Vol. **111** (2007) *ACTA PHYSICA POLONICA A* No. 5

Proceedings of the XII National School "Correlated Electron Systems...", Ustroń 2006

Surface Investigations of Selected Materials by Low-Energy Ion Scattering Technique

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Dedicated to Professor Józef Spałek on the occasion of his 60th birthday

Surfaces of three selected materials were investigated by means of low-energy ion-scattering technique: (1) the magnetite (Fe_3O_4) exhibiting the so-called Verwey transition (T_V(bulk) = 125 K) accompanied by a small cubic-monoclinic crystal distortion, (2) the intermetallic compound $NdMn_2$ undergoing an antiferromagnetic-paramagnetic phase transition (T_N = 104 K) accompanied by a large crystal distortion with a volume change of 1%, and (3) the typical insulator $BaTiO_3$ with two structural transitions below 300 K. The primary energy of the (Ne^+, Ar^+) ion beam was in the range of 4–8 keV, and the low-energy ion-scattering spectra were collected in the temperature range of 85–300 K. A large influence from the Verwey transition on the neutralization and re-ionization of scattered ions from magnetite surface was observed, while no visible change at the magnetic phase transition in $NdMn_2$ was revealed in the low-energy ion-scattering spectra. A strong dependence of the characteristics of the low-energy ion-scattering spectra on the irradiated time was observed for $BaTiO_3$ indicating that this surface was heavily charged by ion bombardments.

PACS numbers: 68.35.Rh, 71.20.Be, 71.20.Eh, 77.80.Bh

1. Introduction

Among different surface methods, the low-energy ion-scattering (LEIS) technique (or ion-scattering spectroscopy, ISS) has been used extensively over the past few decades for analyzing the composition and structure of solid surfaces [1, 2]. In a typical LEIS experiment, a surface is bombarded by noble-gas ions

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($He^+, Ne^+, Ar^+, Kr^+, Xe^+$) having a primary energy in the range of 1–20 keV. The elemental composition of the surface can be identified by the presence of single-scattering peaks in the energy spectra (the LEIS spectra), while the angular distributions of the scattered ions contain certain information about the surface structures. The high surface sensitivity of this technique is attributed to the high differential scattering cross-section in this energy range and to the preferential neutralization of ions scattered from atoms beneath the surface. As a consequence, the majority of the reflected ions are scattered from the outermost surface layer of solids. The phase transitions of the first and second order in metals and alloys are found to affect the ion scattering, sputtering, and all secondary particle emission processes. In recent years we have used the LEIS technique to investigate both MBE and single-crystalline surfaces of magnetite. This technique was proved to be suitable for observation of the so-called Verwey transition (T_V) of the magnetite surfaces: a large change in the ionization and re-ionization of scattered ions was observed shown by a double anomaly in the scattered ion yield curves (the $R^+(T)$ curves) in the temperature region of 100–140 K and a large enhancement of ion-Fe scattering peaks in the low temperature phase [3]. For over 60 years the Verwey transition was described as the metal–insulator phase transition [4]. In order to gain more understanding of the nature of the Verwey transition we have extended our LEIS investigation on other materials focusing on the effect of the phase transition on scattered ions and the scattering process from the surface in an insulator state. In this work we present the LEIS investigations on the surfaces of three selected materials: magnetite (Fe_3O_4), $NdMn_2$, and $BaTiO_3$. Magnetite crystallizes in an inverse spinel structure with a lattice parameter $a = 8.40$ Å. Within the charge-order model, the Verwey transition was considered to be related to the freezing of the electron hopping between Fe^{2+} and Fe^{3+} ions in the octahedral sites. This transition is also accompanied by a structural transition from cubic fcc to monoclinic structure with an atomic displacement of the order of 0.01 nm [4]. $NdMn_2$ is an intermetallic compound crystallizing in the hexagonal $C14$ Laves-phase structure ($a = 5.560$ Å, $c = 9.060$ Å). At 104 K this compound undergoes a first-order antiferromagnetic-paramagnetic phase transition accompanied by a large volume change of about 1% [5]. $BaTiO_3$ is a well-known ferroelectric material crystallizing in a tetragonal structure at room temperature with the lattice parameters $c = 4.036$ Å and $a = b = 3.992$ Å. It is a typical insulator at 300 K with a band gap of about 3.1 eV. Below 300 K this material shows two structural phase transitions from tetragonal ($P4mm$) to orthorhombic ($Amm2$) and then to rhombohedral ($R3m$), respectively, at temperatures 278 K and 183 K [6].

