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MÖSSBAUER EFFECT OF ULTRA-THIN IRON FILMS

A. C. ZUPPERO

ATOMIC ENERGY COMMISSION

TECHNICAL REPORT NO. 62

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TECHNICAL REPORT NO. 62

Department of Physics

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MÖSSBAUER EFFECT OF ULTRA THIN IRON FILMS

Abstract

by

ANTHONY CHARLES ZUPPERO

The properties of ultra thin films of iron have been studied in air using the Mössbauer technique. The surface density of atoms ranged from 10^{13} to 10^{18} atoms/cm². This range corresponds to atomic situations in which 99% of the substrate is empty to the situation where bulk properties have been observed by methods in addition to our own. The method of analysis requires that some of the atoms of the film emit information about their atomic surroundings, in contrast to the usual Mössbauer absorption spectroscopy.

The analyzer system utilized an asymmetric triangle as the velocity relation between source and absorber, which simplified the analysis by not requiring folding of data before observation. A computer CRT interface was used in the computation of spectrum parameters using optical first estimates and thus greatly reduced computation divergences.

The results of the thinnest film seem to indicate that the bonding is that of atoms on a surface and that the type of site occupied by any film atom is equivalent to that occupied by any other. As the surface density of atoms is increased a broad,

almost featureless resonance appears, and this spectrum may be observed to surface densities up to the order of 10^{17} atoms/cm² and to temperatures as low as 5°K. In one sample part of the feature-free spectrum was converted to that spectrum characteristic of stable magnetic behavior by application of small magnetic fields and in others by cooling to liquid nitrogen temperatures. This may indicate that part of the thicker films consisted of clusters of the correct size to be switched to stable magnetic behavior, as predicted in the theory of superparamagnetism. The thickest films exhibited either the bulk value of internal magnetic fields within 20% or non-magnetic spectrum. The latter is interpreted as possibly a new form of iron or iron-oxide.

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PRIOR INVESTIGATIONS

The properties of films of iron the order of a monolayer in thickness have long been a topic of interest because of the questions about ferromagnetism in two dimensions. The experimental presumption of very thin uniform layers of ferromagnetic materials was seldom true.⁽¹⁾ When the films were found not to exist in perfect two dimensional layers interest grew in the properties of the nucleation and growth of films. Many of the questions about the properties of these clusters went unanswered for the lack of a technology capable of observing the properties of so few atoms. With the advent of the "Iron Age" of the Mössbauer resonance effect, interest renewed because the properties of atoms at the surface, the nucleation and subsequent growth of films, and the approach to bulk ferromagnetism in Fe films could in principle all be studied at once.

The magnetic properties of ultra thin iron films in the thickness range from 1.2 to 120 Å were studied by Lee, et al.⁽²⁾ by measuring the resonance absorption of their films. These films were alternate layers of thin film and inert separator material. The surface properties of isolated Fe⁵⁷ atoms at the surface of tungsten and silver substrates were investigated by Godwin.⁽³⁾ Godwin tried to minimize the effects of growth of

clusters by using low surface densities of active material, in the 10^{13} atoms/cm² range. Lindquist, et al.⁽⁴⁾ studied the approach to bulk ferromagnetism in superparamagnetic nickel particles of order 30 Å average size. These particles were formed by impregnation in silica gel, the standard matrix for the large number of investigations of superparamagnetic compounds of Fe. A large number of experiments have been performed on the oxides and metal-oxide compounds of iron in powder and gel matrix forms in investigations into the approach to bulk ferro-, ferri-, and antiferromagnetic properties of iron.⁽⁵⁾ In our investigation we intend to determine how much information could be extracted from a single film of iron whose thickness might range from submonolayer to several hundred angstroms, and whose surface represents a true boundary. We also wished to make a preliminary investigation of the nucleation and growth of vacuum deposited films by this technique.

MÖSSBAUER EMISSION SPECTROSCOPY

The number of atoms per square centimeter for a film of Fe one monolayer thick is 1.2×10^{15} atoms/cm². In order to analyze a film this thin in a conventional Mössbauer analyzer, the film would be used as an absorber. In such an experiment one would find that there is so little iron available, even if the film were made from 100% Fe⁵⁷, that almost none of the incident gamma radiation undergoes absorption in the film. Thus, the number of gammas undergoing resonant absorption in the film are extremely small compared to the number of gammas that pass through the film without undergoing resonance. The signal to background ratio for this thin film absorber is the order of 10^5 times worse than that of a bulk 0.1 mil absorber. This implies that a monolayer film experiment must count gammas for $(10^5)^2$ times as long as a bulk absorber experiment to yield the same signal to noise ratio.

An alternate method⁽⁶⁾ of analyzing a thin sample detects the 6.4 keV x-ray that is emitted by the sample absorber atom of Fe⁵⁷. The 6.4 keV x-ray is emitted only if the Fe⁵⁷ has absorbed the resonant 14.4 keV incident radiation. By arranging the geometry of the experiment properly the detector will not see the incident source beam. In this way the signal to noise

ratios for monolayer thicknesses is only 500 times worse than a bulk absorber experiment.

On the other hand the film could be used as a source of gammas in a Mössbauer analyzer rather than an absorber, which means that some of the film atoms must be radioactive Mössbauer atoms. A single line bulk absorber would be used whose Fe^{57} content is enriched and whose thickness is chosen to optimize the resonance effect. If one chooses an alloy in which only one atom per thousand in the thin film is a radioactive atom, then the signal to noise ratio is 30:1 for a 10 hour counting time. See Appendix A for numerical details of the above methods. We have chosen this latter approach for the analysis of our films.

The nuclear gamma ray from the 14.4 keV first excited state of the iron isotope Fe^{57} exhibits a useful Mössbauer effect. Of all native iron approximately 2.2% is the Fe^{57} isotope, and the isotope is completely stable. By the process of electron capture and with a half life of 270 days the isotope Co^{57} decays into Fe^{57} in the unstable excited state and again decays promptly via gamma transitions in such a way that approximately 92% of the transitions yield the desired gamma ray. Thus, at every location where an excited state Fe^{57} atom is desired as a Mössbauer source atom a Co^{57} atom must be inserted. In a practical Mössbauer analyzer the weakest source acceptable for reasonable (namely one day) counting experiments is the order of one microcurie, or about 10^{12} atoms, provided, as is explained

later on, that the spectrum does not contain too many components. An optimum absorber in such a system has the order of 1 mg/cm^2 of stable Fe^{57} .

Although Mössbauer emission spectroscopy has the required sensitivity for practical investigations on monolayer films, several problems are also introduced. Principle among these are the following:

First, the atomic and electronic environment of newly formed Fe^{57} , or just Co^{57} , is that environment appropriate to cobalt, not iron. Foremost is the empty K shell, whose electron was captured by what was previously Co^{57} . Each property of the environment changes at its own rate from that appropriate to Co to that appropriate to Fe.⁽⁷⁾ Such properties as the s electron density and the electric field gradient at the nucleus greatly affect the magnetic and quadrupole splittings of the spectrum. Consequently when the emission spectrum of excited state Fe^{57} is examined it may be different from the absorption spectrum of Fe^{57} , depending on the relaxation time of the various environmental properties affecting the spectrum. Since the relaxation time for a given property is not a priori a known quantity, it is unwise to plan an experiment that depends on this quantity being small.

