Ferromagnetic resonance (FMR) is a phenomenon of high frequency (HF) electromagnetic field energy in ferromagnetic materials (1). FMR provides a very sensitive tool for studying different contributions to the magnetic anisotropy in thin and ultra thin hematin films like shape, magneto crystalline, magneto elastic, and surface anisotropy.

In the last few years, there has been an increasing interest in FMR investigation of such films, and in particular angle-dependent FMR studies (2-4). In these artificial structures, the intrinsic properties such as crystalline anisotropy can be different from those of bulk materials due to a modified microscopic environment. Surface roughness, interface roughness and Lattice constant mismatch between substrate and film texture cause additional anisotropy, which it’s sensitivity, depends on the preparation conditions. This permits one to grow high quality hematin films and uses novel or elaborate FMR measuring techniques, nowadays, to offer a more refined and reliable experimental investigation of the various anisotropy effects.

1. Introduction

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Figure 1: Schematic diagram of ferromagnetic resonance experiment.
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Theoretical models to describe FMR spectra of bulk samples have been published since 1957 (5). Applying the modified relations to hematin films, all the relevant magnetic parameters can be determined self-consistently by a selected series of high-precision, angle-dependent, FMR measurements, which can be achieved by assuming that the magnetization vector has not pressed around the direction of the external magnetic field (B<sub>ext</sub>), but rather around that of the internal field (6-9).

The purpose of this study is to see how the hematin films with and without acid are responding to the applied magnetic field and to study the FMR for both cases. The hematin films investigated in this work exhibit very small FMR line widths pointing towards a weakly strained layer of high quality, but it gives us an idea about the magnetization and other anisotropy parameters which can be studied by the temperature dependence of magnetic parameters (10-14).

2. Experiment

The specimens used in this work are two hematin samples A and B which consist of a mole of hem, in addition to OH, in which an iron atom is connected in a perpendicular plane with the OH molecule, this is shown in reference (13). The method of preparing the samples A and B is as follows: For sample A (hematin) multilayer LB films of hematin were built on a glass substrates using a KVS 5000 alternate system. A hematin solution in Chloroform (0.25 mg/ml) was spread at a temperature of 17°C onto an aqueous sub-phase (ionized water) containing 1x10<sup>-5</sup> M PH<sub>2</sub>CrO<sub>7</sub> and pH = 8, controlled by NaOH solution. A monolayer film of hematin was formed at the sub-phase surface. Two barriers to a surface pressure of 27x10<sup>-3</sup> N compressed the film, where the collapse pressure of the film was found by an isotherm experiment to be 37x10<sup>-3</sup>N/m<sup>2</sup>. Then the monolayer was transferred onto the glass substrate by lifting the dipped substrates out of the sub-phase at a speed of 5mm/min. Multilayer LB films of Z-type of deposition were built on the substrate up to 20 layers each.

For sample B (hematin + arachidic acid) multilayer LB films of hematin were mixed with arachidic acid (20:1), and then the same procedure is used as in sample A.

The setup of the experiment is shown in (Fig. 1) The conventional FMR investigations were carried out with a commercial electron-paramagnetic resonance spectrometer at 9.2 GHz in a temperature range from 100 to 570 K. The microwave power for the conventional experiments was 0.2 mW. The angle dependence of the resonance absorption was measured at room temperature in three different configurations:

A computer-controlled step motor achieved the sample rotation in the external magnetic field with a gear unit (transmission 1:80). The angular resolution was chosen as 0.1 degree. The absolute positioning error of the system in one revolution of the sample was 0.4 degree.

The signals were recorded by a vector lock-in, the signal consisting of an amplitude and a phase shift, where the latter takes into account the sign change of the derivative absorption signal at the center of the resonance. The resonance fields for symmetrical shaped modes can be deduced simultaneously from the dip in the amplitude and the 180-phase jump. The phase is well defined only in the area where the FMR signal is large enough to prevent the noise causing a sign change in the signal. The microwave frequency ranged between 8.6 and 9.5 GHz. The
frequency 9.2 GHz used here to get the resonance usually depends on the material and size of the sample used.
Two samples (A and B) are used in this work as was explained in the experimental part.

