

## Molecule dissociation at the Fe<sub>3</sub>O<sub>4</sub> (001) surface

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### ABSTRACT

The molecular dissociation at the single-crystalline Fe<sub>3</sub>O<sub>4</sub> (001) surface has been investigated using the diatomic H<sub>2</sub><sup>+</sup>, D<sub>2</sub><sup>+</sup> and N<sub>2</sub><sup>+</sup> molecules in the energy range of 3–8 keV and in the temperature range of 90 K–300 K. The single collision of ions released from dissociation with the surface atoms was observed only for the N<sub>2</sub><sup>+</sup> molecules. The detail analysis confirmed that for the light molecules such as H<sub>2</sub><sup>+</sup> and D<sub>2</sub><sup>+</sup> the charge-transfer process dominate the interaction of a molecule with the magnetite surface. A large change in the scattered ion yields around the Verwey phase transition temperature was observed indicating a strong correlation between the molecule dissociation and the electronic state of the magnetite surface.

### Keywords:

Magnetite surface, low energy ion scattering, molecule dissociation.

## 1. INTRODUCTION

A large interest has been recently focused on magnetite (Fe<sub>3</sub>O<sub>4</sub>), since it is viewed as a promising candidate for use as pure spin sources in spintronic devices at room temperature, such as spin valve, sensitive magneto-resistive devices [1,2]. At room temperature Fe<sub>3</sub>O<sub>4</sub> crystallizes in the cubic inverse spinel structure with a lattice constant of  $a = 8.396 \text{ \AA}$ , in which 32 oxygen anions O<sup>2-</sup> form a close-packed face-centered-cubic *fcc* lattice, 8 Fe<sup>3+</sup> ions locate in the tetrahedrally coordinated A-sites, while 16 octahedrally coordinated B-sites are occupied randomly by 8 Fe<sup>2+</sup> and 8 Fe<sup>3+</sup> ions. Below the Néel temperature of 858 K, magnetite is ferrimagnetic with a net magnetic moment of 4.1 μ<sub>B</sub> per formula unit. A well-known feature of magnetite is the so-called Verwey transition (T<sub>V</sub>) around 123 K. For more than 70 years, since the work of Verwey in 1939 [3], it have been commonly interpreted as a long-range electron charge-ordering in the octahedral Fe sublattice. Recent investigations have revealed that the notion of exact iron of +2 and +3 valence is disproved [4,5] and the charge ordering (CO) and orbital ordering (OO) is suggested [6-8]. Moreover, the dominant role of electron–electron interactions together with electron–phonon correlations has been proved to drive the transition [9]. However, there is still a controversy in the description of the subtle interplay between CO and OO and spin and lattice distortion at the Verwey transition. X-ray diffraction study using the synchrotron light [10] has revealed that the CO and OO set at the same temperature where

the spin reorientation take place at 130 K, i.e. at a temperature of about 10 degrees higher than  $T_V$  and that at  $T_V$  a first order phase transition occurs corresponding to the lattice distortion. A large dependence of the  $T_V$  on the pressure was also observed [11] and the metallization of magnetite could be achieved at the pressure of 8 GPa.

We have investigated the ion-atom collisions on  $Fe_3O_4$  (001) and  $Fe_3O_4$  (111) surfaces using  $He^+$ ,  $Ne^+$  and  $Ar^+$  ion beam (so-called atomic ions) with a primary energy in the range of 3 – 8 keV (the low-energy ion scattering (LEIS) technique) using a large-angle geometry favourable for the single-scattering process [12-14]. In particular we focus on the influence of Verwey transition on the neutralization and re-ionization of ions scattered from the magnetite surfaces. Our results indicate that: 1) the LEIS technique is suitable for observation of the Verwey transition of the magnetite surfaces; a large change in the ionization and re-ionization of scattered ions was observed shown by distinguished anomalies in the scattered ion yield (the  $R^+(T)$  curves) in the temperature range of 100 – 140 K, 2) the Verwey temperature of the  $Fe_3O_4$  surfaces is determined as 138 K, i.e. about 13 K higher than that of the bulk, 3) a large enhancement of ion-Fe scattering peaks in the low temperature phase reveals that the Auger neutralization plays an important role in the ion neutralization especially below the  $T_V$  and 4) the  $Fe_3O_4$  surface even at below  $T_V$  did not behave as a typical insulator.