2. Experimental details

The experiments were performed by using an ISS under UHV conditions and with the primary energy of Ne^+ and Ar^+ ions in the range of 4–8 keV. Details of the setup have been reported elsewhere [3]. Prior to the temperature-dependence investigations of the LEIS spectra we have investigated the characteristics of the LEIS spectra, as a function of the (incident, detection, azimuthal) angle and of the incoming-ion energy at 300 K and 85 K. The so-called optimal angle geometry with $\psi = 34^\circ$ and $\Theta = 68^\circ$ was then used for the temperature-dependent investigations.

The high quality single crystals of magnetite were grown by the Skull–Melter technique in the group of Prof. Honig, Chemistry Department, Purdue University, Indiana, USA. The characterization of the Verwey transition in the bulk has been thoroughly investigated [7]. For the LEIS experiments we have used the surfaces cut perpendicularly to the crystallographic direction (001) and (111). They were checked by the Laue diffractions and polished with a diamond paste with decreasing grain size down to 1 μm. A polycrystal sample of $NdMn_2$ was prepared by arc-melting of 99.9% pure rare-earth and 99.98% pure manganese metals in an argon atmosphere. A polished polycrystalline surface of $NdMn_2$ was used for the LEIS experiments due to the fact that it was difficult to obtain $NdMn_2$ single crystal due to a high evaporation of manganese [5]. The single-crystalline plate $BaTiO_3$ of about 1 mm thickness with the preferable *c*-axis perpendicular to the plate was used for the LEIS investigations. The characterization of the "bulk" Verwey transition of magnetite [7], of the magnetic phase transition of $NdMn_2$ [5] and the ferroelectric properties of $BaTiO_3$ [8] have been thoroughly investigated. For all three surfaces an annealing *in situ* was done at temperatures 500–600 K in UHV. Prior to each measurement the target was cleaned by cycles of 6 keV Ar^+ sputtering in about 2 h. No contamination was detected except a small amount of He^+ recoils.

3. Results and discussions

The LEIS results are analyzed within the framework of the elastic binary collision between the incoming ions and the surface atoms. The relations between the kinetic energy and the scattering angle are expressed as [2]:

$$E_1 = \frac{E_0}{(1+\mu)^2}\left(\cos\Theta + \sqrt{\mu^2 - \sin^2\Theta}\right)^2, \tag{1}$$

$$E_2 = E_0\frac{4\mu}{(1+\mu)^2}\cos^2\Theta_{\rm rec}, \tag{2}$$

where E_0 is the primary energy, E_1 and E_2 is, respectively, the energy of scattered ions and recoil atoms, Θ and $\Theta_{\rm rec}$ is, respectively, the angle between the trajectory of the scattered ion and of the recoil and the incident ion beam, $\mu = m_2/m_1$, is the mass ratio between the target atom and the projectile.

