Magnetoresistance and magnetic properties of epitaxial magnetite thin films

G. Q. Gong
Department of Physics, Brown University, Providence, Rhode Island 02912

A. Gupta
IBM T. J. Watson Research Center, Yorktown Heights, New York 10598

Gang Xiao
Department of Physics, Brown University, Providence, Rhode Island 02912

W. Qian and V. P. Dravid
Department of Materials Science and Engineering, Northwestern University, Evanston, Illinois 60208

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The magnetotransport and magnetic properties of epitaxial Fe_3O_4 thin films grown on (001)-oriented MgO substrates by pulsed-laser deposition have been investigated. The magnetoresistance (MR) exhibits a peak around the Verwey transition (T_v) as has also been reported previously for single crystals. Additionally, we have observed that the MR increases monotonically below 100 K with decreasing temperature. MR values as high as 32% have been observed for a 6600-Å-thick film at 60 K under a 4-T field. The enhanced low-temperature MR is attributed to a magnetic-field-dependent activation energy for electron hopping transport. [S0163-1829(97)01234-4]

The Verwey transition in magnetite (Fe_3O_4) has attracted extensive research interest since its discovery more than fifty years ago.[1] This unusual metal-insulator transition is characterized by a decrease in conductivity by about two orders of magnitude at the transition temperature $T_v \sim 120$ K. Although it is generally accepted that the transition is due to the ordering of the Fe^{3+} and Fe^{2+} ions,[1,2] the mechanism governing the transport and magnetic properties of this material still remains unclear. The magnetotransport behavior of Fe_3O_4 has so far been investigated only by a few groups.[3,4] Early magnetoresistance (MR) studies by Feng *et al.* on polycrystalline thin film samples revealed a negative MR in the temperature range of 105–250 K, reaching 7.5% at about 130 K and 2.3 T.[3] A more recent work on single-crystal samples showed that the MR has a sharp peak around T_v, with a maximum value of 17% under 7.7 T and decreases very rapidly as the temperature deviates from T_v.[4] This MR peak has been explained as resulting from a discontinuous change of thermodynamic quantities accompanying the first-order Verwey transition. It should be noted that the single-crystal measurements[3] have been carried out only in the neighborhood of T_v, covering a small temperature interval of only 114–126 K.

We report the magnetotransport properties of epitaxial Fe_3O_4 films grown on MgO substrates. Around T_v, we have observed a similar peak in MR as reported for single crystals. Moreover, we find that the MR in these films exhibit a monotonic increase with decreasing temperature below 105 K, reaching a value of 32% at 60 K under 4-T field for a 6600-Å-thick film. Our analysis has shown that the cause for the enhanced MR is due to a magnetic-field-induced reduction in the activation energy of the electron-hopping conduction. We have also studied the magnetization of the films as a function of temperature and magnetic field.

The magnetite films have been grown on (001)-oriented MgO substrates using the pulsed-laser deposition technique. The Fe_3O_4 target used for the ablation has been prepared by a standard solid-state reaction method. Resistivity measurement as a function of temperature of the target material shows a very sharp Verwey transition around 119 K, indicating a good oxygen stoichiometry. A focused frequency-tripled Nd:YAG laser (355 nm) has been used for ablation, with a pulse energy of ~ 330 mJ and a fluence of ~ 2 J/ cm^2 at the target. The films have been deposited at a substrate temperature of 350 °C in vacuum. Following deposition, the films are cooled down to room temperature at a rate of 15 °C/min. The film thicknesses have been determined using Rutherford backscattering spectroscopy. In this paper we report the results for two thin film samples with thickness of 6600 and 1500 Å.

The Fe_3O_4 films grow epitaxially on (001) MgO substrate as evidenced by x-ray and transmission electron microscopy (TEM). Figure 1 shows the high-resolution planar view of a Fe_3O_4 film and the corresponding electron-diffraction pattern, with the beam aligned along the [001] direction. The film exhibits a cubic spinel structure with the ⟨100⟩ and ⟨010⟩ axes epitaxially aligned with the respective cubic axes of the substrate. The lattice parameters of Fe_3O_4 (~ 8.4 Å) are almost exactly double of those for MgO. Crossectional micrographs (not shown) have further confirmed the epitaxial growth of the film with relatively few defects in the normal direction, and have shown that the substrate/film interface is very abrupt.

