the sites that iron nuclei occupy are uniform and equivalent. The isomer shift of the samples is 0.17 mm/sec. and is close to that for metallic iron. The tempera-

ture dependence of the isomer shift is negative and the observed value of 4×10^{-4} mm/sec.° K is in close agreement with the value of 7×10^{-4} mm/sec. ° K for metallic iron determined by Hanna. Various possible explanations are included to interpret a slightly lower value of internal magnetic field compared with 330 kilogauss for bulk iron. The variation in magnetic field from 249 kilogauss at room temperature to 298 kilogauss at 15° K for the sample of 12 Å thickness is explained in terms of superparamagnetic fluctuations. The Mössbauer lines in this sample move inwards by about 16% in changing the temperature from 350° K to 15° K, but the lines are still well resolvable and do not show the appreciable broadening that Blume's model suggest. Hence, we have concluded that Blume's theory is not adequate to explain the behavior in our films. No quadrupole splitting was detected in any of the samples thicker than 1 Å.

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TABLE OF CONTENTS

	page
ABSTRACT	ii
ACKNOWLEDGEMENTS	iv
LIST OF FIGURES.	vi
LIST OF TABLES	viii
INTRODUCTION	1
EXPERIMENTAL METHOD.	4
Introduction.	4
Ultra High Vacuum System.	6
UHV Variable Temperature Dewar.	7
Temperature Controller and Sensor	10
Sample Holder	14
Sample Preparation.	16
Mössbauer Drive and Counter	19
Electronics	21
Data Acquisition and Analysis	23
Thickness and Composition Determination	27
THEORETICAL CONSIDERATION.	29
Mössbauer Effect in Iron 57	29
Isomer Shift.	30
Zeeman Splitting Description.	31
Quadrupole Effect	34
Coupled Magnetic and Quadrupole Effect.	39
Mössbauer Line Shape.	42
Saturation Effects.	45
Resonance Fraction.	46
Surface Effects	48
Superparamagnetism in Thin Films.	49
EXPERIMENTAL FINDINGS.	55
Introduction.	55
Results of Group I.	56
Results of Group II	60
Results of Group III.	66
Sample of Thickness Less Than 1 Å	72
CONCLUSIONS.	79

LIST OF FIGURES

Figure		Page
1.	A schematic drawing of the experimental set-up . .	5
2.	Drawing of custom-made Janis research dewar . . .	8
3.	Germanium thermometer resistance vs. the temperature calibration curve	12
4.	The complete electronic circuit of the temperature controller	13
5.	Side view, front view and the top view of the sample holder used in the experiment . . .	15
6.	The basic block diagram of the electronics used in the experiment	22
7.	Energy levels of the 14.4 Kev nuclear transition of Fe^{57} as perturbed by a pure magnetic field	32
8.	Energy levels of the 14.4 Kev nuclear transition of Fe^{57} as perturbed by a quadrupole shift under the influence of a negative electric field gradient	38
9.	Energy levels of the 14.4 Kev nuclear transition of Fe^{57} as perturbed by the isomer shift, the Zeeman splitting, and a quadrupole splitting	41
10.	The data points and the tracing of computer fit for the 3 Å film in group I at room temperature	58
11.	The data points and the tracing of computer fit for a typical film in Group II at room temperature	63
12.	The data points and the tracing of computer fit for the film of 10 Å in Group III at room temperature	69

LIST OF FIGURES (con't)

Figure		page
13.	The data points and the tracing of computer fit for the film of 10 Å in Group III at 100° K	70
14.	Plot showing the normalized resonance area vs. temperature for the film of 10 Å thickness in Group III	73
15.	Plot showing the variation of internal magnetic field with temperature for the sample of 10 Å in Group III.	74
16.	Plot of internal magnetic field with temperature for the sample of 12 Å thickness in Group III	75
17.	Plot of normalized resonance area vs. the temperature for the film of 12 Å thickness in Group III.	76
18.	Typical two-line spectra obtained in film of 0.4 Å thickness at room temperature. Figure shows both the data points and the tracing of the computer fit	77

LIST OF TABLES

Table No.		Page
1.	Mössbauer parameters of samples in thickness range 1 Å to 13 Å in Group I	57
2.	Mössbauer parameters of samples in thickness range 15 Å to 42 Å in Group II	61
3.	Mössbauer parameters of samples in transition thickness range 9 Å to 12 Å in Group III . . .	67

INTRODUCTION

It has long been the goal of physicists to understand ferromagnetism, and the one step toward this end was to learn about one and two dimensional ferromagnetism. Presently, the approach to two dimensional ferromagnetism is a uniform thin film of magnetic material. It is very difficult to obtain a film which is both thin and uniform as has been pointed out by Gradmann.⁽¹⁾ On the contrary films are formed in "clumps" and "clusters" and recently attention was directed towards studying the properties of such clusters. Violet and Lee⁽²⁾ have investigated the ultra thin iron films in the thickness range from $1.2 \text{ \AA}$ to $120 \text{ \AA}$ to determine the critical thickness at which the saturation magnetization and Curie temperature depart from the bulk value by using the Mössbauer resonance technique. Multilayer films were made in a vacuum system at a pressure of 10^{-8} Torr with intermediate layers of SiO_2 . Layering was necessary for sensitivity reasons and to avoid oxidation of the film when it was removed from the vacuum system. A. C. Zuppero⁽³⁾ has also studied the iron films in the thickness range from about a monolayer to about $1000 \text{ \AA}$, but again, in his experiments the films were made at pressure of 10^{-8} Torr and then removed and analyzed at ambient pressures. D. Schroer⁽⁴⁾ has discussed the effects of lattice modifications in microcrystals on the Mössbauer spectra and the Mössbauer parameters. Kündig et al.⁽⁵⁾ have studied the properties of small

α - Fe_2O_3 particles impregnated in silica gel as a function of particle size and temperature. Lindquist et al.⁽⁶⁾ have also studied the effect on Mössbauer spectra of superparamagnetic nickel particles of order $30 \text{ \AA}$ average size. Rabinovitch et al.⁽⁷⁾ have studied the magnetic anisotropy in thin films of iron using the Mössbauer effect. An early treatment on theory of the structure of ferromagnetic domains in films and small particles is given by Kittel.⁽⁸⁾ Magnetic ordering in very thin iron foils using the Mössbauer effect has been done by Walker and Cleveland,⁽⁹⁾ and more recently Guarnieri et al.⁽¹⁰⁾ have studied the Mössbauer effect in ultra thin iron films. In this case the film was made in ultra high vacuum and then coated with a thick layer of aluminum or silver to prevent oxidation. Mössbauer spectra of sputtered Fe^{57} thin films have been studied by Mazak.⁽¹¹⁾ Godwin et al.⁽¹²⁾ have determined the Debye temperature and the surface electric field gradients for the isolated Fe^{57} atoms on tungsten and silver substrates under ultra high vacuum using Mössbauer effect.

The changes in the Mössbauer spectra obtained in the case of iron oxide can be explained in terms of the paramagnetic relaxation of ions. The asymmetry in the quadrupole lines in the Mössbauer spectra has been explained by Goldanskii⁽¹³⁾ in terms of anisotropic Debye-Waller factor and by Blume⁽¹⁴⁾ in terms of paramagnetic relaxation of ions. Blume and Tjon⁽¹⁵⁾ have also considered the effect of fluctuating electric field gradient and the magnetic field at the nuclear site. The literature thus has many examples of

Mössbauer results on a macroscopic sample composed of fine oxide particles, and a few examples of thin films measured under ambient conditions. Usual Mössbauer absorption geometry in which we have a single line source and bulk absorber does not work for very thin films which are to be used as an absorber because the number of iron atoms is very small. The sensitivity needed to examine the monolayer films may be obtained by the Mössbauer technique by using the 6.4 Kev γ -ray which is emitted only if the Fe^{57} has absorbed the resonant 14.4 Kev incident radiation as has been done by Cleveland et al. (9) Another method is to use the film as the source in a Mössbauer experiment with a single line bulk absorber which is enriched in Fe^{57} ; this method has been employed in our experiment. The main object of our experiment was to study the thin films of iron in the oligatonic thickness range over a wide range of temperatures. We wanted to reduce the oxidation or other contamination of the film to a minimum and for this reason the films had to be made and analyzed in ultra high vacuum without losing vacuum integrity. We have constructed such a system. This report describes such a system and reports the Mössbauer spectra of thin films whose superparamagnetic relaxation time varies as a function of thickness and temperature.

EXPERIMENTAL METHOD

Introduction

In most of the experiments studying magnetic properties of thin films of iron using Mössbauer techniques the film is evaporated inside a vacuum system at a pressure of 10^{-8} Torr and then removed from the system to ambient pressure for analysis in standard Mössbauer absorption geometry. This technique has the disadvantage that one can no longer be certain that the films have not oxidized. We have developed a technique in which we can evaporate the films inside the ultra high vacuum at a pressure $< 3 \times 10^{-9}$ Torr and analyze them at a pressure of 10^{-11} Torr without having to remove the films after evaporation. The experimental technique is unique in that it also provides a cold finger whose temperature may be varied from 15° K to 350° K. This dewar has an integral vacuum insulation with the ultra high vacuum system, and thus also is capable of attaining pressures of 10^{-11} Torr. The vacuum system has a large side port to allow the attachment of a re-entrant pipe which houses the Mössbauer absorber and the end window proportional counter. The Mössbauer drive is mounted on the vacuum system to avoid any relative mechanical vibrations of the system and the Mössbauer drive. A schematic drawing of the experimental set up is shown in Figure 1. It is to be pointed out that the Mössbauer drive, the end window pro-

Figure 1

portional counter and the absorber are not inside the ultra high vacuum system; yet the plane of the absorber is only about 22 cms from the plane of the film which is inside the ultra high vacuum. The substrate used in the experiment is a thin cover glass slide and is attached to the cold finger of the ultra high vacuum dewar. The sample holder can be rotated about the axis of the dewar by an external manipulator. We shall proceed to describe the vacuum system and associated Mössbauer drive circuitry and conclude this section with a discussion of the evaporation source, substrate preparation and procedure for evaporating the Co^{57} doped iron films.

Ultra High Vacuum System

The ultra high vacuum system used in the experiment was a Varian Model VI-321A which is equipped with a 140 liter per second Vacion pump, and eight 2-3/4 inch O.D. ports for necessary electrical and mechanical feed throughs. This system is capable of reaching a base pressure of 10^{-11} Torr after the system has been baked for about four hours at a temperature of 250° C. The system also contains a titanium sublimation pump which reduces the time needed to attain the base pressure. The base chamber of the vacuum system is 11-3/4 inch in diameter and thus provides enough work space. Bake-out of the system is monitored by a control unit which can be set to a prespecified time after which the heaters to the base chamber, the variable temperature dewar and the Vacion pump are all

electrically disconnected. In the event that the pressure in the chamber rises above a preset value on the pressure control unit, the unit switches off the power to all the heaters. The circuit of the bake-out control unit was slightly modified so that it was possible to switch off the power to individual heaters of Vacion pump, dewar or the base chamber. The pressure inside the vacuum system is measured by a nude ionization gauge tube, which is located about 2 inches away from the sample. A single 4-1/2 inch O.D. side port on the system is connected to a re-entrant 310 stainless steel pipe of about 7 inches in length at the end of which was heliarc welded a 0.010 inches thick beryllium window to provide the isolation between the UHV and the outside. This re-entrant cavity houses the absorber and the counter and is described in detail in a later section. On the top of this vacuum system is mounted a wheeler flange which has a 10 inch O.D. flange connected to it for the purpose of attaching the variable temperature ultra high vacuum dewar to the system.

UHV Variable Temperature Dewar

The custom-made dewar by Janis Research is shown in Figure 2. The dewar has a unique design in that it is constructed from only materials which satisfy the criteria for ultra high vacuum and thus can attain a pressure of 10^{-11} Torr. A heating tape is wound around the exterior of dewar to give it a mild bake-out at

Figure 2

250° C; the temperature of the dewar during the bake out is controlled by a bimetallic strip attached on to the surface of the dewar. The dewar is built on a 10 inch O.D. Varian flange which mounts directly on the top of the ultra high vacuum system thus providing the common vacuum between the base chamber and the dewar. The dewar has the usual construction of an inner chamber which is separated by vacuum from another chamber which contains liquid nitrogen and this nitrogen container is separated from the outer wall of the dewar by another vacuum space. The liquid from the inner chamber can be forced to pass through a 1/16 inch capillary when the inner reservoir of the dewar is pressurized. The liquid then cools the copper block located about seven and one half inches below the inner chamber and the hot gas passes through a needle valve at the top of the dewar. By adjusting the flow through the needle valve it is possible to crudely vary the temperature of the cold finger. The bottom of the cold finger has a 1/4 - 28 tapped hole in which is screwed a stud to attach the sample holder. A nitrogen shield was provided around the dewar neck to reduce the radiation losses when liquid helium was filled in the inner chamber. We could not put the nitrogen shield all around the cold finger since this would restrict the field of view and also prevent the rotation of the sample holder. With the present radiation shielding it was possible to reach to 15° K when helium was in the inner chamber.

