SCANNING TUNNELING SPECTRA AND LOW ENERGY ION SCATTERING STUDIES OF THE VERWEY TRANSITION IN MBE Fe_3O_4 (100) THIN FILM

N.-T.H. Kim-Ngan, W. Soszka*

Institute of Physics, Pedagogical University
Podchorążych 2, 30-084 Kraków, Poland

and M. Hietschold

Institute of Physics, Chemnitz University of Technology, 09107 Chemnitz, Germany

(Received December 27, 2000)

The (100) surface of magnetite Fe_3O_4 thin film was studied by a UHV low-temperature scanning tunneling microscope and by an ion scattering spectroscopy. The tunneling spectra revealed a widening of the gap with decreasing temperature, which may be related to the metal–insulator phase transition in this material. A strong effect of this phase transition on ion scattering from such a surface was observed. The temperature dependence of the scattered ion yield, $R^+(T)$, revealed two minima at around 100 K and at 125 K under Ne^+ bombardment with the primary energy up to 6 keV. The disappearance of the high-temperature minimum at a bombarding energy of 6.5 keV gave a further evidence for the ion velocity dependence of the character of the $R^+(T)$ curve, which has been first observed for a MBE Fe_3O_4 (111) film surface.

PACS numbers: 61.16.Ch, 61.18.Bn, 71.30.+h

1. Introduction

Magnetite, Fe_3O_4, has a cubic inverse spinel structure with a lattice constant of 8.3967 Å. The valence structure is $[Fe^{3+}](Fe^{3+}Fe^{2+})(O^{2-})_4$, where one half of the Fe^{3+} ions occupies the tetrahedrally-coordinated sites (A-sites) and the other half together with the Fe^{2+} ions are located in the octahedrally-coordinated sites (B-sites). Electron hopping between neighboring Fe^{2+} and Fe^{3+} on B-sites is the reason for the good electrical conductivity at room temperature. Upon cooling, magnetite undergoes a metal–insulator phase transition (MIT), i.e. the Verwey

*corresponding author; e-mail: wsoszka@wsp.krakow.pl

transition, at a temperature in the range of 115–125 K, where the electron hopping is frozen and the crystal becomes insulating [1].

Recently, increasing attention has been focused on the growth and characterizations of epitaxial (MBE) Fe_3O_4 thin films. The surface topology has been intensively investigated by scanning tunneling microscopy (STM) on a number of different surfaces of single crystals and MBE thin films of magnetite [2–8]. On the other hand, low energy ion scattering (LEIS) technique (or ion scattering spectroscopy (ISS)) has been proved to be quite a sensitive technique for solid surface analysis especially for the general phenomena of surface phase transitions [9, 10]. Recently, this technique has been used for investigations of the MIT of several magnetite surfaces [11–13]. Distinct anomalies around 100–130 K in the temper-