The transport measurements have been carried out in a superconducting magnet with field up to 4 T. Figure 2 displays the resistivity as a function of temperature for the two samples together with the magnetization data measured at 300 Oe for the 6600-Å film. From the transport data the

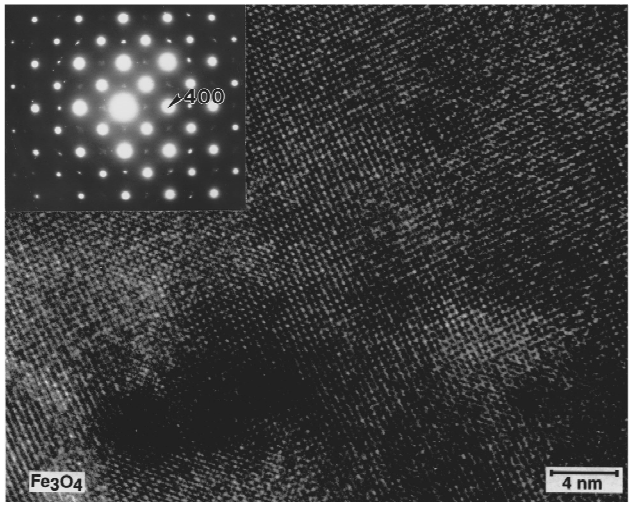

FIG. 1. Plan-view high-resolution electron micrograph of a Fe_3O_4 film with [001] zone axis. The inset shows the corresponding electron-diffraction pattern.

transition temperature (T_v) is determined to be about 120 K for both samples. The magnetization measurement gives a T_v of 123 K for the thick film. Both films exhibit a broadened transition as compared to measurements made on bulk samples. In particular, the thin film's transition is broader than that for the thick film. This is possibly due to the residual strain in the films resulting from the lattice mismatch with the substrate. Previous studies on bulk single crystals have shown that hydrostatic pressure also results in a broadening of the transition and a decrease in T_v.[5] Our measurement of a 670-Å thin film gives a transition temperature of 116.5 K, suggesting that T_v decreases with film thickness. This is also consistent with the results reported by Mangulies *et al.*[6]

As reported by previous investigators, the transport properties of magnetite below T_v is highly dependent on the history of the sample.[7] Thus, the magnetoresistance depends not only on whether the sample is field cooled (FC) or zero-field cooled (ZFC) through the transition, but also on its prior

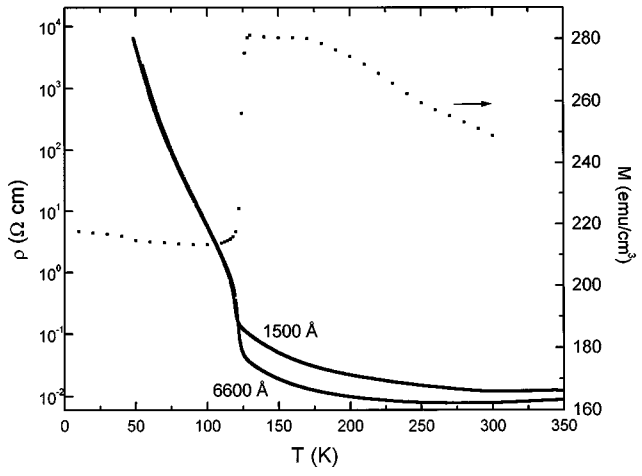

FIG. 2. The resistivity as a function of temperature for 1500-Å- and 6600-Å-thick Fe_3O_4 films in the range of 60–350 K. The magnetization as a function of temperature is also shown for the 6600-Å film measured in a field of 300 Oe.

