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# Some magnetic properties of $\gamma$-$Fe_2O_3$ synthesized from ferrous fumarate half-hydrate

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$\gamma$-$Fe_2O_3$ synthesized from ferrous fumarate half-hydrate was studied by measurements of d.c. electrical conductivity, Seebeck coefficient, initial magnetization and magnetic hysteresis, and by Mössbauer spectroscopy and scanning electron microscopy. The phase transformation observed by electrical conductivity measurements matched well with the phase transformation observed by the variation with temperature of initial magnetization measurements of $\gamma$-$Fe_2O_3$; this magnetic study also established the single-domain character of $\gamma$-$Fe_2O_3$. The magnetic hysteresis values of the $\gamma$-$Fe_2O_3$ synthesized indicated improved values over that of a $\gamma$-$Fe_2O_3$ sample synthesized by established procedures. The scanning electron micrographs showed that the $\gamma$-$Fe_2O_3$ particles were acicular in shape and the Mössbauer spectrum showed a well-resolved six-band spectrum. The presence of a hydrogen ferrite phase was also confirmed by the electrical and magnetic measurements.

## 1. Introduction

Even after decades, $\gamma$-$Fe_2O_3$ maintains its lead over other magnetic tape recording materials [1, 2]. The synthesis of $\gamma$-$Fe_2O_3$ has been studied to some extent in detail [3, 4], but nevertheless research on the newer methods of synthesis for this material and on doped $\gamma$-$Fe_2O_3$ for the improvement of its magnetic properties is still being intensively pursued [1, 2, 4–9]. The reason for the extensive use of this material for magnetic tape recording purposes is because of its ideal combination of such magnetic hysteresis parameters as saturation magnetization ($M_s$), coercive force ($H_c$) and squareness ratio ($M_R/M_s$) [10]. Pure $\gamma$-$Fe_2O_3$, i.e. vacancy-ordered $\gamma$-$Fe_2O_3$, is a ferrimagnetic material with the structural formula $Fe_8^{3+}[Fe_{40/3}^{3+}\square_{1/8}]O_{32}$, where $\square$ indicates vacancy sites present in the lattice. Generally $\gamma$-$Fe_2O_3$ is used in the form of single-domain (SD) particles with acicular shape for a good signal-to-noise ratio on recording [10].

The existence of an intermediate phase, i.e. a hydrogen ferrite phase with a similar structural formulae to $\gamma$-$Fe_2O_3$ (an inverse spinel configuration with A and B sites) such as $Fe_8^{3+}[Fe_{12}^{3+}H_4^{+}]O_{32}$, is established for the synthesis of $\gamma$-$Fe_2O_3$ by thermal decomposition study of ferrous oxalate dihydrate [5].

The use of d.c. electrical conductivity helps in knowing the phase transformation temperature ($\gamma$- to $\alpha$-$Fe_2O_3$), and Seebeck coefficient measurement gives the number and nature of charge carriers as well as the phase transformation temperature. It is generally believed that the permeability ($\mu$) or susceptibility ($\chi_i$) of a magnetic material with SD grains always increases on heating and shows a peak (Hopkinson's peak) just before $T_c$ (the Curie temperature) and then falls to zero rapidly [11]; hence $\gamma$-$Fe_2O_3$ should show this behaviour in the normalized plot of $\chi_i$ against temperature. The Mössbauer spectrum of $\gamma$-$Fe_2O_3$ should show six well-resolved narrow lines in the intensity ratio 3 : 2 : 1 : 1 : 2 : 3 and the effective magnetic fields at A and B sites should be comparable [12].

## 2. Experimental procedures

The procedures for the measurements of d.c. electrical conductivity, Seebeck coefficient, initial magnetization with variation of temperature, high-field magnetic hysteresis loop tracing (HLT) Mössbauer parameters etc. have been reported [5].

$\gamma$-$Fe_2O_3$ was synthesized by the thermal decomposition of ferrous fumarate half-hydrate under a controlled atmosphere of dynamic air containing water vapour [7].