Second, the signal to noise ratio in an emission experiment depends heavily on the number of component lines. Of N_0 emitted gammas, $f_s \times N_0$ resulted from recoilless emission and

thus carry useful information, where f_s is the resonant fraction or Debye-Waller factor for the source. Of these $(A_j/A) \times f_s \times N_0$ gammas carry information about the j^{th} line, where A_j is the resonant area of the j^{th} resonance in arbitrary area units, and $A = \sum_j A_j$. The difference between the on and off resonance counting rate, and consequently the signal to noise ratio, $N_0 - (A_j/A) \times (N_0 \times f_s)$, decreases as the number of lines increases because each A_j decreases as the number of lines increases. In absorption spectroscopy, however, the A_j decreases as the number of lines increases. In absorption spectroscopy, however, the magnitude of the j^{th} resonance peak is proportional to the quantity $[N_0 f_s G(\sigma_0 f_a A_j/A)]$, where f_a is the resonant fraction of the absorber, σ_0 is a constant, and the function G is given as $G(u) = 1 - \exp(-u/2) \times J_0(1/2 u)$. The function J_0 is the zero order Bessel function. The saturating characteristic of the function G implies that for thick absorbers the difference between the on and off resonance counting rate for different lines is not a linear function of (A_j/A) but that the difference changes slowly with the number of lines. Consequently, in an absorber experiment the absorption signal to noise ratio is not a very strong function of the number of resonance components. This condition implies a preference for experiments in which the spectrum of the absorber is of interest.

Third, the chemistry of Co^{57} is slightly different

from that of Fe^{57} . Some method, such as x-ray analysis, other than the Mössbauer effect should be used to assure substitutional replacement by Co. In general, no unexpected problems have arisen for the crystal chemistry of simple iron alloys or compounds as long as the thermal treatment successfully homogenized the specimens. (29)

Last, the specific activity necessary in a monolayer film is the order of one part per thousand. It was necessary to develop a technique for using a milligram alloy source to evaporate micrograms onto a substrate.

The principal and overwhelming advantage of fabricating the monolayer film into a source rather than an absorber is that of the counting time saving of the order 10^4 . An additional benefit is realized when the information desired from a very thin absorber or source is only a true-false answer to the question "has the number of resonances changed?" Such a situation occurs when one investigates transitions from six-line Zeeman spectra to single line or quadrupole doublet spectra. In this case the transitions are quickly verified since a singlet requires a factor of 36 less counting time to establish its presence than a six line spectrum of the same signal to noise ratio.

THEORETICAL CONSIDERATIONS

The four factors that determine the total form of the emission spectrum are the resonant fraction, the isomer shift and the Zeeman and quadrupole effects.

We shall examine each of these contributions from the point of view of our experiment. We must keep in mind when looking at the spectra that we are probing nuclear surroundings.

Resonant Fraction

The resonant fraction, f , is a measure of the mean square excursion of an atom during the emission of the Mössbauer gamma is given by

$$f = \exp(-k^2 \langle x_Y^2 \rangle),$$

where $\langle x_Y^2 \rangle$ is the rms displacement of the emitting nucleus along the direction of the emitted gamma and represents the fraction of gamma rays emitted without recoil. The rms displacement is related to the degree of binding of the emitting nucleus.

Godwin^(3,17) has calculated some values of relative binding for atoms on the surface, in the surface, and in the bulk. His results indicate that the ratio of the surface atom to the bulk atom rms displacement may vary from 1 to 5 depending on the geometry of the site and the direction of gamma emission. He

also notes that the bulk state is reached in practically 2 to 3 atomic layers, so that large and consequently measurable differences occur mainly in the situations of interest, i.e., an atom in or on the surface of bulk material has a significantly different resonant fraction compared to an atom only two layers in the bulk. Thus, a measurement of f for a given spectrum could in principle give information about the relative position of the responsible nuclei.

A measurement of the sum of the areas of all the resonances in the spectrum is proportional to the resonant fraction for that sample. Since the total area of resonance is distributed among the resonances an accurate f measurement is not possible unless all the lines of a spectrum are quantitatively accounted for. In the source experiment f is defined as the total area of resonance in the sample divided by the area under 1 mm/sec of background, or non resonant spectrum, and is proportional to the actual value of f for the sample. The temperature dependence of f can be used to determine the Debye temperature, as the total f decreases with temperature. This determination is more experimentally realistic since a given line will exhibit the appropriate temperature dependence.

Isomer Shift

The isomer shift, or the measured center of gravity of a spectrum with respect to an arbitrary reference, is primarily

related to the electronic wave functions at the various sites. The isomer or chemical, shift, is given by⁽⁹⁾

$$\delta E = \frac{2}{3} \pi Z e^2 [\langle r_B^2 \rangle - \langle r_A^2 \rangle] \{ |\psi_a|^2 - |\psi_e|^2 \}$$

where Ze is the nuclear charge, $\langle r_B^2 \rangle$ and $\langle r_A^2 \rangle$ are the rms radii of the nuclear excited and ground states, and ψ_a and ψ_e are the electronic wave functions at the nucleus for the absorber and emitter respectively.

The most useful property of the measured isomer shift is that of classifying the oxidation state of Fe for the high spin compounds,⁽¹⁰⁾ such as the iron metal and its oxides or as antiferromagnetic FeF_2 (2+) or FePO_4 (3+), although the effect per se measures the nuclear density of electrons. For low spin iron complexes, such as the ferro- and fericyanides, the isomer shift tends to be rather independent of oxidation state from -2 through zero to +2. The (high spin) isomer shift for Fe^{+2} is the order of 1.5 mm/sec, and for Fe^{+3} , 0.7 mm/sec, with respect to a National Bureau of Standards crystal of Sodium Nitroprusside.

Anharmonic binding forces may be able to introduce linear temperature effects, and are estimated by Godwin⁽³⁾ to be the same order of magnitude as the second order doppler shift. The second order doppler shift⁽¹²⁾ is due to the atoms moving at velocities the order of 10^3 meters/second at room temp-

erature while at helium temperatures the velocities are much smaller. Consequently, the time dilation due to the difference in rms velocities is the order of $1/2 \Delta(v^2/c^2)$, which is the order of one linewidth for an Fe^{57} Mössbauer gamma, and therefore observable. Separation of these effects is difficult, however.

Zeeman Effect

The Zeeman effect usually gives information about the magnetization of the system exhibiting the effect. In an Fe film the most important factors that influence the form of the nuclear Zeeman effect spectrum are the effective field and its temporal fluctuations at the nuclear site.

If the magnetic field at the nucleus is constant in time and no other effects are present, then the spectrum should exhibit six lines as shown in the middle of Figure 1 with intensities proportional to⁽¹³⁾

$$I_1 = I_6 = 3(1+\cos^2\theta)$$

$$I_2 = I_5 = 4 \sin^2\theta$$

$$I_3 = I_4 = (1+\cos^2\theta) .$$

Here θ is the angle between the magnetic field and the gamma ray. For a film in which the magnetization is in the plane then the intensities are in the 3-4-1-1-4-3 ratio.

As shown in Figure 1, if the magnetization is random then the second and fifth lines in the figure will have an intensity of 2/3 that of the outer two lines and the intensities are in the familiar 3-2-1-1-2-3 ratio. When there exists a unique angle between the field and the observer, the angle is given by

$$\theta = \text{ARCOS} \left(\sqrt{\frac{4-3a}{4+3a}} \right)$$

where $a = (\text{average area of lines 5 and 2})/(\text{average area of lines 1 and 6})$. In this case the angle 55° gives the same intensity ratio as a random angle. It is also possible to have a distribution of angles in a sample resulting from local homogeneities.

