



Characterization of the metal–insulator phase transition of $\text{Fe}_{3(1-\delta)}\text{O}_4$ surfaces

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Abstract

A sharp specific-heat peak at 123.5 K with an enormous increase of the peak-intensity in a narrow temperature step ΔT of 0.2 K was observed for the perfect stoichiometric magnetite sample, while a broad maximum around 98 K with ΔT of 20 K was found for the non-stoichiometric one. The surface Verwey transition was characterized by means of low-energy ion scattering technique using 4–8 keV He^+ , Ne^+ and Ar^+ beam. The Verwey transition of these surfaces was indicated by a sharp step-rise (under Ne^+ and Ar^+ ion beams) and/or a minimum (under He^+ ion beam) in the temperature dependence of the scattering ion yield at 138 K and around 125 K, respectively.

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1. Introduction

Magnetite (Fe_3O_4) is referred to as a half-metallic material, which is a metal with a Fermi surface in one spin channel and insulator in other spin channel, and is thus considered as a potential

spin-polarized electron source [1]. The well-known feature of magnetite is the metal–insulator phase transition around $T_V \sim 125$ K (the Verwey transition). The nature of this transition has not been yet fully understood. The electronic transport properties were well explained considering the Verwey transition as an electron localization–delocalization transition [2]. X-ray scattering results and NMR suggest a band model with an opening of a gap below T_V [3,4]. Despite of the ongoing debate about its nature, the precise character of the

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Verwey transition in the bulk has been well established. The differences in the sharpness, magnitude and onset temperature of this transition are indications of deviations from a perfect stoichiometry and of the inhomogeneity in the samples. Recently, intensive investigations of the surface structures have been performed on numerous magnetite surfaces by using e.g. scanning tunneling microscopy [5]. Most of the magnetite-surface studies, however, have been carried out at room temperature. The ‘surface’ Verwey transition and its influence on the surface properties remain relatively unexplored, except for a few attempts. Moloni et al. [6] have focused on the domain wall structures in a magnetite single crystal below T_V by using a magnetic force microscope. Kim-Ngan et al. [7] observed a widening of the gap in the tunneling spectra (STS) below T_V on a (001) thin film prepared by MBE. Korecki et al. [8] found a deviation from the bulk properties and a reduction of the Verwey temperature with decreasing the thickness of the MBE (001) magnetite thin film by using in-situ conversion electron Mössbauer spectroscopy. Poddar et al. [9] concluded from the STS on magnetite nanocrystals that an insulator-like gap structure exists below T_V , which gradually disappears with increasing temperature transforming to a small peak structure at the Fermi energy.

We present our results from low-energy ion scattering (LEIS) on the magnetite surfaces of both stoichiometric and non-stoichiometric single crystals. The surface sensitivity of the LEIS technique lays on the fact that the majority of reflected ions are scattered from the outermost surface layers. The influence of the surface structures on the single scattering process, especially in the Verwey-transition region, was underlined elsewhere [10–12]. We focus here on the characteristic of the ‘surface’ Verwey transition. By using the LEIS technique we were concerned to the change in the neutralization and re-ionization during ion–surface atom interactions. The very reproducible LEIS spectra of magnetite surfaces on a time scale indicated a negligible contribution from ion implantation and surface reconstruction to the scattered-ion yield.

2. Experimental details

Several surfaces were prepared from two different single crystals of $\text{Fe}_{3(1-\delta)}\text{O}_4$ grown by the skull-melter technique [13] from 4–9' ($\delta=0$) and 3–9' ($\delta\neq 0$) Fe_2O_3 powder. Specific heat measurements have been performed on these samples from 20 K to 300 K by a quasi-adiabatic method to determine the Verwey transition in the bulk. The LEIS experiments were performed in a standard ion scattering spectroscopy system in UHV in the temperature range from 85 to 300 K using 4–8 keV He^+ , Ne^+ and Ar^+ ion beam. A large scattering-angle geometry was used, favorable for the observation of ion–surface atom binary collisions. For the temperature-dependent investigations, we have used the optimal angle-geometry reported elsewhere [12]. Integration of the energy spectra (the peak area) measured at different temperatures gives the temperature dependence of the scattered-ion yield, $R^+(T)$.

3. Results and discussion

The specific heat (SH) data of the two single-crystalline samples are shown in Fig. 1. For the first sample, the ‘bulk’ metal–insulator phase transition is revealed by a very sharp peak at 123.5 K. The peak-intensity increases enormously in a narrow temperature step ΔT of 0.2 K with a huge value (of 284 kJ/mol K) at the maximum (Fig. 1a) and with a corresponding entropy of the transition ΔS_V of 6.4 J/mol K. The results indicate a perfect stoichiometry of the sample ($\delta=0$). A broad SH peak with ΔT of 20 K with two maxima respectively at 98 and 106 K and with a small peak-intensity is observed for the second sample, revealing its non-stoichiometry (Fig. 1b). The related entropy ΔS_V equals 3.4 J/mol K. The transition point indicates that the δ -value and/or the doping content is above 0.012. The existence of the second maximum at 106 K indicates the existence of an inhomogeneity in the sample.

