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Oxygen Emissions from Single-Crystalline Fe_3O_4 Surfaces Induced by Low-Energy Ion Bombardments

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Negative-charged ion energy spectra of the Fe_3O_4 (001) and (111) surface revealed large peaks attributed to the O^- recoils from a binary collision. Under Ar^+ ion bombardments such an emission was largely affected by the screening effect of the Fe ions. A distinguished peak related to the O^+ recoil ions was observed under Ne^+ ion bombardments, while such a peak was merged into the high background in the case of Ar^+ ion ones. A weak effect from the Verwey transition was found on oxygen emissions. For the (111) surface a small peak characteristic of the O^+ recoils from double collisions appeared in the energy spectra around 140–170 K and a minimum was observed in both $R^+(T)$ and $R^-(T)$ curves under 6 keV Ne^+ ion beam.

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1. Introduction

Among different surface methods, the low-energy ion scattering (LEIS) technique has been used extensively over the past few decades for analyzing the composition and structure of solid surfaces [1, 2]. The high surface sensitivity of this technique is due to the fact that most of the reflected ions are scattered from the outermost surface layers. The LEIS technique affords quantitative data on surface structures but as spatial averages only. The change in the neutralization and ionization of scattered ions is, however, amplified strongly by any small change in the electron state of surface atoms. Recently, the LEIS technique has been proved to be a suitable method for investigations of the metal–insulator phase transition in magnetite surfaces [3–5]. An abrupt increase and/or a large decrease in the

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total ion yield have been revealed in the phase transition region. Moreover, the results indicated that the "surface" Verwey temperature was higher than the "bulk" point.

Another reason why magnetite surfaces attracted our ion-scattering interest is that this material is available for investigations of the oxygen emission. Despite of a large interest in the secondary particle emissions induced by ion bombardments of the solid surfaces, there is a lack of information on the oxygen emission process. The oxygen peaks appearing in the LEIS spectra were mostly originated from the oxidization layers or the absorbed layers. By using the magnetite surfaces, it is possible to investigate the oxygen emission from well-defined lattice positions as well as the influence of the metal–insulator phase transition on such an emission. In this paper we present our investigations of the oxygen emission induced by Ne^+ and Ar^+ ion bombardments on the single-crystalline (001) and (111) magnetite surface.

2. Experimental details

The LEIS experiments were performed in the temperature range from 85 K to 300 K using $4\div8$ keV Ne^+ and Ar^+ ion beam described elsewhere [3, 4]. In general, at room temperature for different detection angle Θ the strongest oxygen-emission peaks were found at the incident angle $\Psi = 25^\circ$. However, the largest temperature effect on the LEIS spectra was obtained for the angle-geometry $\Psi = 34^\circ$, $\Theta = 68^\circ$ and the azimuthal angle $\Phi = 0^\circ$ and $\Phi = +12^\circ$, respectively, for the (001) and (111) surface.

The high quality (5N) single crystals of magnetite were grown by the skull-melter technique in the Chemistry Department of Purdue University [6]. Two surfaces perpendicularly to the crystallographic (001) and (111) direction were prepared. For the LEIS experiments the azimuthal angle $\Phi = 0^\circ$ was fixed at the [010] and $[1\bar{1}0]$ direction (the main crystallographic surface direction), respectively, on the magnetite (001) and (111) surface. The reproducibility of the LEIS spectra showed that for the nA-beam dose the influence from ion implantation and/or surface reconstruction to the scattered-ion yield was negligible in our investigations.

3. Results and discussions

The energy spectra of the negative ions emitted from the magnetite surfaces, under Ne^+ and Ar^+ ion bombardments have revealed a huge peak for the detection angles Θ up to 80°. At higher detection angles ($\Theta > 80^\circ$) only a broad bump was observed. As an example, the data obtained for 6 keV Ne^+ ion bombardments were shown in Fig. 1. The energy position of the peak maximum was found at an expected energy of recoil O^- ions from a binary collision ($E_2 = E_0[4\mu/(1+\mu)^2]\cos^2\Theta_{\mathrm{rec}}$, where E_0 is the primary energy, Θ_{rec} is the scattering angle ($\equiv \Theta$ in the laboratory system), $\mu = m_2/m_1$ is the mass ratio between the target and projectile atoms). Increasing primary energy implied a large widening of the peak

