The surface insulator–metallic phase transition of epitaxial magnetite thin film observed by low-energy ion scattering

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Abstract

The (111) surface of the magnetite thin film has been investigated by low-energy ion scattering (LEIS) in the small-angle geometry and in the temperature range 85–300 K. The thin film has been grown by molecular beam epitaxy (MBE) and characterized by low-energy electron diffraction (LEED), scanning tunneling microscopy (STM) and conversion electron Mössbauer spectroscopy (CEMS). The temperature dependence of the scattered ion yield, \( R^+(T) \), obtained by LEIS technique has shown anomaly around 120 K attributed to the insulator–metallic phase transition of this material. The character of the \( R^+(T) \) curve has been found to depend on the velocity of incoming ions. The resonant and Auger neutralization, which depends on the density of state and on the degree of electron localization, can be responsible for the behavior of the \( R^+(T) \) curve, especially in the phase transition region. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Phase transitions have been found to affect the ion scattering, sputtering and all the secondary particle emission processes. There have been intensive investigations of the general phenomena of surface phase transitions (i.e. surface roughening and surface melting) on a number of fcc (110) surfaces by ion scattering spectroscopy (ISS) or low-energy ion scattering (LEIS) [1,2]. A few investigations have dealt with the influence of the magnetic and structural phase transition on ion scattering [3,4]. Recently, attention has been focused on using this method for investigation of the insulator–metallic phase transition of magnetite [5,6].

The very unique and well-known phenomenon in magnetite (Fe₃O₄) is a rapid electron hopping...
and its termination at low temperatures yielding equal amounts of Fe$^{2+}$ and Fe$^{3+}$ ions in octahedral sites of the spinel structure. The ferrous (Fe$^{2+}$) ions have an electronic configuration $3d^6$, which differs from that of the ferric (Fe$^{3+}$) ions by the presence of an additional single $\downarrow$ electron to the $3d^5 \uparrow$ core. The continuous hopping of the $\downarrow$ electron among all the octahedral site ferric cores implies the high conductivity of the magnetite at room temperature. Below the so-called Verwey transition temperature around 120 K, $T_V$, this electron hopping is frozen out, and the crystal becomes insulating. Such the insulator–metallic transition, related to the charge ordering, is also accompanied by a structural distortion with a displacement of atoms of the order of 0.01 nm [7]. Recently, increasing attention has been focused on the investigation of the geometry of magnetite surfaces by the scanning tunneling microscopy (STM) and by the low-energy electron diffraction (LEED) [8–12], as well as on the growth of magnetic thin films by the molecular beam epitaxy (MBE) [13–18]. The surface properties of magnetite, however, remain relatively unexplored.

In our first investigations by the LEIS technique on a cleavage (213) surface of a single-crystalline magnetite a very deep minimum around 120 K and a small maximum around 135 K in the temperature-dependent curve of scattered ion yield, $R^+(T)$, have been observed [5,6]. These anomalies have been attributed to the Verwey transition of magnetite surface. Such a transition has found to strongly affect the ion scattering. In the present paper, we report our investigations of the Verwey transition of an epitaxial thin film of magnetite and its effect on ion scattering.

2. Experimental

The ion-scattering experiments were performed using a standard ISS with a hemispherical electrostatic analyzer and in the temperature range of 85–300 K described elsewhere [5,6]. We have used a small-angle geometry (the incident angle $\Psi$ relative to the plane and the detection angle $\Theta$ are in the order of 0–10°) favorable for the observation of multiple scattering effects. Irrespective of the primary energy, such a small-angle geometry always results in multiple scattering due to the atomic screening on the incoming and outgoing paths. Moreover, this angle geometry is extremely needed for ion-scattering experiments on a thin-film surface due to the fact that with the large footprint at small angles there was less damage caused by the ion beam.

The 200 Å thick magnetite thin film was grown on 170 Å thick Au/40 Å thick Cr layers on the MgO(001) substrate in the UHV MBE system. The film structure was controlled by a standard four-grid LEED–AES spectrometer. The Fe$_3$O$_4$ layers were deposited by $^{57}$Fe evaporation in O$_2$ ambient pressure at the rate of 14 A/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 Au buffer layer showed a $(28 \times 5)$ reconstruction typical for the bulk (001) Au with two 90° rotated domains, as seen by STM. This reconstruction has been interpreted as coming from a quasi-hexagonal Au monolayer that terminates (001) oriented Au single crystal [19]. A local hexagonal symmetry implied that the Fe$_3$O$_4$ was forced to form the (111) surface in two 90° rotated domains. The in situ LEED image of the magnetite thin film was shown in Fig. 1. Two 90° rotated hexagonal patterns with equal intensity were clearly seen. For magnetite, along the [111] direction Fe ions form an alternating sequence of two distinct layers, as shown in Fig. 2. The first one contains only the Fe ions in octahedral sites (denoted as Fe$_{oct1}$ and Fe$_{oct2}$ occupied randomly by 50% Fe$^{2+}$ and 50% Fe$^{3+}$ ions), while the second one has both octahedral and tetrahedral sites (the tetrahedral sites, denoted as $Fe_{tet1}$ and $Fe_{tet2}$, are occupied by only Fe$^{3+}$ ions). Such two layers were separated by the oxygen layers with a layer spacing of 2.5 Å, as shown in Fig. 2(b). The calculated Fe–O distances are: $d (Fe_{tet1}–O) = 0.61$ Å, $d (Fe_{oct2}–O) = 1.22$ Å, $d (Fe_{tet2}–O) = 1.82$ Å and $d (Fe_{oct1}–O) = 1.21$ Å [11]. The topmost layer (i.e. the surface) has been found to terminate with a Fe–octahedral layer [11,12].