Superparamagnetism

The effect of superparamagnetism is closely linked to the Zeeman splitting of a Mössbauer spectrum for a thin film. Consider a cluster of magnetic atoms that exhibits a magnetic moment resulting from the atomic moments aligned in the same direction. The fact that the direction of the resultant magnetic moment may vary somewhat at random implies that this cluster may be treated as a paramagnetic particle whose total magnetic moment is proportional to a number of atoms in the cluster or particle. A "particle" that exhibits such behavior is said to be superparamagnetic. The internal field found in a superparamagnetic particle is essentially the same magnitude as that observed in a bulk strong magnetic system.

FIGURE 1

The superparamagnetic state can be approximated in terms of single domain particles. A full discussion of this topic is given in a paper by Bean and Livingston.⁽¹⁴⁾ A single domain particle will not be completely isotropic in its magnetic properties since it is a small segment of an anisotropic infinite crystal. Such a particle is assumed to have a constant value of magnetic moment, regardless of the applied field, but not a constant direction. The anisotropy of this magnetization is usually governed by the shape and is given by $E = KV \sin^2(\theta)$, the form for uniaxial symmetry. Here V is the volume of the particle, θ is the angle between the moment and the symmetry axis of the particle, and K is the shape anisotropy energy per unit volume. We shall not include the magnetocrystalline anisotropy energy in this simplified treatment. Note that with respect to θ , the anisotropy represents a potential energy barrier that the moment must penetrate by thermal energy. The probability for the moment rotating through this barrier is proportional to $\exp(-KV/kT)$, and the time constant associated with the penetration is therefore given by $1/\tau = f_0 \exp(-KV/kT)$ where f_0 is the order of 10^{+9} sec^{-1} . This barrier is modified by the magnetostatic energy when external field is applied. For films which consist of isolated clusters magnetic surface anisotropy and strain-induced anisotropy may be expected to play an important role.

When an aggregate of identical uniaxial particles is fully magnetized along the easy symmetry axis the resulting remanence decays as $M_r = M_s \exp(-t/\tau)$, where M_s is the full magnetization, t is the time after removal of the field, and τ is the relaxation time for the process. If the sample consists of a collection of clusters that are reasonably close together, then the dipole-dipole interactions between them will modify the potential barrier. In addition the particle size determines the relaxation time and there will be a distribution of relaxation times in most samples.

Since the Mössbauer effect is observed through the emission of nuclear gamma ray that starts and finishes all in the order of 10^{-7} sec, the magnetic field can be sampled for only that order of time. The rate at which these moments change direction determines whether the resulting field at the nucleus appears constant, resulting in a normal Zeeman splitting, or appears to average to zero, resulting in an apparent paramagnetic spectrum. The rate of change of direction of the moment depends on the thermal energy of the moments, on the strength of the anisotropy forces in the cluster or domain which tend to stabilize the magnetization, and on the applied external magnetic field which also tends to stabilize the magnetization in a similar way as the anisotropy field. Thus, the set of effects characteristic of superparamagnetism are the transition from paramagnetic spectrum to a full Zeeman spectrum as the tempera-

ture decreases, cluster size increases, or external magnetic field is applied. The exponential behavior of the relaxation time implies there is a well-defined particle size at which stable behavior occurs. Stable is defined with respect to the time constant of the observer and is $<10^{-7}$ seconds for Mössbauer experiments, 10^2 seconds for the usual magnetometers. Critical particle sizes range from approximately $5 \text{ \AA}$ at He temperatures $100 \text{ \AA}$ at room temperature for iron and $30 \text{ \AA}^{(4)}$ for nickel. Critical applied field are of order 1000 gauss⁽⁴⁾ for iron.

It should be restated that the magnetic field that a Mössbauer experiment responds to are the effective fields at the nucleus. The fields at the nucleus are typically the order of 300 kilogauss. Numerous experiments^(15,16) have shown that the field sampled by the nucleus is at least proportional to the magnetization. In samples where the magnetic field at the nucleus is fluctuating at rates comparable to the Larmor precession frequencies of the nuclear spins the spectrum exhibits properties analogous to motional narrowing. For each Larmor precession frequency associated with the nuclear spin the rate of fluctuation of the effective nuclear field, which is completely independent of nuclear moment and its motion, will be a) too low to visibly alter the transition energy, b) will be in the correct range to smear the transition and reduce its energy, or c) will be so high that the nuclear spin responds only to the time average of the field, resulting in zero energy.

Since there are three Larmor precession frequencies associated with the Fe^{57} transitions, the effect of a fluctuating field may be different for each frequency depending on whether conditions a, b, or c is satisfied for each Larmor frequency.

The net result is that for field fluctuation rates slightly higher than the highest Larmor frequency condition b is satisfied for the highest and c for the lowest Larmor precession frequency. Thus, the outer lines (1 and 6) in a Zeeman spectrum are smeared and the remaining inner lines are partially collapsed to a central peak. If in addition a quadrupole splitting is present, then the inner four lines of the Zeeman spectrum are associated with one branch and the outer two are associated with the other branch of the splitting as shown in Figure 1. The innermost lines⁽³⁴⁾ contribute fully to the one peak of the quadrupole split line since condition c applies but the outer two lines do not fully contribute to the other peak, since condition b applies. The result is an asymmetry in the intensities. We refer the reader to the discussion of Dekker and Van Der Woude⁽¹⁸⁾ for details of the effects on the magnetic transitions and Blume⁽¹⁹⁾ for details on the quadrupole effect.

Quadrupole Effect

Electric field gradients on atoms at boundary layers can be studied through quadrupole effects. The electric quadrupole shift δE , in the absence of any other effect and in the mathe-

matically simplified case of axial symmetry is given by⁽⁹⁾

$$\delta E = eV_{zz} \frac{Q}{4I(2I-1)} [3m^2 - I(I+1)] \quad (1)$$

where $V_{zz} \equiv \partial^2 V / \partial z^2$ is the electric field gradient, I the nuclear spin state, m the magnetic quantum number, Q the nuclear quadrupole moment. For Fe^{57} in the $I = 1/2$ ground state, $Q =$ zero by measurement, so that δE is given only by the $I = 3/2$ state, and the splitting reduces to

$$\Delta E = \frac{1}{2} eQ V_{zz} . \quad (2)$$

The nuclear quadrupole polarizes the d electrons and thus the actual splitting will be larger than that given by Equation (2) by approximately the Sternheimer anti-shielding factor.⁽⁹⁾ In a crystal where the direction of the electric field gradient is uniform throughout the angular dependence of the quadrupole effect can give the direction of the gradient.⁽²⁰⁾ On a film, however, the microscopic direction may be undefined because of substrate irregularities and because of steps in the film and clusters. Estimates of the parameters in Equation (2) indicate that the surface atoms should experience quadrupole shifts of at least the order of a linewidth.^(3,17)

Mixing of Effects

The four effects described above may all superpose in a given individual class of atomic surroundings. Once the lines

of a given class of surrounding are all identified, the unraveling of the parameters for the four effects is straightforward but not necessarily simple. Kundig⁽²¹⁾ describes in detail the evaluation of Mössbauer spectra whose magnetic and quadrupole effects are coupled and whose quadrupole effect is not simplified through any symmetries. The isomer shift is the geometri centroid of the spectra and the resonant fraction of a source, in a source experiment, is proportional to the total area under the lines. Of course, there may be many classes of atomic surroundings that can give the same value for a given parameter.