The LEIS spectra of 6 keV Ne^+ ions and Ar^+ ions scattered off Fe_3O_4(001), $NdMn_2$, and $BaTiO_3$ surfaces, plotted as E/E_0, were shown in Fig. 1. For each LEIS spectrum, the peak intensity was normalized with respect to the highest scattering peak. Under 6 keV Ne^+ ion bombardments, the LEIS spectrum of Fe_3O_4 has revealed a broad peak resulted from O^+ recoils at the energy ratio $E_2/E_0 = 0.137$ and a very large Ne^+–Fe scattering peak at $E_1/E_0 = 0.625$, in

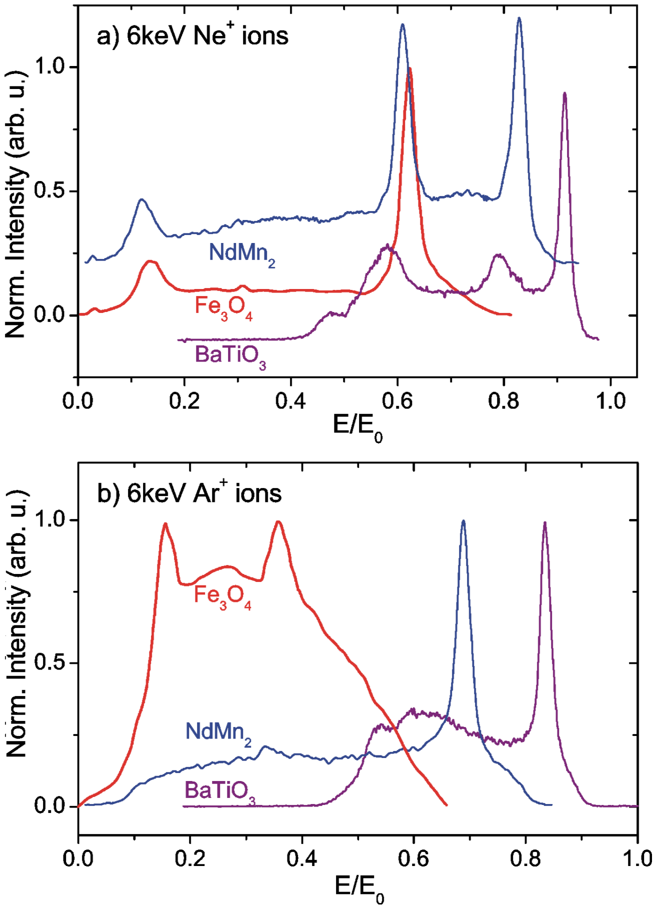

Fig. 1. Comparison of energy spectra, plotted as E/E_0 (E_0 is the primary-energy value), of 6 keV Ne^+ ion (a) and 6 keV Ar^+ ion (b) scattered off Fe_3O_4(100), $NdMn_2$, and $BaTiO_3$ surfaces at the incident angle $\Psi = 34°$ and detection angle $\Theta = 68°$. $T = 300$ K. For each curve the peak intensity was normalized with respect to the largest scattering peak. The curves are shifted to guide the eyes.

good agreement with the estimated values from the elastic binary collision model. In the case of $NdMn_2$, two sharp peaks were observed at $E_1/E_0 = 0.62$ and 0.83 assigned, respectively, to Ne^+–Mn and Ne^+–Nd scattering. The very large Ne^+--surface atom scattering peaks indicated a very high survival probability of Ne^+ ions scattered from $NdMn_2$ surface. A quite large broad peak appeared at the energy ratio of 0.12. This peak is largely decreased with increasing the detection angle (Θ) and disappeared at $\Theta \geq 80°$ indicating that it originated from the secondary ion emission (recoils). We notice here that this peak was located at lower energy compared to that of the O^+ recoils. Moreover, unlike the case of Fe_3O_4, where a huge peak of O^- recoil exhibited at the same energy value of $E_2/E_0 =$