Temperature Controller and Sensor

The temperature sensor mounted on the dewar neck was a Cryocal CR 1000 germanium thermometer with a slight modification that the epoxy normally used to provide protection to the leads at the base was replaced by a special type of epoxy, namely, Stycast 2762 which can withstand a higher temperature of 250° C and is also compatible with the ultra high vacuum. The four leads of the temperature sensor are bare; electrical insulation was provided by threading these wires separately through pieces of aluminum oxide tubes having four holes. In order to provide a reasonable thermal contact of the sensor to the cold finger the sensor was mounted by drilling a hole in a copper ring which has an inner diameter of 1 inch and outer diameter of 1-1/2 inch. This ring was slipped on to the cold finger of the dewar and held in place by two set screws. The four leads of the sensor were then attached to a thermal sink which was coupled to the same copper ring which houses the germanium sensor. The leads from this thermal sink were then connected to a female socket made from aluminum oxide and clamped to the aluminum shield which surrounds the neck of the dewar so that the whole assembly forms a part of the dewar. A 0.005 inch diameter nichrome wire about 6 feet long was used as the 70 ohms heater to control the temperature of the dewar neck. To accomodate the length of wire needed for our controller the

heater wire was first passed four times through the small pieces of aluminum oxide tube having four holes in it, which provided the electrical insulation of the heater wire. The heater was placed in a cavity around the circumference of a second copper ring of 1 inch I.D. and 1-1/2 inch O.D. The thickness of the copper ring was 1/4 inch. This heater was then slipped on to the copper block at the end of the dewar neck and was attached by set screws. The four leads of the germanium sensor and the two heater leads which are on the female socket were finally connected by .002 inch diameter copper wires to the electrical feed-through provided on the vacuum system. In order to calibrate the germanium sensor resistance for temperatures above 200° K a chromel-alumel thermocouple was attached to the sample holder and the needle valve was adjusted to vary the temperature. This calibration graph is plotted in Figure 3. The temperature controller was a standard A.C. bridge circuit which basically works on the principle that when the temperature of the sample changes it changes the resistance of the germanium sensor and hence throws the bridge off balance and in turn controls the power through the heater. The complete electronic circuit of the temperature controller is shown in Figure 4. The detailed circuit is described by Carl Andeen.^(15a) This temperature controller maintains the temperature of the dewar neck to $\pm 0.1^\circ$ K. As the germanium sensor was not at the glass substrate the temperature of the film was not the same

Figure 3

as that of the cold finger to which the sensor was attached. The temperature difference between the cold finger (as measured by the germanium sensor) and the face of the sample holder to which the glass substrate was attached (measured by a chromel-alumel thermocouple) was found to be 5° K at 80° K.

Sample Holder

The sample holder was made out of a single piece of copper from which a disc $1/4$ inch thick and $1-1/2$ inch diameter was cut with a square face of $7/8 \times 7/8$ inch centered in the disc plane and $1/8$ inch thick. The sample holder is shown in Figure 5. Around the circumference of the disc eight small holes were drilled and these were used to rotate the sample inside the vacuum system, by a manipulator. The two threaded holes were used to move the sample holder in and out of the system as described below; this avoided the necessity of removing the dewar every time a new sample was to be made. The $1-1/2$ inch diameter disc of the sample holder had a $1/4$ inch I.D. hole drilled at its center. The sample holder was screwed on to a long rod and was then inserted into the vacuum system through a $2-3/4$ inch O.D. side port; the hole on the sample holder disc was aligned with the stud at the bottom of the cold finger and was gently pushed upwards till it was flush with the flat face of the cold finger. A small stainless steel pin was inserted into the hole on the stud attached to the bottom of

Figure 5

the cold finger and kept the sample holder in reasonably good thermal contact with the cold finger. The substrates used in the experiment were $7/8 \times 7/8$ inch square cover glass slide 0.007 inches thick. In order to put the glass substrate on the square face of the sample holder a thin layer of high purity indium was first coated on one face of the glass substrate. The front face of the square piece on the sample holder was also coated with high purity indium; the substrate and holder were then soldered together and allowed to cool. This way the glass substrate adhered firmly to the sample holder and thus provided a good thermal and mechanical contact.

Sample Preparation

Radioactive cobalt 57 in the form of CoCl_2 in 0.5 N HCl solution was mixed with a measured amount of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ dissolved in distilled water. To this mixture was added radioactive Fe^{59} in the form of FeCl_2 in 0.5 N HCl solution. The maximum amount of doping of Co^{57} and Fe^{59} in this alloy of Co^{57} , Fe^{59} and natural iron was 500 ppm of each; the concentrations were kept low to provide the Fe^{57} with the environment appropriate to natural iron. The mixture of these three elements was then carefully put inside a 1 inch long, $1/4$ inch I.D. and $1/16$ inch thick wall cylindrical tube of pyrolitic boron nitride which was closed at one end. Boron nitride was chosen as the element for evapora-

tion of the films because it is relatively inactive to the elements being evaporated and is a very good thermal conductor, and can also stand large thermal shocks. Due to the anisotropic crystal structure of pyrolitic boron nitride the diffusion of the alloy into boron nitride was negligible, and this was important as we were evaporating very small quantities of material. The mixture in the boron nitride tube was then allowed to dry slowly at room temperature inside a hood. It took about 4 to 5 hours, after which the boron nitride tube was put in a closed furnace at 350° C for fifteen minutes in nitrogen atmosphere and then in hydrogen atmosphere for about eight hours at 500° C, and then finally hydrogen was flushed with nitrogen when the boron nitride tube was cold. This procedure ensured a complete chloride reduction of the mixture. A tungsten wire was wound around the boron nitride tube and then was mounted on to the high current feed-through provided on the vacuum system. In this geometry the plane of the substrate was about 2 inches from the boron nitride. To avoid the heat loss due to thermal radiation from the boron nitride tube it was surrounded by a thin cylinder of tantalum. A tantalum disc, with a hole of 1/2 inch diameter at its center was placed in front of the boron nitride tube. This cut down the thermal radiation reaching the substrate during evaporation and thus avoided unnecessary heating of the substrate. As the boron nitride tube which held the radioactive Co^{57} and Fe^{59} was only about 1-1/2 inch away from the

reentrant pipe which houses the counter, the background radiation was considerable, but was reduced to a reasonable value by wrapping the reentrant stainless steel pipe with 5 layers of .010 inch thick tantalum sheets. The substrate was first cleaned with Alconox and then rinsed with ordinary tap water, and then with deionized water and finally with distilled water. The sample holder and the pin that holds it on the dewar neck were also cleaned in a similar manner. Before any evaporation was made the glass substrate was degassed at 250° C for about 4 hours. A stainless steel rod was connected at the end of a ultra high vacuum compatible stainless steel bellows; this rod had a right angle bend at its other end and was used as a manipulator to turn the sample inside the vacuum system from in front of the boron nitride tube before evaporation to in front of the counter after the evaporation of the film. We will describe below the procedure involved in a typical run.

Before making the evaporation the complete system was baked at 250° C including the substrate at 250° C for about four hours. When the pressure dropped to approximately 2×10^{-10} Torr liquid nitrogen was poured into the inner chamber of the dewar; this was done to avoid heating of the substrate from the thermal radiation coming out from the boron nitride gun during the evaporation. This also prevented the germanium temperature sensor from getting overheated. It was found that the temperature of the cold finger during the evaporation did not rise considerably but remained within 20 degrees of the liquid nitrogen temperature

as was indicated by the germanium sensor. Before evaporating the film the substrate was moved directly opposite the boron nitride tube by the help of the manipulator and the evaporation started. A watt meter was also connected in the circuit to monitor the power at which the films were being made. The rate of evaporation of the films was about $15 \text{ \AA}^{\circ}$ per minute. The films have been made as far as practicable at the same power setting and under the same conditions. During the evaporation the pressure inside the vacuum system was between 1 and 3×10^{-9} Torr for all the films evaporated. After the film was made the manipulator was used to turn the sample in front of the counter face, and collection of the data was started. The procedure of data acquisition and analysis is described in a later section.

Mössbauer Drive and Counter

The Mössbauer transducer is typical in that it consists of a rigid connection between the sensing and drive coils. The springs of the coils were custom made⁽¹⁶⁾ such that they could withstand a relatively large torque. This particular design of the transducer was required to minimize the high frequency vibrations⁽¹⁷⁾ in the transducer and to support the large torque provided by the 8 inch long pipe which carries the absorber at its end. The resistance of the sensing coil was about 5 ohms and that of the drive coil was 300 ohms and was primarily neces-

sitated to satisfy the impedance matching of the servo drive. Attached concentrically to the drive coil was a circular plate of aluminum about 1 inch in diameter and 1/8 inch thick and with a small threaded hole at the center. To this plate was attached an aluminum pipe at the end of which was connected the single line Mössbauer absorber. Special effort was taken to reduce the weight of this aluminum pipe by milling it, reducing the wall thickness and removing sections to minimize the torque that acts on the drive coil. The absorber was in the form of a 310 stainless steel 1 cm x 1 cm square foil of thickness .00015 inch and isotropically enriched in iron 57 so that there was 1 mg/cm² of iron 57 in the absorber. The absorber foil was attached to a plastic disc 1-1/4 inch diameter and 1/16 inch thick by means of Duco cement. The counter used was a proportional counter made by Reuter Stokes Model No. SK-459. This counter had a resolution at full width at half maximum of 14.6% at 14.4 KeV. The counter was filled with Kr-CO₂ gas at a pressure of 380 Torr. The outside diameter of the counter was 1 inch and the length of the counter was 6 inches. The end of the counter had a beryllium window 0.010 inches thick. The counter was put inside the aluminum tube which carried the absorber at its end and was clamped onto the same support which held the transducer. The incoming γ-rays from the film were attenuated by about 4% in passing through the .010 inch thick beryllium window on the re-entrant pipe and the same thickness of the beryllium at the counter.

Electronics

The basic block diagram of the electronics used is shown in Figure 6. The Mössbauer servo-drive and the asymmetric ramp generator are described in detail by A. C. Zuppero.⁽³⁾ The pulses coming from the proportional counter were fed to the Ortec Model 109 PC preamplifier and its output was connected to the linear amplifier Ortec Model 435A; the pulses from the linear amplifier then went to a single channel analyzer Ortec Model 406A. The single channel analyzer was adjusted to select the 14.4 Kev γ -rays which contained the Mössbauer information. Finally the output of the single channel analyzer was fed to the input of 512 channel nuclear data Model ND-510 pulse height analyzer. The PHA was used in a multiscalar mode which implies that each channel of the PHA corresponds to a fixed relative velocity of the source and the absorber. Normally the first half of the PHA memory was used to store the calibration spectrum in which the source was 2 mc Co^{57} in a stainless steel matrix and the absorber was a crystal of sodium nitroprusside whose splitting was known and traceable to the National Bureau of Standards. The second half of the memory was used to store the spectrum obtained from the radioactive evaporated films. In this case the film acts as the source and the absorber is an enriched single line absorber. The reference signal used was an asymmetric ramp; the asymmetric ramp is preferred over the symmetrical triangle for the

Figure 6

convenience of data analysis and avoiding the refolding of the spectrum. The disadvantage of asymmetric ramp is that we discard about 10% of the information. The synchronization of PHA to the ramp is explained in detail by A. C. Zuppero.⁽³⁾

Data Acquisition and Analysis

The output of the pulse height analyzer was connected to a Teletype machine Model No. 33 which had a paper tape punch attached to it. In the "READ OUT" mode of the pulse height analyzer, the contents of each channel was printed out on the Teletype and at the same time was punched onto the paper tape. The data on the paper tape was then transferred to magnetic tape by using the computer program "ACTION".⁽¹⁸⁾ The advantage of data punched out on to a paper tape is that, if accidentally the magnetic tape is wiped out we do not lose the information contained in the paper tape which still contains the valuable data. The data was analyzed on a PDP-9 computer in the following manner: we assume a certain line shape for the spectrum, in our case we have chosen the following expression

$$y(v,H) = \sum_{i=1}^6 \frac{\gamma_i}{1 + (v - H_{g_i} - Q\alpha_i - C)^2 (2/\Gamma)^2}$$

where H is the magnetic field at the nuclear site, Q is the quadrupole splitting, C is the center of the Mössbauer spec-

trum. The six parameters γ_i represent the relative intensity of the six lines. Γ is the full width at half maximum of the resonance line. The other six parameters g_i represent the relative splitting of the six lines and are determined to be -0.01615 , -0.00934 , -0.00254 , 0.00254 , 0.00934 , and 0.01615 millimeter per second per kilogauss respectively. The parameter α_i is $+1$ for line numbers 1 and 6 and -1 for the lines 2, 3, 4 and 5. Here it was assumed that the electric field gradient and the magnetic field are in the same direction. The above formula takes into account the presence of magnetic hyperfine splitting, the quadrupole splitting and the isomer shift. If, in addition, the background term has some terms which vary linearly, quadratically, and cubically in addition to the constant term then the expression for the line shape will be

$$y(v,H) = a + bv + cv^2 + dv^3 + \sum_{i=1}^6 \frac{\gamma_i}{1 + (v - Hg_i - Q\alpha_i - C)^2 (2/\Gamma)^2}$$

The program "GRASP" which is available in the department was used to fit Gaussian curves to the spectra. It was modified to conform with the absorption dips obtained in Mössbauer spectra. The modified "GRASP" can fit either Gaussian or Lorentzian peaks to the data. In our experiment since we expected the shape to be Lorentzian we always fitted the spectrum with Lorentzian peaks. The computer used was Digital Equipment Corporation Model PDP-9. This computer had an added advantage that it has a "Light Pen"

and a display oscilloscope.