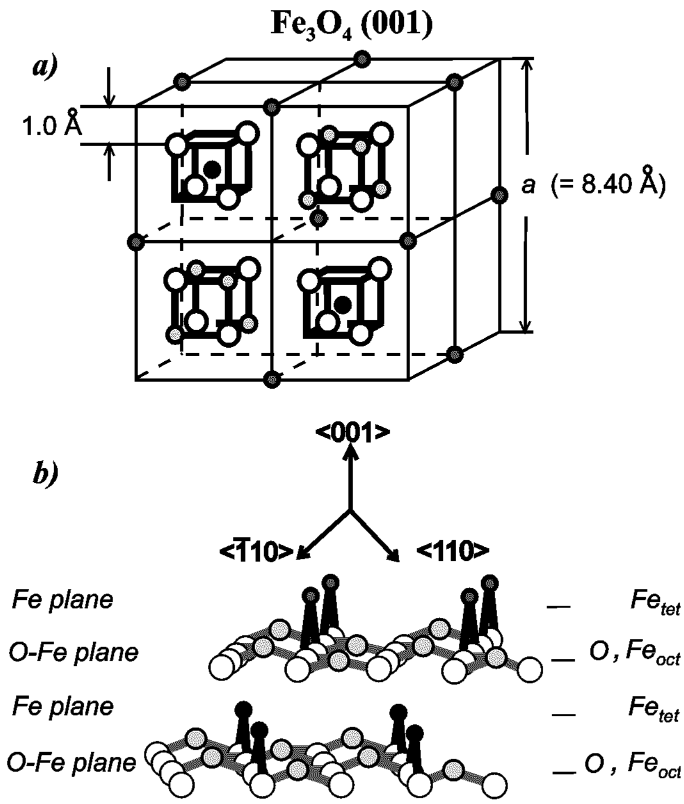


Fig. 1. (a) The cubic inverse spinel structure of Fe_3O_4. For clarity, the atoms are shown only in the front half. Oxygen anions are shown as big open spheres, Fe atoms in octahedral sites as small shaded spheres and those in tetrahedral sites as small solid spheres. (b) The stacking sequence of different (100) layers in magnetite. The crystallographic directions of magnetite are shown. The surface semi-channel with the channel height of 1 Å exists on magnetite surface.

ature dependence of scattered ion yield, $R^+(T)$, have been observed. Moreover, the character of the $R^+(T)$ curve obtained for MBE Fe_3O_4 (111) film surface was found to depend on the velocity of bombarding ion [13].

In this paper we present the STM and ion scattering measurements performed on a (100) surface of MBE Fe_3O_4 thin film. In the bulk, there are two different (100) planes; one built up by the octahedrally-coordinated iron and oxygen atoms and the other one by tetrahedrally-coordinated iron atoms, as shown in Fig. 1. We notice here also the semi-channel formed by Fe ions on the surface (Fig. 1b) favorable for the zigzag collisions of ions [13]. We have focused on investigating the temperature dependence of the tunneling spectra and of the energy spectra of ions scattered from such a surface. It was expected that some visible change would be observed around the Verwey transition temperature.

2. Experimental

The sample discussed in this paper is 200 Å thick Fe_3O_4 film grown on MgO (001) substrate in a UHV MBE system. The film structure was controlled by a standard four-grid low-energy electron diffraction – Auger electron spectroscopy (LEED-AES) spectrometer. Before deposition, the MgO substrate was annealed for 20 min at 600°C. The Fe_3O_4 layers were deposited by evaporation of ^{57}Fe in O_2 ambient pressure at the rate of 14 Å/min and at the substrate temperature of 250°C. The ^{57}Fe isotope has been used as a probe for conversion electron Mössbauer spectroscopy (CEMS). The *in situ* LEED image of this Fe_3O_4 (100) thin film revealed a clean, well-ordered (100) surface [14]. The temperature dependence of CEMS spectra taken *in situ* reflected a good stoichiometry of the thin film. Namely, the spectra at room temperature could be fitted with two magnetic components of "2.5+" and "3+" with the intensity ratio of nearly 1:2, and the drastic change of the spectra related to the Verwey transition occurred at a temperature of 130 K. X-ray photoelectron spectroscopy (XPS) measurements were performed using a spectrometer equipped with Mg K_α radiation source ($h\nu = 1253.6$ eV). The XPS spectrum of the MBE (100) film of magnetite showed the Fe $2p$ lines and O $1s$ transition, similar to that of MBE (111) film and for a single crystal sample. A spin–orbit splitting of the Fe $2p$ core level into $2p_{1/2}$ and $2p_{3/2}$ components was found. The obtained binding energies were in good agreement with those reported earlier [15].

STM investigations have been carried out in an Omicron low-temperature instrument, operating at a base pressure of 1×10^{-10} mbar. Electrochemically etched tungsten tips were used. Beside of taking STM images the collection of local current-versus-voltage $I(U)$ curves (STS) was of special interest. All curves were measured with the feedback loop off. To allow quantitative comparison of the spectra, the $I(U)$ curves at different temperatures were recorded at the same pre-selected tunnel barrier width. The spectral current $1/f$ noise density was detected with a lock-in amplifier at a frequency of 11 kHz. It was recorded as a function of tunneling voltage with the same tip position on the sample surface and at different temperatures.

