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## MAGNETITE TO MAGHEMITE TRANSFORMATION IN ULTRAFINE PARTICLES

K. HANEDA (\*) and A. H. MORRISH

Department of Physics, University of Manitoba, Winnipeg, R3T 2N2 Canada

**Résumé.** — La transition de la magnétite en maghémite fut étudiée du point de vue cinétique pour des grains ultrafins (77-220 Å) au moyen d'analyses chimiques, de mesures de diffraction X et de spectres Mössbauer. La température d'activation est relativement basse (8 250-11 200 K). Le saut d'électrons dans les poudres ultrafines de magnétite est discuté à la lumière des résultats.

**Abstract.** — The conversion of magnetite to maghemite has been studied kinetically in the ultrafine particle range (77-220 Å) by chemical analysis, X-ray diffraction, and Mössbauer measurements. The reaction is third order. The activation temperatures are relatively low (8 250-11 200 K). Electron hopping in ultrafine magnetite powders is discussed on the basis of the results.

**1. Introduction.** — The conversion of magnetite to maghemite has been studied by several investigators [1, 2]; they seem to have established that the oxidation from  $\text{Fe}_3\text{O}_4$  to  $\gamma\text{-Fe}_2\text{O}_3$  can be accomplished at approximately 220 °C [3]. However, almost all these studies have been made on micron- or close-to-micron-sized particles. Such particles of  $\gamma\text{-Fe}_2\text{O}_3$  are commonly used as the active ingredients of magnetic recording tapes. A kinetic study of the transformation of ultrafine magnetite particles to  $\gamma\text{-Fe}_2\text{O}_3$ , made in order to clarify quantitatively the catalytic activity of fine magnetite powders, is reported in this paper.

Gamma ferric oxide,  $\gamma\text{-Fe}_2\text{O}_3$ , is the allotropic form of magnetite,  $\text{Fe}_3\text{O}_4$ . These two iron oxides are crystallographically isomorphous. The main difference is the presence of ferric ions only in  $\gamma\text{-Fe}_2\text{O}_3$ , and both ferrous and ferric ions in  $\text{Fe}_3\text{O}_4$ . Magnetite has the cubic spinel structure. The ferric ions are distributed equally between the tetrahedral (A) and octahedral (B) sites. Above the Verwey transition, a fast-electron exchange occurs between the octahedral ferrous and ferric ions. Maghemite,  $\gamma\text{-Fe}_2\text{O}_3$ , also has the spinel structure. However, its X-ray diffraction pattern possesses additional weak lines that are attributed to vacancy ordering on the B sites [4]. The compound is usually represented by the formula  $(\text{Fe})(\text{Fe}_{5/3}\square_{1/3})\text{O}_4$ , where the two brackets identify A- and B-site cations respectively, and  $\square$  refers to the vacancies [5, 6, 7]. Both  $\text{Fe}_3\text{O}_4$  and  $\gamma\text{-Fe}_2\text{O}_3$  ultrafine powders behave, with respect to their intrinsic properties, in some ways that are still puzzling; further investigation is therefore warranted.

**2. Experiments.** — Micropowders of magnetite were prepared by a chemical precipitation method [8].

(\*) Present address : Research Institute for Scientific Measurement, Tohoku University, Sendai, Japan.

Three samples, each with different particle sizes, and labelled A, B, and C, were made by changing the thermal conditions during preparation. To retard any subsequent oxidation, the samples were kept in an evacuated desiccator until the kinetic run was started. The specific surface area (s. s. a.) of each sample was measured by the BET nitrogen adsorption method. An average diameter for the particles, assumed to be spheres, was calculated; the results are listed in table I.

TABLE I

Activation data for the  $\text{Fe}_3\text{O}_4$  to  $\gamma\text{-Fe}_2\text{O}_3$  conversion in ultrafine particles

Sample	Particle size		$T_A$ (K)	$s$ ( $\text{h}^{-1}$ )
	s. s. a. ( $\text{m}^2 \text{g}^{-1}$ )	diameter (Å)		
A	156	77	8 250	$1.6 \times 10^{11}$
B	101	119	9 850	$1.6 \times 10^{13}$
C	54.1	220	11 200	$5.7 \times 10^{13}$

The amount of X-ray line broadening, together with electron-microscope observations, supported the trend of these size determinations. In addition, the electron microphotographs confirmed that the shape of the particles was either spherical, or at least close to spherical.

The X-ray diffraction patterns for the synthetic samples showed only the presence of the cubic phase. Further, no trace of the extra lines associated with  $\gamma\text{-Fe}_2\text{O}_3$  was detected. In the Mössbauer experiments at room temperature, a spectrum characteristic of a paramagnet was observed for sample A, a spectrum with a small hyperfine splitting for sample B, and a spectrum with a well defined hyperfine splitting for sample C. Thus, the particles range from superparamagnetic to stable for samples A to C, respectively;

the Mössbauer data therefore also support the BET size determinations.