The CEMS spectra were taken in situ. Their temperature dependence has shown that:
1. the room temperature ones could be fitted with two magnetic components of “2.5+” and “3+” with the intensity ratio of nearly 1:2 and
2. the drastic change of the spectra related to the Verwey transition has occurred at temperatures below 130 K.

These results have reflected the good stoichiometry of the thin film.

The magnetite thin film was mounted into ISS and annealed up to 500 K for few hours before each ion-scattering experiment. The scattering plane was parallel to the [1 1 0] direction. For further discussions, we will address this surface of magnetite thin film as the FeO$_4$(1 1 1)-film surface. From all additional investigations, such as the angle and the energy dependence of the energy spectra of the scattered ions, the influence of bombarding time to the film structure, we have found that:

- By choosing magnetite, a fully oxidized material, our investigation could not be disturbed by any problem related to the oxidization of the surface.
- Preferential sputtering has shown only little or no influence on the shape of energy spectra.
- The negative ion yields were negligible.
- The time dependence can also be negligible in the temperature-dependent investigation due to the fact that a very small change in the intensity of a chosen scattering peak was observed within 4 h (i.e. within the time limit of each temperature-dependent run).

For the temperature-dependence investigations we have used mainly Ne$^+$ and Ar$^+$ ions. The measurements have been carried out at different energies between 4.5 and 7.5 keV with an energy step of 0.5 keV (i.e. at 4.5, 5, 5.5 keV, etc.). For a chosen primary energy, almost no change in the position of the scattering peak with temperature as well as with angles was observed. The intensity of the scattering peak, however, decreases very fast with increasing either incident or detection angle. It appeared that the scattering peak was also observed at the grazing angles. This peak was well-separated from the (few times stronger) primary-beam peak observed around the primary energy.
We have chosen such a position of the scattering peak for the temperature-dependent investigations that it was strong enough and that the bombarding-time effect to the thin-film surface was expected to be weakest for this position.

3. Results and discussions

In Fig. 3, the energy spectra of ions scattered from the Fe$_3$O$_4$(111)-film surface under 5.0, 5.5 and 6.5 keV Ne$^+$ bombardments at 90 K are shown. Very broad peaks, typical for multiple scattering were observed. The intensity of the scattering peak was found to increase strongly with increasing primary energies. However, for the same 5.5 keV Ne$^+$ ions, the peak intensity obtained for the thin-film surface was much weaker than that for the cleavage (213) surface of magnetite [5,6]. A very large energy loss was observed. A small downward-shift of the scattering peak has indicated an increase of the energy loss with increasing the primary energy. The elastic energy loss ratio $E_1/E_0$ ($E_0$ is the primary energy value, $E_1$ the energy value at the maximum) was found to be 0.865, 0.861 and 0.852, respectively. For the Ar$^+$ ion bombardments, much broader scattering peaks were observed. Moreover, a larger energy loss was found. The ratio $E_1/E_0$ was about 0.85 for different bombarding energies. The large energy loss for the small angle geometry was well explained in the frame of multiple scattering with participation of scattering with large scattering angle [20]. We notice that the Fe ions always lie higher than the oxygen planes. Moreover, they form different atomic rows with different heights relative to the oxygen plane creating the so-called surface semi-channel. For different magnetite surfaces, the surface semi-channel can have different channel heights [20]. Such surface semi-channel is favorable for the multiple collisions with large scattering angles and with very small outgoing angles from the target surface.
The temperature dependence of the scattered ion yields \( R^+(T) \) from the Fe\(_3\)O\(_4\)(1 1 1)-film surface under the Ne\(^+\) ion bombardments was shown in Fig. 4. A very broad minimum was observed around 125 K for the 5.5 keV Ne\(^+\) ions. Above 150 K, the scattered ion yield was almost constant with temperature. Such a minimum was always found for energies below 5.5 keV. For the 6.5 keV Ne\(^+\) ions bombardment, this minimum had disappeared and only a simple but fast decrease of the scattered ion yield (by a factor of \( \sim 1.8 \)) at the transition point was observed. It indicated that the main trend of the ion scattering variation with temperature was changed with increasing the primary energy. For the Ar\(^+\) ion bombardment, the minimum in the \( R^+(T) \) curve was still observed for the primary energy up to 6.5 keV. However, it is much narrower than that of the Ne\(^+\) ions. With the energy of 7.5 keV, the \( R^+(T) \) curve exhibits a similar behavior as that of the 6.5 keV Ne\(^+\) ions, i.e. the fast decrease with increasing temperature (by a factor of \( \sim 2 \)) at the transition point, as shown in Fig. 5.