In our LEIS investigations under different ion-type bombardments, it was possible to study different ion emissions from the magnetite surfaces. Namely, under He^+ ion bombardments the

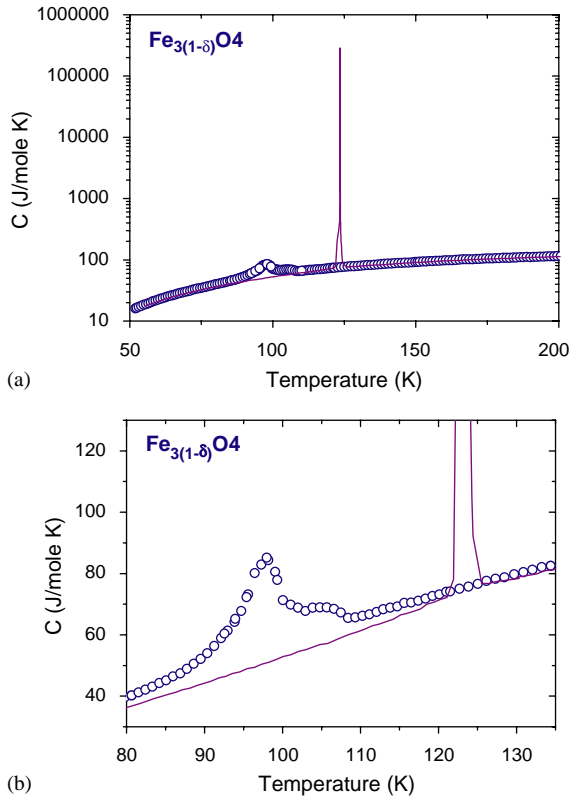


Fig. 1. (a) Comparison of the specific heat data (on a logarithmic scale) of two single crystals of magnetite. (b) The double maximum of the non-stoichiometric sample on a (normal) enlarged scale.

LEIS spectra reveal single-scattering peaks resulting from the $\text{He}^+ - \text{O}$ and $\text{He}^+ - \text{Fe}$ binary collisions. Using a Ne^+ ion beam, the recoil O^{+1} signal and the $\text{Ne}^+ - \text{Fe}$ scattering peak are observed in the positively charged-ion energy spectra, while using an Ar^+ ion beam the recoil O^{+1} signal, the recoil Fe^+ signal and the $\text{Ar}^+ - \text{Fe}$ scattering peak are revealed. The negatively charged-ion spectra for both Ne^+ and Ar^+ ion beam exhibit a strong signal from the recoil O^{-1} ions [10]. The temperature dependence of the normalized yield, $R^+(T)/R_{300\text{K}}^+$, of different positively charged ions scattered off the surface of stoichiometric magnetite sample are shown in Fig. 2. Under He^+ ion bombardment, two wide minima are revealed at 138 and 100 K. A step-rise increase at 138 K and a narrow minimum at 125 K

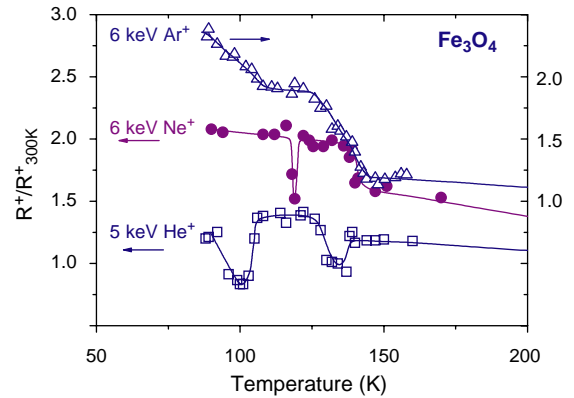


Fig. 2. Normalized yield, $R^+(T)/R_{300\text{K}}^+$, of positively charged ions scattered off the stoichiometric magnetite surface. (LEIS conditions: incident angle $\Psi = 34^\circ$, detection angle $\theta = 68^\circ$, along the $[0\ 1\ 0]$ azimuth on a $(00\ 1)$ surface orientation).

