

MANGANESE FERRITE THIN FILMS PART II: PROPERTIES*

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SUMMARY

Some properties of evaporated manganese ferrite thin films are investigated, e.g. resistivity, magnetization reversal, Curie temperature, Faraday rotation and optical absorption. The properties are partly related to the partial oxygen pressure present during a preceding annealing process.

INTRODUCTION

Thin films of various manganese ferrite compositions ($\text{Mn}_x\text{Fe}_{3-x}\text{O}_{4+y}$) can be made by a reactive evaporation process. The preparation and structure of these films are described in Part I. The as-evaporated films are homogeneous and have the spinel structure. They are composed of very small crystallites ($< 100 \text{ \AA}$). An annealing process of several hours at 750°C increases the crystallite size to typically 1000 \AA . During annealing an appropriate partial oxygen pressure must be maintained to preserve the spinel structure. Some variation in this oxygen pressure is allowed, which may correspond with positive and negative values of γ (metal ion vacancies and oxygen ion vacancies respectively). The small amount of material of the thin films is not suitable for determining the value of γ directly. Some physical properties may however be related to the influence of the partial oxygen pressure during annealing. Unless stated otherwise in the following the annealing process is performed at 750°C in a partial oxygen pressure close to the estimated equilibrium pressure for stoichiometric spinel ($\gamma = 0$) as estimated in Fig. 2 of Part I. The magnetic measurements (magnetization reversal, domains, Curie temperature) are performed by the use of the Faraday effect.

* Part I: Preparation and Structure, see *Thin Solid Films*, 9 (1972) 363–375.

RESISTIVITY

The resistivities of the as-evaporated films are several orders of magnitude higher than the data for bulk material taken from the literature¹. This may be caused by the smallness of the crystallites (which give many crystal boundaries) and also by a very imperfect crystal structure of the as-evaporated films. Support is given to these suppositions by measurements on films which were evaporated at higher substrate temperatures. The latter films show lower resistivities with larger crystallites, whereas it is known that higher substrate temperatures during evaporation give a more perfect crystal structure. For some film compositions the resistivity, ρ , is measured at room temperature as a function of the partial oxygen pressure, P_{O_2} , present during the preceding annealing process of about 3 h at 750 °C. The results are represented in Fig. 1. The measurements suggest linear dependences as indicated in the figure. The values of ρ , which belong to the equilibrium oxygen pressure (as estimated in Fig. 2 of Part I) agree well with the literature data for bulk material, which has been prepared at stoichiometric conditions. This implies a confirmation of our estimates for the equilibrium conditions at 750 °C. The dependence of ρ on $\log P_{O_2}$ can be explained qualitatively in the model of Lotgering¹ on the semiconduction and cation valences in manganese ferrites. Lotgering concludes that the equilibrium of the cations on the octahedral sites: $Mn^{2+} + Fe^{3+} \rightleftharpoons Mn^{3+} + Fe^{2+}$ lies at low temperatures on the left-hand side. So at room temperature the fraction of Fe^{2+} ions on octahedral sites is very small for compositions with $\delta \geq 1$. As the conduction is attributed to the Fe^{2+} content on octahedral sites, the resistivity would be enlarged by a diminishing of the Fe^{2+} fraction. This may be the case in our oxidized samples, which are produced in oxidizing annealing atmospheres. From the strong dependence¹ of ρ on δ in the region near to $\delta = 1$, it may be expected that the resistivity would depend sensitively on the Fe^{2+} content; this is the case for the compositions investigated.

MAGNETIZATION REVERSAL

Some typical magnetization curves of the films are represented in Fig. 2. The films are magnetically isotropic in the plane of the film. The hysteresis loops are strongly sheared if measured in the direction perpendicular to the film plane, which is caused by the large demagnetizing field in that direction. The substrate temperature during evaporation influences the resulting magnetization curve. It is likely that this effect is connected with the degree of perfection of the crystal structure and also with the mean crystallite size. With respect to the latter Néel's theory on the thermal fluctuation aftereffect² must be taken into account. This theory predicts a super-paramagnetic phase for particles below a certain limit of size. This phenomenon is confirmed experimentally by Brook and