The data is first displayed on the oscilloscope; then by light pen "crosses" are adjusted for background and then for peak positions and widths. The parameters that were variable in the fitting were the position of the peak, width of the peak, height of the peak, the constant term in the background, the linear, quadratic and the cubic term in the background. If it is desired to fix the position, width or both of them for any or all the peaks in the spectrum it can be done by the "sense" switches provided on the computer. First, just by visual inspection of the displayed spectrum one determines how many peaks to fit to the spectrum. Then by "PUSH" buttons on the computer the position, height and width of each peak is fixed; the computer takes up these first values and fits a spectrum to the data. This gives an experimenter a feel of how good his initial guess was; if the fit does not seem to be right, the experimenter can change the parameters and try again. This helps in saving a lot of time in the iteration process. Once the initial fit has been obtained the computer is asked to iterate the initial parameters till the best fit is obtained. Once the best fit of the data is obtained the output of the computer is punched onto a paper tape. The program GRASP has been so modified that the punched output of the computer can be fed back into the computer at a later time if required, to inspect a fit spectrum. This results in a great time saving, since to fit a spectrum it takes nearly two hours,

whereas to display it takes only five minutes. The output of GRASP is in terms of channel numbers and this information is converted into millimeters per second by the program called CONVRT. This program in addition to converting into mm/sec. also calculates the isomer shift, the resonance area under the peaks, the magnetic field and the quadrupole shift for the six line Zeeman or the four line Zeeman pattern. The biggest advantage of using this computer was that it was very quick in analyzing the data without giving divergent results. It was possible to take the picture of the raw data, the fit, and the data and the fit together, with a polaroid camera provided on the scope.

Thickness and Composition Determination

In very thin films when we are talking about the thickness of the film in angstroms we generally mean a uniform thin film, but this is seldom the case in films. A better way of representing the thickness of the film is to know the number of atoms per square centimeter or surface density of atoms in the film, and then if one wants to calibrate himself with average thickness of the film he can multiply the surface density of atoms by the volume of the unit cell. We are going to present the thickness both in terms of surface density of atoms and average thickness in angstroms. If we consider the bcc structure of iron so that there are two iron atoms per unit lattice volume then the surface density of atoms is 0.854×10^{15} atoms/cm² for one angstrom average film thickness, and was the number used to calculate the thickness of the films. In our experiment we determined the total number of atoms on the film by the radioactive method. The detailed procedure is described below.

The weight of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ put in the boron nitride tube was known, and the atomic weight of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ was also known, which gives us the total number of Fe^{56} atoms in the tube. Knowing the activity of Co^{57} and Fe^{59} put in the boron nitride tube and their decay constant, one can determine the total number of Co^{57} and Fe^{59} atoms present in the tube separately. So that we knew the initial ratios of $\frac{\text{Co}^{57}}{\text{Fe}^{56}}$ and $\frac{\text{Fe}^{56}}{\text{Fe}^{59}}$ in the boron nitride gun before the evaporation of the film. After the film was evaporated we wanted to know the number of atoms of Fe^{56} present in the film. To get this

information we assumed that the $\frac{\text{Fe}^{56}}{\text{Fe}^{59}}$ ratio in the tube before evaporation was the same as that on the film; this is a good assumption because the vapor pressure for the two isotopes of iron is the same. To determine the activity of Fe^{59} present in the film we used a sodium iodide scintillation counter and counted the 1.05 MeV γ -rays which are characteristic of the decay of Fe^{59} . A standard source of Fe^{59} whose activity is calibrated and is traceable to National Bureau of Standards was used to determine the absolute activity of Fe^{59} in the film. Knowing the activity of Fe^{59} in the film gives the number of atoms of iron present in the film, and hence the surface density of atoms. We wanted to check the uniformity of the films and this was done by a radioactive scanning of the substrate. The activity was found to vary by about 5% in going from edge of the substrate to its center.

It should be pointed out that due to differences in vapor pressure of cobalt and iron the concentration of the cobalt in the successive films made from the same boron nitride gun are slightly different. The concentration of cobalt atoms was very small compared to the iron atoms and hence was neglected in the thickness determination.

THEORETICAL CONSIDERATION

Mössbauer Effect in Iron-57

In simple terms the Mössbauer effect can be thought of as the resonance of absorption of recoil free gamma rays emitted from a radioactive nucleus. In the case of Fe^{57} the pertinent gamma ray is emitted when the nucleus makes a transition from the first excited state to the ground state. The first excited state of the iron 57 nucleus has a half life of 0.14×10^{-6} sec., a magnetic moment $\mu_e = 0.155$ nuclear magneton, a quadrupole moment $Q_e = 0.33$ barn and a spin $I_e = 3/2$. The energy emitted during the transition from the excited state to the ground state is 14.4 Kev and forms the gamma ray that carries Mössbauer information. The ground state has a spin $I_g = 1/2$, a magnetic moment $\mu_g = 0.0903$ nuclear magneton, and quadrupole moment $Q_g = 0$. Thus nuclear properties of Fe^{57} give rise to three kinds of information: (1) Because of the interaction between the positive charge of the nucleus and the electronic charge density that does penetrate the nucleus an isomer shift in the Mössbauer spectra exists. (2) The magnetic dipole moment of the iron nucleus interacts with the magnetic field at the nuclear site and produces the magnetic hyperfine structure in the Mössbauer spectra which normally is called the Zeeman splitting. (3) Finally, since the iron 57 nucleus has an electric quadrupole moment for the excited state this quadrupole moment interacts with the electric

field gradient at the nuclear site and produces a splitting in the Mössbauer spectra.

Isomer Shift

The nuclear isomer shift, also called the chemical shift, is observed as the change in position of the centroid of the Mössbauer resonance spectrum. The expression for this shift is given by⁽¹⁹⁾

$$\text{I.S.} = \frac{2\pi}{3} Ze^2 \{ \langle R^2 \rangle_{\text{ex}} - \langle R^2 \rangle_g \} \{ |\psi_a^2(0)| - |\psi_s^2(0)| \}$$

where $\langle R^2 \rangle_{\text{ex}}$ is the mean square nuclear radius of the excited state and $\langle R^2 \rangle_g$ is the mean square nuclear radius of the ground state, and $|\psi_a^2(0)|$ and $|\psi_s^2(0)|$ are the electronic charge distribution at the nucleus in the absorber and the source respectively. In terms of the change in Doppler velocity the above expression for isomer shift reduces to

$$\Delta V = \left(\frac{4\pi Ze^2 R^2 C}{5E_\gamma} \right) \frac{\Delta R}{R} \{ |\psi_a^2(0)| - |\psi_s^2(0)| \}$$

where R is the radius of the nucleus and E_γ is the energy of the gamma ray that is emitted. The above expression is a simplified one, since it does not take in to account the distortion of the electronic wave function at the origin and also does not consider relativistic corrections. Shirley⁽²⁰⁾ gives a more recent expression for the isomer shift which includes both of these effects. The

isomer shift measurements allow the determination of electronic density at the nucleus and this knowledge is of interest for the molecular structure of the solids. It can also be used to distinguish between the various oxide states of the iron nucleus. For example as the d- electrons are removed in going from the +1 to +6 oxidation state of iron, the shielding of the s- electrons diminishes and their density at the nucleus increases leading to a diminishing chemical shift; this is due to negative value of $\frac{\Delta R}{R}$ for the iron nucleus. The isomer shift of various oxide states of iron is almost independent of the host lattice. The isomer shift for Fe^+ in NaCl (Fe) is 2.3 mm/sec, for Fe^{++} in FeF_2 is 1.5 mm/sec, for Fe^{+++} in FePO_4 is 0.7 mm/sec., for Fe^{++++} in SrFeO_3 is 0.2 mm/sec., and Fe^{+++++} in FeO_4 is -0.6 mm/sec. with respect to the crystal of sodium nitroprusside. (21)

Zeeman Splitting Description

Due to the presence of a magnetic field at the nuclear site the excited state and the ground state will be split into magnetic sublevels; the energy splitting of these levels will depend on the magnitude of the magnetic field and the magnetic dipole moment. As the magnetic dipole moment for the excited and the ground state is different, the splitting for the two states will be different. In Figure 7 is demonstrated the splitting of the excited and the ground state of the iron nucleus in the presence of a magnetic field; the excited state is split into four levels and the ground state is

Figure 7

a doublet. Knowing the energy separation of the lines in the Mössbauer spectra one can determine the magnitude of the internal magnetic field at the nuclear site. The levels shown in Figure 7 indicate that there should be eight possible transitions, but the magnetic dipole interaction selection rules that $\Delta m = 0$ or ± 1 forbid the two transitions which have $\Delta m = \pm 2$. The intensity of the lines in the Mössbauer spectra can be used to determine the direction of the magnetic field relative to the direction of propagation of the gamma ray. For magnetic hyperfine splitting the line intensities are: ⁽²²⁾

Transition	Line No.	Angular Distribution
$-3/2 \rightarrow -1/2$	1	$3(1+\cos^2\theta)$
$+3/2 \rightarrow +1/2$	6	$3(1+\cos^2\theta)$
$-1/2 \rightarrow -1/2$	2	$4\sin^2\theta$
$+1/2 \rightarrow +1/2$	5	$4\sin^2\theta$
$-1/2 \rightarrow +1/2$	4	$(1+\cos^2\theta)$
$+1/2 \rightarrow -1/2$	3	$(1+\cos^2\theta)$

Here θ is the angle between the internal magnetic field and the direction of propagation of the gamma ray. In the case of magnetic hyperfine splitting, if the magnetic field is randomly oriented then $\langle \cos^2\theta \rangle = 1/3$ and $\langle \sin^2\theta \rangle = 2/3$ and the intensity ratio of the lines will be 3:2:1:1:2:3 for the six lines in the Zeeman pattern. However, if the direction of the magnetic field is such

that $\theta = 90^\circ$ then intensity ratio of the lines will be as 3:4:1:1:4:3. Finally, if θ becomes zero or the direction of the magnetic field coincides with the direction of propagation of gamma ray then the intensity ratio will be 3:0:1:1:0:3 and only four lines will be observed in the spectrum. These intensity ratios have been determined on the theoretical basis and can show deviations from the theoretical intensity ratio in an experimental observation due to finite thickness of the absorber, instrumental broadening and field distributions.⁽²³⁾ Krivovalaz⁽²⁴⁾ has also shown that the Mössbauer line intensity is modified if anharmonic binding forces are present. The origin of the magnetic field at the nuclear site is discussed by Watson and Freeman⁽²⁵⁾ and by Marshal and Johnson.⁽²⁶⁾ The value of this field in the case of metallic iron is -330 kG ⁽²⁷⁾ and is mainly due to core polarization.