The actual equation assumed to describe a spectrum whose lines are arbitrarily assigned to correspond to the Zeeman lines of Figure 2 but with quadrupole and isomer shift is:

$$F(v, H, Q, \delta) = A + B(v - v_0) + C(v - v_0)^2 + \sum_{j=1}^6 \frac{A_j}{1 + \left(\frac{v - g_j H - \alpha_j Q - \delta}{(\Gamma/2)} \right)^2} \quad (3)$$

where H is the magnetic field in kilogauss, Q is the quadrupole moment in mm/sec, and δ the isomer shift in mm/sec, and g and α are as follows:

$$(g) = \begin{bmatrix} -.01615 \\ -.00934 \\ -.00254 \\ +.00254 \\ +.00934 \\ +.01615 \end{bmatrix} \frac{\text{mm}}{\text{sec} \cdot \text{kgauss}} \quad (\alpha) = \begin{bmatrix} +1 \\ -1 \\ -1 \\ -1 \\ -1 \\ +1 \end{bmatrix}$$

A, B, v_0 , and C are background parameters, and v is the relative velocity between source and absorber.

The relative f is computed as the normalized resonant area under one millimeter per second of background, as follows:

$$f = \frac{\int_{-10 \text{ mm/sec}}^{+10 \text{ mm/sec}} \{A + B(v - v_0) + C(v - v_0)^2 - F(v, H, Q, \delta)\} dv (\text{mm/sec})}{A} \quad (4)$$

The integral is performed numerically during the fitting, allowing in this way the substitution of a gaussian function, or any other function, for the lorentzian function in the summation. The relative f is sufficient information for our purposes.

EQUIPMENT AND PROCEDURES

Analyzer

A precise definition of a Mössbauer spectrum analyzer is probably the best description of the equipment. A Mössbauer spectrum analyzer requires that there be a record of the number of Mössbauer gammas that are emitted from the source, pass through the absorber, and are detected by a counter, for every increment v to $v + \delta v$ of source to absorber relative velocities between $-V_0$ and $+V_0$ mm/sec. One such system is described in Figure 2. The system operates as follows: The Pulse Height Analyzer (PHA) is used as the master control. The PHA uses 256 channels, numbered from 1 to 256, each channel capable of storing a number from +0 to +999,999. The PHA is operated in the multiscalar mode; here the PHA waits for coincidence commands from the gamma electronics to add one to the contents of the channel determined by the address scaler. At periods of time given by a crystal clock, the address scaler is advanced by one. When the address is 256, the PHA automatically resets the next address to 1. The end result is that the PHA spends an equal amount of time at every address, and the amount of time taken to go from channel 1 to channel 256 is constant. Given this device, it is now a fairly simple matter to arrange for the contents of each channel to represent the Mössbauer gammas counted

in a range of relative velocities ($v, v + \delta v$). An asymmetric ramp generator is synchronized to the signal from the PHA that indicates transition from channel 256 to channel 1 (see Figure 3). The value of the ramp voltage output is proportional to the relative velocity between source and absorber by the action of the velocity drive. Therefore, given a channel number, the relative velocity range between source and absorber is determined. Consequently, the contents of a channel represent the number of Mössbauer gammas that passed through the absorber when the absorber and emitter were moving relative to each other in the velocity increment ($v, v + \delta v$) appropriate for that channel.

The PHA is a Nuclear Data Series 1100, modified only by the addition of three diodes on the address scaler outputs to give a synchronizer signal. The proportional counter is a Xenon-CO₂ Reuter-Stokes model RSG 60-A. The Pre-Amp is an Ortec PC 109-A and the amplifier and pulse-height selector are Ortec 435 and 406 A, all powered by a standard NIM bin.

The transducer is a standard but custom-made device produced by Cleveland Electronics.⁽²²⁾ The transducer assembly was easily operated with an error as low as .2% at 10 mm/sec velocities and 5 hz, and is ideally suited for Fe⁵⁷ Mössbauer work. The device is rugged, compact, and low in price, and is available.

FIGURE 2

FIGURE 3

Electronics

The usual reference velocity used in constant acceleration systems is a symmetric triangle wave. We decided to use an asymmetric ramp as a reference for two main reasons: a) we wished to avoid the psychological and computational handicaps associated with "folding" a spectrum before analysis, and b) we desired to use the nearly factor of two gain in velocity resolution over a symmetric triangle. We decided that the loss of approximately 10% of the information gathered in such a system would be acceptable. The velocity, excursion, and acceleration functions for both triangle and the asymmetric ramp is shown in Figure 4. As can be inferred from Figure 4 the fourier components of the retrace are multiples of the ramp frequency. The necessary presence of these high (audio) frequency components in the motion of the transducer places rather severe requirements on both the mechanics of the transducer and the servo drive unit. For this reason the basic frequency of the system is kept as low as possible between 5 and 10 hz and the retrace/ramp period ratio is kept to the order of 0.1. The use of Fe^{57} is fortunate because the largest velocity ever required is rarely more than 10 mm/sec. This low speed allows the magnitude of the required driving function to be reasonable for the existing electronics.

Servo Drive and Function Generator

In order to reduce the error signal to less than 1 part

FIGURE 4

in 500 (.2%) it was necessary to use two forms of control. The first, suggested by Kankleit,⁽²³⁾ is to control three parameters: total gain, gain at frequencies greater than f_0 , and the frequency f_0 . The second is an old trick long since abandoned by hi-fi enthusiasts: the use of near-critical negative output impedance. In addition, since the servo drive takes the difference between the reference signal and the actual signal, there exists a summing point in the servo drive at which one may insert temperature sensitive components to exactly cancel temperature dependencies in the velocity function reference generator. Inserting compensation at the summing point is the easiest way to almost exactly compensate all the (also non-linear) temperature drifts in the system. (E.G. a carbon resistor here exactly cancels the carbon resistor in the function generator.) A schematic of the servo drive unit is included in the Appendix B since it is not commercially available and is very useful.

The asymmetric ramp generator is adapted from R. L. Cohen.⁽²⁴⁾ The features desired of such a generator are three: a) the output voltages should be linear in time, b) the temperature dependence of the output should be low and known in order that the compensation at the servo drive summing point be a computable second order effect and c) synchronization of the frequency by signals readily available from the PHA should be possible and simple. The linearity of our generator is good to one part in the OP-AMP gain provided the integrator RC time constant is the

order of the period of the system. We have at least 1 in 10^4 . The temperature drifts can all be accounted for in magnitude and sign, and are the order of ± 4 parts in 10^4 per $^{\circ}\text{C}$. Synchronization is accomplished by forcing the sign change in the integrator voltage to be fixed in zero order by the time constants of the function generator and to first order by the change in level of PHA address scalar outputs. A schematic of this generator is included in the Appendix C because of its general usefulness as a synchronizable stable function generator.

Dewar

The low temperature measurements were performed in a dewar made by Cryogenic Associates Model CT14. See Figure 5 for the geometry of the system. The absorber and proportional counter system must be placed as close as possible to the substrate, the source, so that as much of the radiation being emitted can be analyzed. For this reason the distance from source to proportional counter is the order of 1.5 inches. Thermal contact from the copper block to the substrate is made by melting indium on the block and then pushing the substrate flush against the molten metal. Thermal contact from the copper low temperature sink to the copper block was not enhanced by any thermal materials. The copper block was milled flat and screwed as flush as possible against the sink. A reflecting silvered mylar inner window is used as a thermal radiation shield

to exclude room light and heat from the cold sink. A double layer of mylar was used as an air-vacuum membrane and showed irreversible stretching and eventually gas leakage upon cycling.