In the research field of low energy ion-solid surface interactions, beside of the atomic ion-atom interaction, a large interest has been focused also on the interaction of diatomic molecules with solid surfaces [15-20]. It was shown that in general the diatomic molecules are dissociated into atomic ions completely and quickly after resonance neutralization on the incoming path. Thus the molecule impact is equivalent to a pair of atoms hitting independently the solid surface with energy around the half of the primary energy ( $E_0$ ) at different incident or azimuthal angles. However, the interaction between the molecule constituents in which the ions can acquire energy larger than  $E_0$  (revealed by a high energy tail above  $E_0$ ) cannot be neglected completely especially for the large scattering angles [16]. There were several proposed molecule-dissociation mechanisms, e.g. the collision-induced dissociation (or purely impulsive dissociation) and dissociation by resonant neutralization related to the electron capture from a metal into antibonding molecular states (the so-called dissociative neutralisation process) [17,18]. Although the relative contribution of the different dissociation processes depends on the charge state of the bombarding molecules, the geometry of scattering, properties and structure of the target surface, it was revealed that the dissociation of  $H_2$  molecules on metal surfaces is strongly influenced by charge-transfer processes (i.e. minimising the direct collision-induced dissociation), while for e.g.  $N_2$  molecules these processes are of minor importance and the  $N_2$  dissociation was considered to be governed mainly by vibrational and rotational excitation. Moreover, at the low energy (in the range of  $10^2 - 10^4$  eV), the time interval between the successive collisions of the molecule atoms with the local surface area is comparable with the typical times of electron transitions ( $10^{-15} - 10^{-16}$  s) [18]. The surface atoms and also the molecule, excited by the first collision, may not have enough time to relax before the second collision. Thus the molecule-solid-surface interactions may give a more inside look at the electronic processes.

In the present work, we aim at investigations the dissociations of  $H_2$ ,  $D_2$  and  $N_2$  molecules on the  $Fe_3O_4$  (001) surface. We focus also on the influence of Verwey transition on the neutralization and re-ionization of ions resulted from molecule-dissociation (the so-called molecule-dissociated ions) and then scattered from the magnetite surfaces. The experiments have been performed by using similar scattering conditions which allows us to make some comparison of the scattering process between the molecule-dissociated ions and the atomic ions.

## 2. EXPERIMENTS

The experimental data were collected from an apparatus consisted of an ultrahigh-vacuum chamber, equipped with a plasma-ion source, a mass selection magnet and an electrostatic detector. In fact it was the same set-up used for the LEIS experiments reported elsewhere [12]. We have used the diatomic  $H_2^+$ ,  $N_2^+$ ,  $D_2^+$  molecular beam with the primary energy  $2E_0$  in the range of 3 – 8 keV.

The experiments were performed in the temperature range of 90 K–300 K using mostly the optimal angle geometry found from the atomic ion-scattering experiments (i.e. with the incident angle  $\Psi = 34^\circ$  and the detection angle  $\Theta = 68^\circ$  and the azimuthal angle  $\varphi = 0^\circ$  (for which the (001) direction of the sample surface was aligned along the direction of the incoming ion/molecule beam). We used the same monocrystalline  $Fe_3O_4$  (001) target subjected to the ion-scattering experiments. The sample growth and treatment prior to the experiments were similar to those for the LEIS experiments using rare-gas ions described elsewhere [12].

## 3. RESULTS AND DISCUSSION

Ion scattering from the target atoms has been treated within a standard binary elastic collision. The relations between the kinetic energy and the scattering angle are expressed as [15,18]:

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

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

where  $E_0$  is the primary energy,  $E_1$  and  $E_2$  are the energies of scattered ions and recoil atoms, respectively,  $\Theta$  and  $\Theta_{rec}$  is the angle between the trajectory of the scattered ion and/or of the recoil and the incident ion beam (i.e. the detection angle in the experiments, respectively,  $\mu = m_2/m_1$  is the ratio between the target and projectile atomic mass.

We notice here that in order to use the same equation (1-2) for analysing the obtained data for both atomic ions and molecule-dissociated ions with the primary energy of  $E_0$ , the primary energy of molecules were set as  $2E_0$ . In other words, the energy of molecule-dissociated ions amounts to  $2E_0/2 (= E_0)$ , where  $2E_0$  is the set energy for the molecule beam.

Fig. 1 shows the energy spectra of  $H^+$ ,  $D^+$  and  $N^+$  ions scattered off the  $Fe_3O_4$  (001) surface at room temperature, plotted as a function of the relative energy  $E_1/E_0$ . The incident particles are  $H_2^+$ ,  $D_2^+$ ,  $N_2^+$  molecules with a primary energy  $2E_0 = 6$  keV.

A very broad and round-shaped maximum was observed in the case of scattered  $H^+$  and  $D^+$  ions centered at an energy value around  $E_1/E_0 = 0.50$  and  $0.75$  respectively, while the spectrum of the scattered  $N^+$  ions revealed a huge asymmetric peak with a sharp maximum at

the relative energy value of  $E_1/E_0 = 0.730$  and a small shoulder around  $E_1/E_0 = 0.185$  and a plateau between them. In all cases, no any distinguishable signal associated to the scattering of surviving molecules was observed, i.e. no peak was revealed around the energy value  $E_1/E_0 = 1$ . The broad distribution at  $E_1 < E_0$  is related to single ions released by dissociation.