0.137 in the negative-charged LEIS spectra, for the $NdMn_2$ surface no peak was observed in the negative-charged LEIS spectra. Thus the O recoil can be excluded for $NdMn_2$. From the energy consideration, it can be attributed to the Mn^+ recoils. For $BaTiO_3$ surface, four peaks were revealed in the LEIS spectra. Unlike the Fe_3O_4 and $NdMn_2$ surfaces, the peak positions of these peaks in $BaTiO_3$ as well as their relative peak intensity largely depended on the irradiated time. The highest and sharpest peak with the energy ratio $E_1/E_0 = 0.914$ evidently resulted from Ne^+–Ba scattering, while the two large broad peaks at $E_1/E_0 = 0.79$ and 0.58 may result from Ne^+–Ti scattering and Ti^+ recoils. The origin of the small peak at the energy ratio of 0.47 is not clear. No peak was observed in $BaTiO_3$. Thus the possibility of O^+-recoil signal can be excluded. We notice here that although both Fe_3O_4 and $BaTiO_3$ are oxides-surfaces consisting of 3*d* elements, the Ne^+–Fe atom scattering peak is much enhanced than the Ne^+–Ti one. It indicated that the neutralization rate of Ne^+ ions scattered off Ti atoms on $BaTiO_3$ surface was much higher. It may be related to the different electronic states of these oxides; Fe_3O_4 is a half-metal while $BaTiO_3$ is an insulator. In all cases a large contribution from multiple-scattering ions was observed shown by a high background at the low-energy side of the binary scattering peak. The doubly-charged ions scattered from the surfaces (Ne^{2+}) were also observed. It was shown by a small single peak in the case of Fe_3O_4, while a small broad bump was revealed in the case of $NdMn_2$ as a result of overlapping between Ne^{2+}–Mn and Ne^{2+}–Nd scattering. A comparison of the LEIS spectra of 6 keV Ar^+ ions scattered off those three surfaces was shown in Fig. 1b. The LEIS spectra 6 keV Ar^+ ions scattered off the Fe_3O_4 (100) surface exhibited two well-defined peaks on a very high background. The high-energy peak was at the energy where the single binary elastic scattering by iron was expected, i.e. the Ar^+–Fe scattering peak at $E_1/E_0 = 0.352$. The peak width is quite large indicating a large contribution from the quasi-single scattering ions. From the investigation of the angle dependence of the LEIS spectra at different temperatures, the low-energy peak was attributed to the Fe recoils resulted from the binary collision with a large elastic energy loss [9]. In the case of $NdMn_2$ one large peak and a small peak were observed assigned, respectively, to Ar^+–Nd and Ar^+–Mn single scattering peak. The LEIS spectra of 6 keV Ar^+ ions scattered off the $BaTiO_3$ surface have revealed a sharp peak and a broad bump with two distinguished maxima. The sharp peak could be easily contributed to the Ar^+–Ba single scattering, while it is difficult to find the origin of the two maxima, due to the large energy shift of the peaks compared to the estimated values from the binary collision.

The characteristics of LEIS spectra of three surfaces have been thoroughly investigated as a function of (incident and detection) angle by using different ion beams at different primary energies and at 300 K and 85 K. The data for Fe_3O_4 surface have been presented and analyzed in numerous publications [3]. We focus here on the data obtained for $NdMn_2$ and $BaTiO_3$ surfaces. The LEIS spectra of

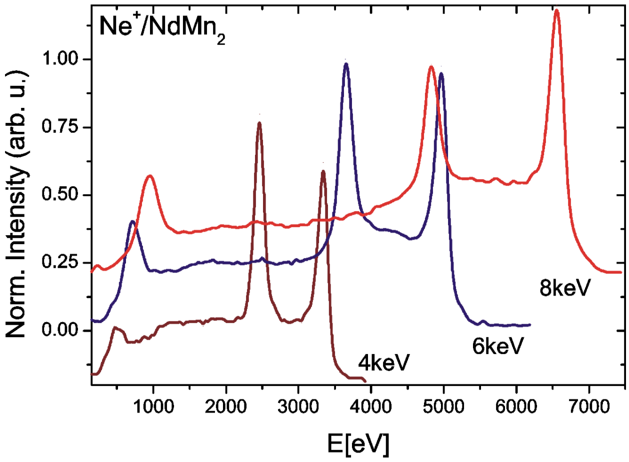

Fig. 2. The LEIS spectra of $NdMn_2$ surface under Ne^+ ion bombardments at different primary energies. $\Psi = 34°$, $\Theta = 68°$, $T = 300$ K. The curves were normalized with respect to the largest scattering peaks and then shifted to guide the eyes.