The temperature of the dewar is controlled by passing He liquid or gas through the cold sink. In this arrangement the lowest temperature used is around 5°K. The temperature was controllable to within 1 degree, but we chose to accept temperature fluctuations from 5°K to 7°K in the interest of conserving He. The temperature of the film side of the glass substrate was assumed to be the same as the copper and indium to which it was attached.

Absorber Optimization

Since the frequency spectrum of the gammas emitted by the Fe^{57} in the thin film source carry the desired information, the absorber in such a system should be chosen to extract as much of this information as possible. The absorber should exhibit as close to the natural linewidth as possible and should exhibit as large a resonance effect as possible. The difficulty arises in that an absorber that provides the maximum ratio of resonant to non-resonant absorption invariably broadens the resonance by several linewidths. A trade must be made between velocity resolution, or linewidth, and resonant effect. When the strength of the source is severely limited the primary criterion in choosing an absorber is to select that thickness which

FIGURE 5

gives a maximum resonance effect per unit incident flux. The velocity resolution or experimental absorber linewidth is then completely determined by the absorber thickness. A very clearly written procedure to compute the thickness that yields optimum absorption is given by Shimony.⁽⁸⁾ A similar paper describing the procedure to determine the linewidth of a Mössbauer absorption is given by Herberle.⁽²⁵⁾

The broadening due to the geometry is determined from the following considerations: the source to absorber distance is about 1 inch, the source areas range from about 1 to 6 (cm)² and the absorber area is approximately 6 cm². Using computations by Nistor and Tinu⁽²⁶⁾ our geometry conditions yield a worst case velocity shift of 1.5% and a linewidth broadening of order 7%. But since our calibrator is subjected to the same geometric handicap as the thin film, the absolute error in velocity is compensated in first order and only the broadening of the line remains. Thus 7% of the linewidth is attributed to the geometric broadening.

Using the weak source criteria we choose an absorber consisting of type 310 stainless steel foil 0.000 15 inch thick and isotopically enriched so that there is 1 mg./cm² of Fe⁵⁷. This absorber yields a linewidth of about 0.45 mm/sec (full width at half maximum) and the resonant effect (signal to background ratio) of about 0.4.

Old PHA Description

Four of the samples (A,B,G, and K) were analyzed on an older Mössbauer analyzer. Rather than describe the old analyzer system it is more useful for these few data runs to describe the system limits of resolution. A triangle drive was used which meant that the spectrum and its mirror image appear next to each other in a plotted output of the PHA. In none of the three above was the spectrum folded since a folding operation required a least squares fit of a special kind, that which takes into account overlapping δv_i ranges. Since no folding was performed, 50% of the available information is discarded. Furthermore, temperature compensation was not explicitly included in either the PHA or servo drive circuitry, which meant that the drifts in room temperature caused zero point shifts in both velocity calibration and the zero velocity channels. The resulting shifts are estimated to be approximately 0.1 mm/sec in the zero point and 1% for absolute velocity calibration drift. The resolution, less drifts, was .65 mm/sec.

Computer Analysis

All of the data was analyzed by the method of least squares for a linearized lorentzian or gaussian based function on a PDP-9 computer using FORTRAN procedures by Bevington.⁽²⁷⁾ The computing system used deserves perhaps special attention because the unusual approach used by Bevington allows very fast

real time analysis-in-depth of a spectrum.

A display oscilloscope and light pen hardware package on the computer seems to be the critical link optimizing the intuitive curve fitting abilities of the experimenter and the severely restricted but fast quantitative iterations performed by the computer.

In a Mössbauer spectrum it almost always happens that a spectrum contains at least one set of lines that are so close together that an arbitrary judgment must be made about the number, position, etc., of the lines so closely grouped. In addition, the experimenter can usually estimate very quickly by sight the positions, widths, and amplitudes of the better defined lines. The computer programs of the type currently used for Mössbauer analysis all require that rather accurate initial conditions be given. This requirement is so because the functions used for fitting the resonances are of the form of Equation 3

$$F(v) = \sum_{j=1}^N \frac{A_j}{1 - \left(\frac{v - a_j}{\sigma_j} \right)^2} \quad (3)$$

where the summation term is the usual form for lorentzian lines. v is the velocity, a_j is the position of the j^{th} line, σ_j the width, A_j the amplitude, and N the number of lines. In a least squares analysis the condition for fit requires that terms of

the form $\frac{\partial F}{\partial \sigma_j}$ and $\frac{\partial F}{\partial a_j}$ be solved for σ_j and a_j . Since these partial derivatives are never linear functions of σ_j and a_j , even for gaussian functions, the method used to solve for σ_j and a_j involves writing $F(v)$ as a Taylor series in σ_j and a_j . Since the Taylor series is truncated to a finite number of terms, and since the partials are fast changing functions, the partials must be evaluated very near to the desired values of parameters σ_j and a_j . This is a very stiff requirement and is the principal reason for frequent divergences in the iterations that yield Mössbauer parameters. In the FORTRAN program the Mössbauer data is displayed on an oscilloscope and a light pen is used to point to and in effect trace out the experimenter's trial initial conditions for the computations. This is the one thing that the eye is extremely good at. This system combines the best abilities of man, that of fast optical best guessing, and that of the machine, that of fast iterative improvement of lengthy and complex approximations. The end result is that an experimenter can now speculate on the parameters of almost unresolved spectra with a much higher degree of non-divergent results than has been possible in the past with older systems.

SAMPLE PREPARATION

Experimental

We consider a film to be satisfactory if the following conditions are met: a) the distribution of surface atoms should be uniform, b) the surface density of atoms, both of natural iron and of cobalt 57, should be measurable, c) the substrate for the film should represent an atomically smooth surface, and d) the effects of oxidation of the film should be minimized. We have chosen to fabricate films in a vacuum system by sublimation of an alloy of iron and cobalt 57 onto glass microscope cover slides. The choice of sublimation was dictated by other experimental considerations, as is shown below.

Deposition of a film of high specific activity is complicated by the fact that conventional devices or methods of film production require bulk amounts, i.e., visible and at least the order of milligram amounts, of radioactive material be used as the source of film material. Since bulk amounts of Co^{57} radioactivity constitute a severe radiation hazard most of the conventional methods of film fabrication are unsatisfactory. Our first approach to the problem was similar to that used by Godwin, namely to in some way deposit the radioactivity onto tantalum, and then heat the tantalum near the substrate

and evaporate. Both Godwin and ourselves find that this method heats the substrate considerably. We abandoned this method after observing that every glass substrate used cracked during evaporation.

We found a method of film deposition that appears to be satisfactory. We used a boat of pyrolytic boron nitride* in the form of a 1/4" I.D. tube closed at one end and with approximately 1/16" thick walls. The pyrolytic form of boron nitride (BN) is different from the usual grades of BN in that it is a crystalline form. It is not hygroscopic, and does not suffer from the high (1%) degree of contamination by impurities that is characteristic of the standard grades of BN. The material boron nitride was chosen as a boat material because it is a refractory material, because it is a good heat conductor, and because it is chemically inert to the HCL in the alloy solution. The alloy to be sublimed is made by mixing the drop of $\text{Co}^{57}\text{Cl}_2$ in 0.5 N HCL, the form the radioactivity is shipped, with a known amount of FeCl_2 in H_2O . The total volume of the order of 0.3 ml is placed in the bottom of the BN tube. The liquid is allowed to evaporate. The BN is then heated in an H_2 atmosphere for at least two hours at a temperature of 930°C . At this temperature and atmosphere powders of CoCl_2 , CoO , FeCl_2 , Fe_2O_3 and FeO were reduced to black conducting amorphous powders which were assumed to be iron or cobalt powders. After this procedure a dark thin coating can be seen on the inside

*Supplied by Union Carbide, Parma, Ohio.

walls of the BN. A Mössbauer spectrum of this dark material always shows at least 90% of the material yields the characteristic 6 line bulk Fe Zeeman spectrum, and the remaining material shows a paramagnetic line. The BN is then fitted into a coil of 0.025 inch diameter tungsten wire which serves as a resistive heater.

