XLI Colloquium on Metal Forming 18.03.2023-21.03.2023, Zauchensee, Austria

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Cel konferencji jest zdefiniowany jako:

“The Colloquium is an opportunity to promote the exchange of ideas, knowledge and experiences between university scientists and industry experts.”

Udział wzięli przedstawiciele przemysłu głównie z Austrii i Niemiec:

- LKR Light Metals Technologies, AIT, Ranshofen
- Voestalpine Tubulars GmbH & Co KG
- IMS Messsysteme GmbH
- LASCO Umformtechnik GmbH
- MICAS Simulations Ltd., Oxford
- Voestalpine BÖHLER Aerospace GmbH & Co KG
- Nokra Optische Prüftechnik und Automatisierung GmbH

Conference Program

Saturday 18th of March 2023

- Martin Stockinger, Chair of Metal Forming, Montanuniversitaet Leoben
  “Opening speech & greeting words”
- Konstantin Prabitz, Chair of Metal Forming, Montanuniversitaet Leoben
  “How to scientifically (not) plan and execute a trip to a non-existing country”

Sunday 19th of March Sunday

- Alexander Wenda, Chair of Metal Forming, Montanuniversitaet Leoben
  “An inverse finite element approach for the evaluation of the hot torsion test”
- Carina Schlögl, LKR Light Metals Technologies, AIT, Ranshofen
  “Modellierung der Texturentwicklung in der FE-Simulation mittels FE-VPSC”
- Thomas Brunner, voestalpine Tubulars GmbH & Co KG
  Burkhard Schöttler, IMS Messsysteme GmbH
  “3-D Oberflächeninspektion - Technologie und Anwendung in der Nahtlosrohrherstellung”
- Maciej Pietrzyk, Department of Applied Computer Science and Modeling, AGH University, Kraków
  Jan Kusiak, Department of Applied Computer Science and Modeling, AGH University, Kraków
  “Uncertainty of Microstructure Modelling during hot rolling of DP steels”

- Marcel Czipin, Chair of Metal Forming, Montanuniversitaet Leoben
  “Feasibility Study for the Finite Element Analysis of Wire-Arc Additive Manufactured Ti-6Al-4V in Deform® 12.1”
- Setiadi Suriana, Chair of Metal Forming, Montanuniversitaet Leoben
  “Numerical Analysis on the influence of the Load Path Distribution on Damage Evolution and Void Closure within the Roll Gap during Hot Rolling”
- Jonas Knoche, Chair of Metal Forming, Universitaet Siegen

Monday 20th of March

- Sebastian Frank, LASCO Umformtechnik GmbH
  “Flexible forming- future technologies”
- Nadine Wurm, Chair of Metal Forming, Universitaet Siegen
  “ Umformverhalten faserverstärkter Thermoplasthalbzeuge beim ebenen Schwenkbiegen ”
- Julius Peddinghaus, Institut für Umformtechnik und Umformmaschinen, Leibniz Universität Hannover
  “ Adhäsions- und Schädigungsverhalten von Duplex-behandelten Werkzeugen beim Gesenkschmieden von Alu-Miniumlegierungen ”
- Zbigniew Kakol, Department of Applied Computer Science and Modeling, AGH University, Kraków
  Konstanty Marszalek, Department of Applied Computer Science and Modeling, AGH University, Kraków
  “Changes of magnetite electronic structure induced by magnetic field – experiment and computations”
- Bastian Zettl, Institute of Manufacturing Technology, FAU Erlangen-Nürnberg
  “Analyse des Einflusses eines Kaltrichtprozesses auf die Eigenschaften mehrlagiger Aluminiumhalbzeuge”
- Nikolay Biba, MICAS Simulations Ltd., Oxford,
  “Automated Process Design integrated with numerical Simulation for Rolling, Forging and Extrusion Technologies”
- Kai Brunotte, Chair of Metal Forming, Universitaet Siegen
  “Einfluss einer kraftschlüssigen Verbindung auf den Wärmetransport zwischen Heatpipe und Schmiedegesenk”

Tuesday 21st of March

- Bernd-Arno Behrens, Chair of Metal Forming, Universitaet Siegen
  “Prozessentwicklung zur Herstellung einer belastungsangepassten hybriden Lagerbuchse durch Tailored Forming”