For the kinetic experiments, the powders were heat-treated in air for various times, from 20 minutes to 2 days, and at various temperatures, from 45 to 125 °C. The conversion was monitored by chemical analysis, X-ray diffraction, and Mössbauer measurements. The fraction of unconverted magnetite was obtained from the  $\text{Fe}^{2+}$  ion concentration, determined by chemical analysis; all the material, other than the residual magnetite, was assumed to be completely transformed to  $\gamma\text{-Fe}_2\text{O}_3$ . This assumption was reasonable since no hematite was observed by X-ray or Mössbauer measurements in any stage of the kinetic experiments. For the chemical analysis the heat-treated sample was dissolved in HCl solution, and then rapidly titrated with  $\text{K}_2\text{Cr}_2\text{O}_7$ , accompanied by a ferricyanide test.

It became evident from the data that the conversion process can be represented by a third-order rate reaction with the form  $-dc/dt = mc^3$ , that is

$$\frac{1}{c^2} = 2mt + \frac{1}{c_0^2},$$

where  $c$  and  $c_0$  are the concentrations of the reactant at the time  $t$  and at the initial time, respectively. Thus the rate constant,  $m$ , is given by the slope of  $1/c^2$  versus  $t$  plot. Figure 1 shows such a plot for sample C

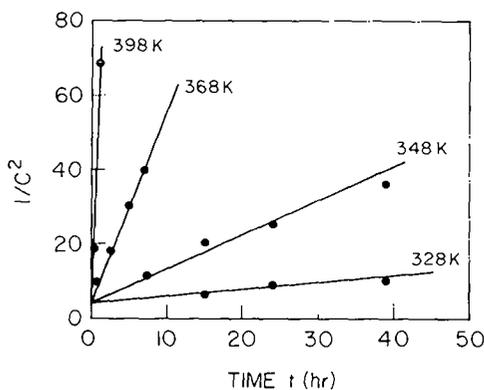


FIG. 1. — The conversion of magnetite to maghemite for sample C ( $d = 220 \text{ \AA}$ ). The fraction of residual magnetite,  $c$ , is shown as a function of time for various temperatures.

( $d = 220 \text{ \AA}$ ). Similar results were obtained for samples A ( $d = 77 \text{ \AA}$ ) and B ( $d = 119 \text{ \AA}$ ). The value of  $c_0$  at the start of the kinetic experiment was not unity for the three samples, but typically ranged from 0.4 to 0.6, with sample A having the smallest value. In other words, the synthetic powders had already become partially oxidized before the kinetic run was started; X-ray observations gave no indication of any oxidation.

Figure 2 shows the Arrhenius plots for the conversion of  $\text{Fe}_3\text{O}_4$  to  $\gamma\text{-Fe}_2\text{O}_3$ . The rate constant can be expressed by the equation  $m(T) = s \exp(-T_A/T)$

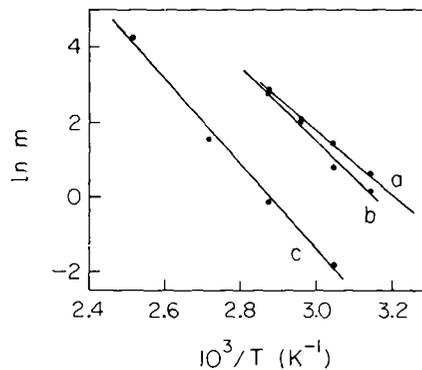


FIG. 2. — Arrhenius plots for three samples with different particle sizes;  $m$  is the rate constant. (a) sample A, (b) sample B, and (c) sample C.

where  $T_A$  is the activation temperature and  $s$  is the frequency factor. The values found for  $T_A$  and  $s$  are given in table I for each of the three samples. As an illustration, a calculation based on table I predicts that sample A, if left in air at room temperature for 50 days, will become 95 % converted to  $\gamma\text{-Fe}_2\text{O}_3$ . It was assumed that  $c_0 = 1$ ; however the results changes by less than 1 % if  $c_0 = 0.3$ , for example. The calculated value was confirmed by experiment.

Figure 3 shows the Mössbauer spectra for sample C at room temperature for three different stages of the