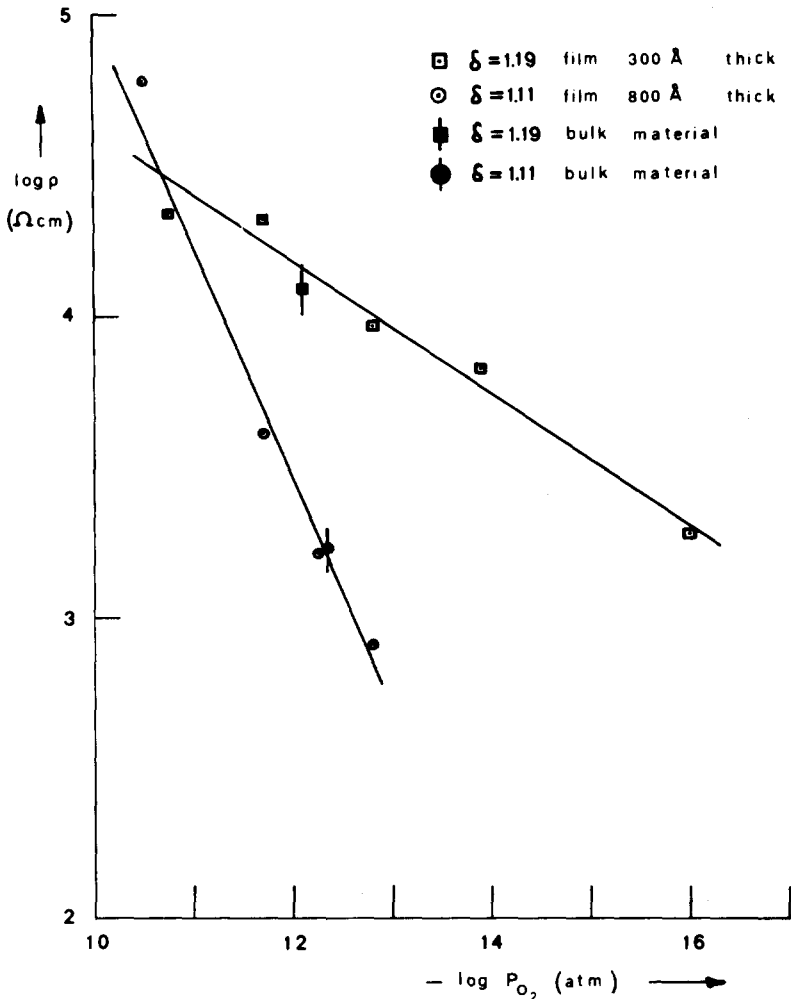


Fig. 1. Resistivity of $\text{Mn}_2\text{Fe}_{3-\delta}\text{O}_{4+\gamma}$ thin films as a function of the partial oxygen pressure, P_{O_2} , present during the preceding annealing process of 3 h at 750 °C. Data from ref. 1 on bulk material are inserted at the equilibrium oxygen pressures at 750 °C for $\gamma = 0$ as estimated in Fig. 2 of Part I.

Kingery³ in micropolycrystalline nickel ferrite films. In their investigation the upper limit for the existence of the super-paramagnetic behaviour appeared at a crystallite size of typically 100 Å at room temperature. It is concluded that the crystal boundaries act as effective barriers for ferrimagnetic exchange interaction. Measurements by Sato⁴ on ultrafine particles determine the upper limit for the existence of the super-paramagnetic behaviour of MnFe_2O_4 at a particle size of 150–200 Å at room temperature. The super-paramagnetic state is possibly the reason for the fact that for a number of our as-evaporated films with small crystallites no hysteresis curve at all can be detected. It appears that by the