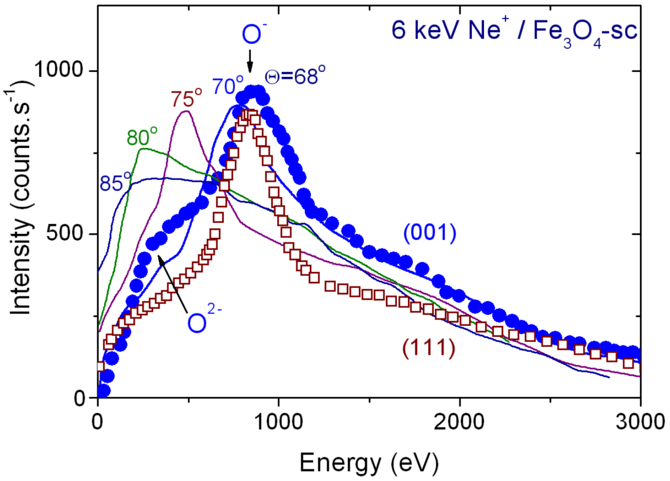

Fig. 1. Negative-charged ion energy spectra of the Fe_3O_4 surfaces under 6 keV Ne^+ ion bombardments at different detection angles. $\Psi = 34°$, $\Phi = 0°$, and $\Phi = 12°$, respectively, for the (001) and the (111) surface, $T = 300$ K. The maximum is at the energy position of the O^- recoils. The broad shoulder revealed the O^{2-} recoils observed only for the (001) surface.

and an enhancement of the background of the high-energy tail related to the multiple scattering. The results indicated that a large amount of oxygen ions were present on the outermost surface layer of magnetite and joined the binary collisions in a negative-charge state. However, while for the (001) surface a broad bump at the left hand side of the maximum was always present contributed to the O^{2-} recoils, no visible O^{2-} signal was observed for the (111) surface. We notice here that the O^{2-} signal is most visible at $\Psi = 25°$ ($T = 300$ K) when also the strongest signal from O^- recoils was found.

For both two surfaces, the oxygen emission was largely enhanced at low temperatures by using the Ne^+ ion beam, whereas the Ar^+ ion beam implied a distinguished decrease in the emission rate (peak intensity). Comparison of the normalized negative-charged ion energy spectra at different temperatures for the (111) surface under 6 keV Ne^+ (with increased ion yield at 90 K) and Ar^+ ion bombardments (with decreased ion yield at 90 K) was given in Fig. 2. Moreover, the relative change of the peak intensity with changing temperature decreased with the increase in the primary energy. We notice here that the Ar^+ ion is twice heavier than the Ne^+ ion ($m_{\mathrm{Ar}} = 40$, $m_{\mathrm{Ne}} = 20$). It was expected that the Ar^+ ion beam would induce a larger amount of emitted oxygen ions. The strong suppression of the O^- recoil signal indicated that the screening effect from the Fe ions gives a dominant contribution to the negative-charged scattered ion yield (R^-) especially at low temperatures. Indeed, the LEIS data have been analyzed within the framework of the screening effect and presented elsewhere [3, 4]. In brief, in the

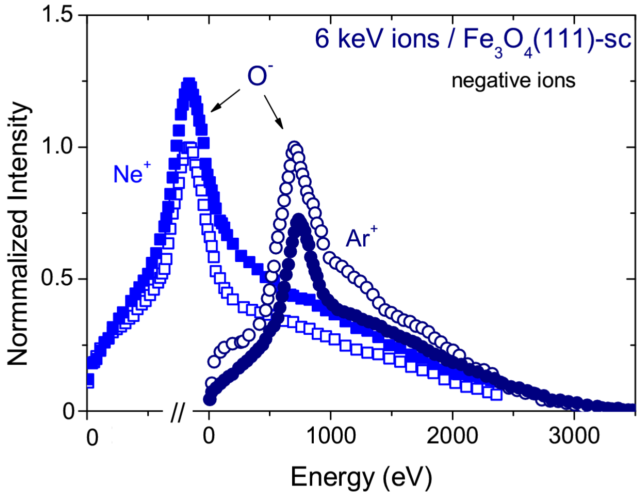

Fig. 2. Normalized negative-charged ion energy spectra of the Fe_3O_4 (111) surface under 6 keV ion bombardments at 300 K (open markers) and at 90 K (solid markers). $\Psi = 34°$, $\Theta = 68°$, $\Phi = 12°$. The maximum is at the energy position of the O^- recoils.

