

# High-field Hall effect and magnetoresistance in Fe<sub>3</sub>O<sub>4</sub> epitaxial thin films up to 30 Tesla

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We have measured the Hall effect and the magnetoresistance of epitaxial Fe<sub>3</sub>O<sub>4</sub> thin films grown on MgO (001) in magnetic fields up to 30 T. Using such high fields, it is possible to magnetically saturate films thicker than 40 nm, providing access to intrinsic conduction properties. We find an effective electron density corresponding to 1 electron per f.u. A smaller value is obtained for thinner films, caused by the increasing density of antiphase boundaries defects. The magnetoresistance is not saturating at 30 T, showing linear dependence at high fields, and peaks at the Verwey transition. © 2009 American Institute of Physics. [doi:10.1063/1.3276696]

Fe<sub>3</sub>O<sub>4</sub> (magnetite) thin films have been subject of thorough studies during the last years, inspired by their possible applications in spintronic devices.<sup>1</sup> Magnetite has a high ferromagnetic Curie temperature ( $T_c=860$  K), a relatively high saturation magnetization [ $M_s=470$  emu/cm<sup>3</sup> at room temperature (RT)], and theoretical predictions indicate it is a half-metallic material,<sup>2</sup> with spin-resolved photoelectron spectroscopic results confirming its high spin polarization.<sup>3</sup> Fe<sub>3</sub>O<sub>4</sub> films can be grown epitaxially on MgO(001) substrates, with a closely matched lattice constant ( $a_{\text{Fe}_3\text{O}_4}=8.397$  Å  $\approx 2 \times a_{\text{MgO}}$ ). All these factors make it a promising material to form magnetic-tunnel-junctions electrodes. The most relevant difference in Fe<sub>3</sub>O<sub>4</sub> thin films with respect to the bulk material is the presence of structural defects, caused by the growth mechanism, called antiphase boundaries (APBs).<sup>4-8</sup> APBs play a major role in the properties of Fe<sub>3</sub>O<sub>4</sub> thin films, mainly due to the antiferromagnetic (AF) superexchange interactions between the spins surrounding the boundary. Recently we studied the anomalous Hall effect (AHE) in Fe<sub>3</sub>O<sub>4</sub>.<sup>9</sup> Using magnetic fields up to 9 T, the lack of magnetic saturation provided evidence for the presence of the APBs. The remaining linear background impedes a clear separation of the ordinary Hall effect (OHE) from the AHE contribution. Nevertheless, in this letter we show how we can separate these two contributions by studying the Hall effect (HE) and the magnetoresistance (MR) of Fe<sub>3</sub>O<sub>4</sub> films in static fields up to 30 T.

Our films were epitaxially grown by pulsed laser deposition on MgO(001) substrates. We have measured the room-temperature HE in four different samples with thicknesses of 200, 41, 27, and 16 nm and a surface area of  $5 \times 5$  mm<sup>2</sup> using the van der Pauw method.<sup>10</sup> Additionally, we have performed HE and MR experiments on a lithographically patterned 40 nm thick film at several temperatures below RT. The transport measurements were carried out by standard ac

or dc modes for temperatures above and below the Verwey transition ( $T_v$ ), respectively, in high magnetic fields.

The RT results are summarized in Fig. 1, where we plot the Hall resistivity,  $\rho_H$ , for the different samples as a function of the magnetic field.  $\rho_H$  has two contributions:

$$\rho_H = \mu_0(R_0H + R_A M), \quad (1)$$

where the first term, proportional to the field  $H$ , is the OHE, and the second one, proportional to the magnetization  $M$ , is the AHE.

The measured resistivity of the thickest film (200 nm) is 4 mΩ cm and identical to the bulk value, which indicates a negligible presence of APBs.<sup>6</sup> In the low field range,  $d\rho_H(H)/d(\mu_0H)$  is never constant, indicating that the magnetization of this film is not saturated. For the higher fields ( $B > 20$  T),  $R_H = d\rho_H/d(\mu_0H) \approx -0.04$  μΩ cm/T is constant, which allows us to extract an effective electron density

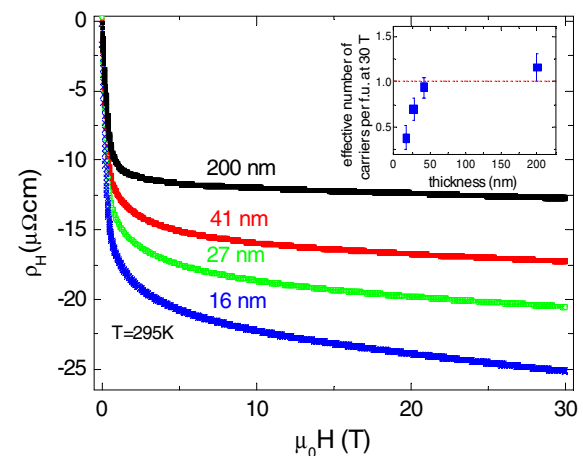


FIG. 1. (Color online) Hall resistivity up to 30 T at RT for four samples, varying in thickness. The inset shows the effective density of electrons at the maximum field. The value associated to 1 e<sup>-</sup> per f.u. is marked by a dashed line.