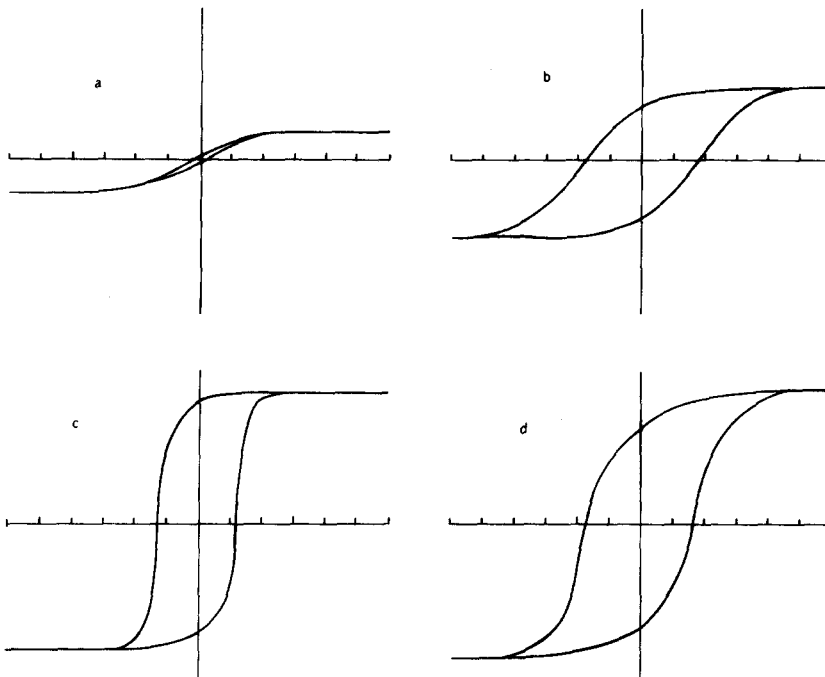


Fig. 2. Magnetization curves of thin films of $\text{Mn}_3\text{Fe}_{3-x}\text{O}_{4+x}$. Horizontal scale: 100 Oe per division; vertical scale: uncalibrated; (a) unannealed, evaporated at substrate temperature 140°C , $\delta = 0.77$; (b) unannealed, substrate temperature 230°C , $\delta = 0.77$; (c) annealed at 750°C , $\delta = 0.68$; (d) annealed at 750°C , $\delta = 2.11$.

annealing process the remanence ratio of the hysteresis curve becomes considerably larger. At the same time the magnetic field strength which is required to achieve saturation becomes lower. The coercivity is a function of the partial oxygen pressure during the annealing process. The lowest coercivity, typically 75 Oe for MnFe_2O_4 , is obtained in the neighbourhood of the conditions for stoichiometric spinel. Oxidizing annealing atmospheres do not give very different results, but reducing atmospheres result in much higher values. The lowest coercivity is two orders of magnitude higher than the usual values for bulk material of the same compositions and even than the values for single crystalline manganese ferrite films⁵⁻⁷. These high coercivities are remarkable for materials with such a low crystal anisotropy as manganese ferrites. This phenomenon is considered in the following. It appears that the origin of the high H_c values is not connected with possible stresses in the films, which could influence the magnetic properties *via* the magnetostriction constant. This is verified by inducing an extra stress in the film during the measurement. Extra (inhomogeneous) stresses up to $3 \times 10^8 \text{ N/m}^2$ are created in the film. These are of the same order of magnitude as the maximum stress which may exist in the film on account of the

thermal history of film and substrate. (Other, intrinsic, stresses of the same order of magnitude are not to be expected in the film material after the annealing process at 750 °C.) It appears however that the extra stress has no influence (with a relative accuracy of 5%) on the coercivity or other characteristics of the hysteresis loops. So the high H_c values must be caused by other factors than stresses in the films. This may be analysed in relation to the process of magnetization reversal.

The nature of the process of magnetization reversal is however not evident, because the presence of magnetic domains and domain walls in the films cannot be observed. Both the demagnetized situation and the transition situations during quasistatic magnetization reversal in a slowly varying magnetic field were investigated. Neither by the Bitter powder technique, nor by direct magneto-optical observation, nor by Lorentz electron microscopy could an indication be obtained concerning the existence of domain walls. There are however indirect indications which make magnetization reversal by domain wall movement plausible. Firstly there is the good rectangularity of the hysteresis loops. In polycrystalline materials this is mostly connected with magnetization reversal by domain wall movement. Secondly it must be considered that the alternative, *e.g.* magnetization reversal by a rotation process, is not possible, since coherent rotation of the magnetization (as for example occurs in permalloy films under certain conditions) is not possible due to lack of an overall magnetic easy-direction in our films. The local easy-direction will vary from crystallite to crystallite and this dispersion means that a rotation process could only be incoherent. However incoherent rotation (as for example may occur at high field strengths in an aggregate of single-domain particles) would require that a large magnetostatic energy should be overcome. For during magnetization reversal by incoherent rotation the normal component of the magnetization would be discontinuous at the crystal boundaries of a large number of crystallites. The field to deliver this energy should be of the order of magnitude of the demagnetizing field, which is about 1700 Oe (for spherical crystallites of MnFe_2O_4). Our measured coercivities are however lower by one order of magnitude. Thirdly the temperature dependence of the coercive force provides an indication that magnetization reversal takes place by domain wall movement. This may be concluded from the following rather simplified argument.