Moreover, no high energy tail in the energy region  $E > E_0$  was revealed, i.e. no re-distribution of the energy of the molecule atoms colliding with each other after the dissociation (which acquired a higher energy than  $E_0$ ) was observed. In the case of scattered  $H^+$  and  $D^+$  ions, no signal from a single ion-surface atom collision was revealed. Namely, no peak-like feature was found at the energy position corresponded to the relative energy value of single ion-iron ( $H^+$ -Fe and  $D^+$ -Fe) and ion-oxygen ( $H^+$ -O and  $D^+$ -O) collision. ( $E_1/E_0(H^+$ -Fe) = 0.978,  $E_1/E_0(D^+$ -Fe) = 0.956,  $E_1/E_0(H^+$ -O) = 0.925,  $E_1/E_0(D^+$ -O) = 0.855)). In both cases, the broad maximum in the spectra are energetically shifted with respect to the theoretical  $E_1$ -value due to a large inelastic energy loss.

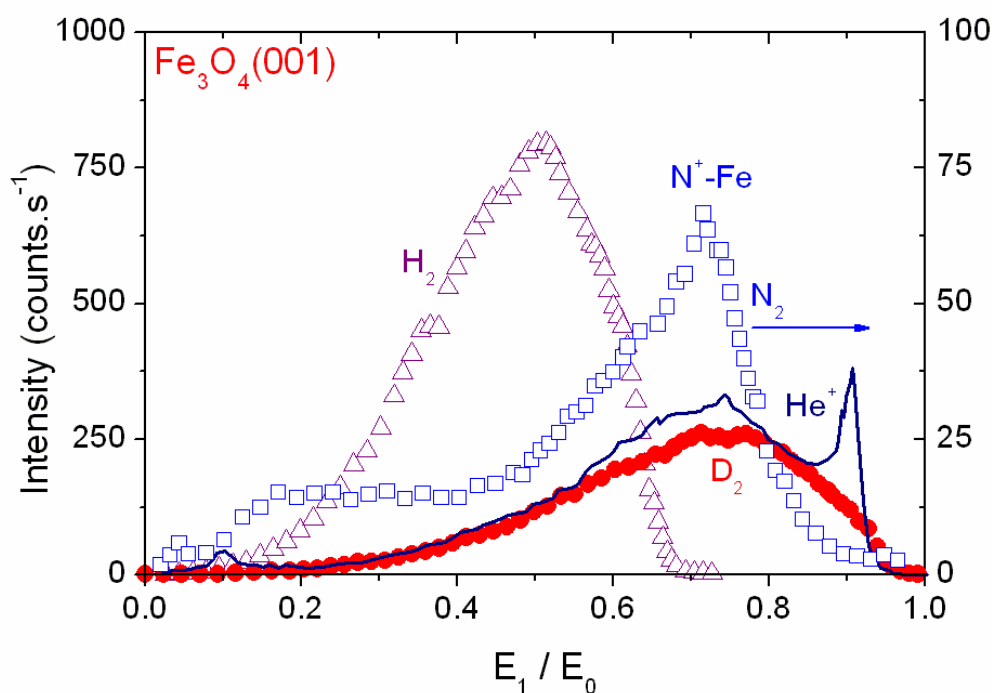
The results indicated that bombardments the  $Fe_3O_4(001)$  surface with  $H_2^+$  and  $D_2^+$  molecules imply a very low survival-probability of the  $H^+$  and  $D^+$  ions resulted from the dissociation after a binary collision with the atoms on the surface layers. A major part of the scattered ions off the  $Fe_3O_4$  surface would be from the particles penetrated in deep layers which suffer re-ionization in the out-coming path. In the case of scattered  $N^+$  ions under  $N_2^+$  molecule bombardment, the energy position of the huge peak in the energy spectra is in a good agreement to that from  $N^+$ -Fe elastic binary collision ( $E_1/E_0(N^+$ -Fe) = 0.728). It was hard to define the origin of the small shoulder at around  $E_1/E_0 = 0.185$ . It can be attributed to the scattered  $N^+$  ions or oxygen recoil  $O^{+1}_{rec.}$  from the  $N^+$ /O collision.

The theoretical energy value for scattered  $N^+$  ions is  $E_1/E_0(N^+$ -O) = 0.237. Thus if only  $N^+$ -O collision was taken into account, then the scattered-off ions must be from multiple collisions with a considerable large energy loss. On the other hand, the energy value is quite close to that from the oxygen recoil ( $O^{+1}_{rec.}$ ),  $E_2/E_0(N^+$ -O) = 0.140. We notice here that in the energy spectrum of the negative-charge scattered ions (see Fig. 3) a huge signal was observed at almost the same energy value. Thus the possibility seems to be only (negative-charged) oxygen recoils ( $O^{-1}_{rec.}$ ) in our case and the shoulder in the energy spectra of positive-charge scattered ions was attributed to the oxygen recoils.

The large  $N^+$ -Fe peak indicates that a quite large amount of  $N^+$  ions can maintain the ionized state during the binary collision with the Fe atoms located on magnetite surface. However, a large broadening of the  $N^+$ -Fe peak at the left-hand side and a very high background (the plateau between  $N^+$ -Fe peak and  $N^+$ -O shoulder) revealed a considerably large contribution from the multiple ion-Fe scattering as well as from the re-ionization of the particles penetrated in the deep layers.