## 3. Results and discussion

Fig. 1 shows the plot of log $\sigma$ against $1/T$ for $\gamma$-$Fe_2O_3$ under a static air atmosphere. First a decrease in conductivity $\sigma$ up to 123° C was seen (Region A). The $\sigma$ value then increased showing a kink (K), then on a further increase of temperature the $\sigma$ value increased till there was a phase transformation to $\alpha$-$Fe_2O_3$ with a broadening at this transformation temperature ($T_D - T_E$). The cooling curve shows a hysteresis curve in which $\sigma$ does not show any observable variation between 180° C and room temperature.

For the determination of factors responsible for the

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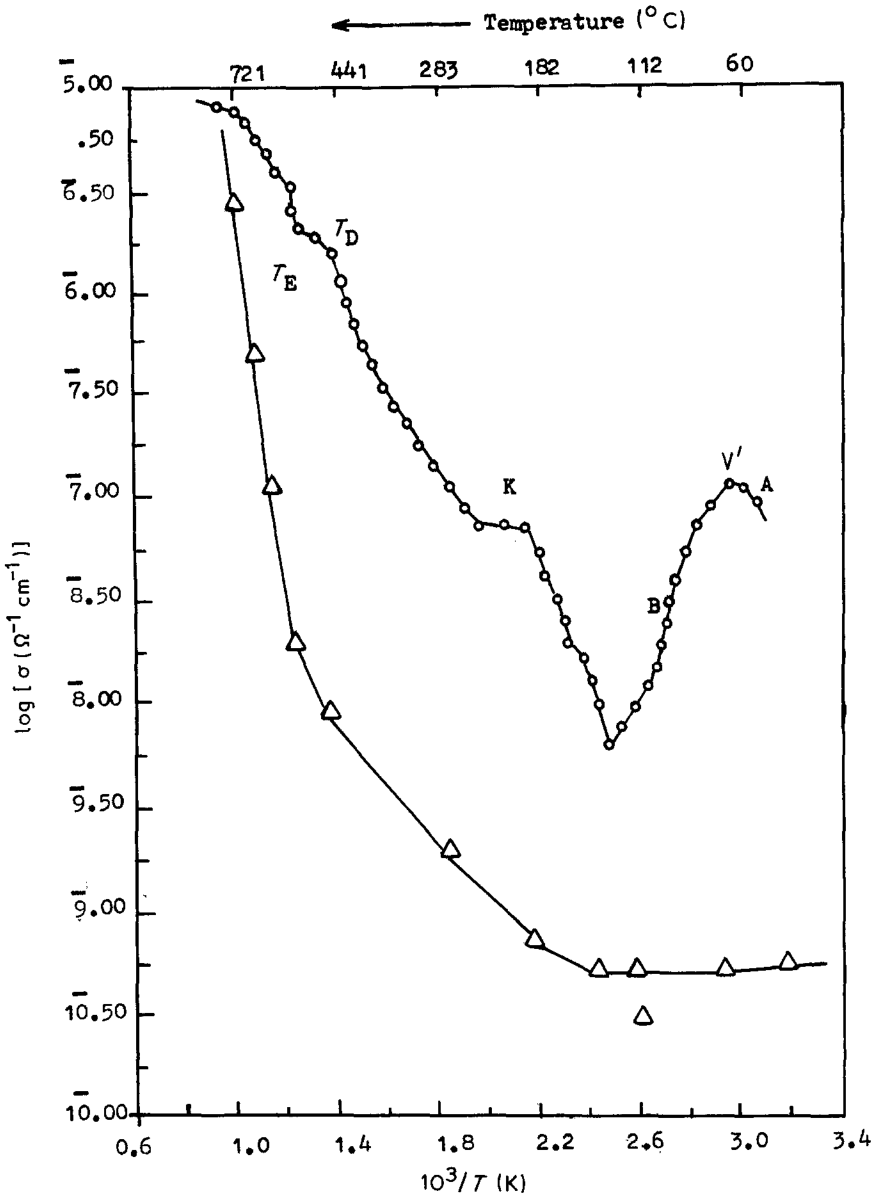