are observed under Ne^+ ion bombardment. Two-step increases located at 138 and 104 K are found under Ar^+ ion bombardment with primary energy of 6 keV. Increasing the primary energy implied a relative change of the ion yield (i.e. the ratio $R^+(T)/R_{300\text{K}}^+$), of the depth of the minimum (under He^+ and Ne^+ ion beam) and a widening of the plateau (under Ar^+ ion beam). However, no change in the character of the $R^+(T)$ curve is observed. In other words, irrespective of the different ion types and energies, the high-temperature anomaly in the $R^+(T)$ curve is always observed at 138 K, attributed to the surface Verwey temperature for the perfect stoichiometric surface. We notice here that the minimum under Ne^+ ion bombardment is observed to be close to the ‘bulk’ Verwey temperature. Evidently, a large change of the target material transparency due to the crystal distortion at T_V of the bulk implies a large decrease of R^+ . The $R(T)/R_{300\text{K}}$ curves for the non-stoichiometric magnetite surface under Ne^+ ion bombardment are shown in Fig. 3. The $R^+(T)$ curve of positively charged-ions exhibits a wide minimum around 125 K and a maximum around 135 K. No change in the tendency of the $R^+(T)$ curve is observed under different energies. Increasing the primary energy from 6 to 7 keV implies only an increase of the $R_{90\text{K}}^+/R_{300\text{K}}^+$ ratio from a value of 1.1 to 1.4. The same characteristic was observed for the negatively charged ion yield

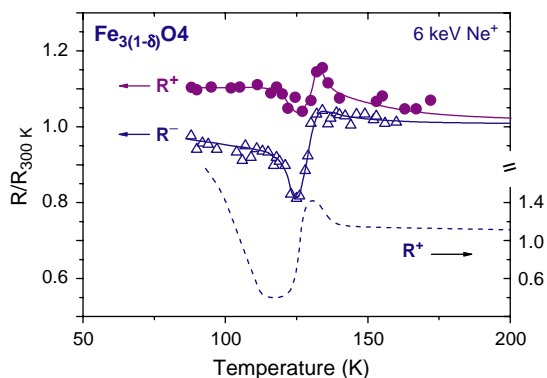


Fig. 3. Normalized yield, $R(T)/R_{300\text{K}}$, of positively charged ions (R^+) and of negatively charged ions (R^-) scattered off the non-stoichiometric magnetite surface. (LEIS conditions: $\Psi = 34^\circ$, $\Theta = 68^\circ$, azimuthal angle $\Phi = 12^\circ$ with respect to the $[1\bar{1}0]$ azimuth on a (111) surface orientation) The dashed line shows the LEIS results for a cleavage surface from the non-stoichiometric sample.

curve, $R^-(T)$, except for the fact that the minimum is deeper and the maximum is less pronounced. We show in Fig. 3 the $R^+(T)$ curve of a cleavage surface from the same non-stoichiometric magnetite sample. Under very different conditions applied to LEIS investigations of the multiple-scattering process, it exhibits very similar features. The different shapes of the $R(T)$ curves of the two surfaces obviously indicate a large influence from the surface-channel structures on the contributions from the neutralization and re-ionization. However, in all cases a wide minimum at 125 K and a small maximum around 135 K exist. The minimum is attributed to the surface Verwey transition, while the maximum is an evidence of some surface effects related to the sample inhomogeneity. Thus for stoichiometric and non-stoichiometric magnetite samples the ‘surface’ Verwey point is found at higher temperatures (about 15 and 25 K, respectively). Moreover, the imperfect stoichiometry and inhomogeneity of the sample are found to be reflected also in the surface processes.

The fine structure of the $R(T)$ curves indicates a complicated interplay between the neutralization and re-ionization processes in the phase transition region. The step-rise increase (under Ne^+ and Ar^+ ion bombardments) in the ordered-state (below T_V) indicates a dominant contribution from Auger

neutralization. This is supported by another fact: a widening of the plateau between two step rises (under Ar^+ ion beam) and an enhancement of the fast increase below 100 K (under Ne^+ ion beam) with increasing primary energy, i.e. with increasing ion velocity. Unlike the Ne^+ and Ar^+ ions, the He^+ ions suffer re-ionization in a collision with an oxygen atom on the magnetite surfaces. Moreover, they have a very high probability of penetration into the sample. In such a case, the re-ionization would play a more dominant role.

Auger neutralization is one of the basic mechanisms for the charge-exchange between an incident ion and a surface atom. An increase in the Auger neutralization can be easily explained as due to an increase of the electron-localization degree. Moreover, we notice here that no typical effect for an ‘ordinary’ insulator is revealed in the LEIS spectra of magnetite. Namely, no energy shift of the peak-position or any peak-splitting is observed in the insulator phase of magnetite.

4. Summary

Specific heat measurements indicate a perfect stoichiometry of one magnetite sample shown by a sharp peak at 123.5 K, while double maxima at 98 and 106 K are observed in another sample indicating its imperfect stoichiometry. From the LEIS investigations, the anomaly at 138 K (the minimum under He^+ -ion bombardment and/or the sharp step-rise under Ne^+ and Ar^+ bombardments) in the temperature dependence of the scattering ion yield $R^+(T)$ is attributed to the ‘surface’ Verwey transition for the stoichiometric sample while, for the imperfect-stoichiometric sample, it is revealed by a wide minimum around 125 K. The LEIS results indicate a dominant contribution originating from Auger neutralization of ions scattered from these surfaces.

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