Both two contributions imply a large energy loss. However, the re-ionization may play a more dominant role in the case of  $N^+$ -O collision implying a large energy shift of the  $N^+$ -O signal. In Fig. 1, for a comparison, the energy spectrum of scattered  $He^+$  ions as results of bombarding the magnetite surface with 6keV  $He^+$  ion beam was also shown. In this case, a large contribution from the multiple scattering and re-ionization also lead to a broad maximum related to the  $He^+$ -O collision.

However, the  $He^+$ -Fe signal formed a very sharp peak indicating a much higher survival probability of the  $He^+$  ions after a single collision with Fe atoms from the magnetite surface.

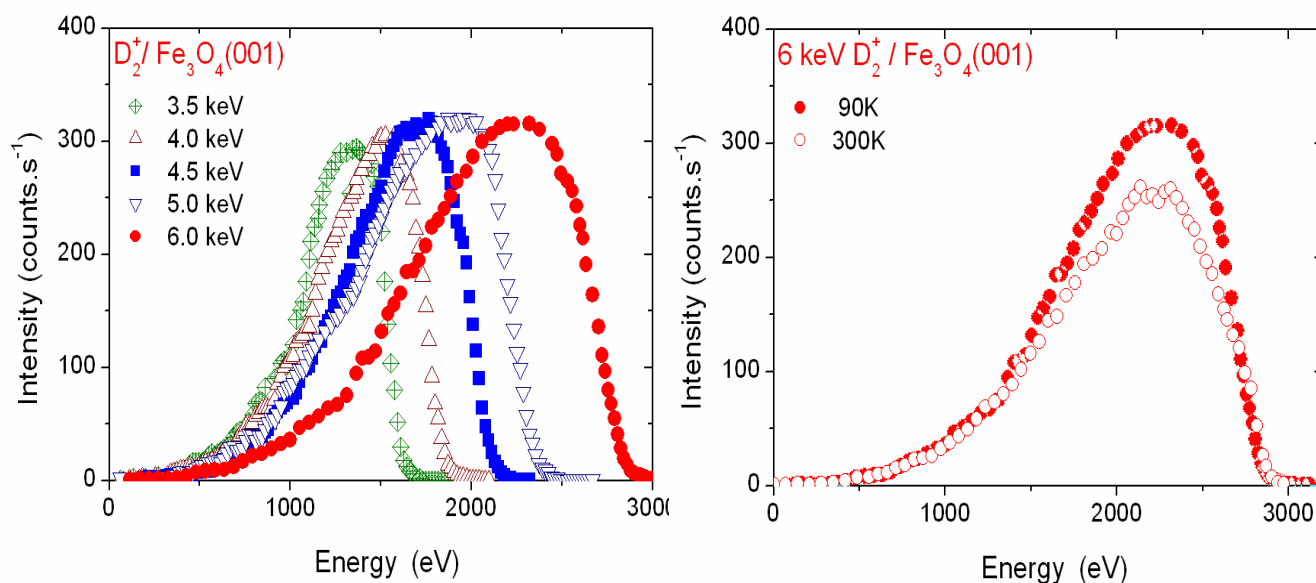


**Fig. 1:** Energy spectra of  $H^+$ ,  $D^+$  and  $N^+$  ions scattered off the  $Fe_3O_4(001)$  surface. The incident particles are  $H_2^+$ ,  $D_2^+$ ,  $N_2^+$  molecules with primary energy  $2E_0 = 6$  keV.  $\Psi = 34^\circ$ ,  $\Theta = 68^\circ$ ,  $\varphi = 0^\circ$ .  $T = 300$  K. For a comparison the energy spectrum of scattered  $He^+$  ions resulted from  $He^+$  ion beam was also shown revealing a sharp  $He^+$ -Fe peak from single elastic  $He^+$ -Fe collisions.

In Fig. 2 the energy- and temperature dependence of the energy spectra for  $D^+$  ions scattered off the  $Fe_3O_4(001)$  surface were shown. The spectra at different energies (i.e. the energy dependence) were presented at 90 K (Fig. 2, left), since the peak intensity is larger at low temperatures. Increasing the primary energy ( $2E_0$ ) from 3.5 keV to 6 keV implied a shift of the maximum to a higher energy accordingly, but there was no change in the relative energy position. Namely, the energy value of at the maximum is  $E_1/E_0 = 0.75$  and is constant: it does not change with changing the energy of the incoming molecule beam. However, a visible widening of the peak with increasing the primary energy was observed. Moreover, the spectra become more asymmetric, mostly due to an enhancement of the signal at the low energy side.

The results indicate that with increasing primary energy the ion penetration depth was increased leading to a larger contribution of the re-ionized particles from deeper layers. The energy spectra at different energies were also collected at different temperatures. As an example, a comparison of the energy spectra of  $D^+$  ions with a primary energy  $2E_0 = 6$  keV scattered off the  $Fe_3O_4(001)$  surface at 300 K and 90 K was shown in Fig. 2-right. No shift or broadening of the broad peak was observed.