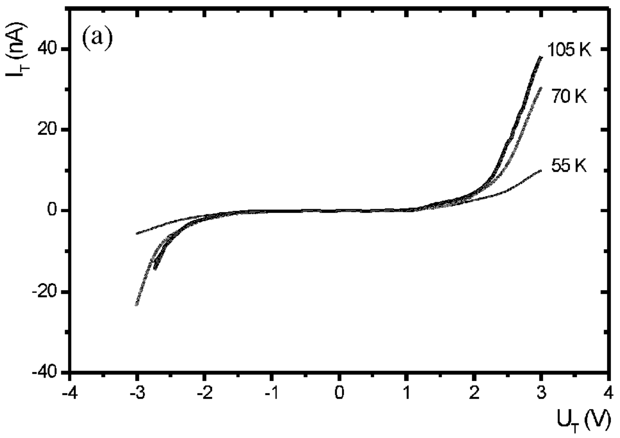
The ion-scattering experiments were performed using a standard ISS in the temperature range of 85–300 K. A small-angle geometry has been developed for ion-scattering experiments on the thin-film surfaces, as described earlier [13]. There was less damage caused by the ion beam to the film surface due to the large footprint at small angles. He^+ and Ne^+ ion beams at energies between 5.0 keV and 6.5 keV with an energy step of 0.5 keV were used. We optimized the scattering peak at grazing angles for the temperature-dependent investigations. Such a peak was found to be the most suitable since it was strong enough and the bombarding-time effect on the thin-film surface was weakest for this position [13].

3. Results and discussions

STM image of the MBE Fe_3O_4 (100) surface at room temperature showed a rough surface with the presence of several small features that were supposed to be contaminations. Our sample had to be exposed to air for some time. Possibly, the film surface stoichiometry has changed as well [16]. There is always the question for an *ex situ* STM experiment whether the obtained STM images represent the actual surface during growth. However, multiple steps of about 2 Å high between large terraces were observed. This step height is corresponding to 1/4 of the bulk spinel lattice constant of magnetite. The observed surface step might correspond to the distance between two adjacent planes of oxygen atoms or equivalently of iron atoms.

Figure 2 shows the local tunneling spectra (STS) recorded at the same selected tunnel barrier width and at different temperatures. The $I(U)$ curves are significantly non-ohmic. The tunneling current I_{T} was close to zero in a voltage range between −2.1 V to +0.9 V. There was almost no change in the curve shape with decreasing temperature down to 70 K. Some inner structure in the $\mathrm{d}I/\mathrm{d}U$ versus U_{T} curves, however, was revealed at this temperature (Fig. 2b). A visible widening of the gap was observed at 55 K. We assumed that for the tunneling current spectra, a visible gap change related to the energy gap upon the charge-ordering transition in magnetite can be observed when the electron hopping is completely frozen out, i.e. when the sample is in a complete insulator state.

The intensity of the $1/f$ current noise measured as a function of the tunneling voltage is shown in Fig. 3. At room temperature, i.e. in the metallic phase, no tunneling voltage dependence was observed. At low temperature, i.e. in the insulator phase, the noise exhibited a much lower background. Moreover, it was increased with increasing tunneling voltage. Until now there are only two factors taken into account for explaining the origin of the STM $1/f$ spectra: (1) the fluctuation of the tunneling barrier height affected by physical conditions of the surface, and (2) the fluctuation of the phonon density [17]. However, for magnetite the fluctuations of the density of carriers in a critical network of conduction can play an important role [18]. Namely, when the number of carriers involved in the hopping conduction decreases, the conductivity becomes more sensitive to the fluctuation of the number of charges in the network; it provokes an increase in the $1/f$ noise level.



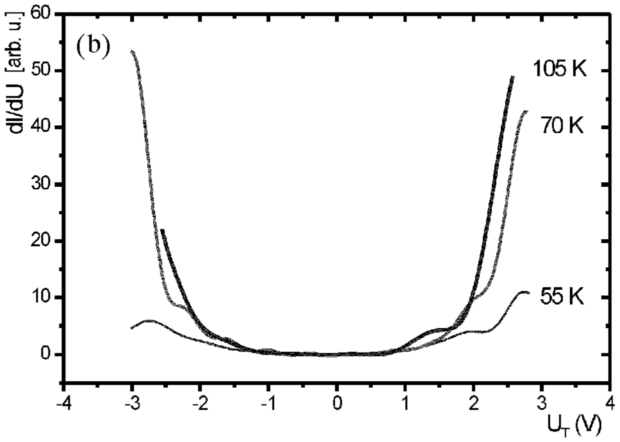


Fig. 2. Tunneling spectra (a) and local conductivity spectra (b) of MBE Fe_3O_4 (100) film at low temperatures. A widening of the gap was observed at 55 K.