3. Theory
The theoretical model used to analyze the experimental data follows the FMR dispersion relation expressed in terms of partial derivatives of the free-energy density \( F \) as shown in references (5, 6, 14)

\[
\left( \frac{\omega}{\gamma} \right)^2 = \frac{1 + \alpha^2}{M^2 \sin^2(\theta)} \left[ \frac{\partial^2 F}{\partial \theta^2} \frac{\partial^2 F}{\partial \Phi^2} - \left( \frac{\partial^3 F}{\partial \theta \partial \Phi} \right)^2 \right] \quad \text{..................(1)}
\]

\[
\Delta \omega = \frac{\gamma \alpha}{M} \left( \frac{\partial^2 F}{\partial \theta^2} + \frac{1}{\sin^2(\theta)} \frac{\partial^3 F}{\partial \Phi^2} \right) \quad \text{..................(2)}
\]

Where \( \omega \) is the microwave frequency, \( \Delta \omega \) is the line width, \( \gamma \) the gyro magnetic ratio, \( M \) the saturation magnetization, and \( \alpha \) the damping parameter. \( \theta \) and \( \phi \) are the polar and azimuth angles, respectively, of the magnetization \( M \) relative to the film plane.

The model used proceeds from the free-energy density \( F \) of the system consisting of the following major contributions, given in the order of appearance in the subsequent equation:
Zeeman energy, demagnetizing energy, surface anisotropy energy of the cubic thin film, magnetocrystalline anisotropy energy (first and second order), and uniaxial anisotropy energy in the film plane, giving the magnetization a preferential direction \( B \).

\[
F = -M \cdot B_{ext} + \frac{1}{2} \mu_0 M^2 \cos^2(\theta) + \frac{2K_2}{d} \sin^2 \theta \\
+ \frac{1}{4} K_1 \left[ \sin^2(2\theta) + \sin^4 \theta \sin^2(2\Phi) \right] \\
+ \frac{1}{16} K_3 \sin^2 \theta \sin^2(2\theta) \sin^2(2\Phi) \\
+ K_u \sin^2 \theta \cos^2(\Phi - \beta) \quad \text{..................(3)}
\]

Where \( K_1 \) and \( K_2 \) are the first and second order crystalline anisotropy constants. \( K_s \) are the surface anisotropy constant, \( K_u \) is the uniaxial anisotropy constant and \( \beta \) is the phase shift.
Figure 2: The angle dependence of high field lines for hematine sample (A). The in-plane magnetic field angle (degree) versus the magnetic field (mT) is shown in the graph.
Figure 3: The absorption derivative (au) as a function of the magnetic field (mT) for sample A, at 0, 45 and 90 degrees with respect to the field.
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The resonance fields are obtained from Eq. (1) by minimizing the free energy $F$ [Eq. (2)] with respect to the two angular variables $\theta$ and $\Phi$.

$$\frac{\partial F}{\partial \theta} = 0 \quad \cdots \cdots \cdots \cdots (4)$$

$$\frac{\partial F}{\partial \Phi} = 0 \quad \cdots \cdots \cdots \cdots (5)$$

The three equations (1), (4) and (5) depend on the microwave frequency $w$, external magnetic field $B_{\text{ext}}$ at resonance, and its orientation angles and (Fig. 2). Which are defined by the experimental setup. The solutions of the differential equations yield the magnetization $M$ as a function of the orientation angles $\theta$ and $\Phi$. The anisotropy constants in Eq. (3) serve as fitting parameters.

For the angle-dependent measurements, the equations are solved simultaneously. It is essential that we allow for solutions where the magnetization and the external field are not aligned. For that reason we can fit all the resonance of the different angle dependent measurements, which show there individual effect on the various anisotropy contributions.

4. Results and discussion

Figure 2, shows the in – plane magnetic field angle (degrees) plotted versus the applied external magnetic field for sample A. The figure shows that there is angle dependence of high field lines for that plot with respect to the applied external magnetic field for sample A because of the magnetization. The first peak is due to iron impurity, the second one due to an impurity or due to ionized iron (Fe $^{+2}$ or Fe $^{+3}$). These ions could also be seen in sample B because of the addition of the acid to the hematin. The resonance peak is taking place at field of 155 mT for the two samples (A and B) and for all rotations as shown in figures 3 to 7, because for these materials (hematin) the resonance occurred at this field since the resonance field ($H_{\text{ext}}$) is proportional to the microwave frequency ($w$) and inversely proportional to the factor of the atomic system ($g$). The structural formulae for hem is C$_{34}$ H$_{33}$ Fe N$_4$ O and from this structural one can see that there is only one mole of iron among the seventy seven molecules, which the hem is constructed from. This is the main reason for the small changes, which are taking place as will be shown in the coming figures for the different rotations for the two samples.