$NdMn_2$ surface under Ne^+ ion bombardments at different primary energies were shown in Fig. 2. The main characteristic of the LEIS spectra was unchanged with increasing energy: one broad peak and two sharp peaks on a high background were always observed. A larger enhancement of the Ne^+–Nd scattering peak was observed shown by a large increase in the peak ratio between the Ne^+–Mn^+ and Ne^+–Nd scattering peak (I_{Mn}/I_{Nd}). Namely a value of 0.9, 1.0, and 1.2 was found for I_{Mn}/I_{Nd}, respectively, at the energy of 4, 6, and 8 keV. The results indicated a large decrease in the neutralization degree and/or a large increase in the reionization degree of the scattered ions from Nd atoms on $NdMn_2$ surface with increasing ion energy.

The LEIS spectra of $BaTiO_3$ surface under 6 keV Ar^+ ion bombardments as a function of irradiated time was shown in Fig. 3a. A large energy shift of the peak position from the "theoretical" binary-collision value was observed. Moreover, a large increase in not only the peak intensity but also the relative peak ratio of those peaks with increasing irradiated time was observed. The LEIS spectra under 5 and 6 keV Ne^+ ion bombardments collected at a similar irradiated time of 1 h (plotted as E/E_0) was shown in Fig. 3b. While the shift of the Ne^+–Ba scattering was quite small, a much larger shift was observed for the two broad peaks related to Ne^+–Ti scattering. The results indicate that the $BaTiO_3$ surface is heavily charged during ion bombardments. The deflection of ions leaving the surface was largely influenced from the "extra" electronic field due to a charged surface. The energy difference between the theoretical and observed value was estimated for the Ne^+– and Ar^+–Ba peak, $\Delta E = [E_1(\text{cal}) - E(\text{observed})]/E_0$. It appeared that ΔE first increased rapidly with increasing irradiated time. However, after 10 h no saturation was reached. Moreover, the fluctuation of ΔE was quite large and no

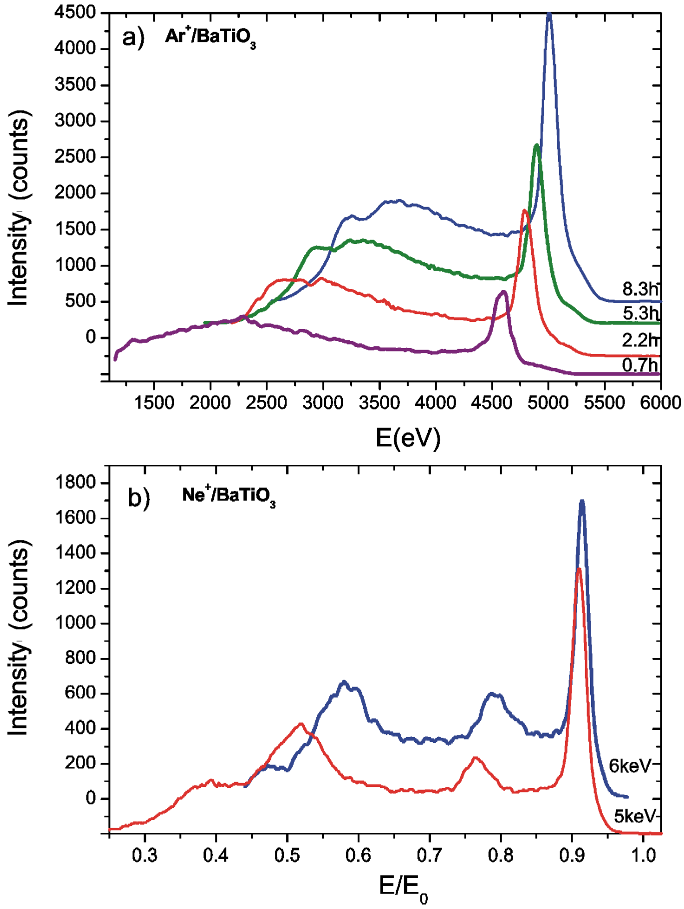

Fig. 3. The LEIS spectra of $BaTiO_3$ surface as a function of irradiated time under 6 keV Ar^+ ion bombardments (a) and at similar irradiated time under 5 and 6 keV Ne^+ ion bombardments (b). $\Psi = 34°$, $\Theta = 68°$, $T = 300$ K.