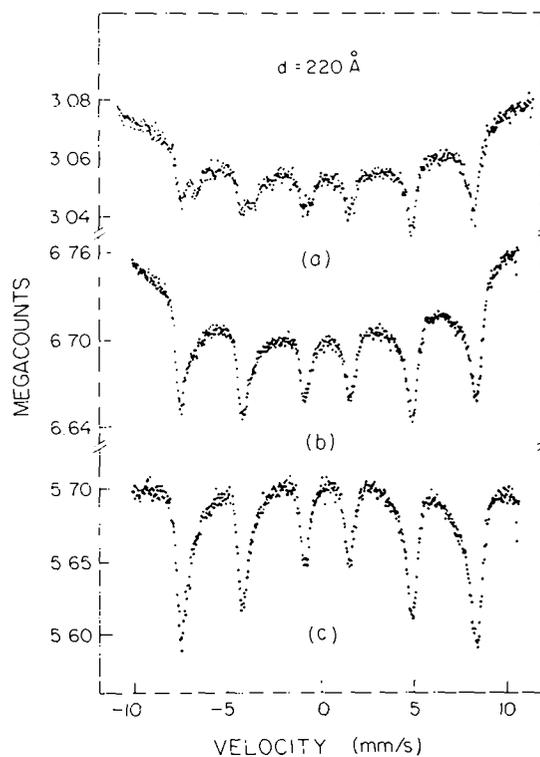


FIG. 3. — Mössbauer spectra for sample C ( $d = 220 \text{ \AA}$ ) at room temperature taken at three different stages of the conversion process. (a) No heat treatment, residual magnetite 50 %, (b) heated at 125 °C for 20 min., residual magnetite 20 %, and (c) heated at 125 °C for 1 hr., residual magnetite 12 %.

conversion process. As is well known, the Mössbauer spectra of magnetite possesses two six-line patterns above the Verwey temperature. One is associated with the tetrahedral ferric ions. The other is attributed to the ensemble of octahedral ferrous and ferric ions; they produce only one pattern because the electron hopping is much faster than the nuclear Larmor precession period. As the number of ferrous ions decrease on oxidation, the area of the absorption pattern corresponding to the B-site ions of magnetite decreases. The absorption profile then gradually approaches that for pure  $\gamma\text{-Fe}_2\text{O}_3$ .

**3. Discussion.** — A relationship between the kinetic parameters,  $T_A$  and  $s$ , and the particle sizes is implied in table I. The activation temperature,  $T_A$ , is relatively small, and is least for the smallest particles. In other words, conversion takes place at relatively low temperatures in ultrafine magnetite powders, and occurs most easily for the smallest particles. The frequency factor is relatively large, but is the least for the smallest particles. Thus it appears that  $s$  is some function of the particle volume. It is interesting to note that the volume ratio of sample C to sample A is about  $10^{1.3}$ , whereas the ratio of the corresponding frequency factor is  $\approx 10^2$ . The large value of  $s$  may imply that once conversion commences it tends to go to completion within one particle. The dependence of  $T_A$  and  $s$  on the particle size appears to be related to the relatively large surface area exposed in smaller particles. Then oxidation and other processes in which the surface plays a role are enhanced.

It is pertinent to consider electron hopping in ultrafine magnetite powders in the light of the present results. The conversion experiments make it probable that a partially oxidized ultrafine magnetite powder is actually a mixture of fully oxidized ( $\gamma\text{-Fe}_2\text{O}_3$ ) particles together with stoichiometric  $\text{Fe}_3\text{O}_4$  particles. The alternative possibility that the particles are a uniformly oxidized solid solution with the composition  $(\text{Fe}_2\text{O}_3)_x(\text{Fe}_3\text{O}_4)_{1-x}$  seems less likely. Consequently, electron hopping should be observable in those particles that are still magnetite. Figures 4a and b show the Mössbauer spectra at 293 and 77 K of

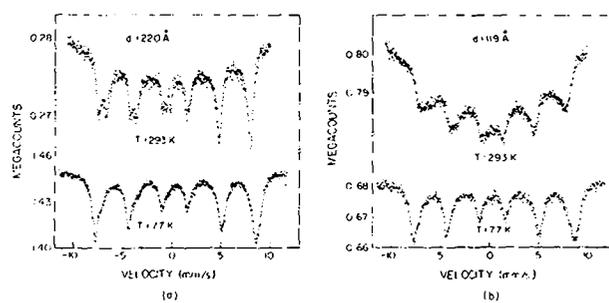


Fig. 4. — Mössbauer spectra taken at 293 and 77 K for (a) sample C ( $d = 220 \text{ \AA}$ ), and (b) sample B ( $d = 119 \text{ \AA}$ ).

sample C with  $c = 0.50$  and of sample B with  $c = 0.15$ , respectively. The difference in the absorption profiles between 293 and 77 K clearly establishes that electron hopping occurs in the ultrafine powders at room temperature. This result is in complete disagreement with that found in previous studies on ultrafine  $\text{Fe}_3\text{O}_4$  powders made by McNab *et al.* [9] and by Roggwiler and Kündig [10]. Their Mössbauer spectra were not characteristic of magnetite above the Verwey temperature, but instead consisted of one broad six-line pattern. It was suggested that the structure of ultrafine magnetite particles resembled that possessed by magnetite below the Verwey temperature.

Further, from figure 4 it is certain that the Verwey transition occurs between 77 and 293 K. This observation is contrary to that reported by Krupyanski *et al.* [11], who claim that the Verwey temperature is above 300 K for their 200 Å particles.

The present study, together with that by Topsøe *et al.* [12], therefore appears to provide the reason for the failure, up to now, to observe electron-hopping phenomena in ultrafine magnetite powders. Namely, considerable oxidation can occur even at room temperature.

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