However, the peak intensity at low temperature was increased: at 90K the peak-intensity was about 1.2 larger than that at 300 K indicating a larger amount of ions scattered off the  $Fe_3O_4(001)$  surface. It may contribute to a large decrease of the free electron concentration in the low-temperature phase of the magnetite.



**Fig. 2.** a) Energy dependence (left,  $T = 90$  K) and temperature dependence (right,  $2E_0 = 6$  keV) of the energy spectra of  $D^+$  ions scattered off the  $Fe_3O_4(001)$  surface. The incident particles are  $D_2^+$  molecules with primary energy  $2E_0 = 3.5 - 8$  keV.  $\Psi = 34^\circ$ ,  $\Theta = 68^\circ$ ,  $\phi = 0^\circ$ .

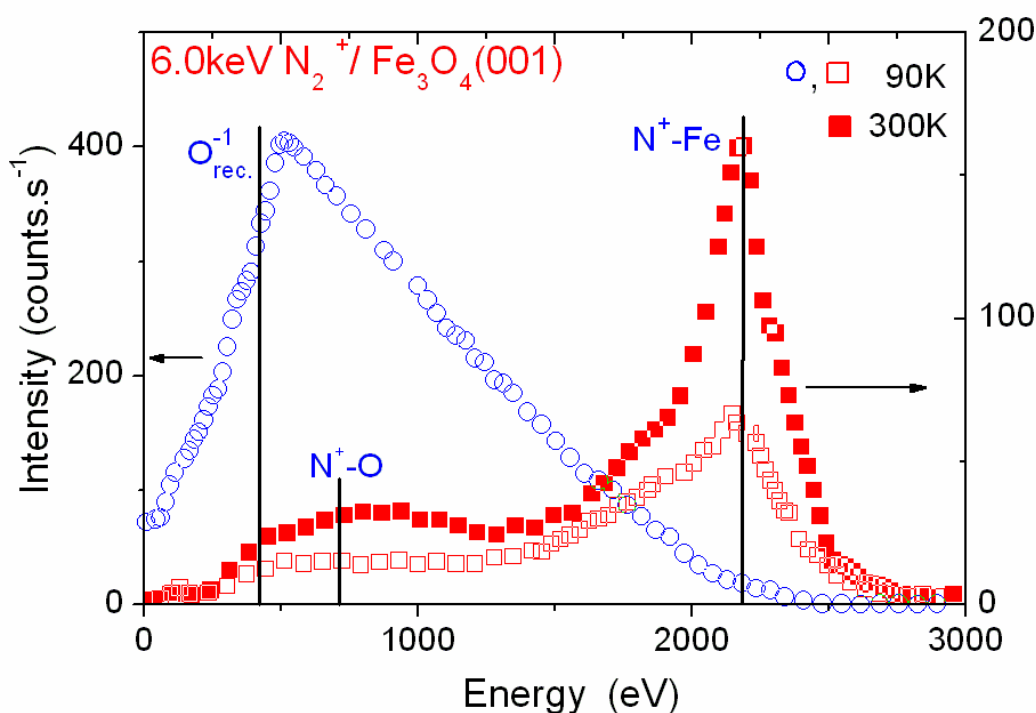
An enormous increase of the peak intensity was observed in the low-temperature phase for  $N^+$  ions scattered from magnetite surface, as shown in Fig. 3.

The peak-intensity of the  $N^+$ -Fe peak at 90 K is about 2.5 times larger than that at 300K. Moreover, a broad minimum was revealed around the energy value related to  $N^+$  ions scattered off from Oxygen atoms on the surface.

The theoretical energy value for the  $N^+$ -Fe and  $N^+$ -O elastic binary collision indicated by the vertical lines in the Figure 3. We notice here that the visible shoulder observed at 300 K was attributed to the oxygen recoils. However, the appearance of the broad maximum at low temperatures at a higher energy value (instead of the shoulder-like feature at high temperature) clearly indicates that the contribution from  $N^+$  ions scattered off the magnetite surface after collision with the oxygen atoms was much enhanced.

The spectra of the negative-charged ions emitted from the  $Fe_3O_4(001)$  surface under  $N_2^+$  molecule bombardments was also shown in the same Figure. Only one huge peak was observed. The maximum of this peak was located at the relative energy value of  $E_2/E_0 = 0.185$ , i.e. in a good agreement with that for the shoulder-like feature in the LEIS spectra of the positive-charged ions at 300 K.

As we mentioned earlier it was attributed to the  $O^{-1}$  recoils. However, the energy is quite high in comparison with the theoretical value for the oxygen-recoil ( $E_2/E_0(O) = 0.140$ , shown by a vertical line in Fig. 3). Besides, this peak contains a very long high-energy tails, to the relative energy value of  $E/E_0 = 0.80$ .

