INFLUENCE OF CHEMICAL ADSORPTION ON THE EFFECTIVE ANISOTROPY CONSTANT OF α $-Fe_2O_3$ FINE PARTICLES

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ABSTRACT

The properties of α $-Fe_2O_3$ fine particles with and without adsorbed pyridine were studied by Mössbauer spectra. The effective anisotropy constant K were calculated. The K of pyridine-adsorbed α $-Fe_2O_3$ particles is smaller than that of pure α $-Fe_2O_3$ particles. A probable mechanism of the decreasing effective anisotropy constant K is discussed.

Keywords: α $-Fe_2O_3$ Mössbauer spectroscopy Effective anisotropy constant

1 INTRODUCTION

The electron cloud density and spin of Fe ions on the surface of α $-Fe_2O_3$ fine particles can be changed by pyridine adsorption[1]. In order to make clear further the influence of surface adsorption on the properties of α $-Fe_2O_3$ particles, the Mossbauer spectra of α $-Fe_2O_3$ particles with and without adsorbed pyridine have been measured to get the effective anisotropy constants K of them. This paper presents the experimental results. The probable mechanism has been discussed.

2 EXPERIMENTS AND RESULTS

2.1 Sample preparation

Samples were prepared as follows[2]: Sample A—1.0 g analytically pure $Fe(NO_3)_3 \cdot 9H_2O$ was dissolved in 500 ml distilled water, held at 95 °C for dehydration, and kept at 150 °C for 48 h. α $-Fe_2O_3$ fine particles were obtained.

Sample B was obtained by chemical adsorption of pyridine on the surface of sample A at 120 °C.

2.2 The dimension and structure determination of α $-Fe_2O_3$ fine particles

The shape and dimension of sample A was determined by high resolution

transmission electron microscopy. The average size of sample A is near 15 nm and that of sample B is the same as sample A. The phase structure was determined by electron diffraction. From its electron diffraction pattern the structure of sample A is identified as pure α -Fe_2O_3.

2.3 Mössbauer spectrum measurement

A Co (Rh) source of 1.85×10^9 Bq was used. The adsorption Mössbauer spectra were measured at temperatures from 80 to 295K and calibrated by α -Fe at room temperature. These spectra were fitted by a least square procedure. For fine particles with constant volume, the relaxation time of the electron spin may be written as[3]

$$\tau_s=(1/af)\exp(2KV/kT) \quad (1)$$

where a is a geometrical factor which for trigonal α -Fe_2O_3 $a=2$, f the frequency factor of the Larmor precession, V the average volume of particles, T the absolute temperature, K the effctive anisotropy constant, and k the Boltzmann constant. When ferromagnetic and superparamagnetic parts are equal in the analysis of Mössbauer spectrum, f is equal to 7.7×10^3 K · cm · s · g. Using these values, Eq.(1) can be written as

$$\ln(4\times 10^{-4}K)=(2KV/kT) \quad (2)$$

The temperature T, at which the ferromagnetic and superparamagnetic Mössbauer spectra are equal, may be determined from the Mössbauer spectra measured at different temperatures. The particle volume V of sample A can be calculated from the particle diameter. Substituting the T and V into Eq.(2) the effective anisotropy constant K may be calculated.

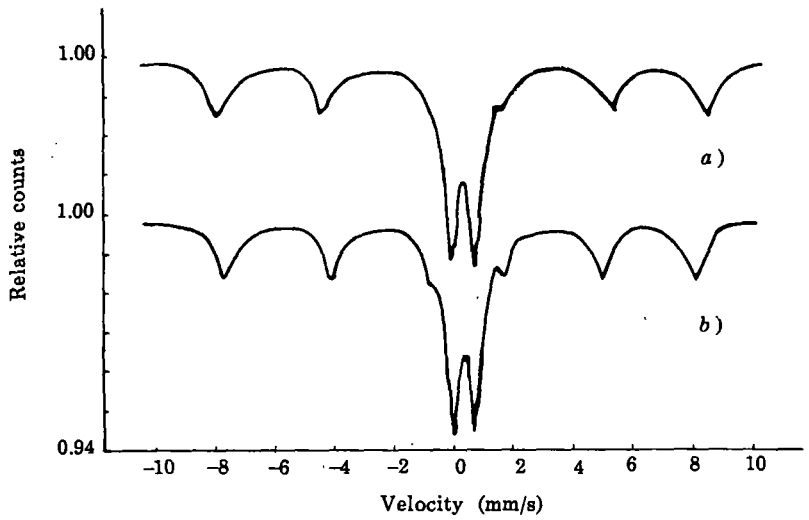

Fig.1 Mössbauer spectra of *a*) sample A and *b*) sample B measured at 200 K

Mössbauer spectra of samples A and B were measured at 295, 200, 150, 100 and

80 K, respectively. Fig.1 shows the Mössbauer spectra of samples A and B measured at 200 K.

The area ratios of each subspectrum to the total spectrum of samples A and B are listed in Table 1.