*Figure 1* Plot of log $\sigma$ against $T^{-1}$ for $\gamma$-$Fe_2O_3$: (○) heating curve, (△) cooling curve.

observed maximum (V′) in Region A, and the kink (K) in the curve, the $\sigma$ measurements were carried out under different atmospheres. The results observed for the maximum V′ and the kink K are similar to those observed for $\gamma$-$Fe_2O_3$ synthesized from ferrous oxalate dihydrate [5]. Hence these results for the kink (K) analysis indicate that a hydrogen ferrite phase with the formulae $Fe_8^{3+}[Fe_{12}^{3+}H_4^{+}]O_{32}$ is present up to 180° C and at this temperature the hydrogen ferrite phase decomposes to give a vacancy-ordered $\gamma$-$Fe_2O_3$; on further raising the temperature there is a slow transformation of $\gamma$-$Fe_2O_3$ to $\alpha$-$Fe_2O_3$ as indicated in Fig. 1 by the temperature regions $T_D$ to $T_E$ (i.e. 403 to 468° C).

The Seebeck coefficient measurements in Fig. 2 showed a fall in the number of charge carriers (negative charge carriers) in the temperature region 115 to 145° C, and the number then remains almost constant up to 180° C. A further rise of temperature showed a rise in the number of charge carriers up to the transformation temperature. After the complete phase transformation from $\gamma$-$Fe_2O_3$ to $\alpha$-$Fe_2O_3$ the nature of the charge carriers changes from negative to positive.

TABLE I Magnetic parameters

| Material | Saturation magnetization, $M_s$ (e.m.u. g$^{-1}$) | Coercive force, $H_c$ (Oe) | Squareness ratio, $M_r/M_s$ |
|---|---|---|---|
| Hydrogen ferrite phase | 62.0 | 200.0 | 0.51 |
| Vacancy-ordered $\gamma$-$Fe_2O_3$ | 71.0 | 300.0 | 0.56 |

$\gamma$-$Fe_2O_3$ used for magnetic tape recording should have SD grains with an acicular shape. Hence $\gamma$-$Fe_2O_3$ should show a slightly temperature-dependent magnetic hysteresis and a temperature-independent initial susceptibility below $T_c$ (the Curie temperature) with the presence of a Hopkinson peak below $T_c$ [11, 13]. The hydrogen ferrite phase should have a lower saturation magnetization ($M_s$) value than the vacancy-ordered $\gamma$-$Fe_2O_3$ [14, 15].

The magnetic hysteresis parameters for the hydrogen ferrite phase and vacancy-ordered $\gamma$-$Fe_2O_3$ (obtained by heating hydrogen ferrite under a dry dynamic nitrogen atmosphere at 200° C for four hours) are tabulated in Table I. The $M_s$ value for vacancy-ordered $\gamma$-$Fe_2O_3$ is found to be higher than the $M_s$ value observed for the hydrogen ferrite phase, as expected. All the magnetic parameters compare quite well with the expected values.