The Verwey transition of the MBE Fe_3O_4 (100) film surface has been thoroughly investigated by ion scattering experiments. In this paper we focus on the ion scattering data under Ne^+ bombardments. The energy spectra of ions scattered from such a surface under 5.0, 5.5, 6.0, and 6.5 keV Ne^+ bombardments at 87 K, plotted in a relative energy scale of E_1/E_0 (where E_1 is the energy of the scattered ions and E_0 — the primary energy), are shown in Fig. 4. Two maxima were observed, which became more visible with increase in the bombarding energy. For energies higher than 5.0 keV, the maximum at the low-energy side (the low-energy maximum) increases enormously with increasing primary energies, while no change in the intensity of the maximum at the high-energy side was observed. The minimum between two maxima was found to locate at the same relative energy loss ratio, E_1/E_0, of 0.865, as shown by the vertical line in Fig. 4. In the case of ion scattering from the cleaved surface and (111) film surface, only broad scattering peaks have been observed [12, 13]. The broad scattering peak is

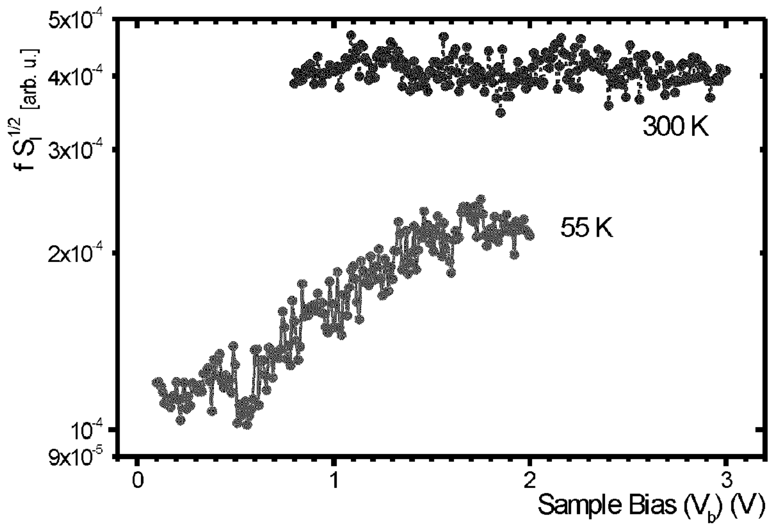


Fig. 3. Sample bias dependence of the noise intensity for MBE Fe_3O_4 (100) film measured at room temperature (i.e. in the metal phase) and at 55 K (i.e. in the insulator phase).

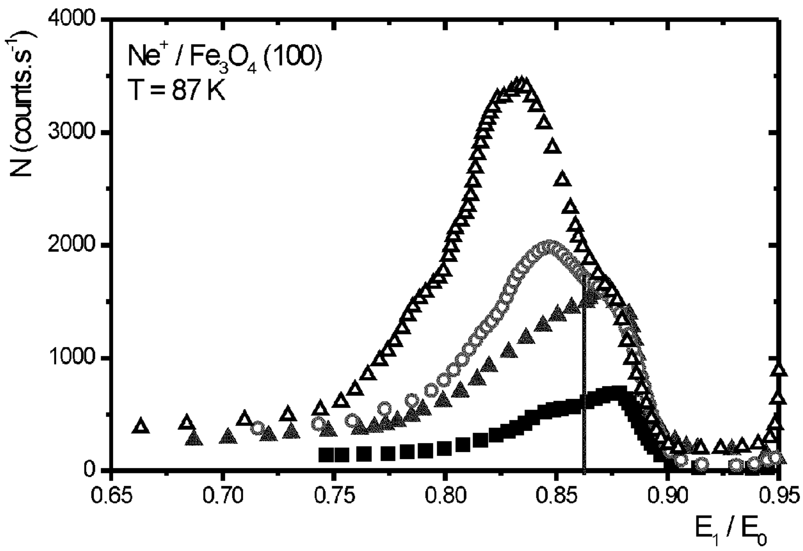


Fig. 4. Energy spectra of 5.0 keV, (■), 5.5 keV (full triangle), 6.0 keV (∘), and 6.5 keV (△) Ne^+ ions scattered from MBE Fe_3O_4 (100) film surface at grazing angles and at the target temperature of 87 K. The vertical line shows the position of the minimum between two maxima, which is at the same relative energy loss ratio, E_1/E_0, of 0.865 for different bombarding energies.