Table 1

Area ratios of each subspectrum to the total spectrum in percentage

T(K)	Sample A		Sample B	
	FM*	STM* *	FM	STM
295	48.8	51.2	42.4	57.6
200	50.9	49.1	46.0	54.0
150	53.3	46.7	48.9	51.1
100	54.8	45.2	53.5	46.5
80	64.6	35.4	59.0	41.0

* Ferromagnetic phase * * Superparamagnetic phase

From Fig.1 it is shown that the spectra of samples A and B were composed of two components, one is ferromagnetic and the other a doublet. With decreasing temperature the ferromagnetic peak area increases gradually, while the superparamagnetic decreases. But the area changes with temperature of samples A and B are different. At 295 K the ferromagnetic and superparamagnetic peak areas are 48.8% and 57.6%, respectively. The area ratios of the ferromagnetic to the superparamagnetic peak of A and B were calculated directly from the Mössbauer spectrum peaks. The ratio versus temperature is shown in Fig.2.

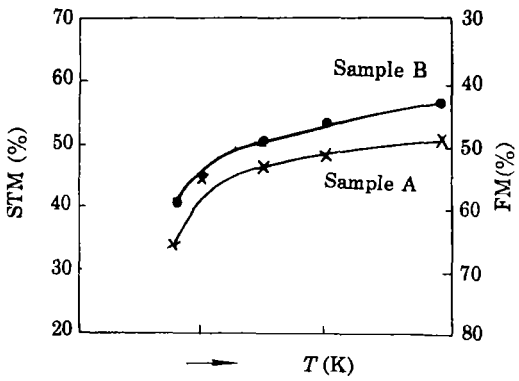

Fig.2 Percentage of superparamagnetic (STM) and ferromagnetic (FM) parts of samples A and B changed with the temperature

From Fig.2 the temperature T at which the ferromagnetic and superparamagnetic parts become equal could be determined that $T=240$ K for sample A and $T=110$ K for sample B, respectively. Substituting the values of T and V into Eq.(2), the effective anisotropy constants K may be calculated.

for sample A, $K_1=1.04\times10^4$ J/m^3; for sample B, $K_2=5.17\times10^3$ J/m.^{3}

K_2 is smaller than K_1, this means that the effective anisotropy constant K of the α –Fe_2O_3 fine particles after pyridine adsorption decreases.

3 DISCUSSION

The above experimental results showed the effective anisotropy constant K of

sample B adsorbed with pyridine decreases by about 50% compared with that of sample A. The mechanism is probably as follow:

Pyridine is the nonmagnetic organic compound with ring structure, it contains one N atom in its ring. In tems of the result of quantum chemical calculation, the charge distribution of pyridine can be written like Fig.3.[4]

As reported by us in a previous paper[5] the isomer shifts (IS) of α -Fe_2O_3 particles adsorbed with pyridine are larger than that of α -Fe_2O_3 particles without pyridine and the quadrupole splittings (QS) increased rapidly with decreasing temperature. These results means that when pyridine is adsorbed on the surface of α -Fe_2O_3 fine particles the electrons can be partially transmigrated from pyridine molecules to the Fe ions on the surface of α -Fe_2O_3 particles.

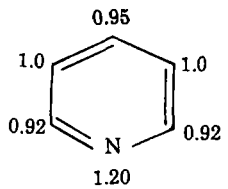

Fig.3 Charge distribution of pyridine

Because of the charge transmigration the spin of Fe ions on the surface of α -Fe_2O_3 particles adsorbed pyridine has been changed,[5] which decreases the effective anisotropy constant K. However the reason that charge transmigration from pyridine molecules to Fe ions can change the effective anisotropy constant K is not yet clear.

REFERENCES

[1] Morrison S Roy. The chemical physics of surface. New York: Plenum Press, 1977.

[2] Nininger R C, Jr, Schroeer D. *J Phys Chem Solids*, 1978, 39:137.

[3] Kundig W, Bommel H, Constabris G *et al. Phys Rev*, 1966, 142:327.

[4] Jin S S. Bases and applications of quantum chemistry (in Chinese). Shanghai Press of Science and Techniques, 1980.

[5] Wang G H, Li S, Xiao F M et al. ICAME 1991 Nanjing Abstracts. International Conference on the Applications of the Mössbauer Effect, Nanjing, 1991. p.2.59.