Quadrupole Effect

The electric quadrupole moment of the excited state of the iron nucleus demonstrates the fact that the nucleus is not spherically symmetric. An oblate nucleus has a negative quadrupole moment and a prolate one has positive quadrupole moment. The electric field gradient is a 3×3 tensor but can be reduced to diagonal form in proper coordinate system, so that it is completely specified by three components, $\frac{\partial^2 V}{\partial x^2}$, $\frac{\partial^2 V}{\partial y^2}$, and $\frac{\partial^2 V}{\partial z^2}$. These three components are not all independent since they must obey the Laplace equation.

$$V_{xx} + V_{yy} + V_{zz} = 0 \quad (1)$$

where $V_{xx} \equiv \frac{\partial^2 V}{\partial x^2}$; $V_{yy} \equiv \frac{\partial^2 V}{\partial y^2}$ and $V_{zz} \equiv \frac{\partial^2 V}{\partial z^2}$. If we define η as

the asymmetry parameter such that

$$\eta \equiv \frac{V_{xx} - V_{yy}}{V_{zz}} \quad \text{and} \quad -1 \leq \eta \leq 1 \quad \text{then this implies that}$$

$$|V_{zz}| > |V_{xx}| \geq |V_{yy}|$$

and the Hamiltonian expressing the quadrupole interaction is given by (28)

$$H = \frac{eqQ}{4I(2I-1)} [3I_z^2 - I(I+1) + \frac{\eta}{2} (I_+^2 + I_-^2)] \quad (2)$$

where $eq \equiv V_{zz}$ and $I_{\pm} = I_x \pm iI_y$

The Hamiltonian mentioned in Equation 2 has eigenvalues given by

$$E_Q = \frac{eqQ}{4I(2I-1)} (3m_I^2 - I(I+1)) (1+\eta^2/3)^{1/2}$$

where $m_I = I, I-1, \dots, -I$ For an axially symmetric case $\eta = 0$ and this implies that

$$E_Q = \frac{eqQ}{4I(2I-1)} (3m_I^2 - I(I+1))$$

For the excited state of Fe^{57} , the nuclear spin is $3/2$ and m_I can be $3/2$ or $1/2$ so that

$$E_Q \Big|_{3/2} = \frac{eqQ}{4}$$

and

$$E_Q \Big|_{1/2} = -\frac{eqQ}{4}$$

so that total splitting of the level is

$$\Delta E_Q = E_Q \Big|_{3/2} - E_Q \Big|_{1/2} = \frac{eqQ}{2} = \frac{V_{zz}Q}{2} \quad (3)$$

The case of origin of electric field gradient in metals is discussed in detail by Watson et al.^(29,30) The actual splitting of the levels is not as given by the equation (3) since we have neglected the effect of polarization of the d-electrons by the nuclear quadrupole moment. Due to this polarization the resulting electric field gradient is given by the expression

$$q = q_{\text{lat}}(1-\gamma_\infty) + q_{\text{loc}}(1-R_Q)$$

where q_{lat} is the electric field gradient due to charges outside an atomic sphere centered at the nucleus, and q_{loc} is the electric field gradient due to electrons within the atomic sphere and γ_{∞} and R_Q are the Sternheimer antishielding factors. (31) Figure 8 shows the transitions for a quadrupole split excited state; the ground state of the nucleus is ~~unsplit~~ since the ground state has no quadrupole moment. The angular distribution of the intensities for quadrupole split lines is

Transition	Line No.	Angular Distribution
$\pm 3/2 \rightarrow \pm 1/2$	1	$(1 + \cos^2 \phi)$
$\pm 1/2 \rightarrow \pm 1/2$	2	$(5/3 - \cos^2 \phi)$

where ϕ is the angle between the principal axis of the electric field gradient and the direction of the gamma ray propagation.

If the angle ϕ is random then the two lines of the quadrupole pattern should be symmetrical since the average value of $\cos^2 \theta$ is $1/3$. If the recoil free fraction has angular dependence then the average intensity for the two lines will be different, and thus produce an asymmetric doublet in the spectra, known as the Goldanskii effect. (13) An asymmetry in the quadrupole spectra has also been explained by Blume in terms of paramagnetic relaxation of ions. This asymmetry has temperature dependence in the opposite sense as predicted by Goldanskii effect.

Figure 8

Coupled Magnetic and Quadrupole Effect

In previous paragraphs we have discussed mainly three effects, the isomer shift, quadrupole shift and the magnetic hyperfine effect separately. But in some cases it is possible that all these effects may simultaneously be present. It is easy to write down a Hamiltonian describing the hyperfine coupling of both the magnetic and electric terms but in general, it is not possible to get a solution in a closed form. One example of this situation will be the case in which the principal axis of the electric field gradient tensor is not in the same direction as the magnetic field direction. It has been shown that in general the magnetic sublevels will be coupled with quadrupole interaction and in this case the selection rules allow all the eight transitions to occur and this results in a complex Mössbauer spectra. Now, if the quadrupole interaction is much smaller than the magnetic interaction, i.e.,

$$\frac{e^2qQ}{\mu H} \ll 1 \quad (4)$$

and if the electric field gradient is axially symmetric the energy levels of the excited state is given by:

$$E = -\mu_e H m_I + (-1)^{|m_I|+1/2} \frac{eqQ}{4} \frac{3\cos^2\alpha - 1}{2} \quad (5)$$

where μ_e is the magnetic moment of the excited state and α is the angle between the magnetic field and the electric field gradient.

If the direction of the magnetic field and the direction of the electric field gradient coincide the formula reduces to:

$$E = -\mu_e H m_I + (-1)^{|m_I|+1/2} \frac{eqQ}{4} \quad (6)$$

If the condition (4) is not satisfied, but other conditions remain the same, computer calculations can be made and this has been done for the case of $I = 1, 3/2, 2$, etc., by Parker⁽³²⁾ and Matthias.⁽³³⁾ The use of these calculations for the case of iron 57 has been made by Collins and Travis.⁽³⁴⁾ Note that equations (5) and (6) can not be distinguished experimentally unless q and Q are independently known since the equations (5) and (6) are identical if q and Q are redefined as q' and Q' . The shifts in energy of the excited and ground states of the iron nucleus when isomer shift, quadrupole shift and a magnetic hyperfine splitting all are present at the same time are given schematically in Figure 9. The figure shows only the transitions that are allowed according to the selection rules, and assumes that the electric field gradient and the magnetic field are parallel. The general case of the electric field gradient tensor with the magnetic field along one of its principal axis, which is the case with FeF_2 is discussed by Wertheim.⁽³⁵⁾

Mössbauer Line Shape.

Lines arising from the Mössbauer spectra should exhibit a Lorentzian shape⁽³⁶⁾ whose width is determined by the lifetime of the excited state of the nucleus. But the width of the line is increased due to the geometrical broadening and also due to the finite thickness of the absorber used. Line broadening also arises from thermal excitations of the solid which lead to a temperature dependent shift in the Mössbauer line and this has been discussed in great detail by Snyder and Wick.⁽³⁷⁾ The line widths have been calculated by J. Heberle⁽³⁸⁾ for various thicknesses of the absorber. The effect of finite thickness of the absorber has also been studied by Frauenfelder et al.⁽³⁹⁾ Frauenfelder finds that for $t < 10$ the shape of the Mössbauer line is Lorentzian to within 1/2 percent, meaning the deviation of any point on the Mössbauer line from the true Lorentzian curve is within 1/2 percent. Thickness t has been defined to be equal to the dimensionless quantity $f \sigma_0 n$ where f is the recoil free fraction, σ_0 the resonance absorption cross-section for a single nucleus of the absorber and n is the number of Fe^{57} nuclei per unit area in the absorber. The line shape of the Mössbauer line determined by Frauenfelder is the following:

$$\Gamma_a = 2\Gamma(1+0.135t) \quad 0 \leq t < 5 \quad (7)$$

$$\Gamma_a = 2\Gamma(1.01 + 0.145t - 0.0025t^2) \quad 4 < t < 10 \quad (8)$$

where Γ_a is the width of the line when the finite thickness of the absorber is considered and Γ is the natural line width of the excited state. Heberle has extended the formula of Frauenfelder to a larger value of thickness of the absorber and has replaced two different formulas (7) and (8) by a single one which is valid in the thickness range $0 \leq t < 12$ and is given below:

$$\Gamma_a = 2\Gamma(1 + 0.1288t + 4.733 \times 10^{-3}t^2 - 9.21 \times 10^{-4}t^3 + 3.63 \times 10^{-5}t^4)$$

$$0 \leq t \leq 12 \quad (9)$$

From the above discussion it is clear that increasing the thickness of the absorber will increase the width of the Mössbauer line. However, increasing the thickness of the absorber has the advantage that it increases the resonant absorption and thus the signal to noise ratio increases. This is due to the increase in the number of absorbing nuclei in the absorber. The thickness can not be increased indefinitely to increase the signal to noise ratio as this will broaden the line considerably and hence the line will be masked in the background. Another disadvantage of

having a very thick absorber is the reduction in the overall intensity due to electronic absorption and this will mean that to get good statistics a very long time will be required. On the other hand if the absorber is very thin the total radiation will be strong but the resonance effect is considerably reduced. A very good discussion of the condition on the thickness for maximum single line absorption is given by U. Shimony,⁽⁴⁰⁾ who has taken into consideration the line broadening due to absorber thickness and also the time required to get reasonably good statistics. Nistor and Tinu⁽⁴¹⁾ computed the velocity shift and line broadening due to geometrical effects. For our geometry of the experiment in which the area of the film is 5 cm^2 , the area of the absorber is one cm^2 , and the distance between the film and the absorber about 2 cm, the velocity shift is about two percent,⁽⁴²⁾ and the line width increase is about seven percent. As the calibration spectrum is taken with the same geometrical consideration as the thin film spectrum the velocity shift cancels to first order. In our experiment the source was very weak (about 5 micro curie), and we chose an absorber consisting of one cm^2 square 310 stainless steel foil of thickness 0.00015 inch and enriched to 1 mg/cm^2 of Fe^{57} . This absorber yields a single line spectrum with a Co^{57} source in 310 stainless steel matrix. The full width at half maximum is found to be 0.724 mm/sec and the resonance dip is about forty percent. Using Eq. 9 the full width at half maximum is

expected to be 0.5 mm/sec which is five times the natural line width. The line width is further broadened due to geometrical broadening and this broadening is expected to be .035 mm/sec. so that the total expected width of the line is about 0.535 mm/sec. In the above calculation it has been assumed that the width of the single line source is the natural width. The difference in the observed width of 0.7 mm/sec and the calculated width of 0.535 mm/sec. can be attributed to the finite width of the single line source.

Saturation Effects

In general if we have a source of gamma rays and a resonant absorber, then the absorption peak observed is sharp if the thickness of the absorber is small. However, increasing the thickness of the absorber would increase the width of the line and hence eventually the line would become very flat. This is called the saturation effect. In the standard Mössbauer absorption geometry in which the source is a single line and the absorber is a bulk natural iron foil the theoretical intensity ratios for a random distribution of angle between the magnetic field and the direction of γ -ray emission is 3:2:1. This theoretical ratio is achieved only if the absorber is very thin. However, for very thick absorbers the intensity ratio of the lines will be 1:1:1.⁽⁴³⁾ In intermediate thickness of the

absorber the intensity of lines will be somewhere in between 3:2:1 and 1:1:1. The above effect is observed due to saturation in the absorber and increases as the thickness of the absorber is increased. However, in our experiment the absorber is a single line absorber and the source is a very thin radioactive film so that saturation effects are negligible. Hence no correction is needed in the relative intensities of the line.

Resonance Fraction

The recoil-free resonance fraction f may be written as

$$f = \text{exponential } (-4\pi^2 \langle x^2 \rangle / \lambda^2) \quad (10)$$

where $\langle x^2 \rangle$ is the mean square amplitude of the vibration in the direction of gamma ray averaged over an interval equal to the lifetime of the nuclear level involved in the gamma ray emission process and λ is the wave length of the emitted gamma ray. Eq. 10 clearly indicates that if $\langle x^2 \rangle$ is not bounded then the resonance fraction will vanish. This implies that no Mössbauer effect can take place in a liquid where the molecular motion is not restricted. For example, the Mössbauer effect is seen in metallic Sn^{119} below the melting point but is not observed at higher temperatures. (44) The root mean square displacement of the gamma ray emitting nucleus reflects the binding

of this nucleus to the lattice. If the nucleus is bound in a lattice with high Debye temperature the root mean square displacement of the nucleus will be small and the resonance effect will be pronounced. Thus, in a bulk sample the resonance fraction is a measure of the Debye temperature of the solid. In the case of iron the Debye temperature has been determined by Freston⁽²⁷⁾ from the temperature dependence of the resonance fraction. Eq. 10 also exhibits that if the wavelength of the gamma ray is very small then the resonance fraction will be very small and no Mössbauer effect can be seen. In case of bulk material like iron the Mössbauer resonance fraction is about 0.7⁽⁴⁵⁾ at room temperature and increases to 0.92 at 0° K. It has been shown by Shirley and Kaplan⁽⁴²⁾ that the absorption area under a Mössbauer curve for small t is given by

$$\text{Area} = \pi/2 \frac{c}{E_Y} n \sigma_0 f f' (1 - 0.24t + 0.04t^2) \quad (11)$$

where $t \equiv n \sigma_0 f' \Gamma / \Gamma'$. Here Γ' is the experimental width of the line. Equation 11 makes it obvious that f for a source could be determined precisely only if f' is known for the absorber. On the other hand if f' is not known then one could determine the product ff' but not f and f' individually. In our experiment as the absolute value of f' for the absorber was not known the resonance fraction of our samples is not

the absolute resonance fraction of the sample, but is known only in a relative sense.