always considered as a superposition of many scattering peaks in which each one is with different scattering configuration (sub-scattering peak), i.e. each at different scattering angles. We assumed that due to the effect of neutralization some of the sub-scattering peaks at certain scattering angles may disappear resulting in the minimum observed in the scattering peak of the (100) film surface. Moreover, this minimum became more visible with increase in the primary energy. Since the shadow cone is decreased at larger bombarding energies, probably the ions can go deeper into the semi-channel and reach the bottom. As a consequence, the neutralization by the surface semi-channel became more distinct with increasing primary energies. Although beyond the scope of this article, it would be interesting to perform the measurements of the energy spectra of neutrals, by a time of flight (TOF) spectrometer for instance. The comparison of energy spectra of neutral scattered particles with ion scattering spectra would provide information on neutralization.

Energy losses up to 1 keV were found, similar to that for the single crystal surface and MBE (111) film surface of magnetite. Such a large energy loss for small angle symmetry has been well explained in the framework of the zigzag collisions of ions from the semi-channel surface (see e.g. Ref. [12]). The channel height in this case, i.e. for the (100) magnetite surface, is 1 Å.

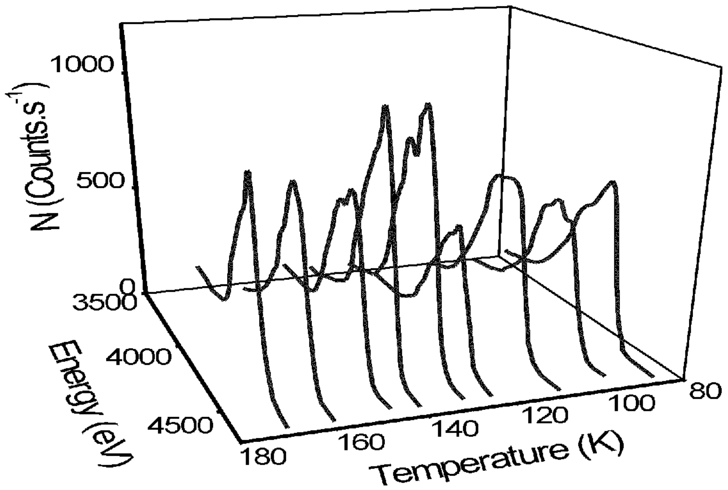


Fig. 5. Temperature dependence of the energy spectra of 5.0 keV Ne^+ ions scattered from MBE Fe_3O_4 (100) film surface at grazing angles. For clarification of the minima and maximum, results were shown by smoothed curves through the data points.

No change in the position of the scattering peaks with temperature was observed. However, a strong temperature-dependence of the peak intensity was found. Figure 5 shows the temperature dependence of the energy spectra of ions scattered from MBE Fe_3O_4 (100) film surface under 5.0 keV Ne^+ ion bombardment. A decrease in the peak intensity around 100 K and then again around 125 K was found. Above these temperatures, it increases and reaches a maximum around 135 K and then gradually decreases with increasing temperature. Such a temper-

