

# Magnetic hysteresis and Mössbauer studies in ultrafine iron particles

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The magnetic hysteresis behavior of ultrafine Fe particles has been examined by SQUID magnetometry and Mössbauer spectroscopy. Ultrafine Fe particles have been prepared by vapor deposition under argon atmosphere in pressures from 1 to 6 Torr and passivated by exposure to oxygen at low pressure. Particles with size below 10 nm showed a small coercivity ( $\sim 100$  Oe) at room temperature, which increased drastically upon cooling to cryogenic temperatures (1000–1500 Oe). The larger particles had the highest coercivity at room temperature ( $\sim 1000$  Oe) which increased by 100% at 10 K. Mössbauer studies revealed that the Fe particles are surrounded by an Fe oxide layer composed of ultrafine  $\text{Fe}_3\text{O}_4$  or  $\gamma\text{-Fe}_2\text{O}_3$  grains. At room temperature the oxide component gives a very broad absorption superimposed on an  $\alpha\text{-Fe}$  spectrum. The enhanced coercivity at room temperature may be attributed to anisotropy induced by exchange interaction between the ferromagnetic core and the ferri- or antiferromagnetic oxide layer.

## INTRODUCTION

Ultrafine metallic iron particles have attracted considerable interest recently in view of their potential applications in ferrofluids and high density magnetic recording. The study of their magnetic properties is also of interest in itself, with regard to magnetic anisotropy vis à vis the bulk material and to the effect of the surface on the magnetic properties. Since fine iron particles are pyrophoric in air, some protection must be applied to avoid oxidation. In early studies this has been achieved by fine dispersion of Fe in mercury using electrolytic methods.<sup>1</sup> Later, aerosol techniques have been developed for the production of fine particles and passivation is effected by controlled exposure to oxygen which creates a protective oxide layer.<sup>2</sup>

Mössbauer spectroscopy can provide detailed information on the nature and magnetic state both for the oxide layer and the iron core. In a study of this type Haneda and Morish<sup>3</sup> have found that the surface layer consists of iron oxide with a spinel structure ( $\text{Fe}_3\text{O}_4$  or  $\gamma\text{-Fe}_2\text{O}_3$ ), probably in the form of small crystallites. There is, however, lack of detailed data on the magnetic properties of ultrafine iron particles and more specifically on anisotropy and coercivity in relation to the preparation conditions and the structure and phase constitution of the particles.

In this paper we present preliminary results from a study of iron particles by both Mössbauer and magnetic measurements for samples prepared under various experimental conditions. The Mössbauer results determine the relative amounts of Fe metal and oxide in particles of different sizes and illustrate the effect of these parameters on the magnetization and coercivity of the particles.

## EXPERIMENTAL METHODS

Powder specimens were prepared by evaporation of Fe metal in an Ar atmosphere at pressures in the range of 1–6 Torr from  $\text{Al}_2\text{O}_3$ -coated tungsten filaments. Metal particles

were collected on a water-cooled Cu cold finger. The samples were then subjected to a dilute air-argon atmosphere for a few hours in order to passivate the surface. For magnetization measurements, samples were immobilized and sealed from further contact with the atmosphere by mixing with molten wax in a quartz capsule. Mössbauer samples were prepared by sealing the powder in perspex holders under inert  $\text{N}_2$  atmosphere.

Mössbauer data were obtained with a conventional constant acceleration spectrometer using a  $^{57}\text{Co}(\text{Rh})$  source at temperatures from 4.2 to 300 K. Magnetization measurements were made with a SQUID magnetometer. The particle size and morphology were examined by transmission electron microscopy and further characterization of the phase constitution and structure was done by powder x-ray diffraction.

## RESULTS AND DISCUSSION

The particle shape as revealed by transmission electron micrographs is roughly spherical with slight distortion. The diameters of the particles used in this study ranged from 9 to 20 nm as determined from the electron micrographs and are listed in Table I. X-ray and selected area diffraction patterns (SAD) showed relatively well defined  $\alpha\text{-Fe}$  lines especially in the samples of larger sizes and additional diffuse lines which are assigned to a spinel-type Fe oxide. The detailed results of the electron micrograph study will be described in another publication. In this paper we shall concentrate on the magnetic and Mössbauer results.

The magnetization of the samples  $\sigma_s$  and the coercivity  $H_c$  are listed in Table I. The magnetization is essentially the same at 10 K and room temperature. The values of magnetization are from 30% to 60% lower than the magnetization of bulk  $\alpha\text{-Fe}$  (220 emu/g) with the highest reduction generally occurring in the particles of smaller size. This can be attributed to the presence of the Fe-oxide shell as will be

TABLE I. Constitution and magnetic properties of ultrafine iron particles derived from TEM, magnetization, and Mössbauer measurements.

Sample No.	Press. (Torr)	Average diameter (nm)	$\sigma_s^a$ (emu/g)	$H_c$ (Oe)		Phase constitution	
				10 K	RT	Fe-oxide %	$\alpha$ -Fe %
122	4	13 <sup>b</sup>	110	1613	507	72	28
123	4	20	130	1700	800	65	35
125	1	...	106	1400	225	77	23
131	4	9	95	1300	100	> 90	
132	4	10	106	1500	100	62	38
133	4	10	103	1500	25	61	39
134	6	13	160	1700	900	36	64

<sup>a</sup> Values at room temperature.<sup>b</sup> The dispersion in the particle diameter was about 2 nm.

discussed below in connection with the Mössbauer data. Values of up to 200 emu/g have been achieved in other preparations. With the available data, no clear correlation can be established between magnetization and the Ar pressure during evaporation. The coercivity  $H_c$  varies strongly between 10 K and room temperature, the difference being generally most pronounced for the particles with the smaller diameter. For example, particles with average diameter 9 nm (sample No. 131) have coercivities of 1300 and 100 Oe at 10 K and room temperature respectively, while sample No. 132 with average particle diameter 130 nm shows coercivities of 1700 Oe (10 K) and 900 Oe (RT).