(Fig.3.) shows the plot of FMR absorption derivative (au) versus magnetic field in (mT) for sample A. The absorption derivative is about 1.5x10 $^{-4}$ (au) at 155 mT for 90 degree rotation and it is larger this value for 45 degree rotation, this is due to more interactions with iron atoms at this angle and due to the second term in equation 3 will contribute to the energy density as demagnetizing energy, but at 90 degree this term and the Zeeman energy are vanishing because cos 90 = zero. At 80 mT, the FMR absorption derivative is zero because for the anisotropy to take place, it needs more external field, but as the field increasing and at 125 mT, there is 5x10 $^{-5}$ (au), then it goes to about 2.5x10 $^{-5}$ (au) between 160 and 280 mT, then
Figure 4: The absorption derivative (au) as a function of the magnetic field (mT) for sample with an-acid (B), at 0, 45 and 90 degrees with respect to the field.
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Figure 5: The absorption derivative (au) as a function of the magnetic field (mT) for sample A and B.
it picks up after 300 mT to reach $5 \times 10^{-5}$ (au) At 45 degree there is almost nothing at low fields, but at high fields of 280 mT and more there is an increase in the absorption derivative. This is due to the anisotropy in the sample, which is a combination of the angle and surface anisotropies. The absorption derivative (au) versus magnetic field (mT) is shown in (Fig. 4) for sample A with different rotations. When it is rotated by 90 degrees, there is a peak at 125 mT and the FMR absorption derivative (au) is $2 \times 10^{-5}$, while at high fields around 300 mT, there is a shift in the resonance width of $10$ mT for the 90 and 45 degrees. Also the FMR absorption derivative (au) at 45 degrees is more than at 90 degrees, which is due to the high magnetization in the sample. From the same figure, we can see that at 90 degrees there is a change at low fields and this shows that sample A has a two fold rotation.

For sample B, an acid is added to the hematin, which causes the iron to be oxidized. The same previous FMR measurements were carried out for sample B. Figure 4. Shows the plot of FMR absorption derivative (au) versus magnetic field for different rotations, from which one can see that the resonance is taking place at the same field 155 mT. There is no resonance for fields less than 150 mT, and there is a small shift at high fields, around 300 mT, which shows that there is anisotropy at that field.

(Fig. 5) we see that the FMR for sample A is almost double that for sample B at a field of 50mT, while for high fields (300mT) there is very small resonance with larger FMR.

As shown in (Fig. 6) when both samples A and B are rotated by 90 degrees, the absorption derivative (au) at fields below 200mT for sample A is larger than that for sample B, and this is due to the existence of iron without the addition of the acid. For fields greater than 200mT, both samples behave about the same.

(Fig. 7) Shows the absorption derivative (au) versus magnetic field for microwave powers of 0.5mW and 5mW. We see from the graph that for fields less than 50mT, the absorption derivative is $8 \times 10^{-5}$ au and almost zero between 50 to 125 mT, while at 155 mT it is $-3.2 \times 10^{-4}$ au and then goes back to zero beyond 200mT when using high powers.

5. Conclusion
The anisotropy takes place here in sample A more than in sample B which they are identical by having the same magnetic volume; this is because when the acid is added to sample B then the iron ionizes and this reduces the effect of its magnetization, which is the magnetic moment per unit volume (13). Magnetization in the samples is high; the first line is due to impure iron, while the second line is due impurity or due to the iron ions. For pure iron we used a low power as 0.21 mw, while when a high field is used then the magnetization is small.

Sample A seems to behave as if it has a two-fold symmetry when it is rotated by 90 degrees because it has the same value and the same direction. The main difference between samples A and B is the amplitudes about 150mT. This is due to the acid in sample B that changes the iron-to-iron ions.
Figure 6: The absorption derivative (au) as a function of the magnetic field (mT) for sample A and B when they rotated by 90 degrees.
Figure 7: The absorption derivative (au) as a function of the magnetic field (mT) for sample B at different powers.
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Acknowledgment
The author greatly appreciates the support provided by the DAAD and also the invitation by Prof. Pelzel to do this work at the Ruhr University in Bochum (Germany).

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