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TABLE I. Electrical conduction properties of Fe<sub>3</sub>O<sub>4</sub> epitaxial thin films. The first four rows refer to the van der Pauw measurements at RT, varying the sample thickness. The last four rows are obtained for a 40 nm thick lithographically patterned sample as a function of temperature ( $T > T_v$ ). The effective quantities are derived from the slope at 30 T.

$t$ (nm)	$T$ (K)	$\sigma$ ( $\Omega \text{ cm}$ ) <sup>-1</sup>	$R_0^{\text{eff}}$ ( $\mu\Omega \text{ cm/T}$ )	$N^{\text{eff}}$ ( $\text{e}^-/\text{cm}^3$ )	$n^{\text{eff}}$ ( $\text{e}^-/\text{f.u.}$ )	$\mu_H^{\text{eff}}$ ( $\text{cm}^2/\text{V s}$ )
200	295	245.2	-0.04	$1.56 \times 10^{22}$	1.15	0.09
41	295	129.6	-0.05	$1.25 \times 10^{22}$	0.93	0.065
27	295	102.2	-0.07	$8.93 \times 10^{21}$	0.67	0.072
16	295	59.9	-0.12	$5.22 \times 10^{21}$	0.38	0.074
40	285	112.6	-0.06	$1.08 \times 10^{22}$	0.80	0.065
40	242	88.3	-0.07	$9.65 \times 10^{21}$	0.71	0.057
40	150	20.9	-0.11	$5.58 \times 10^{21}$	0.41	0.023
40	120	9.0	-0.27	$2.29 \times 10^{21}$	0.17	0.025

for this film,  $N^{\text{eff}} = 1/(eR_0) = 1.56 \times 10^{22} \text{ cm}^{-3}$  corresponding to  $n^{\text{eff}} \approx 1.15$  electrons per f.u. (as calculated from 1/8 of the volume of a unit cell =  $7.41 \times 10^{-23} \text{ cm}^{-3}$ ). This result is in agreement with the value found by Feng *et al.*<sup>11</sup> in polycrystalline Fe<sub>3</sub>O<sub>4</sub> thin films, and by Siemons<sup>12</sup> in a single crystal, although in this case he reported a positive  $R_H$  (conduction by holes).

Using the same analysis for the 41 nm thick film, yields  $n^{\text{eff}} \approx 1 \text{ e}^-/\text{f.u.}$ , a value in striking contradiction to results by Lavine *et al.*<sup>13</sup> in a single crystal, and by Reisinger *et al.*<sup>14</sup> in a 40–50 nm thick epitaxial film, who both reported  $n^{\text{eff}} \approx 0.25 \text{ e}^-$  per f.u. In the latter case, the value was extracted from  $\rho_H$  measurements up to 7 T. We indeed find a similar result from the slope of  $\rho_H$  in the low-field data of our 41 nm film ( $R_H = -0.2 \mu\Omega \text{ cm/T}$ , i.e.,  $0.22 \text{ e}^-/\text{f.u.}$ ). Margulies *et al.*<sup>4</sup> demonstrated that thin films are not well saturated up to 9 T, due to the AF interactions in APBs. The description of the conduction in Fe<sub>3</sub>O<sub>4</sub> at RT by Verwey,<sup>15</sup> given in terms of thermally activated hopping between octahedral sites, provides us with a simple interpretation of the experimentally obtained  $n^{\text{eff}} \approx 1 \text{ e}^-/\text{f.u.}$

We have performed the same analysis for the two thinnest samples and obtained decreased values for  $n^{\text{eff}}$ , shown in Table I and Fig. 1. The decrease in  $n^{\text{eff}}$  is due to the density of APBs which varies with  $t^{-1/2}$ .<sup>6–8</sup> This effect could either be extrinsic, caused by a progressive lack of magnetic saturation with decreasing film thickness, or intrinsic, due to the electron localization around the increasing density of APBs.<sup>4,6–8</sup> The calculated Hall mobility for the 200 nm thick film is  $\mu_H = |R_0|\sigma \approx 0.09 \text{ cm}^2/\text{V s}$ , and a similar value of  $\mu_H \approx 0.07 \text{ cm}^2/\text{V s}$  is obtained for the three thinner films.