Surface Effects

It is very interesting to note that the resonance fraction in a Mössbauer experiment as has been discussed before depends on the root mean square displacement of the atom which in turn gives the clue on the binding of the atom to the lattice; this property of the Mössbauer effect can be effectively used to study the surface effects in thin films. The difficulties involved in such an experiment are manifold. The most difficult part is to get a clean surface and then to maintain it "clean" during the experimental observation; the latter part is not too difficult thanks to modern ultra high vacuum technology. Another difficulty is the interpretation of the spectrum itself which to start with is very complex and due to large widths of the lines, it is difficult to identify all the lines in the Mössbauer spectrum. The relative binding for the atoms on the surface in the bulk and in the surface is estimated by Godwin⁽⁴⁶⁾ who finds that the ratio of the root mean square displacement of atoms on the surface to that in the bulk can vary from one to five. The few experiments that have been performed to study the surface effects are given in References 47, 48, 49 and 50.

Superparamagnetism In Thin Films

It was shown by Frenkel and Dorfman⁽⁵¹⁾ that below a critical particle size a particle of ferromagnetic material consists of a single magnetic domain. This critical diameter of about 150 Å^o for spherical samples of ferromagnetic materials was estimated by Kittel.⁽⁸⁾ During the growth of the films some atoms cluster together in one place so that the individual magnetic moments of the atoms in this cluster point in the same direction and result in a net magnetization. The direction of this magnetization is random if no interactions between clusters are present. Thus, this cluster of atoms may be treated as a small ferromagnetic particle whose magnetic moment is proportional to the number of atoms in that cluster, but whose direction of magnetization undergoes the same type of thermal motion as a paramagnetic atom. A cluster which exhibits the above property is called superparamagnetic. The superparamagnetic state of the system can be represented in terms of a collection of single domain particles as has been done by Bean and Livingston.⁽⁵²⁾ Each single domain particle possesses a complex anisotropy energy arising from magnetocrystalline, shape, strain, and even external origin. We assume a simple uniaxial anisotropy energy given by $KV\sin^2\beta$. Here V is the volume of the particle, K is the effective anisotropy energy per unit volume and β is the angle between

the direction of the magnetic moment and the anisotropy axis of the particle. As the magnetization may only rotate the probability that the moment will rotate through this potential barrier is given by $\exp(-KV/kT)$ where kT is the thermal energy. The superparamagnetic relaxation time is given by

$$\tau_p = \tau_o e^{KV/kT} \quad (12)$$

where τ_o is called the frequency factor and is of the order of 10^{-9} seconds. The appearance of V in the exponential implies that there is a critical size or temperature of the particle at which the magnetization oscillates rapidly between the easy directions and the superparamagnetic effects start to appear. The value of the frequency factor has been calculated by Néel⁽⁵³⁾ and more recently by W. F. Brown, Jr.⁽⁵⁴⁾ For an understanding of Eq.12, let us follow the approach given by Brown. Consider a single domain ferromagnetic particle with spontaneous magnetization M . We assume that to start with the magnetization is parallel to the applied field H . Now consider the effect of changing the direction of the field. If the particle size is very large and temperature is low, then the particle behaves almost like a static system and hence the magnetization either remains in its original position or rotates immediately through 180° , depending upon whether $|H| < H_c$ or $|H| > H_c$ where H_c is some

critical field and will be different for different materials. However, if the particle size is small and temperature is high and H is less than H_c then the magnetization may rotate through 180° some time after the field reversal as a result of thermal agitation. So that the mean magnetization takes a certain time τ_p to reverse its direction, and this time is referred to as the superparamagnetic relaxation time. It is obvious from Eq. 12 that the relaxation time for bulk material is very large since the particle volume in bulk is infinite. Hence the magnetization does not reverse in zero applied field and this is called stable magnetic behavior. If the direction of H is taken along the positive z axis then the probability for M to change from orientation 1 (along z) to orientation 2 (along $-z$ axis) is given by

$$v_{12} = c_{12} e^{-(w_m - w_1)/kT}$$

and similarly

$$v_{21} = c_{21} e^{-(w_m - w_2)/kT}$$

where v_{12} and v_{21} is the probability of changing M from orientation 1 to 2 and vice versa. w_m is the energy in the intermediate orientation of highest energy and w_1 and w_2 are

energies in the orientation 1 and 2.

The value of the coefficients c_{12} and c_{21} are determined by Brown. In the case of zero applied field these values are given by

$$c_{12} = c_{21} = 1/2 \gamma' \left(\frac{VMH^3}{2\pi kT} \right)^{1/2}$$

where γ' is a constant, and is approximately equal to ratio of the magnetic moment to the angular momentum. The frequency factor τ_0 in Eq. 12 is defined as

$$1/\tau_0 = (c_{12} + c_{21}) = \gamma' \left(\frac{VMH^3}{2\pi kT} \right)^{1/2}$$

or

$$\tau_0 = \frac{1}{\gamma'} \left(\frac{2\pi kT}{VMH^3} \right)^{1/2}$$

Clearly, then τ_0 depends on the particle size and the temperature but the dependence is $\left(\frac{T}{V}\right)^{1/2}$ which is much slower change than $\left(\frac{T}{V}\right)$ in the exponential of Eq. 12 and hence in comparison to the exponential change can be assumed constant.

The relation between the superparamagnetic relaxation

time τ_p and the characteristic time of the measurement τ_c determines the magnetic behavior of the system. Whereas τ_c is about 100 seconds for a static experiment, for a Mössbauer experiment τ_c is defined as the reciprocal of the Larmour precession frequency of the nucleus in an average field and is of the order 10^{-8} second for the case of iron. If $\tau_c \gg \tau_p$ then the average value of M will be zero and hence the system behaves paramagnetically. On the other hand if $\tau_c \ll \tau_p$ the magnetization will not be averaged to zero and the system will behave as a ferromagnet. For the situation in which $\tau_c \approx \tau_p$ the system should exhibit a transitional behavior. In general the superparamagnetic fluctuations or reversals of the magnetization can be brought about by applying an external field, changing the particle size, or varying the temperature of the system. The superparamagnetic fluctuations are analogous to the case of spin-spin and spin-lattice relaxation, and hence below we will briefly review the theory developed by Blume⁽¹⁴⁾ and van der Woude⁽⁵⁵⁾ for spin relaxations. Consider that due to spin-lattice relaxation the internal magnetic field at the nucleus changes from a value $+h_0$ (along the z axis) to a value $-h_0$ (along the $-z$ axis). The rate of change of field depends on the spin lattice relaxation time. If the rate of change of field direction at the nucleus is small compared to the Larmour precession frequency of the nucleus then the nucleus will experience an average magnetic field and thus the nuclear level will be split and will produce

a full six line Zeeman magnetic hyperfine pattern. However, if the field direction at the nucleus changes rapidly compared to the Larmour precession frequency, the nucleus will be unable to precess and the net effect will be no field at the nucleus. This will mean that the nuclear levels will not be split and the full six-line Zeeman pattern will collapse into a single paramagnetic line. This implies that as the reversal frequency of the field direction at the nucleus increases from a value much below the Larmour precession frequency, the inner most lines in the Zeeman pattern collapse first into a single line and at the same time the outer four lines are broadened. These outer lines eventually collapse into the central line as the reversal frequency of the field direction at the nucleus becomes much larger compared to Larmour precession frequency. It has been shown by Anderson⁽⁵⁶⁾ that the lines in the Zeeman pattern move inwards by about 16% before they become so broad that they overlap and form what appears to be a single line.

EXPERIMENTAL FINDINGS

Introduction

The results of the experiment are classified into three groups: one group containing the films in the thickness range from 1 to 6 Å (8.5×10^{14} atoms/cm² to 5.1×10^{15} atoms/cm²); the second containing the films in the thickness range from approximately 15 Å to 45 Å; the third group containing those samples in the transition region between the first two groups. All the spectral data were obtained while the samples were inside the ultra high vacuum at a pressure of 10^{-11} Torr. The spectra were observed over a temperature range from 15° K to 350° K.

From the experimental spectra we calculated the following parameters: The normalized resonance area of the spectra was determined by dividing the total resonance area under all the absorption peaks in a spectrum by one mm/sec. times the background. The magnetic fraction F for the samples was defined as the ratio of the resonance area of the peaks whose positions lie outside ± 2.5 mm/sec. to the total resonance area. Any resonance that lies outside the velocity range ± 2.5 mm/sec. is due to the magnetic hyperfine splitting so this parameter measures the fraction of the sample that behaves ferromagnetically. It has been shown⁽⁵⁷⁾ that only 16% of the Zeeman spectrum of bulk iron and less of the iron oxides, and practically all the quadrupole

spectra and the paramagnetic singlet spectra lie in the velocity range ± 2.5 mm/sec. If one considers an intensity ratio of 3:48:1:1:48:3 for the six lines of the magnetic hyperfine spectrum where $0 \leq \beta \leq 1$ then the magnetic fraction for $\beta = 0$ will be 0.75 and for $\beta = 1$ its value will be 0.875. Hence under these conditions the value of magnetic fraction will depend on the intensity of the lines in the spectrum. The isomer shifts presented in the tables are with respect to a crystal of sodium nitroprusside traceable to the National Bureau of Standards and with a quadrupole splitting of 1.702 mm/sec. The velocity in our experiment was positive when the source and the absorber were moving towards each other and negative when they were moving away from each other. The intensity ratio of the lines presented in Table 2 are determined by dividing the average normalized resonance area of peaks 1 and 6, and 2 and 5 by the average normalized area of peaks 3 and 4. The error bars shown in the Tables are statistical fluctuations of the given quantity.

Results of Group I

The results of the samples in this group are presented in Table 1. We also present a representative Mössbauer spectrum for the 3 A° film in Figure 10. The figure shows both the data points and the tracing of the computer fit. The spectrum for samples in this group showed two lines with an average

Table - 1

Mössbauer Parameters of Group I

	1 Å	3 Å	6 Å	13 Å*	
Thickness	$(8.5 \times 10^{14} \frac{\text{atoms}}{\text{cm}^2})$	$(2.4 \times 10^{15} \frac{\text{atoms}}{\text{cm}^2})$	$(5.2 \times 10^{15} \frac{\text{atoms}}{\text{cm}^2})$	$(1.1 \times 10^{16} \frac{\text{atoms}}{\text{cm}^2})$	
Temperature					
300° K	0.55 ± 0.21	$0.59 \pm .10$	$.54 \pm 0.16$	$0.66 \pm .04$	Doublet Separation in mm/sec.
80° K	0.64 ± 0.27	$0.56 \pm .11$	0.74 ± 0.05	$0.56 \pm .28$	
15° K	- - -	$0.56 \pm .17$	0.70 ± 0.11	$0.73 \pm .16$	
300° K	0.15 ± 0.01	$.04 \pm .01$	$.02 \pm 0.01$	$.09 \pm .01$	Isomer shift in mm/sec
80° K	-0.10 ± 0.01	$.02 \pm .01$	$-.16 \pm 0.01$	$-.12 \pm .01$	
15° K	- - -	$-.06 \pm .01$	$-.22 \pm 0.01$	$-.11 \pm .01$	
300° K	0.58 ± 0.28	$0.95 \pm .14$	0.64 ± 0.21	$0.60 \pm .08$	Width of left line in mm/sec
80 K	1.23 ± 0.56	$1.18 \pm .15$	0.90 ± 0.07	$1.23 \pm .32$	
15° K	- - -	$1.32 \pm .16$	1.22 ± 0.20	$1.04 \pm .29$	
300° K	0.91 ± 0.31	$0.79 \pm .10$	1.03 ± 0.19	$0.90 \pm .08$	Width of right line in mm/sec
80° K	0.76 ± 0.32	$0.86 \pm .10$	0.67 ± 0.07	0.84 ± 0.36	
15° K	- - -	$0.70 \pm .28$	0.56 ± 0.07	0.76 ± 0.21	
300° K	$0.16 \pm .07$	$0.19 \pm .03$	$0.13 \pm .04$	$0.17 \pm .02$	Normalized Resonance area
80° K	$0.26 \pm .15$	$0.17 \pm .03$	$0.14 \pm .01$	$0.13 \pm .07$	
15° K	- - -	$0.16 \pm .05$	$0.13 \pm .03$	$0.11 \pm .03$	