It was found that the pressure in the vacuum system was roughly proportional to the power input to the tungsten surrounding the BN. Even with stainless steel heat shields surrounding the evaporator assembly it was found that the temperature of the BN was considerably less than that of the tungsten wire surrounding it. At a system pressure of 3×10^{-8} torr the temperature of the BN is approximately 1400 °K, as measured by an optical pyrometer. Iron and cobalt sublime at this temperature⁽²⁸⁾ with a vapor pressure ratio of $3.1 \pm .15$ over ± 100 degree range around 1400 °K.

THICKNESS DETERMINATION

Units of Thickness

We compute the thickness of a sample as a surface density with units of atoms/cm². Reference to an average thickness implies a continuous film with no irregularities or clusters, whereas reference to a surface density is not so misleading for monolayer films. In order to give an approximate relation between surface density and film thickness we assume that the area times the thickness of the film is equal to the number of atoms times the volume per atom calculated from the lattice constant. This computation gives the result that $120 \text{ \AA} = 100 \times 10^{15} \text{ atoms/cm}^2$, or that thickness (Å) = $1.2 \times 10^{-15} \times \text{surface density (atoms/cm}^2\text{)}$. The surface density corresponding to a monolayer of iron depends on which crystallographic plane is parallel to the substrate. The (100) orientation yields $1.2 \times 10^{15} \text{ atoms/cm}^2$ for a monolayer while the (110) orientation yields $1.7 \times 10^{15} \text{ atoms/cm}^2$.

Surface Density Computation

The surface density of iron on the film is computed from the measured surface density of Co⁵⁷. The composition of the alloy in the BN cylinder is fixed before deposition, as indicated previously. The sublimation temperature is measured by an

optical pyrometer and is 1400 ± 50 °K. The vapor pressure ratio of Fe to Co may be determined at this temperature and it is assumed that the alloy is evaporating under equilibrium conditions. Thus, the composition of the final film is determined by the initial alloy composition modified by the effects of fractional distillation. The amount of Co^{57} in the sample is measured using a standard of radioactivity traceable to NBS. The number of iron atoms on the film is thus computed given the number of cobalt atoms and the computed iron to cobalt ratio. The area of the film is measured optically where possible or by a profile of radioactivity. Thus, the surface density is computed as the ratio of the number of film atoms divided by the film area.

Uncertainties in Measurement

The determination of the surface density for some of the thickest films, G, H, and K, was complicated by the fact that the optical estimates of thickness are approximately a factor of five less than the radioactive estimate. This uncertainty is included in the surface density uncertainty for the samples involved. Since the amount of source material was very small it is possible that the final alloy would be enriched in cobalt for these thicker films. Assuming the thin film composition to be the same as original alloy the surface densities quoted would be too high by a factor of about three. The optical den-

sity of samples H and K also varied over the surface in a highly irregular manner, complicating the area determination. The radioactive and optical density of samples G and I varied smoothly, requiring Pb masking to exclude those portions of the film which appeared to be a factor of two optically thinner. These uncertainties are also included in the surface density uncertainties.

It should be possible in future experiments to include another isotope of iron, say iron 59, in the deposition alloy. A measurement of the radiation of the two radioactive components would then reduce the uncertainty of composition between different elements to that of differences between isotopes of the same element.

Fe/Co⁵⁷ Concentration Ratio

The surface density for a monolayer of iron is taken as 1.2×10^{15} atoms/cm². The surface density of cobalt 57 atoms used in films of thickness the order of a monolayer or greater is the order of one microcurie, or 8.6×10^{11} atoms/cm². The ratio of cobalt to iron in a monolayer film with a microcurie of cobalt is thus 700 parts per million. Since the natural isotopic abundance of iron 57 is about 1 part in 50, the total change in the isotope ratio after all of the cobalt 57 has decayed into iron 57 is then only 35 parts per thousand.

RESULTS

Introduction

In presenting the results of our investigation we will give a general overview of the entire set of results in the form of graphs, followed by a description of individual samples in detail. We will also try to summarize the new or important findings.

Every sample was removed from the vacuum after evaporation and analyzed at room temperature and atmospheric pressure. In addition some samples were subjected to various other environments detailed below.

Samples C, D, and F, in the surface density region 5×10^{15} to 7×10^{16} atoms/cm², were examined at three temperatures: room temperature, 79°K, and 5°K. The heat treatment given to samples D and E in a hydrogen atmosphere at 930°C for 2 hours is the same as that used to reduce Co⁵⁷Cl₂ and FeCl₂ to native metals. This temperature did not mechanically deform the substrates in any observable irreversible manner. A magnetic field was applied to samples E and I. This field was produced by a small magnetron magnet and was between 800 and 1000 gauss as measured with a Hall probe in the region where the samples were placed. The field was always in the plane of the film, and

TABLE 1

A Brief Summary of the Results and Environments of Each Sample

Sample Label	Surface Density Atoms/cm ²	f	F	Internal Field Value (kilogauss)	Environment	Spectra
A	$1.0-1.5 \times 10^{13}$	.04-.08	0	0	300°K	Quadrupole & Isomer
B	$1.5-4 \times 10^{15}$	.06-.12	0	0	300°K	Characteristic
C	$7.6-19 \times 10^{15}$	.07 .14	0	0	300, 79, 5°K	Characteristic
D	$7-12 \times 10^{15}$	.15 .22	.1-.33	Not Available (NA)	H ₂ Heat 300, 79°K, 5°K	Characteristic Plus Some Magnetic
E	$6-9 \times 10^{16}$	.08 .15	.4-1	354 ± 10 340 ± 5	B in film plane H ₂ Heat	Characteristic Plus Some Magnetic/Pure Magnetic
F	$3-7 \times 10^{16}$	.14 .18	0-.28	N.A.	High Resolution Scan 300, 79, 5°K	Characteristic
G	$.5-5 \times 10^{17}$	.2 .24	0	0	300°K	Characteristic
H	$.5-5 \times 10^{17}$	.3 .34	1	323 ± 5	300°K	Pure Magnetic
I	$.5-4 \times 10^{17}$	.31 .35	0	0	B in plane 300°K	Characteristic
J	$.1-10 \times 10^{18}$	.3 .4	.9	335 ± 10	300°K (BN cylinder)	Magnetic plus Weak Singlet (All H ₂)
K	$.5-5 \times 10^{18}$	N.A.	1.0	265 ± 15	300°K	Pure Magnetic <u>B</u> in plane

FIGURE 6

FIGURE 7

FIGURE 8

the sample temperature was only room temperature when the field was applied. Table 1 summarizes briefly the results and environments of each sample.