According to the general theory² the energy γ of a domain wall per unit area of the wall may be expressed as:

$$\gamma = \sqrt{AK} \cdot f$$

with A = exchange constant, K = anisotropy constant, and f is a function of the geometrical coordinates of the domain wall. The function f is determined by the position of the wall with regard to the local easy-directions of the magnetization and with regard to, for example, the local irregularities in the structure of the

magnetic lattice. Displacement of the domain wall in the x -direction requires an energy E_1 :

$$E_1 = \frac{\partial \gamma}{\partial x} = \sqrt{AK} \frac{\partial f}{\partial x}.$$

As $\partial f / \partial x$ is independent of the temperature T :

$$E_1(T) \propto \sqrt{A(T)K(T)}.$$

This energy can be acquired by the reduction of the magnetostatic energy $E_2(T)$ of the material in an external field H :

$$E_2(T) = I(T) \cdot H.$$

With I = magnetization of the material. Magnetization reversal by an external field is achieved if $H \approx H_c$. This means $E_1(T) \approx E_2(T)$, so:

$$H_c(T) \propto \frac{\sqrt{A(T)K(T)}}{I(T)}.$$

It is generally accepted^{8,9} that the exchange constant depends on the temperature in the same way as the square of the magnetization: $A(T) \propto I^2(T)$ which gives: $H_c(T) \propto \sqrt{K(T)}$. According to our experiments there is no significant influence of a stress anisotropy on the coercivity. So K must be determined by the crystal anisotropy and can be put equal to K_1 . According to the theory of Yosida and Tachiki¹⁰ the temperature dependence of K_1 for MnFe_2O_4 between room temperature and the Curie temperature T_c is: $K(T) \propto (T_c - T)^2$ which results in:

$$H_c(T) \propto (T_c - T).$$

This implies that the coercivity must decrease linearly to the Curie temperature. Our measurements (Fig. 3) show a good agreement with this theory. For comparison a check can be made of the temperature dependence of H_c if the magnetization reversed by rotation. In that case the following should hold:

$$H_c(T) \propto H_k(T) \propto \frac{K(T)}{I(T)}$$

with H_k = anisotropy field. The temperature dependence of $K(T)/I(T)$ is taken from Yosida and Tachiki¹⁰ and represented in Fig. 3 in arbitrary units. It is clear that the rotation process is not confirmed by our measurements.

From the foregoing three arguments it is very probable that magnetization reversal is performed by domain wall motion notwithstanding the lack of direct observation of these walls. The thickness of these domain walls may be estimated according to the theory²: $d = \pi(A/|K|)^{1/2} \approx 800 \text{ \AA}$ for MnFe_2O_4 at room