*Condition under which evaporation was made was different than the other samples

COUNTS IN ARBITRARY UNITS

Figure 10

splitting of 0.6 mm/sec. This splitting was almost constant with a change in either the thickness or the temperature of the samples. The isomer shift for these samples was small and showed a definite temperature dependence in that the isomer shift decreased as the temperature was lowered. The width of the line on the negative velocity side, called the left line, showed an increase as the temperature was lowered and the width of the line on the positive velocity side, called the right line, remained fairly constant or at the most showed a slight decrease in the width. The normalized resonance area for all these samples was relatively invariant with temperature and thickness; if anything it showed a slight decrease with decreasing temperature. The normalized resonance area for these samples was about 0.16. As the resonance area is proportional to the Mössbauer resonance fraction, the temperature shift is opposite to that expected from theory. Magnetic fraction for all these samples was zero as no magnetic hyperfine structure was observable. Mention must be made of the sample of ^{13}A average thickness which has a spectrum typical of group I even though its thickness would place it in group III. This film was made at a substrate temperature which was higher than the room temperature and this would differ in molecular and growth habit. No transitional behavior from two-line spectra to Zeeman six line spectra was observed for this film as will then be noted for group III spectra. Isomer shift for this film

showed a slight decrease in going from room temperature to 80° K and then remained constant at 15° K. The doublet splitting was approximately 0.6 mm/sec. and independent of temperature. Hence this sample exhibited group I characteristics.

Results of Group II

Data from the samples in this group are given in Table 2. A typical six line Mössbauer spectrum representative of these films is shown in Figure 11. Again, the figure shows both the data points and the tracing of the computer fit to the data points. The films in this group showed the six line Zeeman spectrum which is indicative of the magnetic hyperfine structure. No significant quadrupole moment was detectable in these samples when the thickness or the temperature of the film was varied. The isomer shift for these samples was also found to be small, about 0.17 mm/sec, and showed a slight decrease as the temperature was lowered. The normalized resonance area showed an increase as the samples became thicker. The resonance area also showed a systematic increase with lowering of temperature for these films. The outermost pair of lines in the spectrum are called 1 and 6 lines, the next two outer lines are called 2 and 5 and the inner pair of lines are called 3 and 4. The widths of the lines presented in Table 2 are average widths of each corresponding pair. The widths of line 1 and 6 for these films almost remain constant

Table - 2

Mössbauer Parameters of Group II

	15.5 Å ^o	20 Å ^o	42 Å ^o	36 Å ^{o*}	
Thickness	$(1.3 \times 10^{16} \frac{\text{atoms}}{\text{cm}^2})$	$(1.7 \times 10^{16} \frac{\text{atoms}}{\text{cm}^2})$	$(3.6 \times 10^{16} \frac{\text{atoms}}{\text{cm}^2})$	$3.1 \times 10^{16} \frac{\text{atoms}}{\text{cm}^2}$	
Temperature					
300° K	0	0.09 ± .05	-.05 ± .05	0	Quadrupole
80° K	-.02 ± .05	0.05 ± .05	- - -	.08 ± .05	Splitting in
15° K	- - -	- - -	- - -	.03 ± .05	mm/sec
300° K	0.2 ± 0.01	0.17 ± .01	0.15 ± .01	.07 ± .01	Isomer shift
80° K	0.18 ± .01	0.14 ± 0.01	- - -	.02 ± .01	in mm/sec
15° K	- - -	- - -	- - -	.08 ± .01	
300° K	0.12 ± .01	0.16 ± .03	0.24 ± .01	0.34 ± .02	Normalized
80° K	0.13 ± .01	0.19 ± .02	- - -	0.52 ± .03	Resonance
15° K	- - -	- - -	- - -	0.53 ± .03	area
300° K	0.69 ± .15	0.58 ± .19	0.45 ± .05	Not seen	Width of lines
80° K	0.53 ± .16	0.94 ± .21	- - -	1.43 ± .24	1 and 6 in
15° K	- - -	- - -	- - -	1.53 ± .30	mm/sec
300° K	0.50 ± .15	1.46 ± .65	0.30 ± .06	0.80 ± .16	Width of lines
80° K	0.90 ± .38	1.57 ± .40	- - -	1.38 ± .28	3 and 4 in mm/sec
15° K	- - -	- - -	- - -	1.13 ± .23	
300° K	313 ± 5	319 ± 5	326 ± 5	225 ± 3	Internal magnetic
80° K	319 ± 5	314 ± 5	- - -	328 ± 5	field in Kilo-
15° K	- - -	- - -	- - -	312 ± 5	Gauss

*Condition under which evaporation was made was different than the other samples.

Table - 2 (con't)

Thick- ness	Mössbauer Parameters of Group II				
	15.5 Å ^o	20 Å ^o	42 Å ^o	36 Å ^{o*}	
Tempera- ture	(1.3 x 10 ¹⁶ $\frac{\text{atoms}}{\text{cm}^2}$)	(1.7 x 10 ¹⁶ $\frac{\text{atoms}}{\text{cm}^2}$)	3.6 x 10 ¹⁶ $\frac{\text{atoms}}{\text{cm}^2}$	(3.1x10 ¹⁶ $\frac{\text{atoms}}{\text{cm}^2}$)	
300° K	1.8:2.5:1:1:2.5:1.8	0.5:1.1:1:1:1.1:0.5	2.7:1.7:1:1:1.7:2.7	0:3.7:1:1:3.7:0	Inten- sity Ratios
80° K	1.1:1.6:1:1:1.6:1.1	1.5:1.9:1:1:1.9:1.5	- - -	0.9:2.5:1:1:2.5:0.9	
15° K	- - -	- - -	- - -	1.1:3.5:1:1:3.5:1.1	
300° K	0.69 ± .10	1.28 ± .37	0.35 ± .05	2.83 ± .28	Width of lines 2 and 5 in mm/sec
80° K	0.60 ± .12	1.03 ± .18	- - -	1.75 ± .14	
15° K	- - -	- - -	- - -	2.07 ± .18	

*Condition under which evaporation was made was different than the other samples.

Figure 11

as the thickness of the samples was increased, or at the best showed a slight decrease in width. The width of these lines was also relatively invariant with temperature. The widths of lines 2 and 5 and 3 and 4 increased as the thickness was increased, but did not show any significant change with temperature. It should be pointed out that the line width that one observes in these films may be different from the width of single line observed with the Co^{57} source in a stainless steel matrix and the same enriched absorber because now the single line source is replaced by a Co^{57} doped thin iron film. The internal magnetic field for these films as determined from the separation of the Mössbauer lines increased from 313 Kilo-Gauss to 326 Kilo-Gauss as the thickness of the samples was increased from $15 \text{ \AA}$ to $42 \text{ \AA}$. The internal field of these samples never reached the value of 330 Kilo-Gauss which is the field expected in bulk iron, but was consistently lower for all the films in this thickness range. The magnetic fraction F for these samples was of the order of 0.75 and was indicative of the stable magnetic behavior in all films. The magnetic fraction was relatively invariant with a change in temperature.

Table 2 also includes a sample of film thickness $36 \text{ \AA}$ which was made with four successive evaporations. For this film there were four lines in the Mössbauer spectrum at room temperature and the spectrum changed into a full six line Zeeman spectrum as the temperature was lowered to 80° K . No quadrupole splitting

was detected in the six line or the four line Zeeman pattern. The isomer shift for this film was also very small. The normalized resonance area for this film was large compared with other samples which showed a full six line Zeeman pattern. The normalized resonance area showed a definite increase as the temperature was lowered. In the four line spectrum which was observed at room temperature it seemed as though the outermost lines 1 and 6 of the usual six line Zeeman spectrum were missing. Using the separation of the outer lines in the four line spectrum as the 2 and 5 line in the normal six line spectrum the internal magnetic field is calculated to be 225 Kilo-Gauss. The internal magnetic field as calculated from the separation of the six line Zeeman pattern at 80° K and 15° K was 328 Kilo-Gauss and 312 Kilo-Gauss respectively.

As the positions of the lines in the four line spectrum are within ± 2.5 mm/sec the F fraction for this film is zero by our definition. But one must realize that the widths of these lines extend beyond ± 2.5 mm/sec and thus even though the magnetic fraction is zero there is partial stable magnetic behavior present in the film. The magnetic fraction reached a value of 0.77 at 80° K and increased to 0.88 as the temperature of the film was lowered to 15° K. So then this film exhibits a stable magnetic behavior below a temperature of 80° K. It is inferred from the magnetic F fraction that the film may be partially stable in between room temperature and 80° K.

Results of Group III

There are three films in this transition group, one of average thickness $9 \text{ \AA}$ and the other about $10 \text{ \AA}$ and a third one of about $12 \text{ \AA}$. The results of these films are given in Table 3. It will be easier to discuss the results of these three samples separately.

(i) The $10 \text{ \AA}$ film showed a two-line spectrum at room temperature whose splitting was 0.52 mm/sec . The isomer shift of the sample was 0.13 mm/sec and the normalized resonance area was 0.21 . The width of the two lines of the spectrum was also nearly equal. This spectrum is shown in Figure 12. As the temperature of this sample was lowered to 100° K the two-line spectrum transformed to a full six-line Zeeman spectrum as shown in Figure 13. No quadrupole moment was detectable in this six-line spectrum. The magnetic field as calculated from the line separation was 307 kG . The normalized resonance area also showed an increase to 0.24 upon cooling. The widths of all the six lines were approximately the same but were slightly broader than the room temperature values. Finally when the sample was cooled to 15° K the normalized resonance area increased to 0.30 and the internal magnetic field to 321 kG . No appreciable change was observed in the small value of the isomer shift.

The magnetic fraction F for this sample was zero at room temperature and jumped to 0.7 as the temperature was lowered

Table - 3

Mössbauer Parameters of Group III

Thick- ness	9 Å	10 Å	12 Å	
Tempera- ture	$(8.1 \times 10^{15} \frac{\text{atoms}}{\text{cm}^2})$	$(9 \times 10^{15} \frac{\text{atoms}}{\text{cm}^2})$	$(1 \times 10^{16} \frac{\text{atoms}}{\text{cm}^2})$	
350° K	- - -	- - -	≈ 0	Quadrupole splitting in mm/sec.
300° K	- - -	$0.52 \pm .10$	≈ 0	
240° K	- - -	- - -	$.09 \pm .05$	
200° K	- - -	- - -	$.03 \pm .05$	
170° K	$.08 \pm .05$	- - -	- - -	
120° K	$.05 \pm .05$	- - -	- - -	
100° K	$.05 \pm .05$	$.04 \pm .05$	- - -	
80° K	$.03 \pm .05$	$.05 \pm .05$	$.05 \pm .05$	
40° K	- - -	- - -	$.05 \pm .05$	
15° K	- - -	- - -	$.01 \pm .05$	
350° K	$0.16 \pm .01$	- - -	$0.10 \pm .01$	Isomer shift in in mm/sec
300° K	$0.31 \pm .01$	$0.13 \pm .01$	$0.11 \pm .01$	
240° K	- - -	- - -	$0.09 \pm .01$	
200° K	$0.21 \pm .01$	- - -	$0.10 \pm .01$	
170° K	$-0.28 \pm .01$	- - -	- - -	
120° K	$-0.34 \pm .01$	- - -	- - -	
100° K	$-0.24 \pm .01$	$0.28 \pm .01$	- - -	
80° K	$-0.23 \pm .01$	$0.26 \pm .01$	$.04 \pm .01$	
40° K	- - -	- - -	$.04 \pm .01$	
15° K	- - -	- - -	$.01 \pm .01$	
350° K	- - -	- - -	248 ± 3	Internal Magnetic Field in Kilo-Gauss
300° K	- - -	- - -	257 ± 3	
240° K	- - -	- - -	272 ± 3	
200° K	- - -	- - -	277 ± 3	
170° K	295 ± 3	- - -	- - -	
120° K	301 ± 5	- - -	- - -	
100° K	302 ± 5	307 ± 5	- - -	
80° K	324 ± 5	321 ± 5	291 ± 3	
40° K	- - -	- - -	287 ± 3	
15° K	- - -	- - -	298 ± 3	