- Johannes Hoffer, voestalpine BÖHLER Aerospace GmbH & Co KG
  “Prediction of Non-Conformity in Aerospace Production with Deep Learning and Explainable AI”
- Günther Lauven, nokra Optische Prüftechnik und Automatisierung GmbH
  “alpha.hot3D: Kaltmaß-Geometrieauswertung von warmen Prüflingen aus Schnellschmiedepressen mit objektiver Beurteilung des Werkzeugzustands”
- Manuel Reck, Institute of Manufacturing Technology, FAU Erlangen-Nürnberg
  “Wear Analysis of Micro Textured Coining Tools”
- Konstantin Prabitz, Chair of Metal Forming, Montanuniversitaet Leoben
  “Prozessoptimierung mittels multiphysikalischer Modellierung des Widertsandspunktschweissens”

W trakcie konferencji, na której wystąpiliśmy z referatem naukowym (w załączeniu), opublikowanym w materiałach konferencji, prowadziliśmy z przedstawicielami przemysłu rozmowy dotyczące:

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- zapotrzebowania na badania, zapytań przemysłu o projekty, ZAMÓWIEŃ NA PROJEKTY
- finansowania badań
- transferu wiedzy

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CHANGES OF MAGNETITE ELECTRONIC STRUCTURE INDUCED BY MAGNETIC FIELD – EXPERIMENT AND COMPUTATIONS

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ABSTRACT: When the magnetic field is applied on a single crystal of magnetite at 50K < T < 124K, the monoclinic c_m axis, which is the easy magnetization axis, switches to one of the <100> cubic directions, nearest to the direction of the magnetic field, and the phenomenon known as an axis switching (AS) occurs. The results of magnetic and structural studies of magnetic easy axis switching in magnetite observed via different experimental techniques are presented. In this review article, we show that this process is linked to electronic order alteration.

KEYWORDS: metal–insulator phase transition; magnetite; charge order; orbital order; strongly correlated systems

1. INTRODUCTION

Magnetic materials are now becoming more and more important in the development of modern society. They have a wide range of applications being used in the creation and distribution of electricity in generators, transformers and transducers, and in a large variety of devices that use electricity. They can be found in home appliances and home entertainment systems. In medicine, they are used in body scanners. They are also used for the storage of data on audio and video tape as well as on computer disks.

Recently, these materials are undergoing deep transformation towards the applications in nanometer scale electronic devices where both charge and spin (spintronic devices) can be used to carry and manipulate information, instead of charge only, like in traditional electronics. This way new types of junctions, transistors, logic gates, sensors, and devices can be built. For the development of these spin-based electronics the understanding of interplay of electronic and magnetic properties is crucial.

Magnetite Fe_3O_4 is the first magnetic material known by the mankind being utilized to enable navigation in the world. Biogenic magnetite nanoparticles have found great interest in medicine and pharmacology as a drug delivery system and also as a magnetic contrast agent in MRI diagnostic. Magnetite is also one of the model magnetic materials that, due to its spin-polarized transport, can be a testing ground for spin electronics [1].

Finally, magnetite is the first material where the concept of a strong correlations driven metal-insulator transition was suggested and found at T_V = 124 K in the so-called Verwey phase transformation named after one of its discoverers [2]. This metal-insulator phase transformation is the main reason, that apart from its wide applications, magnetite attracts the attention and serves as a test ground for solid-state physicists, geophysicists, and material scientists.

Understanding of magnetic, electronic and structural properties of magnetite and the related phenomena, all strictly linked to the Verwey transition, is essential both, for science and applications. One of such important phenomena is the magnetic axis switching (AS); below, the background of AS and its experimental observation is presented and discussed.

2. VERWEY TRANSITION

The Verwey transition is reflected in practically all physical characteristics, with the best known being a resistivity drop by two orders of magnitude on heating [3] and the spectacular increase in heat capacity [4], proving a discontinuous character of this phase transformation. The anomaly is present in magnetic susceptibility as well [5].

Also, the structure changes at the transition: from high–temperature cubic [6] to low-temperature monoclinic [7].

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When the material is cooled down, the distortion of the cubic lattice occurs and the symmetry turns from cubic to monoclinic, with one of cubic axes doubled. Iron atoms have two surroundings: tetrahedral (A), where the valence is +3 and octahedral (B), where the valance is a subject of discussion.

The magnetite cubic structure together with iron atoms surroundings and the relation between high-temperature cubic and low-temperature monoclinic structures are presented in Figure 1a and 1b respectively. Crystal lattice and iron positions play a crucial role in the understanding of the Verwey transition and axis switching phenomenon.