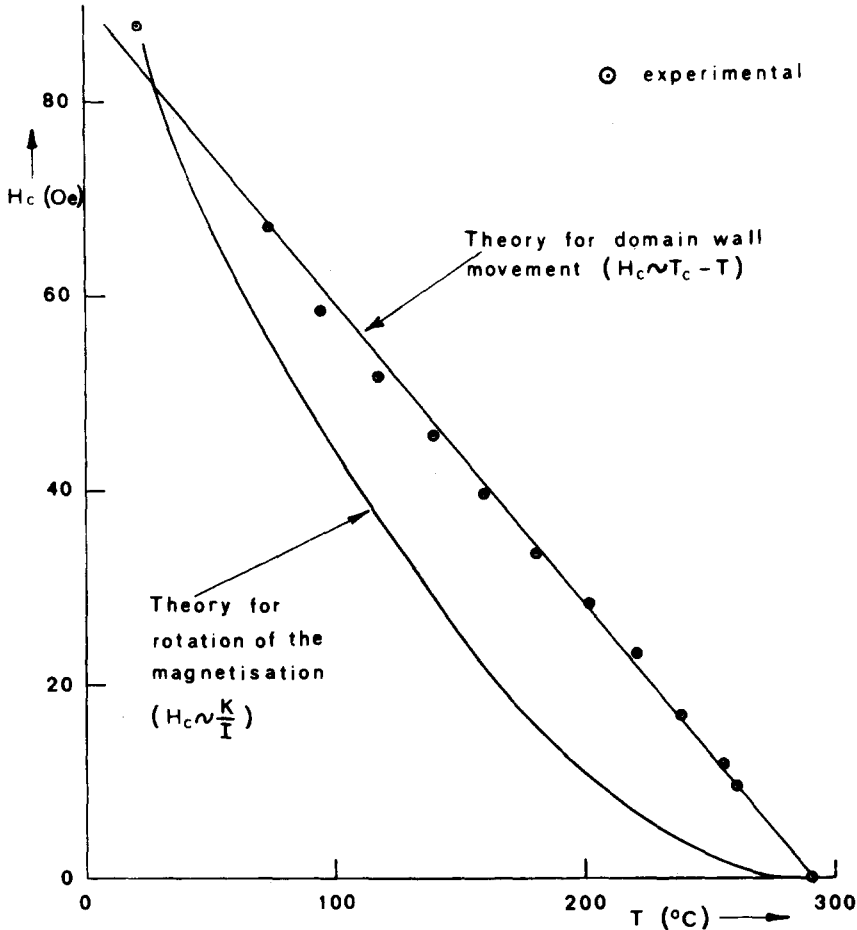


Fig. 3. Coercivity of a $Mn_{0.97}Fe_{2.03}O_4$ thin film as a function of the temperature.

temperature. (A is estimated to be 3×10^{-12} J/m, see also ref. 8; K is taken from ref. 11.) This value of d is in the same order of magnitude as the dimensions of the crystallites in the films. A high coercivity is, therefore, not surprising. Following the theory developed for permalloy films¹² coercivity is largest when the domain wall thickness is comparable with the period of the local variations of those parameters which influence the wall energy. One of these parameters is the anisotropy. In our films the crystal anisotropy may disperse from crystallite to crystallite, which gives an important contribution to the wall energy. So displacement of domain walls implies strong variations of the domain wall energy. This requires a large applied field and thus a high coercivity is found.

However in an important respect the process of wall displacement in polycrystalline manganese ferrite films differs from the process of wall displacement in permalloy films. For in a ferromagnetic material the exchange interaction acts

across the crystal boundaries. This applies because the ferromagnetic exchange is just a function of the distance between the neighbouring magnetic moments. But in a ferrimagnetic material a local symmetry of cations and anions is required for the exchange interaction. At the crystal boundaries this symmetry, and by that the exchange interaction, is disrupted. This is already mentioned above in relation to the super-paramagnetic state. This implies that in a ferrimagnetic material the coupling of the magnetization between two neighbouring crystallites is only magnetostatic. The magnetostatic coupling is weak compared to the exchange interaction. So a definite distribution of the magnetization in a ferrimagnetic material will meet with more disruptions from crystal boundaries than in a ferromagnetic material. This means that a domain wall in our films can hardly move across a large number of crystallites, in contrast to walls in, for example, permalloy films. So magnetization reversal in micropolycrystalline manganese ferrites requires nucleation of a large number of domain walls, each of which may move along a short distance. The many domain walls contain much energy, which implies a high coercivity for magnetization reversal. Now it is not surprising that direct observation of domain walls in our manganese ferrite films is difficult. For instance, the fact that the thickness of the domain walls is of the same order of magnitude as the crystallites hampers the observation. Moreover, the distance between two domain walls will be small, while each wall will move only over a small distance.

INDUCED MAGNETIC DOMAINS

With the help of a magnetic head close to the surface of the film magnetic domains can be induced in the film material which was saturated previously along a direction in the plane of the film. The shape of such an induced domain is a regular reproduction of the split in the magnetic head. The domain can be detected with the help of the Faraday effect. Its position appears to be very stable. A homogeneous magnetic field of increasing intensity does not cause any visible displacement of the domain. In a field of sufficient strength the domain seems to fade away on the spot. With reference to the conclusions of the last section concerning the process of magnetization reversal, it can be concluded that the vanishing of an induced domain takes place *via* the nucleation of a number of domain walls on a microscale. The saturated condition must be attained by movements of these walls by a very short distance.