regularity in the $\Delta E(t)$ curve was found. It indicated that the extra electric field on the surface is not constant due to the "arbitrary" discharging and charging of the surface. Due to such a large fluctuation, it is impossible to properly identify the observed peaks from the $BaTiO_3$ surface. These results showed that $BaTiO_3$ is a typical insulator surface at room temperature and that the surface-terminated layer of $BaTiO_3$ consists of Ti and Ba atoms. If the oxygen ions are present in the surface layers, then the oxygen neutralization rate would be 100%, since no signal from oxygen ions was found in the LEIS spectra.

Integration of the LEIS spectra yields the total scattered ion yield R. The temperature dependence of the yield of both positive-charged ($R^+(T)$) and negative-charged ($R^-(T)$) ions, scattered off Fe_3O_4 surfaces has been thoroughly investigated and a detailed analysis of the influence of the Verwey transition on neutralization and re-ionization of scattered ions has been reported elsewhere [3, 9]. In brief, in all cases a double anomaly was observed in the $R^+(T)$ curve in the temperature range of 100–140 K. The high-temperature anomaly always observed at 138 K was attributed to the "surface" Verwey temperature for magnetite surfaces, i.e. about 13 K higher than the Verwey temperature of the bulk (= 125 K). The strong effect of the Verwey transition on the scattered ions from Fe_3O_4 surfaces was considered to be related to a large change in the electron concentration/state. Thus our LEIS investigations rather support the charge-order model. Besides, no energy shift and no energy splitting of the scattering peaks were observed at low temperatures indicating that magnetite surface does not behave as a typical insulator. This suggestion was strongly supported by the results obtained on the insulator surface $BaTiO_3$. Due to a strong dependence of the LEIS spectra of $BaTiO_3$ surface on irradiated time it was impossible to investigate the effect of structural phase transition on scattered ions. For $NdMn_2$ surface, we did expect to see a large change at the magnetic phase transition due to a large change in the ion penetration and/or in the neutralization of ions scattered from sub-surface layer related to a large crystal distortion and a big volume change in this material. Surprisingly, except a small increase in the peak intensity, no visible change was observed at T_N for $NdMn_2$ surface. The results further support that the change of the electron state and concentration give a dominant contribution to the large change in the neutralization and re-ionization of ions scattered from Fe_3O_4 surfaces, and the change in the ion penetration rate related to crystal transparency plays a minor role.

4. Summary

Our LEIS results have shown that the LEIS technique is quite suitable for surface investigations of metallic and/or half-metallic materials. The huge single--scattering peaks were observed for Fe_3O_4 and $NdMn_2$ surfaces indicating a high ion-survival probability of ions scattered from surface atoms on these surfaces. A large energy shift of the scattering-peak positions observed for $BaTiO_3$ surface indicated that this surface is heavily charged during ion bombardment. No visible effect from magnetic phase transition in $NdMn_2$ accompanied by a large volume change due to crystal distortion on the scattered ion yield was observed indicating a minor contribution from a change in the ion penetration rate (related to the crystal transparency). This gives a further evidence that the large influence from the Verwey transition on the neutralization and re-ionization of ions scattered off the magnetite surfaces were strongly related to a change in the electron state/concentration.

Acknowledgments

The authors express their thanks to Dr. A. Kozłowski (Faculty of Physics and Computer Science, AGH, Kraków) and Dr. J. Suchanicz (Institute of Physics, AP, Kraków) for supplying Fe_3O_4 and $BaTiO_3$ samples.

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