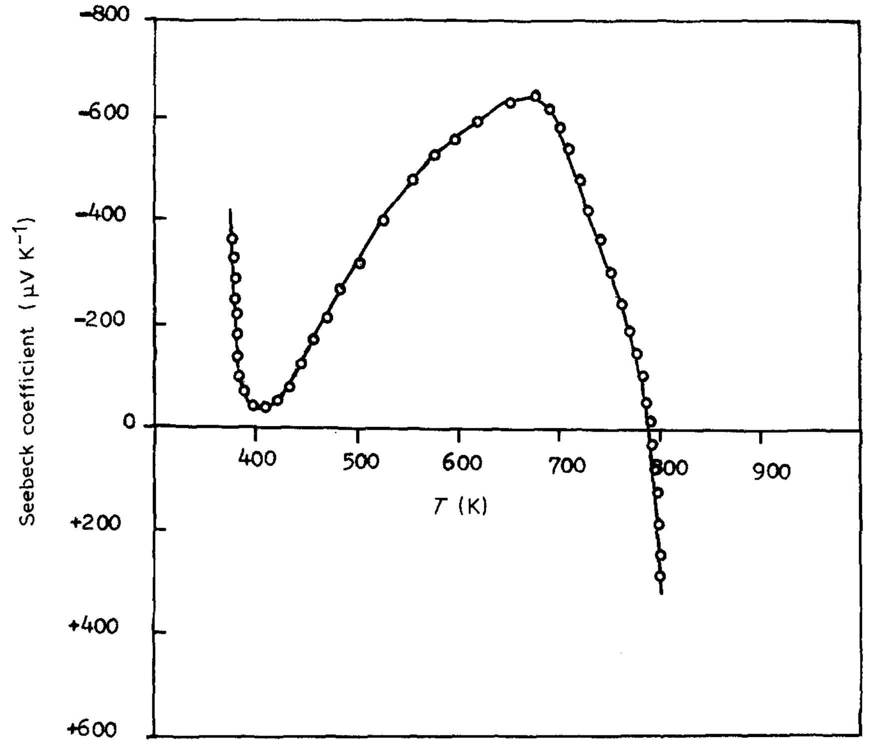

*Figure 2* Plot of Seebeck coefficient against temperature $T$ for $\gamma$-$Fe_2O_3$.

Fig. 3 shows the normalized $\chi_i$–$T$ curve obtained for vacancy-ordered $\gamma$-$Fe_2O_3$. The normalized $\chi_i$ values vary with temperature before the Hopkinson peak, indicating the SD behaviour of the sample, after this the $\chi_i$ value falls to zero ($T_c$) with some tailing.

The Mössbauer spectra of $\gamma$-$Fe_2O_3$ and that of hydrogen ferrite are very similar, with six well-resolved narrow lines (half-bandwidth of 0.285 mm sec$^{-1}$) in the intensity ratio 3 : 2 : 1 : 1 : 2 : 3. This nature of the spectra suggests that the effective magnetic fields at the A and B sites of $\gamma$-$Fe_2O_3$ are comparable, and that the magnetic SD grains are randomly oriented. The isomer shift (with respect to iron foil) and hyperfine field of these samples are very comparable (Table II). Hence