Table - 3 (con't)

Thick- ness	9 Å	10 Å	12 Å	
Tempera- ture	$(8.1 \times 10^{15} \frac{\text{atoms}}{\text{cm}^2})$	$(9 \times 10^{15} \frac{\text{atoms}}{\text{cm}^2})$	$(1 \times 10^{15} \frac{\text{atoms}}{\text{cm}^2})$	
350° K	2.83 ± .32	- - -	1.14 ± .28	Width of lines 1 and 6 in mm/sec
300° K	3.65 ± .54	0.70 ± .15	1.17 ± .28	
240° K	- - -	- - -	1.47 ± .34	
200° K	2.86 ± .49	- - -	1.01 ± .29	
170° K	1.22 ± .35	- - -	- - -	
120° K	1.33 ± .28	- - -	- - -	
100° K	1.14 ± .26	0.72 ± .06	- - -	
80° K	1.46 ± .23	0.88 ± .10	1.01 ± .16	Width of lines 2 and 5 in mm/sec.
40° K	- - -	- - -	1.01 ± .20	
15° K	- - -	- - -	1.25 ± .24	
350° K	1.61 ± .32	- - -	1.57 ± .18	
300° K	1.51 ± .39	0.67 ± .11	1.61 ± .19	
240° K	- - -	- - -	1.64 ± .16	
200° K	1.14 ± .46	- - -	1.74 ± .20	
170° K	1.77 ± .25	- - -	- - -	Width of lines 3 and 4 in mm/sec.
120° K	1.66 ± .18	- - -	- - -	
100° K	2.03 ± .20	0.81 ± .08	- - -	
80° K	1.52 ± .14	0.88 ± .08	1.29 ± .10	
40° K	- - -	- - -	1.28 ± .14	
15° K	- - -	- - -	1.17 ± .14	
350° K	- - -	- - -	1.10 ± .41	Width of lines 3 and 4 in mm/sec.
300° K	- - -	- - -	1.15 ± .43	
240° K	- - -	- - -	1.14 ± .32	
200° K	- - -	- - -	1.19 ± .51	
170° K	1.08 ± .43	- - -	- - -	
120° K	1.32 ± .43	- - -	- - -	
100° K	1.26 ± .45	0.93 ± .15	- - -	
80° K	1.18 ± .23	0.83 ± .15	1.39 ± .23	Normalized Resonance area
40° K	- - -	- - -	1.33 ± .25	
15° K	- - -	- - -	0.82 ± .25	
350° K	0.24 ± .02	- - -	0.27 ± .02	
300° K	0.27 ± .03	0.21 ± .05	0.28 ± .03	
240° K	- - -	- - -	0.31 ± .03	
200° K	0.27 ± .03	- - -	0.31 ± .03	
170° K	0.30 ± .02	- - -	- - -	Normalized Resonance area
120° K	0.31 ± .02	- - -	- - -	
100° K	0.31 ± .02	0.24 ± .01	- - -	
80° K	0.32 ± .02	0.30 ± .01	0.33 ± .01	
40° K	- - -	- - -	0.33 ± .02	
15° K	- - -	- - -	0.36 ± .02	

Figure 12

Figure 13

indicating that the film became magnetically stable. The plot of the normalized resonance area for this sample as a function of temperature is shown in Figure 14 and the temperature dependence of magnetic field is shown in Figure 15.

(ii) The $12 \text{ \AA}$ sample is unique in that we observed a six-line Mössbauer spectrum at room temperature but the internal magnetic field was found to be only 248 Kg which was much smaller than the bulk value of 330 Kg. We varied the temperature of this sample from 350° K to 15° K and observed a systematic increase in the internal magnetic field which reached a value of 298 Kg at 15° K . This temperature dependence is shown in Figure 16. No quadrupole moment was detectable for this film. The normalized resonance area of this film also increased slowly from a value of 0.27 to 0.33 as the temperature was varied from 350° K to 15° K , and is shown in Figure 17. The width of the lines was about 1-1/2 times the experimental width and was relatively invariant with temperature. The experimental width is defined as the observed full width at half maximum for the single line obtained from a Co^{57} source in stainless steel matrix and an enriched absorber. The magnetic F fraction for this sample was 0.7 and was approximately constant with temperature variation.

(iii) The $9 \text{ \AA}$ film also falls in the transition thickness range. This film showed a three-line spectrum at 350° K which developed into a six-line Zeeman spectrum when cooled to about 170° K . No quadrupole splitting was observed in this six-line spec-

Figure 14

Figure 15

Figure 16

Figure 17

trum. The internal magnetic field was calculated to be 295 Kilo-Gauss at a temperature of 170° K which increased to 324 Kilo-Gauss as the temperature was lowered to 80° K. The normalized resonance area of this film was 0.24 at 35° K and consistently increased to 0.32 as the temperature was lowered to 80° K. The magnetic F fraction of the sample was 0.8 at room temperature and remained approximately constant as the temperature was lowered to 80° K.

Sample of Thickness $< 1 \overset{\circ}{\text{A}}$: $(0.4 \overset{\circ}{\text{A}})$

This sample has only 3.7×10^{14} atoms/cm² and is expected to be discontinuous. This film showed a well defined two-line spectrum and is shown in Figure 18. The separation of this doublet was about 2 mm/sec. and is roughly 3-1/2 times the separation obtained in the case of group I samples. This large separation is relatively insensitive to the temperature change from room temperature to 80° K. The isomer shift was -0.98 mm/sec. at room temperature and increased slightly to -0.96 mm/sec. at 80° K. The normalized resonance area of this sample increased from about .11 to about 0.18 as the temperature was lowered from room temperature to 80° K. The widths of the two lines are approximately 1-1/2 times the experimental width and are independent of temperature. The magnetic fraction for the film is zero since no spectrum was observed beyond ± 2.5 mm/sec.

Figure 18

From our results it appears that the isomer shift of all the films made was small, except for the case of $.4^{\circ}$ Å thick film for which the isomer shift was very large compared to that of metallic iron. The small isomer shift in these samples indicates that the films are not oxidized. The isomer shift for these films also show a trend to decrease as the temperature is lowered. No quadrupole splitting in these films is detectable except for the $.4^{\circ}$ Å thick film for which the quadrupole splitting was very large. The origin of the two-line spectrum in group I is not considered to be arising from quadrupole splitting. When the films show a magnetic behavior the magnetic fraction F for these films is of the order of 0.7 and is nearly invariant with thickness and temperature. The normalized resonance area for all these films with variation of temperature ranged from about 0.12 to 0.54. The internal magnetic field of the samples showing six-line spectra varied from 245 to 326 Kilo-Gauss as the temperature changed from 350° K to 15° K.

CONCLUSIONS

In this section we will present a discussion and interpretation of the results given in the previous section. We know that iron has a cubic structure and thus does not possess any electric field gradient at a point of cubic symmetry. One would therefore not expect to find any quadrupole splitting in the Mössbauer spectra of iron. In our experiment if we assume the two-line spectra that one observes in group I films are not due to quadrupole splitting then our data indicates that by definition no electric quadrupole interaction is present in our films. There is an explanation for the film of $0.4 \text{ \AA}$ thickness for which the splitting was very large, $2.2 \pm .02 \text{ mm/sec}$. We feel that this large splitting is due to isolated atoms of iron experiencing an electric field gradient from the glass substrate or some other contamination present on the surface of the substrate. This value of quadrupole splitting gives an electric field gradient of $6.4 \times 10^{17} \text{ volts/cm}^2$. This value of electric field gradient is much larger than $4 \times 10^{16} \text{ volts/cm}^2$ as observed by Godwin⁽⁴⁶⁾ for iron atoms on the surface of silver. To calibrate the reader $2.5 \times 10^{17} \text{ volts/cm}^2$ is the electric field gradient due to an electron at about $1 \text{ \AA}$ distance. One could consider the two lines arising from two different species of iron, for example, if one peak is due to Fe^{++} and another

due to Fe then since the isomer shift of Fe^{++} is 1.5 mm/sec. and that of Fe is 0.27 mm/sec. the maximum separation will be 1.77 mm/sec. which is smaller than the value of 2.2 mm/sec. for our film. Also convincing is the fact that the widths of the two lines in this film are narrow and are of almost equal intensity. If the peaks arose from two different valence states, it would be coincidental that the intensities are equal; a quadrupole splitting assumes only that each iron atom is at an equivalent site. Hence we are led to believe that the two-line spectrum is due to quadrupole interaction. The sign of the electric field gradient can not be determined from our experiment.

The isomer shifts of the films in group I and group II are small and close to the value of 0.27 mm/sec. for metallic iron. Thus we can conclude that the films are representative of iron and not iron oxide. The closest iron oxide having the isomer shift of 0.2 mm/sec. is Fe^{++++} which is very unlikely. Another reason to believe that the films are metallic iron is that the internal field observed was never above 326 kilogauss, whereas the field representative of an iron oxide is of the order 500 kilogauss. We observed a temperature dependence in the isomer shift of these samples. A possible explanation for this could be the second order doppler shift in the iron nuclei. The isomer shift for our samples decreased as the temperature was lowered and implies that $\frac{d\Delta v}{dT}$ is negative where Δv is the isomer shift. If one averages the difference of isomer shift in the temperature range from 300° K to

80° K for all the samples and then calculates $\frac{d\Delta v}{dT}$ the result is -5×10^{-4} mm/sec. which is in close agreement with the value of -7×10^{-4} mm/sec.° K as calculated by Hanna et al. (27)

The internal magnetic field at the iron nucleus as determined by our experiment for the group II films is slightly lower than 330 kilogauss observed for bulk iron at room temperature. This decrease in field could be explained in one of the following ways. i) The films in the thickness range we have studied may still be considered as consisting of superparamagnetic particles which interact with each other and thus do not correspond to the situation in bulk and this may produce variations in the magnetic field observed. ii) As in our films cobalt is doped in iron one could expect the internal magnetic field to depend slightly on the relaxation time of the cobalt atom. As the cobalt nucleus goes to an iron nucleus by capturing a K electron there is a relaxation time of the order of 10^{-8} seconds (58) after which the electronic configuration changes to that appropriate to iron. So that if a γ -ray is emitted by Fe^{57} which carries the Mössbauer information before the electronic configuration has relaxed to that appropriate to iron then this γ -ray may sample a field which is not appropriate to iron and thus may show a slight deviation. iii) The third possibility could be the presence of Co^{57} in iron films. The concentration is about 0.05 atomic percent of cobalt. C. E. Johnson et al. (59) have found that the

hyperfine field in Fe-Co alloys can increase to about 365 kilogauss at 30 atomic percent of cobalt and then decrease to about 165 kilogauss as the concentration is increased. For such low concentrations as in our experiment, no change in hyperfine field would be observed, hence this possibility is ruled out.

We feel that the reasoning in (ii) is more likely to explain this small decrease in the internal magnetic field since the field appropriate to the electronic configuration of cobalt in iron is 300 kilogauss⁽⁶⁰⁾ at 4.2° K and that for bulk iron is 330 kilogauss at room temperature. Thus the Mössbauer gamma ray can sense a field below the bulk value of 330 kilogauss.

The temperature dependence of the magnetic field for the sample of 12 Å in the transition thickness range may be interpreted if one considers that the frequency of superparamagnetic fluctuations is such that the average value of magnetization and hence the field is less than the bulk value. If the superparamagnetic fluctuations are rapid but still slow compared to the Larmour precession frequency of about 10^8 radian/sec. the average value of field seen by the nucleus will be small and would increase as the superparamagnetic fluctuations are slowed down by lowering the temperature of the system. This would then mean that the magnetic field would increase as the temperature was lowered. This was the case found in our observation. The reason why we do not see such large changes in magnetic field in

thicker samples of group II can be because the fluctuation time is already so large that the system is almost behaving like bulk. Assuming that the above is correct one can conclude that the Zeeman hyperfine lines in the spectrum start to come closer as the temperature is raised or the superparamagnetic fluctuations time is reduced as the films are made thinner. From our results we find that the lines in the Zeeman hyperfine spectrum move inwards by about 16% in going from 15° K to 350° K. One should point out at this point that even though the lines have moved in by 16% the lines are well resolved and are not appreciably broadened. Van der Woude⁽⁵⁵⁾ theory suggests that when the lines move in by about 16% the lines are considerably broadened and are no longer able to be resolved. This implies that the model of Blume and Van der Woude is not sufficient to explain the phenomenon observed in our films.