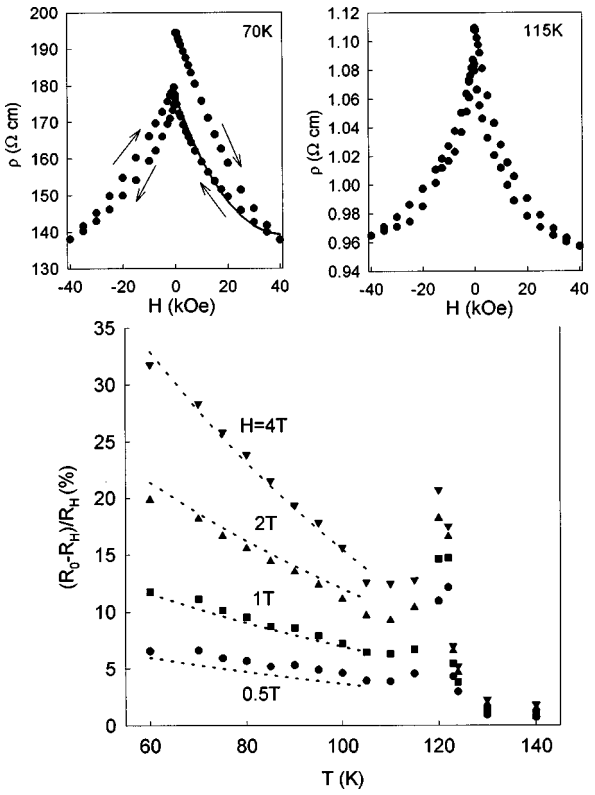

FIG. 3. Magnetoresistance at $H=0.5$, 1, 2, 4 T in the temperature range 60–140 K for the 6600-Å-thick Fe_3O_4 film along with its field dependence at two fixed temperatures. The dotted lines are simulations using Mott's formula, as described in the text.

magnetic state. To be consistent, we have adopted the following procedure for the magnetotransport measurements of all our films. The sample was initially ZFC from 300 K to the target temperature for the field-dependence measurement at this temperature. Subsequently, the sample was warmed up to 300 K to eliminate the history effect and again ZFC to the next measurement temperature. Since our measurements have been done in a region where the resistivity is very sensitive to temperature changes, extra care had to be taken to ensure that the temperature fluctuations remained less than ± 0.02 K.

Figure 3 (top) shows the field dependence of the 6600-Å film at two different temperatures. The hysteresis effect during the measurement cycle is quite apparent. At the starting point, the film has the highest resistivity in zero field. As the field is increased to 4 T and then returned to zero, the resistivity does not return to its original value, but settles at a smaller value. As the field is again increased up to 4 T in the other direction, the resistivity data become more reproducible as the field is swept back and forth. In order to calculate the MR, we have taken the values on the return curve where the reproducibility is within 0.4%. The MR ratio for the different fields are defined according to $\Delta R/R=(R_0-R_H)/R_H$, where R_0 is the zero-field resistance and R_H is the resistance in the applied field H.

Figure 3 (bottom) shows the MR data for the 6600-Å sample at 0.5, 1, 2, and 4 T. The peaks around T_v for the different fields are consistent with the single crystal results.[4] However, the MR peak is observed over a wider temperature range, possibly because of the broadened transition. Above

T_v the MR decreases rapidly and remains at a level below 2% at temperatures above 150 K. On the other hand, below the transition, the MR first decreases, as in the single-crystal case, and then shows a dramatic upturn below ~ 105 K. Apparently, some mechanism other than the suggested thermodynamic one governing the behavior in the neighborhood of T_v is effective in the low-temperature regime. As the films are cooled to 60 K in 4-T field, the MR reaches 18% for the 1500-Å film and 32% for the 6600-Å film, respectively, and shows no sign of saturation.

Our transport data below the Verwey transition can be fitted to Mott's formula for the variable range-hopping mechanism, as has been shown by Drabble *et al.*[8] for single crystals;

$$\rho = A \exp(B/T)^{1/4}, \tag{1}$$

where ρ is the resistivity and B is the activation energy (in units of K). Our fit to the zero-field transport data gives $B = 1.61 \times 10^8$(K). Phenomenologically, when the field effect is small, the field dependence of the Mott activation energy can be represented in the Taylor series as