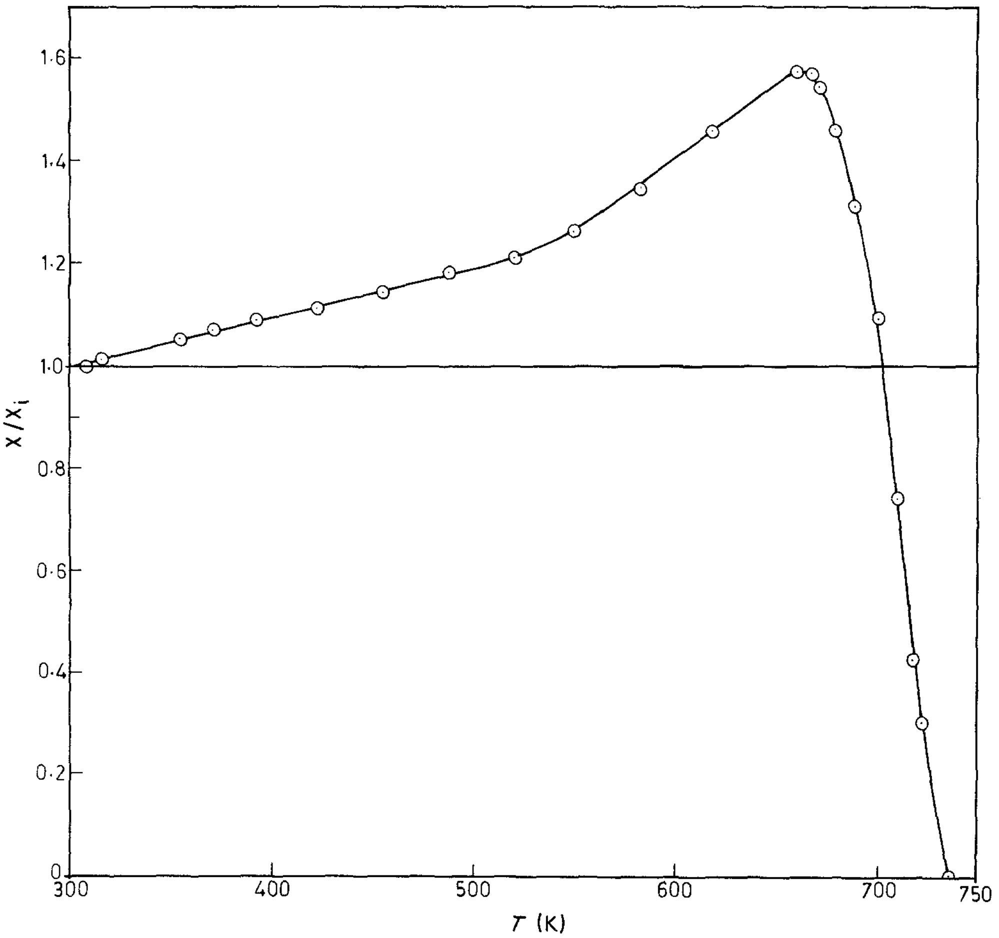

*Figure 3* Plot of normalized susceptibility ($\chi/\chi_i$) against temperature $T$ for $\gamma$-$Fe_2O_3$.

TABLE II Mössbauer parameter (hyperfine field, kOe ± 5.0)

| | |
|---|---|
| Hydrogen ferrite phase | 493.8 |
| Vacancy-ordered $\gamma$-$Fe_2O_3$ | 493.8 |

it can be said that the presence of the non-magnetic dopant $H^+$ at the lattice points does not affect the magnetic fields at the A and B sites.

The SEM photographs obtained for $\gamma$-$Fe_2O_3$ indicated that the particles were mostly of acicular shape.

## 4. Conclusions

The present study suggests the following important points.

1. The heating curve (log $\sigma$ against $1/T$) for $\gamma$-$Fe_2O_3$ under a static air atmosphere showed a decrease in $\sigma$ up to 123°C, indicating the desorption of adsorbed water molecules. There was then an increase in the $\sigma$ value with increase in temperature, with a kink indicating the presence of a hydrogen ferrite phase in the sample. Finally the transformation of $\gamma$-$Fe_2O_3$ to $\alpha$-$Fe_2O_3$ occurred with a broadening in the curve.
2. The sign of the Seebeck coefficient for $\gamma$-$Fe_2O_3$ was negative until the phase transformation temperature.
3. There was a significant increase in the $M_s$ values for a $\gamma$-$Fe_2O_3$ sample compared to that of the hydrogen ferrite phase, and all the magnetic parameters were in close agreement with reported values.
4. The normalized $\chi_i$–$T$ graph suggested that $\gamma$-$Fe_2O_3$ had SD grains.
5. The Mössbauer spectra for the hydrogen ferrite phase and vacancy-ordered $\gamma$-$Fe_2O_3$ were similar, indicating that the effect of the non-magnetic dopant $H^+$ does not have any observable effect on the Mössbauer spectrum.
6. The scanning electron micrographs showed the particles to be 1.0 to 2.0 nm in size with an acicular shape.

Hence on the basis of the above study it can be said that the $\gamma$-$Fe_2O_3$ synthesized from $FeC_4H_2O_4 \cdot \frac{1}{2}H_2O$ had all the necessary parameters for being used as an efficient tape recording material.

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