CURIE TEMPERATURE

Figure 4 shows a typical example of the dependence of the Faraday rotation of an annealed film on the temperature. The temperature at which the Faraday rotation is just zero, is taken as the Curie temperature. In general this point

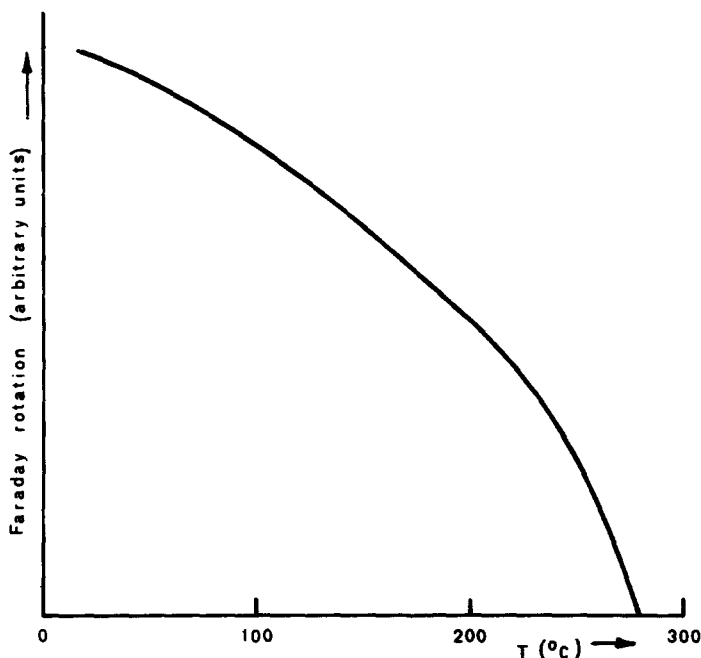


Fig. 4. Faraday rotation of a $\text{Mn}_{0.97}\text{Fe}_{2.03}\text{O}_4$ thin film as a function of the temperature.

appears to be sharply defined in our films. If the composition of the material were less homogeneous, the curve would have some sort of tail to higher temperatures¹³. Figure 5 gives the Curie temperature, measured on annealed films, as a function of composition. The results agree well with the measurements of Brabers¹⁴ on bulk crystals. Some points, as indicated in Fig. 5, are taken on films which have been annealed in a reducing atmosphere. One sees that the Curie temperature of these films is considerably higher. This is in qualitative agreement with the results of Gerber¹⁵. The origin of this influence of the oxygen pressure during annealing on T_c may be a valence change of the cations, but also a change in the cation distribution on the lattice positions during the annealing process. Our measurements indicate that an oxidizing atmosphere during annealing has a less pronounced influence on T_c .

FARADAY ROTATION AND ABSORPTION

The Faraday rotation of the manganese ferrite films is a function of the temperature of the material and of the wave length of the incident light. An example of the former dependence is represented in Fig. 4. Some results of the latter dependence for thin films of $\text{Mn}_{0.97}\text{Fe}_{2.03}\text{O}_4$ at room temperature are given in Table I. The Faraday rotation, F , is negative for visible light. For magneto-optical detection of magnetization curves and domain structures the Faraday