$$B = B_0 - \alpha(T)H + \beta(T)H^2, \tag{2}$$

while the change in the pre-exponential factor A should be small enough to neglect. The signs before the first-order and second-order expansion terms have been chosen such that α and β would be positive. Substituting Eq. (2) into Eq. (1), we can fit the ρ vs H data on the return path at a fixed temperature, as presented in Fig. 3 for $T = 70$ K. This fitting procedure has been repeated for each measurement temperature up to 105 K. The two parameters $\alpha(T)$ and $\beta(T)$ are found to be only slightly depend on temperature, varying in the range of $\pm 15\%$ of their values at 105 K. It is found that in the field range of the measurement, the second term of Eq. (2) is an order of magnitude smaller than B_0, while the third term is still another order of magnitude smaller than the second term. This gives the self-consistency check of the expansion in Eq. (2). The MR calculated using Eqs. (1) and (2) are plotted as dotted lines in Fig. 2, and are seen to be in good agreement with the experimental data. This phenomenological model does not account for any hysteresis or history effect as is experimentally observed. This is likely caused by the twinning which occurs during zero-field cooling through the Verwey transition,[7,9] i.e., the orthorhombic axes of the low-temperature phase do not have the same orientation throughout the film. Thus, because of the transport anisotropy in Fe_3O_4, some history effect will set in if the local axes can be switched by applying a field.

Finally, we briefly discuss the magnetic properties of the magnetite films. The magnetization has been measured using a Quantum Design superconducting quantum interference device magnetometer in a magnetic field up to 5.5 T. Figure 4 displays the in-plane hysteresis loops measured at two different temperatures for the 6600-Å film. The saturation moment (M_s) is 458 emu/cc for the thick film and 427 emu/cc for the thin film at 90 K, while at 300 K the M_s for the

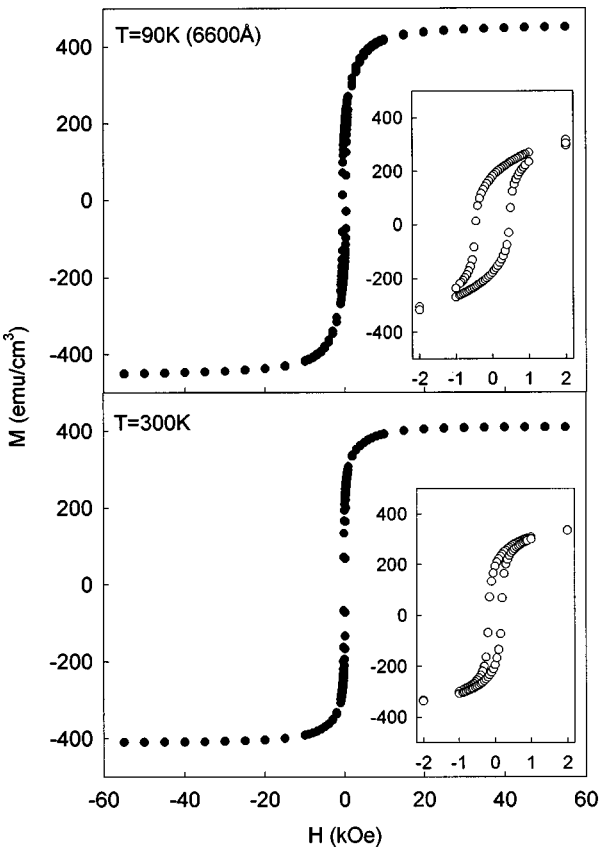

FIG. 4. Magnetization hysteresis loops at $T = 90$ and 300 K for the 6600-Å film with field scans up to 5.5 T. The insets show the expanded hysteresis behavior at low fields.

6600-Å film is 415 emu/cc, less than the reported bulk value of 471 emu/cc.[10] The even lower M_s value for the thinner film suggests that strain may play a role in the reduction of magnetization. It has also been suggested that the reduction may be caused by a thin layer of α-Fe_2O_3 present on the surface.[11] The insets show the expanded low-field hysteresis behavior at the two temperatures. The coercivity increases from 200 to 470 Oe, going from 300 to 90 K.

In summary, we have grown high-quality, epitaxial Fe_3O_4 films on (001) MgO substrates and measured their magnetotransport and magnetic properties. A sharp peak in the MR is observed at the Verwey transition. Furthermore, a monotonic increase in the MR with decreasing temperature has been noted below 105 K and reaches 32% at 4 T. The latter has been phenomenologically attributed to the field dependence of the activation energy for hopping conduction below the transition temperature, while the physical mechanism responsible for the unusual MR effect remains to be understood.

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