case of Ne^+ ion bombardments, the shadow radius R_S is small and the ion–surface atom collision is not affected by the screening effect; every incoming ions can knock out the oxygen ion implying a large ion yield. The shadow radius in the case of Ar^+ ion bombardments is about 1.5 times larger ($R_S(\mathrm{Ar})/R_S(\mathrm{Ne}) \approx 1.5$). A large part of the incoming ions had to be scattered due to a strong screening effect from the neighboring Fe ions. Only a small part of ions with "adequate" trajectories can knock out the oxygen ions and thus a much smaller emitted-ion rate was obtained. At low temperatures, the strong suppression of the O^- emission was an indication of a strong enhancement of the screening effect (due to a change in the atomic distance related to the crystal distortion) which compensated an increase in ion yield resulting from e.g. the electron-state change. The significant role of the screening action was also indicated by a large influence from the surface-channel structure on the Fe-ion emission especially from the (111) surface [5]. Namely, under Ne^+ ion bombardments a value of 2.5 was obtained for the relative ion rate, $I_{90\mathrm{K}}/I_{300\mathrm{K}}$, for the wide square-shaped channels on the (001) surface, while a (smaller) value of 1.3 was found for the narrow triangular-shaped ones on the (111) surface.

A large difference between the Ne^+ and Ar^+ ion beam was also revealed in the energy spectra of the emitted positive-charged ions. Under Ar^+ ion bombardments a very small O^+ recoil peak on the very high background from Fe recoils and multiple scattering was present. Under Ne^+ ion bombardments, a distinguished O^+ recoil peak was observed indicating that the re-ionization plays an important role. The oxygen recoil signal was found to disappear at $\Theta \geq 76°$, whereas a visible Ne^+–Fe peak is still existing at $\Theta = 94°$. The peak intensity was increased

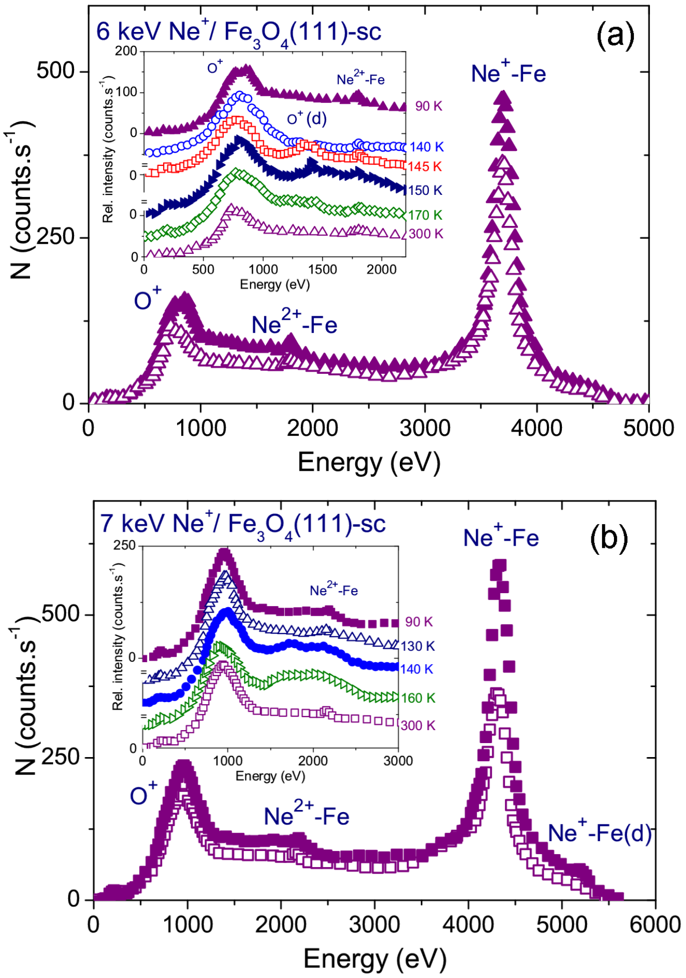

Fig. 3. Temperature dependence of the positive-charged ion energy spectra for the Fe_3O_4 (111)-sc surface under 6 keV (a) and 7 keV (b) Ne^+ ion bombardments. $\Psi = 34°$, $\Theta = 68°$, $\Phi = 12°$. Insets: enlarged oxygen peaks from a single binary collision (O^+) and from a double-collision (O^+(d)). The zero-point of the curves was shifted in order to have a clear view of the peaks.

at low temperatures, as shown in Fig. 3. The relative change of the peak intensity, i.e. the I_{90K}/I_{300K} ratio was found to be much larger for the (001) surface than that for the (111) one. The results indicated that a dominant contribution to the positive-charged scattered ion yield (R^+) comes from the ion–atom interactions inside the channels. Moreover, the interacting rate was smaller for the narrow triangular-shaped channels on the (111) surface than that for the wide square--shaped channels on the (001) surface implying a smaller contribution and a less enhancement of R^+ at low temperatures.