The anomaly in the \( R^+(T) \) curve of Fe\(_3\)O\(_4\)(1 1 1)-film surface was attributed to the Verwey phase transition. Some different behaviors with those of the cleavage (2 1 3) surface were observed:

1. the broadening of the minimum in the \( R^+(T) \) curves,

2. the disappearance of the small maximum around 135 K, and

3. the change of the character of the \( R^+(T) \) curve at higher primary energies.

For explanation of the phase transition effect on ion scattering from magnetite surface, three factors have been taken into account:

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

2. the change of the crystal transparency, and

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

The last one was found to play the most important role for ion scattering from the cleavage (2 1 3) surface of magnetite in the phase transition region [20]. A very narrow choice of ionizing trajectories was found in case of the small angle geometry. For example, the scattering angles for the double scattering can only be in the range: \( 15^\circ \leq \theta_1 \leq 25^\circ \) and consequently \( 26^\circ \geq \theta_2 \geq 17^\circ \) for the 5.5 keV Ar\(^+\) ions. On the one hand, with such trajectories, the ions should be directed to the detector placed under small detection angles. On the other hand, the ions should fulfill the re-ionization criterion namely they should suffer the last ionizing collision. Around the phase transition temperature, a small change of the atomic position of the target atoms (for example due to the crystal distortion)
can easily affect such a narrow group of ion trajectories. Consequently, a large effect from the phase transition on the scattered ion yield was observed. For the Fe₃O₄(1 1 1)-film surface, much weaker scattering peaks were observed. It indicates that in this case the scattering peak was composed mainly by ions with the trajectories, which do not contain ionizing collisions, contrary to that for the surface of single-crystalline magnetite. The character of the scattered ion yield has shown the dependence on the velocity of the incoming ions, but not on the primary energy value. The change in its temperature-dependence variation has been observed at 6.5 keV Ne⁺ ion bombardment. For the Ar⁺ ions, the minimum at the Verwey point was still present at the same bombarding energy, and the character of the R⁺(T) curve has changed at higher primary energy, i.e. at 7.5 keV. Moreover, a smaller effect of the phase transition on ion scattering was observed for the thin film surface. These results indicate that only neutralization effects occur along the ion trajectory and they are the main factors influencing the character of the R⁺(T) curve. In the previous paper [20], the change in the neutralization probability has been considered to be related to the increase in the density of states (DOS) near the Fermi level (E_F) as well as to the increase of the electron localization degree below the Verwey temperature of magnetite. The observed velocity dependence of the scattered ion yield can be an indication of significant contributions from basic processes such as the resonant and Auger neutralization. The resonant neutralization involves the tunneling of an electron from the solid surface valence band into an unoccupied state of the ion incoming to the surface, while Auger neutralization returns the ion to its ground state involving the loss of two electrons from the solid valence band. For basic neutralization mechanisms the probability of remaining as an ion is [21]: \( P_{\text{ion}} = \exp\left(-\frac{A}{a V_\perp}\right) \), 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 exponential in the reciprocal of \( V_\perp \). An increase of the ion velocity implies an increase of the remaining ion probability (i.e. the probability that the ion escapes neutralizations). Such an increase can cause the disappearance of the minimum at the Verwey point. For magnetite, on the one hand, a certain amount of “free” electrons exist in the high temperature phase, which hop between the Fe ions. On the other hand, 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. Thus contributions from these neutralization processes certainly play very important roles. In some cases, they can exceed the contribution of the neutralization from binary collisions where the remaining ion probability is exponentially proportional to the reciprocal of the velocity on the trajectory. Binary collision neutralization effects occur in the full temperature range and they depend on the kind of projectiles.

4. Conclusion

The anomalies around 125 K in the temperature-dependent curve of the scattered ion yield, R⁺(T), from the surface of Fe₃O₄(1 1 1) thin film were attributed to the Verwey transition. The observed large effect of the Verwey transition on ion scattering has shown that our ISS with the small-angle geometry is a suitable technique for investigation of the insulator–metallic transition in magnetite. Moreover, with this small-angle geometry, we were able to carry out the ion-scattering experiments on a thin film surface.

The large elastic energy loss has also been observed in case of ion scattering from the surface of magnetite thin film. However, the broad scattering peak was considered as a result of multiple scattering. The ionizing trajectories, along which the ions suffer the last ionizing collision, can be hardly existed in this case. It implies that the re-ionization criterion can play minor role in the Verwey transition effect on ion scattering from such a surface, opposite to that from the surface of a single-crystalline magnetite. The fine structure of the R⁺(T) curve near the Verwey point indicates the involvement of different processes in the ion scattering. However, the velocity dependence of the character of the R⁺(T) curve shows that the
resonant and the Auger neutralization involving the tunneling or the loss of electrons from the solid surface valence band can give dominant contributions affecting the ion scattering at the Verwey phase transition.

References