Magnetic Fraction

The fraction, F , of the atoms exhibiting stable magnetic behavior is plotted in Figure 6 versus surface density of atoms. F is computed by dividing the resonance area found outside the velocity region ± 2.5 mm/sec by the total resonance area, which is equivalent to assuming that any resonance not in that portion of the spectrum associated with paramagnetism is characteristic of stable magnetic behavior. This is also equivalent, roughly, to assuming all magnetic fields are greater than about 50 kilogauss and are fixed in space for a time greater than about 10^{-8} sec. Since only 16% of the bulk Fe Zeeman spectrum and even less of iron oxide systems, and virtually all quadrupole and singlet spectra lie within this velocity range,⁽³⁰⁾ a worst case error of about 16% may occur in the estimate of F . The quantity F is displayed in the figure as that entire range of values that the magnetic fraction assumed when the sample was observed and subjected to various environment discussed above. Each sample is thus represented by an area in Figures 6, 7, and 8, and is labelled by a letter. The vertical ranges for a given sample include at least one and probably many data points with the uncertainties included. The horizontal range may include

many points and always includes the uncertainty in the thickness measurement.

The plot of F in Figure 6 shows that there were two samples, J and G, in the density range greater than 5×10^{16} atoms/cm² that exhibited no stable magnetic behavior. This is unusual in that the expected spectrum for surface densities this large is that of either iron or iron oxide: a set of lines whose Zeeman splitting is characteristic of between 300 and 600 kilogauss at the nucleus. It is observed that a thinner sample, E, could be switched from a partially stable $F < 0.5$ condition to be entirely stable $F = 1$ condition by a heat treatment. Sample J were the films formed on the BN cylinder after hydrogen heat treatment. This sample is assumed to be the order of 10^{17} atoms/cm² or greater from both numerical and optical estimates of thickness and shows consistently $F > .9$.

Computational smoothing of the spectra made it possible to resolve with confidence lines whose intensities were close to the noise level. The smoothing process trades a factor N in the velocity resolution, or energy resolution, for a factor N in the data amplitude, or $\sqrt{N}$ in the signal to noise ratio-- a worthwhile trade only for small N , e.g., $N = 2$ to 3. Unfortunately, the existence of the four Zeeman lines in sample E was discovered in the above manner during the computer analysis, after an irreversible heat treatment was performed. We would like to have analyzed this sample at 78 or 5°K as this should also have

caused Zeeman lines to appear.

Internal Fields

We have plotted the internal fields wherever computable versus the surface density in Figure 8. Several samples, A, B, C, I, and G, exhibited from the point of view of the Zeeman effect zero stable magnetic field. Samples E, H, J, and K exhibited measurable Zeeman fields with value varying from approximately 265 kg to 354 kg. In sample D the spectrum consisted of a characteristic spectrum, to be defined later, and a set of lines outside the velocity range ± 2.5 mm/sec that consistently appeared when the sample was cooled to nitrogen temperature but whose number and position did not correspond to any known bulk Zeeman spectra. Lines were observed out to velocities of ± 9 mm/sec after an $N = 3$ computational smoothing. While the nuclear field of sample D was not computable, and thus not plotted in Figure 8, it should be implied that some stable magnetic phenomenon was being induced when the temperature was lowered from room to 78°K. A heat treatment of sample D did not appear to affect the spectrum (and its temperature dependence) in any observable fashion.

All the predominantly magnetic samples, those for which $F > 0.4$, exhibited nuclear fields within 20% of 330 kilogauss, the bulk value. Sample K gave a field of 265 ± 15 kg (kilogauss). This is approximately 20% lower than bulk, and is yet unex-

plained. Sample H, fabricated in the same fashion as sample K, yielded 323 ± 5 kg, also slightly lower than bulk. The fields of sample J were always within 5% of the bulk value. Before a heat treatment, sample E exhibited a "characteristic spectrum", to be described later. Upon application of a 1 kg bias field four lines appeared in the velocity region greater than ± 2.5 mm/sec and whose positions and widths were approximately in those of the outer four lines of a bulk Zeeman spectrum. The area of resonance of these lines compared to the total resonance area of the sample implies that these four lines comprise 40% of the sample corresponding to $F = .4$. Under the assumption that these lines correspond to lines 1, 2, 5, and 6 in Figure 1 the nuclear field is computed to be 354 ± 10 kg. Presumably, in sample E about 0.4 of the volume of the sample contained particles whose cluster size was in the correct range so that the 1 kg bias field was sufficient to induce the Zeeman splitting. After a heat treatment sample E exhibited the bulk field of 340 ± 5 kg and was entirely magnetic, $F = 1$.

In summary, the internal field properties of the films appear to follow the behavior predicted by superparamagnetic theory. In thicker samples the field is stable at room temperature. As the surface density decreases to lower than approximately 7×10^{15} atoms/cm² the internal fields disappear completely. Also, either a small bias field or a reduction in temperature was sufficient to induce stable magnetic effects in at least some

fraction, up to .4, of the atomic clusters for the films of range 7×10^{15} to 10^{17} atoms/cm².

Resonant Fraction f

Presented in Figure 7 is the resonant fraction expressed as the total area of resonance divided by the area under 1 mm/sec of background. The fraction f is presented as that entire set of values assumed by the sample under all experimental conditions, plotted versus the surface density of atoms. This measurement will always be incorrect by an additive factor proportional to the response of the electronics to the other unused gamma energies. The variation in this error is estimated to be less than 10% since the f obtained for the 310 Stainless standard source varied by approximately this much with different electronics. Thus, the factor f plotted is proportional to the Debye-Waller factor of the source and is estimated to be approximately half its value. As in the F measurement, the regions enclosed by a shaded rectangle in the figure may include more than one point and always include the uncertainties of the data point or points.

In the surface density region of 10^{17} atoms/cm² the resonant fraction approaches that for bulk sources. The resonant fraction generally decreases as surface density of atoms decreases, but appears to approach a constant of about 1/6 of the bulk value when the surface density decreases to about 10^{13} atoms/cm². The resonant fraction approaches a lower limit consistent with the

assumption of atoms on the surface. Surface atoms may experience a factor of 2 increase in the mean square displacement over a bulk sample atom giving a factor of e^{-2} decrease in f , according to a bond counting approach.⁽¹⁷⁾ This would yield an f the order of 1/7 that of bulk. In the mid-range of surface densities samples B, C, D, E, F and G exhibit f factors strongly suggesting that the bonding of the clusters or of the atoms on or near the surface of the substrate was different from sample to sample.

This could be expected since the temperature of the substrates during the evaporations was dependent on the particular geometry of the evaporation, and the temperature of the substrates determines the mobility of surface atoms. Consequently the degree of cluster formation and the average value of cluster size could be different from sample to sample.

All these samples suggest that the bonding was predominantly characteristic of atoms embedded not more than two or at most three atoms into the substrate or cluster.

Sample F was unusual in that its measured f , in the central velocity region of ± 3 mm/sec, decreased with a decrease in temperature to 5°K. This temperature dependence implies that either the nuclear mean square displacement increased as the temperature decreased or that some of the resonance appeared out of the central region due to stable magnetic behavior. Since the spectrometer was adjusted to scan the region ± 3 mm/sec in an

effort to resolve possible fine structure we choose the latter alternative explanation.

We did not compute Debye temperatures since we did not have a complete set of data for all samples.

Quadrupole and Isomer Shifts

Except for the thinnest sample to be discussed later, no clearly recognizable quadrupole splitting was observed. In the computation the parameters of the Zeeman lines, the quadrupole parameter fluctuated about zero within $1/3$ the experimental linewidth even for the bias-field-induced Zeeman lines of sample E, the thinnest sample showing $F = 1$ after a heat treatment.

The computation of isomer shifts made sense only for the thinnest and thickest samples because the linewidths of the remaining spectra ranged from 0.45 to 1.5 mm/sec for a given sample. This situation implied that a superposition of spectra of moderately different parameters was being observed. In this case the average isomer shift would be computed, not a very meaningful quantity in our studies. For the thinnest sample the isomer shift was $-1.23 \pm .1$ mm/sec with respect to the NBS standard of Sodium Nitroprusside. For the thickest samples yielded $-.2 \pm .1$ mm/sec, the bulk value, with respect to the standard.

