UHV MÖSSBAUER EMISSION SPECTRA OF THIN IRON FILMS*

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Abstract

Mössbauer emission spectra are used to determine relaxation effects of $\text{Fe}^{57\text{m}}$ in thin iron films deposited at 10^{-9} Torr and measured at 10^{-11} Torr. The spectra from the radioactive films have been analysed at room temperature, liquid nitrogen and 15°K over a range of thickness from 3×10^{16} atoms/cm² to 0.12×10^{16} atoms/cm² ($25 \text{ \AA}$ to $1 \text{ \AA}$). Samples thinner than $7 \text{ \AA}$ show the following characteristics: a positively resolved doublet interpreted as quadrupole splitting of about 0.6 mm/sec . independent of thickness and temperature; a Mössbauer fraction roughly constant with temperature; one line increases in width and area and the other decreases as the temperature is lowered. Samples thicker than $10 \text{ \AA}$ are approximately characteristic of bulk iron. The transition is ascribed to superparamagnetic fluctuations in the internal field but the detailed line shapes are not simply explained. A multilayer $25 \text{ \AA}$ sample has six lines in the normal positions at 15 and 80°K , but the outer lines show a decreasing intensity as the temperature increases until they vanish at room temperature.

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INTRODUCTION:

The asymmetry in the quadrupole lines in Mössbauer spectra of Fe^{57} have been explained by Goldanskii et. al.⁽¹⁾ in terms of an anisotropic Debye-Waller factor and by Blume⁽²⁾ in terms of paramagnetic relaxation of ions. Violet and Lee⁽³⁾ have investigated ultra-thin iron films to determine the critical thickness at which the saturation magnetization and Curie temperature depart from the bulk value. Cleveland et al.⁽⁴⁾ have studied the magnetic ordering in very thin iron films by detecting the internal conversion of the 6.4 keV γ -ray. These experiments all use absorption geometry, and in most of the experiments the sample was prepared in a vacuum system at a pressure of 10^{-8} Torr and then removed from the system for analysis. This way of sample preparation and analysis suffers from serious defects due to oxidation of the film and resultant changes in the characteristics of the spectra. We should like to report on the experimental technique we have developed to make films without losing the ultra-high vacuum integrity of the system. We have analysed films in the thickness range $1 \text{ \AA}$ to $25 \text{ \AA}$ (0.12×10^{16} to 3×10^{16} atoms/cm²) at 300, 80, and 15° K.

EXPERIMENTAL METHOD:

The Varian UHV system used is capable of attaining base pressures of 10^{-11} Torr, as measured by a nude ionization gauge, after four hours of bakeout at 250° C. The system is unique in that the variable temperature Janis dewar mounted at the top has its vacuum insulation common to the UHV. A re-entrant stainless steel pipe is connected to a flange,

at the end of which is heliarc welded a 10 mil thick berillium window which allows the γ -rays to come out of the vacuum system, pass through the absorber and finally reach the end window proportional counter which is adjusted to detect 14.4 keV γ -rays. In this geometry all the moving parts e.g. counter, Mössbauer drive, absorber etc. are all external to the vacuum system yet the sample plane is only 2 cm from the counter face.

The sample holder is in the form of a copper ring which is attached to the neck of the dewar and can be rotated about the axis of the dewar by means of a manipulator. The substrate used is a cover glass slide, which is attached to the sample holder by a thin layer of high purity indium. The film is made by evaporating an alloy of Co^{57} , Fe^{59} and Fe^{56} slowly from a boron nitride tube. A detailed account of cleaning the substrate and preparation of sample is given by Zuppero and Hoffman.⁽⁵⁾ The film thus made was used as a source; the absorber in the experiment was an enriched absorber in 310 stainless steel foil. The sample is prepared at a pressure of 10^{-9} Torr and then is rotated towards the counter by the manipulator without breaking vacuum. An asymmetric constant acceleration drive is used to aid the data analysis of fitting Lorentzian functions with the aid of the DEC PDP9 computer.⁽⁶⁾

RESULTS:

The results of the experiment can be classified mainly in two groups, one represented by the two-line spectra with quadrupole splitting of approximately 0.6 mm/sec and the other group exhibiting the six-line Zeeman spectra. We present in Table I various parameters that have been calculated from the

Mössbauer spectra. It appears from our results that the quadrupole splitting of the samples below about seven angstroms remains fairly invariant with temperature and thickness at about 0.6 mm/sec. The Mössbauer resonance fraction, which is calculated as the total area under the resonance divided by a 1 mm/sec of background, also appears to be constant. The isomer shifts in the table are those with respect to a crystal of sodium nitroprusside traceable to the National Bureau of Standards. The magnetic fraction has been defined as the ratio of the resonance area found outside the velocity range ± 2.5 mm/sec to the total resonance area. The magnetic fraction for these samples is zero and indicates that there is no stable magnetic behavior present in these films. This is also reflected in the internal magnetic field being zero for these samples. The isomer shift of these samples is very small. The width and area of one of the lines in the Mössbauer spectra of these samples increases as the temperature is decreased and the other line shows a decrease in width and area as the temperature is decreased. It appears that the widths are equal at about 200° K. The maximum width of the lines in the samples is about twice the minimum resolution width of 0.7 mm/sec. This asymmetrical behavior in the quadrupole spectra of these films can not be explained on the basis of paramagnetic relaxation of ions as suggested by Blume. It is to be remarked that for film thicknesses below one angstrom a doublet spectra was observed with a large quadrupole splitting of about 2 mm/sec.