A striking feature of the (111) surface is the appearance of an extra peak in the temperature region of 140–170 K under Ne^+ ion bombardments. With the primary energy up to 6 keV, it was well separated from the Ne^{2+}–Fe scattering peak (Fig. 3a, inset). At 7 keV and higher, such a peak was merged with the Ne^{2+}–Fe scattering peak due to a very close energy position between them and only one broad peak was observed (Fig. 3b, inset). The large peak represented the O^+ recoil ions from a single binary collision at the scattering angle θ_s ($\equiv \Theta$), while the additional peak was attributed to those resulting from the double collisions at the scattering angles $\theta_i \leq \frac{1}{2}\theta_s$ ($i = 1, 2$). The results showed that the re-ionization of the oxygen ions is strongly dependent on the surface structure.

The temperature dependence of the normalized ion yield ($R(T)/R_{300\mathrm{K}}$) for 6 keV ions scattered from the two surfaces was shown in Fig. 4. Unlike the temperature variation of the positive-charged ion yield R^+ revealing double anomalies, no visible change was observed for the negative-charged ion yield R^- in the Verwey transition region. The $R^-(T)$ curve showed only a smooth decrease or increase below 170 K. A similar trend of the $R^-(T)$ curve was observed at different primary energy. Besides, a weak azimuthal-angle dependence of the negative-charged oxygen emissions was found. The positive-charged ion yield was largely contributed from the ion–Fe scattering (and the Fe^+ recoils under Ar^+ ion bombardments). The positive-charged emitted ions was largely governed by the neutralization pro-

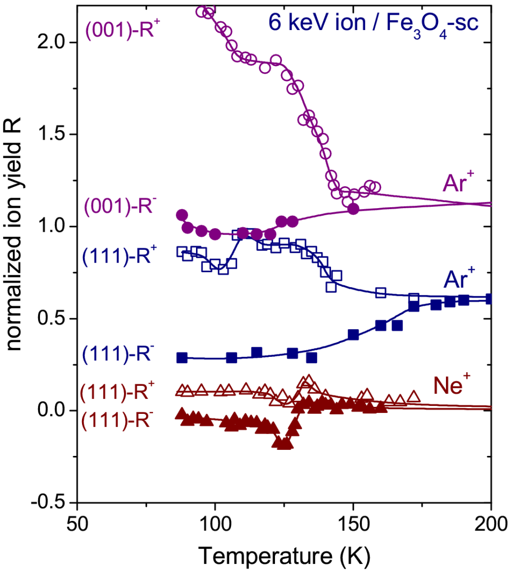

Fig. 4. The normalized ion yield, $R(T)/R_{300\mathrm{K}}$, of the negative-charged (R^-) ions (solid markers) in comparison to the positive-charged (R^+) ions (open markers) emitted from the Fe_3O_4 (001) and (111) surface under 6 keV ion bombardments.

cess and thus a strong influence from the Verwey transition was observed related to e.g. an increase in the electron localization degree. Such an electron state-change was found to affect weakly on both negative- and positive-charged oxygen emission in which the re-ionization process plays a dominant role especially for the particles escaping from the inside surface-channels. It was expected that the re-ionization and thus its surface-structure dependence would be enhanced by using the Ne^+ ion beam with which a larger contribution to the total ion yield originated from the ion–surface atom interaction inside the surface-channels. Indeed, a visible phase transition effect on oxygen emissions was found for the case of 6 keV Ne^+ ion beam onto the (111) surface: a minimum was revealed around 125 K in the $R^-(T)$ curve (Fig. 4). Such a minimum was somewhat deeper than that in the $R^+(T)$ curve. However, no maximum was revealed around 135 K in the $R^-(T)$ curve as that in the $R^+(T)$ curve.

4. Summary

A very strong negative-charged oxygen emission induced by ion bombardments onto the magnetite surfaces was obtained indicating that a large amount of oxygen ions joined the binary collisions in a negative-charge state. Such an emission was found largely influenced by the screening action of the Fe ions indicated by a less enhanced ion yield under bombarding the surfaces by the heavier ions (Ar^+) than the lighter one (Ne^+). The existence of the O^+ recoil signal indicated a dominant role of the re-ionization process. A weak effect from the Verwey transition was found on both the negative- and positive-charged oxygen emissions. The appearance of the O^+ recoil peak from double collisions and the visible phase transition effect in an exceptional case of 6 keV Ne^+ ion onto the (111) surface indicated a large influence from the surface structure on the re-ionization process.

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