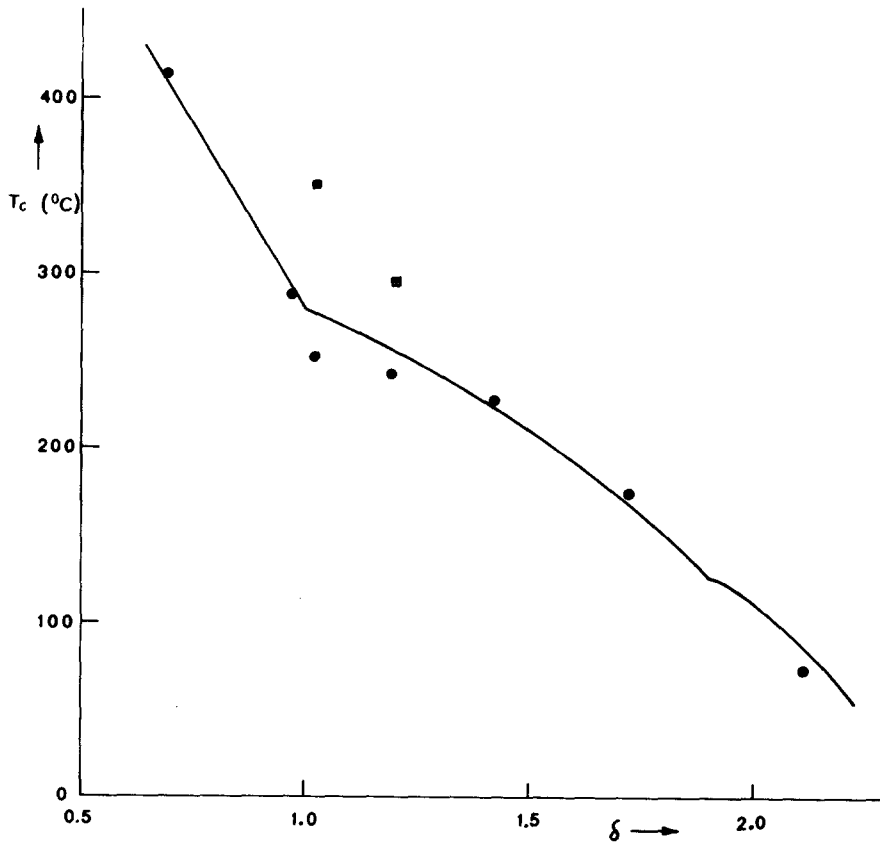


Fig. 5. Curie temperature of $Mn_3Fe_{3-\delta}O_{4+\gamma}$ as a function of δ . Circles: present study on evaporated films annealed at 750 °C in approximate equilibrium atmosphere for $\gamma = 0$. Squares: present study on evaporated films annealed at 750 °C in a reducing atmosphere. Full line: measurements on bulk material (ref. 14).

rotation as well as the absorption coefficient of the material are essential. Table I shows that the absorption coefficient, α , increases with decreasing wave length. Aagard *et al.*¹⁶ calculated that optimal magneto-optical contrast between forward and reversed magnetization direction is obtained at a film thickness of $2/\alpha$. The contrast is determined by the value $2F/\alpha$. Table I shows that this latter value has a weak maximum for the material investigated at a wavelength of about 4900 Å. The Faraday rotation and absorption of manganese ferrite can be compared with the measurements of Coren and Francombe¹⁷ on some other spinel ferrites, e.g. $NiFe_2O_4$ and $CoFe_2O_4$. They found the reversed sign of the Faraday rotation below a certain wave length of the light.

TABLE I*

FARADAY ROTATION AND ABSORPTION COEFFICIENT OF $\text{Mn}_{0.97}\text{Fe}_{2.03}\text{O}_4$
(FOR EXPLANATION SEE TEXT)

λ (\AA)	$-F$ ($10^3 \text{ deg. cm}^{-1}$)	α (10^4 cm^{-1})	$\frac{2}{\alpha}$ (10^{-8} cm)	$\left \frac{2F}{\alpha} \right $ (deg)
3980	16.5	10.3	1950	0.32
4350	17.0	8.1	2480	0.42
4920	13.1	5.5	3630	0.48
5480	8.2	3.8	5300	0.43
5870	5.2	2.6	7670	0.40
6490	4.2	2.3	8700	0.37

* Note: The Faraday rotation has been measured with the magnetization of the material in the plane of the film, while the angle of incidence of the light beam has been 43° . The Faraday rotation F has been calculated from $F = \theta/D \text{ tg } r$ with θ = measured rotation, D = film thickness, and r = angle of refraction in the manganese ferrite film. To compute r from the angle of incidence, the refractive index of the material has been approximated by $n = 2.8$ for all wavelengths of the light (cf. ref. 18).

DISCUSSION

Ferrimagnetic materials show a large variety of properties like magnetization, Curie temperatures, crystal anisotropy, magnetostriction, conductivity and optical properties. Influencing these properties to a desired value is in general possible by variation of the metal-iron ratio and by preparation of mixed ferrites. Thus a large field of application exists for these magnetic materials. Manganese ferrite takes an important place in this field. In the literature little attention is given to the properties of ferrimagnetic films, in contrast to the many publications on ferromagnetic films (especially permalloy films). However ferrite films form an interesting field for research with electron microscopy and Faraday rotation as valuable aids for investigations.

In the foregoing it has been shown with the help of electron microscopy that the structure of manganese ferrite films can be controlled well. With the help of magneto-optical detection some magnetic properties have been investigated. In doing so the Faraday rotation in combination with the absorption coefficient takes the place of the magnetization for inductive measurements.

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