Characteristic Spectrum

The "characteristic spectrum" or spectrum that seems to dominate in films from 10^{16} to 5×10^{17} atoms/cm² is typified by

FIGURE 9

that of sample C, shown in Figure 9. There is a broad resonance of width approximately 1.5 mm/sec, or approximately three times the experimental resolution, and a satellite resonance always less than about 20% of the amplitude of the main resonance and varying between -1.5 and -2.5 mm/sec in position. The satellite resonance shape often appears and is better described as rectangular rather than as a usual gaussian or lorentzian. The samples B, C, D, E, F, G and I, i.e., those in Figure 6 with F less than 0.5 and surface density greater than 10^{15} atoms/cm², all exhibited this spectrum.

A search for the temperature dependence of the characteristic spectrum was performed on sample F from room temperature to 5°K by scanning the velocity region from -3 to 3 mm/sec. The only changes observable with any degree of confidence were a) a decrease in the resonance area versus temperature, and b) a shift in the position and shape of the satellite line, which broadened by about .5 mm/sec without changing amplitude. This means that while the satellite resonance increased in area the total resonance area decreased.

The characteristic spectrum appears to be the only feature exhibited by a magnetically unstable film. We choose not to assume any specific form for the spectrum in our computations since the spectrum should arise as the result of a distribution of sizes and shapes of atomic clusters.

The rather constant form of the characteristic spectrum in the 10^{15} to 5×10^{17} atoms/cm² surface density range indicates that the distribution of atomic positions, or more precisely of a nuclear electric field gradients and electron densities, is constant in spite of the fact that the resonant fraction varies from sample to sample. A model describing the configurations taken on by the film atoms must satisfy the condition that changing the surface density by two orders of magnitude does not alter the relative numbers of atoms at different types of sites but does allow the Debye-Waller factor to fluctuate.

Solely on the basis of two samples, G and I, we propose another explanation for at least part of the characteristic spectrum. Samples G and I, non-magnetic, were as thick as or thicker than H, K, and J. In samples H and K the surface density of iron atoms was enough to cause stable magnetic ordering at room temperature. In samples G and I this same or more surface density of iron atoms should also imply stable magnetic order. The lack of stable magnetic order implies that a) in these samples the anisotropy constant is lower than in H, K, and J, or b) that the particle size and shape are such that magnetic effects are unstable, or c) that a different form of material exists. At high surface densities of samples G and I alternatives a) and b) are usually considered unlikely. This suggests that these films may consist of a form of iron or iron oxide that is sufficiently different from normal iron or iron oxide that the form remains paramagnetic even in bulk amounts. The existence of two forms of cobalt oxide has been reported,⁽³¹⁾ the second form being the same as the first form with

half the positive and half the negative ion sites vacant. Co O is found to be magnetic at nitrogen temperatures, below 120°K, in bulk quantities.⁽³²⁾ A large number of vacancies may occur in our films because the evaporation rates are the order of an angstrom per second to an angstrom per minute, allowing the possibility that oxygen contamination is uniform but not equivalent to the oxidation of a uniform film exposed to oxygen. Since the evaporations were made in a 3×10^{-8} torr pressure the rate of arrival of oxygen atoms is equivalent to approximately 30 seconds per atomic layer. The evaporations were made over a period of as long as 5 minutes, allowing the possibility of collecting up to 10 layers of oxygen per film.

Thinnest Sample

The spectrum of the thinnest film, sample A, is shown in Figure 10. This spectrum shows a splitting of 2.2 mm/sec, interpreted as a quadrupole splitting, and an isomer shift possibly corresponding to Fe^{2+} .⁽¹¹⁾ The width of the lines was about 1.5 times the experimental resolution. The continuous function superimposed on the data is a lorentzian function, used in preference to a gaussian because of a slightly lower Chi square value in the fitting computation and from which the parameters of the lines were taken.

The distinct features of the spectrum for the thinnest sample are consistent with the assumption of isolated atoms on the surface. At this low surface density the distance between atoms is about 10 atomic iron diameters, implying that about 99% of the substrate area is empty. This would indicate that the resonant

FIGURE 10

fraction is for the most part due to substrate-iron bonding, and may thus be characteristic of isolated atoms on the surface.

It is also possible that monomers are not stable on the surface and the smallest stable nucleus consists of 3 or more atoms.⁽³³⁾

The spectrum of sample A implies if this were the case, then the majority of emitting atoms have roughly the same quadrupole splitting, and isomer shift, and consequently implies that the majority of film atoms are either clusters of one atom, two atoms, three atoms, etc., but not an equal mixture of one, two, etc., atoms. This is in contrast to the normal interpretation of the nucleation and growth models which would predict a distribution of sizes of atomic cluster.

Summary

The general observations about cluster growth and nucleation effects are the following: At extremely low densities of iron on a surface each iron atom sits in a site very similar to every other iron atom. As surface densities increase a distribution of sites also builds up and for two decades of surface density this distribution of atomic types of site changes little. It appears that this distribution may in some case also persist for another decade in surface density. Some form of iron or iron oxide appears whose spectrum is similar to that of the distribution and which is magnetically unstable. The formation of stable superparamagnetic particles eventually becomes the

dominant process for the highest thicknesses and first appears at surface densities corresponding to a few monolayers. The resonant fraction suggests atoms on a surface at very low densities and gradually increases its value with surface density to that of atoms in bulk at the highest thicknesses. The internal fields when computable, ranged within 20% of bulk iron values.

APPENDIX A

The following is a table of the derivations and approximate values for the counting statistics for varying systems of analysis. I_0 represents the total 14.4 gammas incident on an absorber from an assumed 10 millicurie source, I^s represents the gammas emitted from a microcurie of Co^{57} monolayer film. The noise is always the square root of the background. t_A is the thickness of the sample in $\text{\AA}$, and is chosen to be $1 \text{ \AA}$. ϵ is an efficiency factor indicating how well a counter for the 6.4 keV experiment approaches a 4 π counter of efficiency unity.

Incident	Background	Signal	Signal/Noise	Method
I_0	I_0	$(\frac{1}{4} \times \frac{t_A}{2.5 \times 10^4}) I_0$	$(t_A/10^5) \sqrt{I_0}$	Standard Analyzer Method
I_0	$(\frac{3}{4} \times \frac{t_A}{2.5 \times 10^4}) I_0$	$(\frac{1}{4} \times \frac{t_A}{2.5 \times 10^4}) I_0 \epsilon$	$\frac{1}{3} \sqrt{\frac{t_A}{10}} \sqrt{I_0} \epsilon$	6.4 keV Analysis
$I^s t_A$	$I^s t_A$	$\frac{1}{2} I^s t_A$	$\frac{1}{2} \sqrt{t_A} \sqrt{I^s}$	film radioactive method

$$\frac{\text{Standard analyzer method } 1 \text{ \AA film}}{\text{Standard analyzer method bulk}} = 10^{-5}$$

$$\frac{6.4 \text{ keV analysis (with } \epsilon=1) 1 \text{ \AA}}{\text{Standard analyzer method } 1 \text{ \AA}} = 240 = \frac{(\text{signal/noise}) \text{ method 1}}{(\text{signal/noise}) \text{ method 2}}$$

$$\frac{\text{film radioactive method } 1 \text{ \AA}}{\text{Standard analyzer method } 1 \text{ \AA}} = 500$$

APPENDIX B

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