In the second group of films, which had thickness greater than about $10 \text{ \AA}$, we find a six-line Zeeman spectrum representative of the usual magnetic hyperfine spectrum. The analysis shows that these samples have a very small

quadrupole splitting. The room temperature internal magnetic field in these samples is - 320 Kgauss and is only about 3% lower than the bulk value of - 330 Kgauss.⁽⁷⁾ The magnetic field increases slightly as the temperature is lowered. The magnetic fraction F for the samples is of the order of 0.75 and is representative of stable magnetic behavior. The Mössbauer resonance fraction f is found to be approximately invariant with temperature and does show a slight increase as the thickness is increased. The isomer shift of these samples is small. In conclusion these samples can be considered as those representing the stable magnetic behavior. It appears from the intensity ratios that the magnetization vector lies in the plane of the film.

A film in the critical thickness range of $7.5 \text{ \AA}$ showed a two-line spectra at room temperature with a quadrupole splitting of 0.5 mm/sec. The magnetic fraction and the internal magnetic field for this sample was zero. As the temperature of this sample is lowered to 100° K a six-line Zeeman pattern appeared. The internal magnetic field and the magnetic fraction were calculated as - 307 Kgauss and 0.71 respectively. The Mössbauer resonance fraction increased slightly. Finally, when the temperature was lowered to 80° K the magnetic field and the magnetic fraction both showed an increase. This sample suggests that the critical thickness at which the transition to the ferromagnetic state occurs is in the vicinity of seven angstroms or $0.84 \times 10^{16} \text{ atoms/cm}^2$ at room temperature. This type of transition is representative of superparamagnetic fluctuations in the internal field and has been reviewed by Collins et al.⁽⁸⁾ It should be pointed out that the critical thickness will change somewhat depending upon how the film was made, as it depends on the anisotropy and volume. For

example, when the evaporation rate was slow and the temperature of the substrate increased beyond room temperature the transition was observed at 11 Å.

Mention must be made of the sample of 25.6 Å thickness which was made by successive evaporation. This sample showed a four-line spectrum at room temperature, which developed into a six-line spectrum as the temperature was lowered to 80 and 15° K. The internal magnetic field increased as the temperature was lowered from - 100 Kgauss to - 327 Kgauss. If the layers were well matched so that the film grew in a continuous manner then we would expect a pure six-line Zeeman pattern. As the film did not show bulk behavior at room temperature it implies the layers are at least partially magnetically isolated.

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Table I Mössbauer Parameters of Iron Films

Thickness	5.6 Å ($6.7 \times 10^{15} \frac{\text{atoms}}{\text{cm}^2}$)	7.5 Å ($9.0 \times 10^{15} \frac{\text{atoms}}{\text{cm}^2}$)	11 Å ($1.3 \times 10^{16} \frac{\text{atoms}}{\text{cm}^2}$)	25.6 Å ($3.0 \times 10^{16} \frac{\text{atoms}}{\text{cm}^2}$)	Properties
Temperature					
300° K	0.54	0.52	.005	-0.003	Quadrupole Splitting in mm/sec.
80° K	0.72	-0.06	-.02	-0.079	
15° K	0.69	-0.04(a)	--	0.031	
300° K	0	0	-313	-100	Internal Magnetic field in kilo-Gauss
80° K	0	-321	-319	-327	
15° K	0	-307(a)	--	-311	
300° K	0	0	0.81	0	Magnetic Fraction F
80° K	0	0.78	0.73	0.77	
15° K	0	0.71(a)	--	0.82	
300° K	0.13	0.21	0.12	0.34	Mössbauer Resonance Fraction f
80° K	0.14	0.30	0.13	0.52	
15° K	0.13	0.24(a)	--	0.53	
300° K	0.021	0.132	0.20	0.065	Isomer Shift In mm/sec.
80° K	-0.16	0.127	0.18	0.027	
15° K	-0.22	0.196(a)	--	0.084	
300° K	Two	Two	Six	Four	# of Lines in the Spectrum
80° K	Two	Six	Six	Six	
15° K	Two	Six(a)	--	Six	

(a) These parameters measured at 100° K