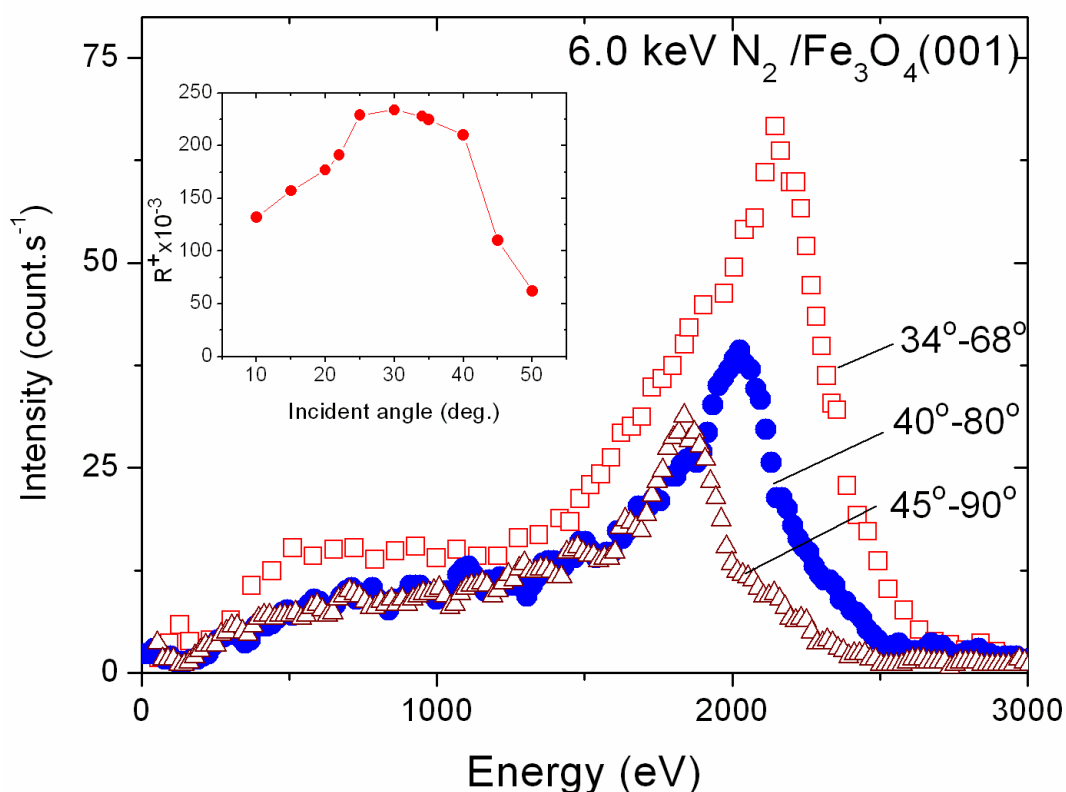


**Fig. 3.** Comparison of the energy spectra of  $N^+$  ions scattered off the  $Fe_3O_4(001)$  surface at 300 K and 90 K. The spectrum of the emitted negative-charge ions collected at 300 K was also shown. The incident particles are  $N_2^+$  molecules.  $2E_0 = 6$  keV.  $\Psi = 34^\circ$ ,  $\Theta = 68^\circ$ ,  $\varphi = 0$ . Vertical lines show theoretical values for elastic binary collision for  $N^+$ -Fe and  $N^+$ -O collision and for the oxygen-recoils ( $O_{rec.}$ ).

We have performed the measurements at different energy values of the incoming  $N_2^+$  beam. The results show that, while increasing the primary energy up to 8 keV lead to only a small increase of the peak intensity of the  $N^+$ -Fe peak, a large enhancement of the peak-intensity of the  $N^+$ -O shoulder and the plateau were observed. It indicates a complicated interplay between different processes upon  $N_2^+$  molecule dissociation on magnetite surface, in particular with the presence of the oxygen on the surface.

Since it is visible single ion-surface atom collision in the case of bombarding the magnetite surface with molecule  $N_2^+$  beam, we have performed also angle-dependence of the energy spectra for the incoming energy of 6 keV. We first collected the energy spectra at an symmetric angle geometry (i.e. the detection angle is always  $\Theta = 2\Psi$ ) with  $\Theta$  in the range of  $66^\circ - 94^\circ$ . Then we collected the spectra at different incident angles in the range  $10^\circ - 50^\circ$  at a fixed detection angle  $\Theta = 68^\circ$ . As an example, we show in Fig. 4 selected energy spectra at  $\Theta = 2\Psi = 68^\circ, 80^\circ$  and  $90^\circ$ .