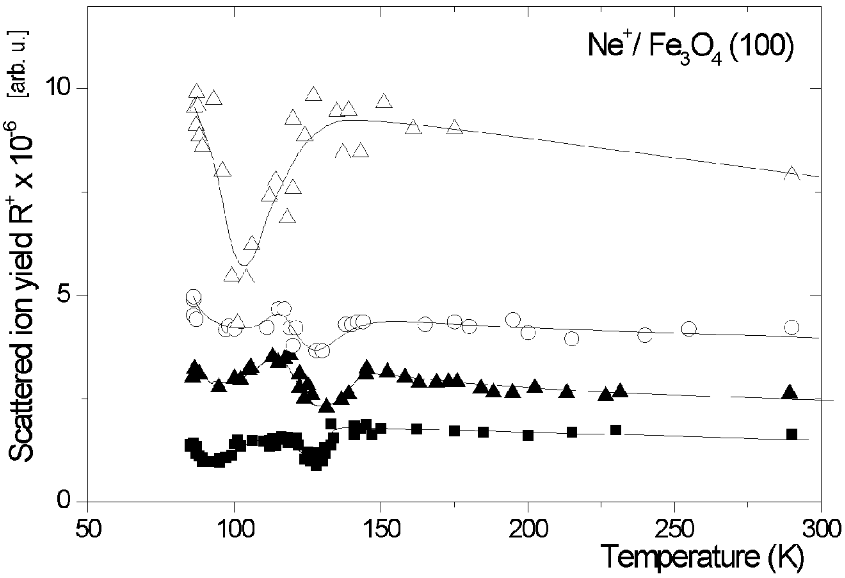


Fig. 6. Temperature dependence of the scattered ion yield, $R^+(T)$, for 5.0 keV (■), 5.5 keV (full triangle), 6.0 keV (○), and 6.5 keV (△) Ne^+ ions scattered from MBE Fe_3O_4 (100) film surface. Solid curves serve to guide the eyes.

ature effect on the scattered ions in this temperature can be seen clearly in the $R^+(T)$ curves, as shown in Fig. 6. Two minima, one located around 100 K and the other one at around 125 K, were observed for the $R(T)$ curves obtained at the bombarding energy of 5.0, 5.5, and 6.0 keV. The scattered ion yields decrease by about 20% of magnitude at the minimum. Above 150 K, they were almost constant with temperature. For the 6.5 keV Ne^+ ion bombardment, only one deep minimum existed at around 100 K. Moreover, a bigger decrease in the scattered ion yield, by twice of magnitude at the minimum, at the transition point was observed. Those anomalies were certainly related to the Verwey transition of MBE Fe_3O_4 (100) film surface. The strong effect of MIT on the ion scattering from such a surface, similarly to other investigated surfaces of magnetite, have been considered as the results of:

1) the change of the neutralization probability of incoming and outgoing ions,

2) the change of the crystal transparency, and

3) the existence of the so-called ionizing trajectories, i.e. trajectories along which the particles become re-ionized (in other words, ion trajectories containing ionizing collision).

The last one was found to play an important role in the phase transition region. A very narrow choice of ionizing trajectories was found in case of the small angle geometry. Any small influence on such a narrow group of ion trajectories can cause a large change in the scattered ion yield [12].

The character of the temperature-dependent scattered ion yield curve of the Fe_3O_4 (100) film surface at the same bombarding energy differs from that of the (111) one. For both surfaces, however, we have observed the change of the character of the $R^+(T)$ curve at higher primary energies. Namely, for the (111) film surface, only one broad minimum in the $R(T)$ curves around 125 K was observed at low energies. Under the 6.5 keV Ne^+ bombardment this minimum has disappeared and only a very fast decrease in the scattered ion yield around 100 K was observed. For the latter one (i.e. for the (100) film surface) two minima were found. Under 6.5 keV Ne^+ ion bombardment only the minimum around 100 K was left. Thus the change of the character of the ion scattering variation with temperature was indicated by the disappearance of the minimum around 125 K. Detailed analysis of ion scattering from the (111) film surface has shown that the character of the scattered ion yield curve is dependent on the velocity of the incoming ions, indicating that the neutralization from the resonant and Auger processes plays an important role [13]. The existence of the minimum in the energy spectra and the disappearance of the high-temperature minimum in case of 6.5 keV Ne^+ ion scattering from the (100) film surface has given a further proof for such a neutralization effect. For basic neutralization mechanisms the probability of remaining as an ion is [19] $P_{\text{ion}} = \exp(-A/aV_\perp)$, where $V_\perp$ is the component of the ions velocity perpendicular to the surface. A and a are parameters depending on the specific process. Thus the loss of ions from the ultimate scattered signal is proportional exponentially to the reciprocal of $V_\perp$. In case of the small-angle geometry, where the perpendicular component of the velocity, $V_\perp$, is small, the remaining-ion probability should be very sensitive to the change of such a component. An increase in the ion velocity implies an increase in the remaining-ion probability. Such an increase can cause the disappearance of the minimum at 125 K for both two thin film surfaces.

4. Summary

The primary temperature dependence investigations of the tunneling spectra of the MBE Fe_3O_4 (100) thin film have revealed a widening of the gap at 55 K, i.e. at temperature lower than the Verwey temperature defined from other experiments. The ion scattering experiment on such a surface has revealed a large effect from the Verwey transition. Namely, two minima respectively at around 100 K and at 125 K were observed in the temperature dependence of the scattered ion yield, $R^+(T)$. The disappearance of the high-temperature minimum under 6.5 keV Ne^+ ion bombardment was an evidence of the character change of the $R^+(T)$ curve, which can be explained in the framework of the resonant and the Auger neutralization.