In Fig. 2 we show the evolution of  $\rho_H(H)$  with temperature for a lithographically patterned 40 nm thick film at temperatures above the Verwey transition (in this film  $T_v = 110 \text{ K}$ ). Complementary to the increase in  $\rho_H$  upon temperature decrease due to the AHE,<sup>9</sup> the absolute value of the high-field slope increases. This results in an evolution of the effective number of carriers from  $\sim 1 \text{ e}^-/\text{f.u.}$  at 285 K, down to  $\sim 0.2 \text{ e}^-/\text{f.u.}$  at 120 K, close to  $T_v$ . Above the Verwey transition, we use the Ihle–Lorenz model to explain the conduction in Fe<sub>3</sub>O<sub>4</sub>,<sup>16</sup> combining small-polaron (SP) band and hopping conductivity. For  $T_v < T < 285 \text{ K}$  we can consider an Arrhenius dependence for  $n^{\text{eff}}(T)$  and  $\mu_H(T)$ . We obtain activation energies  $E_A(n) = 26 \pm 4 \text{ meV}$  and  $E_A(\mu_H) = 20 \pm 5 \text{ meV}$ , both in good agreement with the values reported in Ref. 11. The positive temperature dependence for

$\mu_H$  can be understood by the decrease in the effective mass of the SP with temperature. The sum of both obtained activation energies is approximately 50 meV, which is a typical value for the activation energy of conductivity in this temperature range.<sup>11,13,16</sup> Unfortunately, minimal thermal drifts ( $< 1 \text{ K}$ ) at temperatures near  $T_v$  hinder an accurate determination of the Hall slope, due to the large changes in magnitude that  $\sigma(T)$  and  $\rho_H$  present there.<sup>9</sup> Therefore, we are unable to show the results for the OHE at these temperatures.

In Fig. 3 we show the MR for the lithographically patterned sample, which was used in our HE studies, at temperatures from RT down to 77 K (including  $T < T_v$ ), defined as

$$\text{MR}(\%) = 100 \frac{[R(H) - R_0]}{R_0}. \quad (2)$$

The MR in epitaxial Fe<sub>3</sub>O<sub>4</sub> thin films in moderate magnetic fields has been widely studied.<sup>5,7,8,17</sup> Their results have led to the explanation of the observed negative MR, substantially higher than in single crystals, in terms of spin-polarized transport of electrons through the APBs.<sup>5</sup>

The MR curves are fitted to the model developed in Refs. 7 and 8 for  $T > T_v$ , excluding the range  $H < H_a$  ( $H_a$ : anisotropy field) where MR is quadratic,<sup>7</sup>

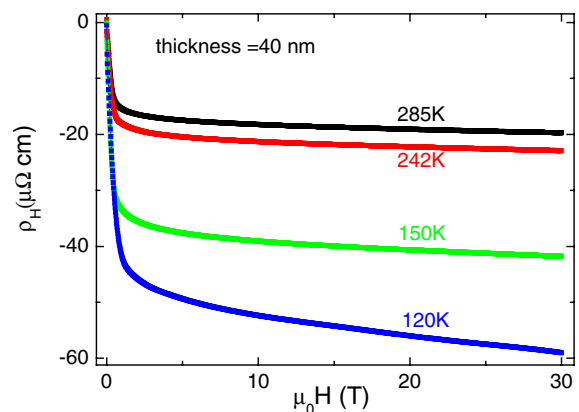


FIG. 2. (Color online) Hall resistivity up to 30 T for temperatures above the Verwey transition, measured in a lithographically patterned 40 nm thick sample.