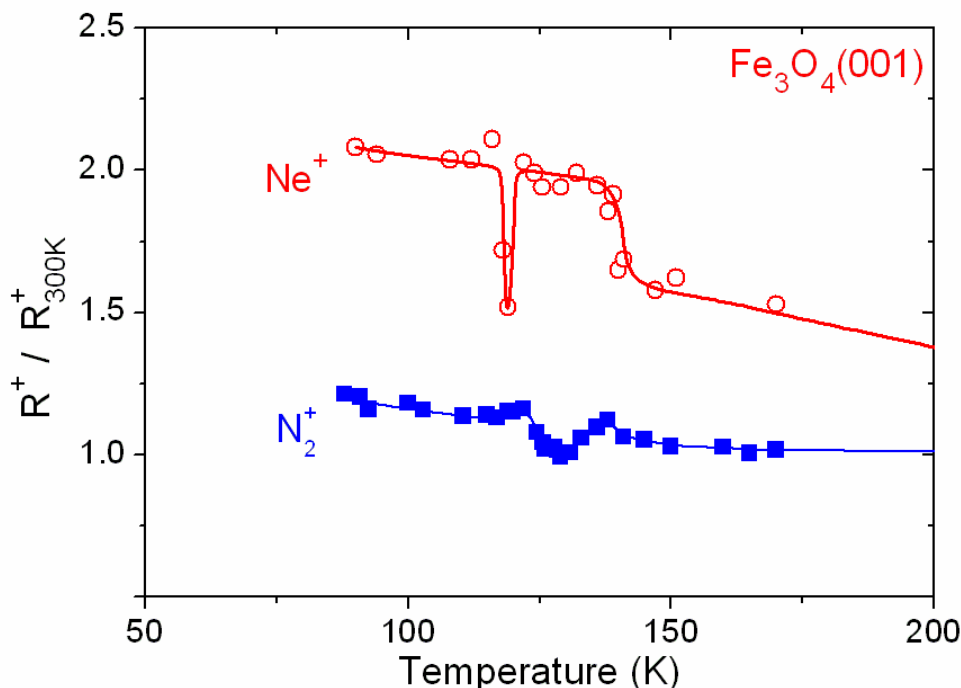
The sharp peak was always observed (even if at the detection angle  $\Theta > 90^\circ$ ) confirming that it originated from the  $N^+$ -Fe collision. The energy shift with increasing detection angle value was in a good agreement with that estimated from the binary collision model (i.e. the energy of scattered ions  $E_1$  is as a function of  $\cos(\Theta)$ ). At a fixed detection angle  $\Theta = 68^\circ$ , the peak-intensity and the related ion yield revealed a broad maximum for the incident angle in the range of  $30^\circ - 40^\circ$  (the inset of Fig. 4). Just like the case with rare-gas ions, the geometry  $\Psi = 34^\circ$  and  $\Theta = 68^\circ$  is optimal also for our LEIS experiments using the molecule beam.



**Fig. 4.** Angle dependence of the energy spectra of  $N^+$  ions scattered off the  $Fe_3O_4(001)$  surface. Inset shows the incident-angle dependence of the ion yield ( $R^+$ ) collected at a detection angle  $\Theta = 68^\circ$ . The incident particles are  $N_2^+$  molecules.  $2E_0 = 6$  keV.  $T = 300$  K.

The temperature dependence of the energy spectra as well as of scattered ion yield ( $R^+$ ) was investigated further for the whole temperature range 90 K – 300 K for the  $N^+$  ions scattered off the magnetite surface under 6keV  $N_2^+$  molecule bombardment. Fig. 5 shows the temperature dependence of the normalized scattered yield  $R^+(T)/R_{300K}$ . One wide minimum was revealed in the temperature range of 125K – 140 K. For a comparison, the  $R^+(T)$  curves obtained for 6keV  $Ne^+$  scattered ions was also shown. In fact the minimum under 6 keV  $N_2^+$  molecule bombardment was located in the temperature range between the Verwey temperature of the bulk (the sharp minimum at 125 K of the  $R^+(T)$  curves of scattered  $Ne^+$  ions) and that of magnetite surface (the sharp drop at 138 K) defined from the LEIS experiments using the rare-gas ions. In general, our results give a good evidence that for the light molecules, the re-ionization of the dissociated ions plays a very dominant role and that the charge-transfer processes is mainly governed the dissociation of  $H_2$  and  $D_2$  molecules on  $Fe_3O_4$  surfaces. The distinguishingly large survival probability of the scattered  $N^+$  ions confirmed that the charge-transfer process plays a minor role for the  $N_2$  dissociations. The different shape of the energy spectra with a visible single-collision  $N^+$ -Fe signal in the case of bombardment the magnetite surface with  $N_2$  molecule beam indicates that the registered ions by the electrostatic detector were from the single-scattered ions which maintain the charge state. Moreover, the contribution from multiple scattering to the total out-coming signal may be more dominant in the case of  $N^+$  ions scattering than that of  $H^+$  and  $D^+$  scattered ions (for which the re-ionization path was dominant).





**Fig. 5.** The normalised scattered ion yield curve ( $R^+(T)/R_{300K}$ ) for  $N^+$  ions scattered off  $Fe_3O_4(001)$  surface. The incident particles are  $N_2^+$  molecules with primary energy  $2E_0 = 6$  keV.  $\Psi = 34^\circ$ ,  $\Theta = 68^\circ$ ,  $\phi = 0^\circ$ . The  $R^+(T)$  curve of 6 keV scattered  $Ne^+$  ions was shown for a comparison.