Acknowledgments

One of the authors (N.-T.H. Kim-Ngan) would like to thank Prof. J. Korecki and Mr. B. Handke (Department of Solid State Physics, Faculty of Physics and Nuclear Techniques, University of Mining and Metallurgy, Kraków, Poland) for supplying the MBE samples of magnetite and for their fruitful discussions. The helpful assistance of Dr. F. Müller and Mr. M. Lackinger (Institute of Physics, Chemnitz University of Technology) with STM investigations are highly acknowledged.

References

[1] N. Tsuda, K. Nasu, Y. Yanase, K. Siratori, in: *Electronic Conductions in Oxides*, Vol. 94, Eds. M. Cardona, P. Fulde, K. von Klitzing, H.-J. Queisser, Springer-Verlag Series in Solid-State Sciences, Springer, Berlin 1990, p. 207.

[2] R. Wiesendanger, I.V. Shvets, J.M.D. Coey, *Vac. Sci. Technol. B* **12,** 2118 (1994); R. Wiesendanger, I.V. Shvets, D. Bürgler, G. Tarrach, H.-J. Guntherodt, J.M.D. Coey, S. Gräser, *Science* **255,** 583 (1992).

[3] R. Jansen, V.A.M. Brabers, H. Van Kempen, *Surf. Sci.* **328,** 237 (1995).

[4] A.R. Lennie, N.G. Condon, F.M. Leibsle, P.W. Murray, G. Thornton, D.J. Vaughan, *Phys. Rev. B* **53,** 10244 (1996).

[5] N.G. Condon, F.M. Leibsle, T. Parker, A.R. Lennie, D.J. Vaughan, G. Thornton, *Phys. Rev. B* **55,** 15885 (1997).

[6] W. Weiss, A. Barbieri, M.A. Van Hove, G.A. Somorjai, *Phys. Rev. Lett.* **71,** 1848 (1993).

[7] J.M. Gaines, P.J.H. Bloemen, J.T. Kohlhepp, C.W.T. Bulle-Lieuwma, R.M. Wolf, A. Reinders, R.M. Jungblut, P.A.A. van der Heijden, J.T.W.M. van Eemeren, J. aan de Stegge, W.J.M. de Jonge, *Surf. Sci.* **373,** 85 (1997) and references therein.

[8] J.M. Gaines, J.T. Kohlhepp, J.T.W.M. van Eemeren, R.J.G. Elfrink, F. Roozeboom, W.J.M. de Jonge, *Mater. Res. Soc. Symp. Proc.* **474,** 191 (1997).

[9] S. Speller, M. Schleberger, H. Franke, C. Muller, W. Heiland, *Mod. Phys. Lett. B* **8,** 491 (1994) and references therein.

[10] E. van de Riet, H. Derks, W. Heiland, *Surf. Sci.* **234,** 53 (1990).

[11] N.-T.H. Kim-Ngan, W. Soszka, *J. Magn. Magn. Mater.* **202,** 327 (1999).

[12] W. Soszka, N.-T.H. Kim-Ngan, *Surf. Sci.* **441,** 331 (1999).

[13] N.-T.H. Kim-Ngan, W. Soszka, D. Sitko, G. Jagło, J. Korecki, B. Handke, *Nucl. Instrum. Methods Phys. Res. B* **164-165,** 992 (2000).

[14] W. Soszka, N.-T.H. Kim-Ngan, D. Sitko, G. Jagło, J. Korecki, B. Handke, *Vacuum* **59,** 868 (2000).

[15] A. Barbieri, W. Wiess, M.A. van Hove, G.A. Somorjai, *Surf. Sci.* **302,** 259 (1994).

[16] B. Handke, J. Haber, T. lzak, M. Kubik, J. Korecki, *Vacuum*, in press.

[17] S. Sugita, Y. Mera, K. Maeda, *J. Appl. Phys.* **79,** 4166 (1996).

[18] B. Raquet, J.M.D. Coey, S. Wirth, S. von Molnár, *Phys. Rev. B* **59,** 12435 (1999).

[19] D.P. Woodruff, *Nucl. Instrum. Methods* **194,** 639 (1982).