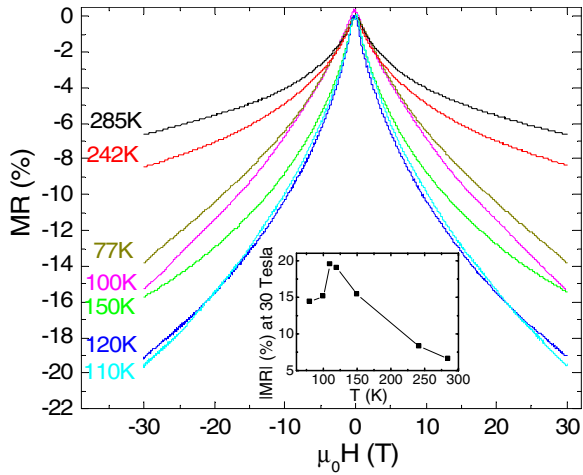


FIG. 3. (Color online) MR up to 30 T in a lithographically patterned 40 nm thick sample for temperatures above and below the Verwey transition, with the magnetic field applied perpendicular to the substrate plane. The inset shows the absolute MR at 30 T as a function of temperature, with a maximum value of 20% at  $T_v$ .

$$\text{MR}(\%) = - \left[ C \frac{M_\infty}{W_{\text{AF}}} \mu_0 H - \left( \frac{M_\infty}{W_{\text{AF}}} \mu_0 H \right)^{3/2} \right] \quad (3)$$

(in which  $\mu_0$  is the vacuum permeability, and  $C$  and  $M_\infty/W_{\text{AF}}$  are fitting constants). Good fits to the experimental data were obtained for the magnetic field range  $H_a < H < H_{\text{max}}$ , with  $H_{\text{max}}$  between 8 and 10 T, depending on the temperature. Fitting MR at 242 K results in  $C = 35.0 \pm 0.1$  and  $M_\infty/W_{\text{AF}} = (0.03 \pm 10^{-4}) \text{ T}^{-1}$ , both values in good agreement with results reported by Ramos *et al.*,<sup>8</sup> who studied the MR up to 7 T. For  $H_{\text{max}} < H < 30 \text{ T}$ , a field range not studied before, the MR is not saturated and becomes more linear with magnetic field than the model's prediction. For  $T < T_v$  the MR changes its shape, and this model is no longer applicable. Additionally, the MR curves are fitted to the model used in Ref. 18 for Zn-doped- $\text{Fe}_3\text{O}_4$  films studied up to 15 T. This model has previously been used for perovskite manganites,<sup>19</sup> in which the MR is explained by the spin-polarized hopping of localized carriers in the presence of magnetic disorder. In this case the MR follows the Brillouin function  $B_J$

$$\text{MR}(\%) \approx - \beta \frac{B_J(\mu_{\text{eff}} \mu_0 H / k_B T)}{k_B T}, \quad (4)$$

where  $\mu_{\text{eff}}$  is the effective magnetic moment of the local spins and  $J=2$ . The model is in good agreement with our results for temperatures above  $T_v$  and fields lower than 15 T. We obtain  $\mu_{\text{eff}} \approx 90 \mu_B$ , which is similar to the value found in Ref. 18, in which the MR was assigned to small misalignments of the spins between  $\sim 3$  unit cell sized clusters. Below  $T_v$  the model fits well our data in the complete field range, since the conduction becomes more localized due to a variable-range-hopping mechanism,<sup>16</sup> yielding  $\mu_{\text{eff}} \approx 10 \mu_B$ . This value is substantially smaller than for  $T > T_v$ , and suggests that only 2 to 3  $\text{Fe}^{2+}$  ions would contribute to the MR, casting doubts about the suitability of the model in this case.

The magnitude of the MR at maximum field as a function of the temperature is shown in the inset of Fig. 3, presenting a maximum at  $T_v$  corresponding to  $\sim 20\%$ . This peak in  $T_v$  has previously been observed in single crystals,<sup>20</sup> and both polycrystalline<sup>11</sup> and epitaxial<sup>17</sup> thin films, in which differences in magnetocrystalline anisotropy play an important role.<sup>17</sup>

Our experiments provide a wide experimental picture of the MR in epitaxial (001)  $\text{Fe}_3\text{O}_4$  thin films, where the extrinsic effect of APBs and intrinsic phenomena intermix, disclosing an overall temperature-dependent MR, which does not saturate up to 30 T. A full understanding of this complex scenario is beyond the scope of this Letter.

In summary, we have measured the HE and the MR in epitaxial  $\text{Fe}_3\text{O}_4$  thin films on  $\text{MgO}(001)$  for magnetic fields up to 30 T. At these high fields the thickest samples are magnetically saturated, providing the possibility to separate the OHE from the anomalous one. We derive that  $\sim 1$  electron per f.u. contributes to the conduction at room temperature. Thinner samples have a smaller effective density of conducting electrons, as a consequence of the APBs. The density of electrons as well as the Hall mobility fit well to an Arrhenius thermal dependence. The MR is not saturated in the high magnetic fields we applied, and presents a peak at the Verwey transition of  $\sim -20\%$  at maximum field.

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