Our results indicated a large influence of the change in the electron concentration on the scattered  $H^+$ ,  $D^+$ , and  $N^+$  ions. It is a good evidence for a strong correlation between molecule dissociations and a change of the electronic state of the surface. We empathize here that such results are in a good agreement with those obtained by (the LEIS technique) using the atomic ions of rare gases ( $He^+$ ,  $Ne^+$ ,  $Ar^+$  ions).

Namely, according to the charge-order model accounted for a freezing of the electron hopping between  $Fe^{2+}$  and  $Fe^{3+}$  sites, an increase of the electron localization below the Verwey transition leads to a large decrease of the concentration of 'free' electrons implying a large decrease of the neutralization probability (i.e. an increase of the survival probability) of the scattered ions (a less charge-transfer rate).

Such an effect would become enhanced in the case of  $N^+$  ions for which the single and multiple scattering of ions scattered from the atoms in the surface and subsurface layers play a dominant role. In all cases, it revealed a complicated interplay between neutralization and re-ionization mechanisms.

#### 4. CONCLUSIONS

Molecular dissociations on the  $Fe_3O_4(001)$  surface has been investigated using the diatomic  $H_2^+$ ,  $D_2^+$  and  $N_2^+$  molecules in the energy range of 3 – 8 keV and in the temperature range of 90 K – 300 K. Our results confirm that for the light molecules such as  $H_2^+$  and  $D_2^+$  the charge-transfer process dominates the interaction of a molecule with the magnetite surface. The single collision of the ions released from dissociation with the surface atoms was observed only for the  $N_2^+$  molecules.

A large change in the scattered ion yields around the Verwey phase transition temperature of magnetite surface was observed indicating a strong correlation between the molecule dissociation and the electronic state of the magnetite surface.

## REFERENCES

- [1] P. J. van der Zaag et al., *J. Magn. Magn. Mater.* 211 (2000) 301-308
- [2] W. Kim, K. Kawaguchi, N. Koshizaki, M. Sohma, T. Matsumoto, *J. Appl. Phys.* 93 (2003) 8032-8034
- [3] E. J. W. Verwey, *Nature* 144 (1939) 327-328
- [4] G. Subías, J. García, J. Blasco, M. Grazia Proietti, H. Renevier, M. C. Sanchez, *Phys. Rev. Lett.* 93 (2004) 156408-156411
- [5] P. Novak, H. Stepankova, J. Englich, J. Kohout, V. A. M. Brabers, *Phys. Rev. B* 61 (2000) 1256-1260
- [6] J. P. Wright, J. P. Attfield, P. G. Radaelli, *Phys. Rev. B* 66 (2002) 214422-214436
- [7] E. Nazarenko, J. E. Lorenzo, Y. Joly, J. L. Hodeau, D. Mannix, C. Marin, *Phys. Rev. Lett.* 97 (2006) 056403-1-4.
- [8] J. Schlappa et al., *Phys. Rev. Lett.* 100 (2008) 026406-026409
- [9] P. Piekarczyk, K. Parliński, A. M. Oleś, *Phys. Rev. B* 76 (2007) 165124-165139
- [10] J. E. Lorenzo et al., *Phys. Rev. Lett.* 101 (2008) 226401-1-4
- [11] J. Spalek, A. Kozłowski, Z. Tarnawski, Z. Kakol, Y. Fukami, F. Ono, L. J. Spalek, J. M. Honig, *Phys. Rev. B* 78 (2008) 100401(R)
- [12] N.-T. H. Kim-Ngan, W. Soszka, *Surf. Sci.* 536 (2003) 24-32
- [13] N.-T. H. Kim-Ngan, W. Soszka, A. Kozłowski, *J. Magn. Magn. Mater.* 279 (2004) 125-133
- [14] N.-T. H. Kim-Ngan, W. Soszka, *Acta Phys. Pol. A* 109 (2006) 715-721
- [15] W. Heiland, in: *Low Energy Ion-Surface Interactions*, Ed. J.W. Rabalais, Wiley, New York, 1994.
- [16] I. A. Wojciechowski, M. V. Medvedeva, V. Kh. Ferleger, K. Bruning, W. Heiland, *Nucl. Instr. and Methods B* 164-165 (2000) 626-632
- [17] J. M. Schins, R. B. Vrijen, W. J. van der Zande, J. Los, *Surf. Sci.* 280, 145 (1993).
- [18] L. M. Kishinevsky, E. S. Parilis, V. Kh. Ferleger et al., *Atomic Collisions on Solid Surface*, North-Holland, Amsterdam (1993)
- [19] M. Hamhami, N. Djouhri, A. C. Chami, M. Richard-Viard, M. Boudjema, *Nucl. Instr. and Methods B* 266 (2008) 3359-3364
- [20] K. Bruning, T. Schlatholter, W. Heiland, *Nucl. Instr. and Methods B* 182 (2001) 162-166 and references therein.