Typical Mössbauer spectra at three different temperatures obtained with sample No. 122 are shown in Fig. 1. At the two lower temperatures (85 and 4.2 K) the spectra consist clearly of two magnetic hyperfine patterns. The first component with narrow lines and an effective field near 34 T is readily recognized as  $\alpha$ -Fe. The second component shows asymmetrically broadened lines, the broadening being less pronounced at 4.2 K. The average hyperfine field and the pattern of the spectra are similar to previously reported results on small particles of  $\text{Fe}_3\text{O}_4$ .<sup>4</sup> Similar patterns, however, may arise from  $\gamma$ - $\text{Fe}_2\text{O}_3$ . In fact, it has been shown that the transformation from  $\text{Fe}_3\text{O}_4$  to  $\gamma$ - $\text{Fe}_2\text{O}_3$  takes place with good probability in the small particle region.<sup>5</sup> An additional complication is that the occurrence of the Verwey transition, if it takes place, may further change the shape of the spectra due to multiple twinning. In view of these difficulties the fitting of the spectra was made with one component for  $\alpha$ -Fe and two or three components for the Fe oxide in order to take into account the asymmetric broadening. This procedure is adequate for the calculation of the relative areas of the iron oxides and  $\alpha$ -Fe. Assuming equal Debye-Waller factors at 85 K the relative amounts of  $\text{Fe}_3\text{O}_4/\gamma$ - $\text{Fe}_2\text{O}_3$  and  $\alpha$ -Fe have been calculated from the corresponding spectra and are included in Table I.

On the other hand, the relative areas of the Fe and Fe-oxide components as shown in the fit of Fig. 1 (c) are within experimental error the same as at 85 K. In this respect our data differ from a study of surface oxides on iron particles by Haneda and Morrish, who have noted a strong reduction of

the recoilless fraction for the iron oxides at room temperature.

Our results, as well as other measurements at intermediate temperatures which will be reported elsewhere lead to the tentative conclusion that the superparamagnetic behavior is modified by the proximity of the ferromagnetic iron core.

We turn now to a discussion of the magnetic properties in the light of the Mössbauer results concerning the constitution of the samples. We observe first that there is an approxi-

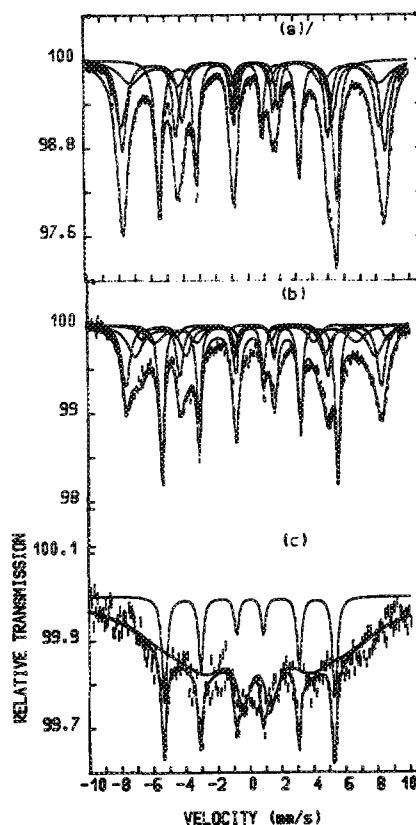


FIG. 1. Mössbauer spectra of a sample of ultrafine iron particles ( $D = 13$  nm) at three different temperatures: (a) 4.2 K, (b) 85 K, (c) 300 K.

mate correlation between the value of the saturation magnetization and the oxide content of the particles. The general trend is that the magnetization decreases as the oxide content increases. An approximate value of the magnetization can be calculated assuming a value for the oxide component of 80 emu/g (average of  $\text{Fe}_3\text{O}_4$  and  $\gamma\text{-Fe}_2\text{O}_3$ ) and 220 emu/g for  $\alpha\text{-Fe}$ . For samples No. 132 and No. 134 this calculation gives 133 and 170 emu/g, respectively.

The second point which emerges from Table I is that the retention of a high value of coercivity at room temperature may be connected with the relative oxide content and the size of the iron core. Although the available data are not sufficient to substantiate with certainty this conclusion, the following observations may be considered as supporting evidence. The highest coercivity is observed in sample No. 134 which has the highest iron content. A slightly smaller coercivity is exhibited by sample 123 which has a higher oxide content. Here, however, the size of the particles is larger, so that, in spite of the higher oxide content, the iron core remains large enough to retain a high coercivity. Low coercivities are observed in samples No. 131 and No. 132 which have the smallest size. Again the data for sample No. 133 do not

conform with these qualitative trends.

The origin of the anisotropy induced in the iron core leading to the observed high coercivities can be attributed to the exchange interaction between the ferromagnetic core and the ferri- or antiferromagnetic oxide layer as suggested many years ago by Darnell.<sup>6</sup> Further studies will be required to ascertain the nature of this interaction and determine the optimum conditions of particle constitution for the control of magnetic properties.

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