Before discussing the films in group I and group II we want to point out that the two line spectrum observed in group I is not due to iron atoms at two different sites. If this were the case then one could not construct two lines with a separation of 0.6 mm/sec. and an isomer shift of about 0.17 mm/sec. for the spectrum. We also have discarded the possibility that this doublet could be due to quadrupole splitting by observing that no quadrupole was detectable in the full six line Zeeman spectra, and moreover, one does not expect a quadrupole splitting if the

iron remains cubic and no oxides are present.

Now we will give a possible explanation of the transition thickness range sample and the two-line spectra in the films of group I. The Larmour precession frequency of the excited state of Fe^{57} nucleus is 1.6×10^8 radians/sec. and that of the ground state is 2.8×10^8 radians/sec. in the bulk iron field of 330 kilogauss. If the superparamagnetic fluctuation frequency is much smaller than any of the above frequencies the nucleus will precess and thus magnetic levels will be split and one will observe the full six-line hyperfine spectrum, as was observed in the case of films in group II. Assuming the anisotropy constant value of 5×10^5 ergs/cm³ for the bulk iron and 10^{-7} seconds as the superparamagnetic relaxation time which is larger than the reciprocal of the Larmour precession frequency one could calculate the particle size for the films in the thickness range of group II. As the films in this group show a six-line spectrum at room temperature the choice of 10^{-7} seconds for the smallest superparamagnetic fluctuation time is reasonable. The particle size as calculated by using Equation 12 is $90 \text{ \AA}$ at room temperature. We therefore conclude that a film with particle size of $90 \text{ \AA}$ at room temperature will exhibit bulk behavior. If the superparamagnetic fluctuation frequency is much greater than the Larmour precession frequency of the nucleus, the nucleus will not be able to precess and thus magnetic sub levels will not be split and one would expect a

single paramagnetic line. Blume's calculation shows that the complete collapse of the lines occur at fluctuation time of the order of 10^{-10} seconds, but Equation 12 tells that we cannot go below 10^{-9} sec. and hence complete collapse of the spectrum cannot be obtained in the case of iron.

Now consider the case where the superparamagnetic fluctuation frequency becomes comparable to the Larmour precession frequency, the magnetization will wander around as it changes direction and this may lead to complex spectra. We feel that in this frequency range the magnetic sub levels start to come closer together faster in the case of the excited state as compared to the ground state because the splitting of sub levels in ground state is 3.8 mm/sec. and that of excited is 2.2 mm/sec. and also because the Larmour precession frequency is smaller for excited states as compared to the ground state. In these circumstances then it is possible that the excited state sub levels have come very close to each other so that they are not resolvable but the ground state is still split a little bit more so that it can be resolved. Hence in a Mössbauer spectrum one still observes two lines resulting from the transition from the excited state to the two sub levels of the ground state, though the splitting is much smaller than the full splitting of the ground state. Our data for the ^{57}Fe 10 Å thick film shows that the separation of lines is about 0.6 mm/sec. which is about 1/6 the total splitting of the

ground state when the fluctuation time is of the order of 10^{-7} sec. and thus supports the above model. This particular sample was used to estimate the superparamagnetic fluctuation frequency at which this transition can be observed. As the full Zeeman pattern was observed at 100° K one can assume that the fluctuation time is of the order of 10^{-7} sec. Now by changing the temperature to 300° K the sample showed a two-line spectrum. Knowing these temperatures we have calculated the fluctuation time to be approximately 5×10^{-8} sec. corresponding to a frequency of 1.2×10^8 radians/sec. which is very close to the Larmour precession frequency of the excited state and about half the Larmour frequency for the ground state. Using the value 5×10^{-8} sec. for the superparamagnetic fluctuation time we have calculated the critical particle size of $85 \text{ \AA}$ at room temperature. For the films in group I we observed a two-line spectrum at all temperatures which would imply that the superparamagnetic fluctuation time is smaller than 5×10^{-8} seconds, and we have assumed a value of 1×10^{-8} sec. as the fluctuation time for these films. The particle size at room temperature for these films has been calculated using the above fluctuation time and is found to be $71 \text{ \AA}$. For the films in group I a two-line Mössbauer spectra was observed. This spectrum was relatively insensitive to temperature variations and the particle size in this thickness range. This could be because the superparamagnetic fluctuation time is limited to a value of approximately 10^{-9} sec. due to the frequency factor in

Equation 12, so that we would expect that in this group the maximum particle size at 15° K is such that the superparamagnetic fluctuation time is of the order of 10^{-9} seconds and thus the spectrum that one observes is independent of temperature and particle size. The superparamagnetic fluctuation frequency will also affect the width of the lines in the spectrum. One would expect that as the fluctuation frequency is increased there will be more uncertainty in the energy of the levels and thus the line will broaden. This means that the lines will broaden as the temperature is increased or the thickness is decreased. Solely on the basis of data on the 20 Å and 42 Å thick film we can see that the width of lines increases as the thickness is decreased, but we cannot be absolutely certain of this behavior and more experiments at various thickness ranges should be done to confirm this.

In summary we find that the particle size above which a stable magnetic behavior is observed is of the order of 90 Å at room temperature assuming a simple uniaxial anisotropy. The particle size at which the Zeeman pattern collapses to two lines is about 85 Å at room temperature and corresponds to a superparamagnetic fluctuation frequency of about 1.2×10^8 radian/second. For smaller particles only a two-line spectrum is seen, resulting from the excited state splitting decreasing to zero while the ground state is still partially split. The isomer shift of the films indicate presence of metallic iron as opposed to iron

oxides. No quadrupole splitting is observed in the samples except for monolayer films.

REFERENCES

- (1) U. Gradmann, J. Appl. Phys. 40, 1182 (1969).
- (2) C. E. Violet and E. L. Lee, Mössbauer Effect Methodology, Edited by I. J. Gruverman (Plenum Press New York, 1967) 2, 171-179.
- (3) A. C. Zuppero and R. W. Hoffman, J. Vac. Sci. and Technol. I, 118-121 (1970).
- (4) D. Schroerer, Mössbauer Effect Methodology, Edited by I. J. Gruverman (Plenum Press New York, 1969) 5, 141-162.
- (5) W. Kündig, H. Bömmel, G. Constabaris and R. H. Lindquist, Phys. Rev. 142, 327 (1966).
- (6) R. H. Lindquist, G. Constabaris, W. Kündig and A. M. Portis, J. Appl. Phys. 39, 1001 (1968).
- (7) K. Rabinovitch and H. Shechter, J. Appl. Phys. 39, 2464 (1968).
- (8) C. Kittel, Phys. Rev. 70, 965 (1946).
- (9) J. C. Walker and B. Cleveland, Bul. Amer. Phys. Soc. 15, 108 (1970).
- (10) C. R. Guarnieri, B. T. Cleveland and J. C. Walker, Bul. Amer. Phys. Soc. January 1971.
- (11) R. A. Mazak, Bul. Amer. Phys. Soc. January 1971.
- (12) J. W. Burton and R. P. Godwin, Phys. Rev. 158, 218 (1967).
- (13) V. I. Goldanskii, E. F. Makarov, and V. V. Khrapov, Phys. Letters, 3, 344 (1963).
- (14) M. Blume, Phys. Rev. Letters 14, 96 (1965).
- (15) M. Blume and J. A. Tjon, Phys. Rev. 165, 446 (1968).
- (15a) Carl Andeen, Private Communications.

- (16) Cleveland Electronics, 1974 East 61st Street, Cleveland Ohio, 44103, U.S.A. The device is named Mössbauer Transducer.
- (17) E. Kankaleit, Mössbauer Effect Methodology, Edited by I. J. Gruverman (Plenum Press New York, 1965) 1, 47-66.
- (18) P. R. Bevington, "Data Reduction and Error Analysis For the Physical Sciences", (McGraw Hill Book Co., New York, 1969).
- (19) Lectures on the Mössbauer Effect by J. Danon (Gordon and Breach, Science Publishers New York, 1968).
- (20) D. A. Shirley, Rev. Mod. Phys. 36, 339 (1964).
- (21) N. N. Greenwood, Chemistry in Britain, February, 1967 Vol. 3, No. 2, 56-72.
- (22) L. W. Fagg and S. S. Hanna, Revs. Modern Phys. 31, 711 (1959).
- (23) NBS. Technical Note No. 463, Issued August 1968.
- (24) M. A. Krivoglaz, JETP, 19, 432 (1964).
- (25) R. E. Watson and A. J. Freeman, Phys. Rev. 123, 2027 (1961).
- (26) W. Marshall and C. E. Johnson, Metallic Solid Solutions, editors J. Friedel and A. Guinier, (W. A. Benjamin Ind., New York, 1963) Ch. 29.
- (27) R. S. Preston, S. S. Hanna, and J. Heberle, Phys. Rev. 128, 2207 (1962).
- (28) Mössbauer Effect Principles and Application by G. K. Wertheim (Academic Press, New York, and London) Page 61.
- (29) R. E. Watson, A. C. Gossard and Y. Yafet, Phys. Rev. 140, A375 (1965).
- (30) R. E. Watson and A. J. Freeman, Phys. Rev. 131, 250 (1963).
- (31) H. Frauenfelder, The Mössbauer Effect, (W. A. Benjamin Inc., New York, 1963).

- (32) P. M. Parker, J. Chem. Phys. 24, 1096 (1956).
- (33) E. Matthias, W. Schneider, and R. M. Steffen, Phys. Rev. 125, 261 (1962).
- (34) R. L. Collins and J. C. Travis, Mössbauer Effect Methodology, Vol. 3, edited by I. J. Gruverman, (Plenum Press, New York, 1967) P. 123.
- (35) G. K. Wertheim, Phys. Rev. 121, 63 (1961).
- (36) W. Heitler "Quantum Theory of Radiation", Clarendon Press, Oxford, 1949.
- (37) H. S. Snyder and G. C. Wick, Phys. Rev. 120, 128 (1960).
- (38) J. Heberle, Nucl. Inst. and Methods, 58 90-92 (1968)
- (39) H. Frauenfelder, D. E. Nagle, R. D. Taylor, D.R.F. Cochran, and W. M. Visscher, Phys. Rev. 126, 1065 (1962).
- (40) U. Shimony, Nucl. Inst. and Methods 37, 348-350 (1965)
- (41) C. Nistor and T. Tinu, Rev. Roum. Phys. 11, 551 (1966).
- (42) A. C. Zupperero, A.E.C. Technical Report No. 62, January 1970.
- (43) S. S. Hanna and R. S. Preston, Phys. Rev. 139, A722 (1965).
- (44) A.J.F. Boyle, D. St. P. Bunbury, C. Edwards, and M. E. Hall Proc. Phys. Soc. (London) 77, 129 (1961).
- (45) R. V. Pound and G. A. Rebka Jr., Phys. Rev. Letters 3, 554 (1959).
- (46) R. P. Godwin, The Mössbauer Effect In Surface Studies, Ph.D. Thesis University of Illinois (1966).
- (47) F. G. Allen, Bul. Am. Phys. Soc. 9, 296 (1964).
- (48) J. W. Burton, "The Mössbauer Effect of Fe⁵⁷ on the Surface of Tungsten", Ph.D. Thesis, University of Illinois (1965).
- (49) P. A. Flinn, S. L. Ruby and W. L. Kehl, Science 143, 1434 (1964).

- (50) B. J. Bowles and T.E. Cranshaw Phys. Letters 3, 258 (1965).
- (51) J. Frenkel and J. Dorfman, Nature, 126, 274 (1930).
- (52) C. P. Bean and J. D. Livingston J. Appl. Physics, supplement to Vol. 30, 120s (1960).
- (53) L. Néel, Ann. Géophys. 5, 99 (1949).
- (54) W. F. Brown, Jr., J. Appl. Phys. 30, 130s (1959).
- (55) A. J. Dekker and F. van der Woude, Physica 33, Zeeman centennial conference, Amsterdam, pages 195-201.
- (56) P. W. Anderson, J. of the Phys. Soc. of Japan 2, 316 (1954).
- (57) V. I. Goldanskii "The Mössbauer Effect and its Application in Chemistry". (Consultant's Bureau, New York, 1964) P. 25.
- (58) H. Pollak, Phys. Stat. Sol. 2, 720 (1962).
- (59) C. E. Johnson, M. S. Ridout and T. E. Cranshaw. "Proceedings of the Second International Conference on the Mössbauer Effect" Sept. 1961, Page 142-145.
- (60) "The Physical Principles of Magnetism" by Allan H. Morrish, John Wiley and Sons Inc., page 634.