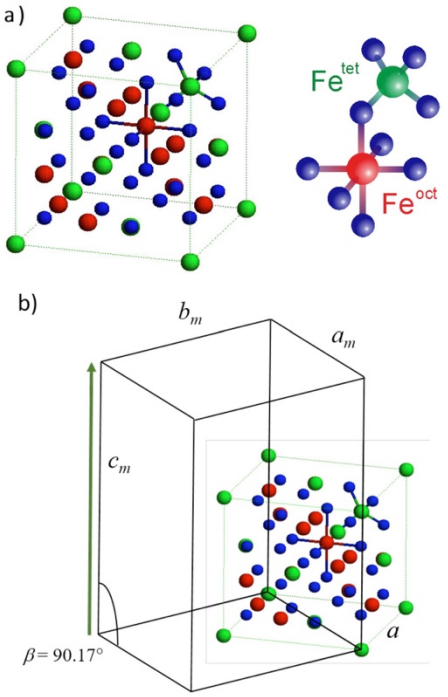

Figure 1 (a) Magnetite cubic structure with tetrahedral and octahedral iron surroundings, (b) relation between high-temperature cubic and low-temperature monoclinic structures. Oxygen atoms are shown as blue spheres.

3. CHARGE ORDER IN THE VERWEY STRUCTURE OF MAGNETITE

Already in the first papers of Verwey [1] the following mechanism of the transition was suggested. First, iron cations that occupy tetrahedral positions are trivalent (+3), and both trivalent (+3) and bivalent (+2) iron cations reside on octahedral positions. At high temperatures one electron from iron on these octahedral positions may be treated as jumping on all octahedral sites, establishing the mean valance as +2.5. When the material is cooled down, due to strong Coulomb interaction between those octahedral electrons, they freeze on certain regular lattice positions arranged in certain charge order. This picture of strongly correlated electrons freezing into the well-defined ionic charge order at T_V was questioned when the exact low temperature structure was resolved [8]. It exposed very complicated structure, with iron atoms on octahedral sites arranged in characteristic three atoms cigar-like structures (Figure 2), trimerons, with valences 2.3–2.95 within one trimeron. Generally, the central atom is less positive than the end atoms and the Verwey model may only be treated as a useful but physically simple approximation.

A more detailed analysis of resonant X-ray scattering (RXS) spectra [9] shows that three subsystems changed their ordering below T_V : atomic arrangement (causing lattice distortion), charge and the way the charge is organized in orbitals.

It was then interesting to study how the manipulation of the magnetic easy axis by the magnetic field is reflected in the changes of these three subsystems.

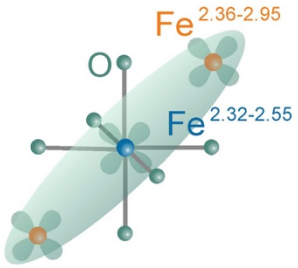

Figure 2 An example of trimeron with the valence range of the central and end atoms marked [8].

The Verwey transition and subsequently charge and orbital ordering are very subtle phenomena. Even very small amount of spurious atoms or nonstoichiometry dramatically changes the transition. Departure from ideal stoichiometry in $Fe_{3(1-\delta)}O_4$ or the presence of spurious atoms lowers the transition temperature T_V. When 3δ exceeds 0.012 the transition changes from discontinuous to continuous one. Finally, the transition disappears when doping or nonstoichiometry parameter 3δ exceeds one Fe-atomic percent. These findings were revealed by specific heat and electrical transport measurements [10 - 13].

So, since already a tiny amount of dopants or nonstoichiometry can substantially change the transition, the special treatment is needed to prepare those materials.

4. SAMPLE PREPARATION

Synthetic samples were 99.999% pure single crystals grown at Purdue University by the skull melter, cruciibleless technique [14,15]. This technique allows for the control of the oxygen partial pressure during growth, thereby ensuring that the melt remains within the stability range of the material. After preparation, the crystals were subjected to subsolidus annealing under CO/CO_2 gas mixtures to establish the appropriate metal/oxygen ratio [16].

5. MAGNETIC PROPERTIES

At high temperatures magnetic easy, intermediate and hard axis of Fe_3O_4 are along cubic <111>, <110> and <001> directions, respectively. Below T_V, each of cubic <100> can become an easy axis and the c_m monoclinic axis as well [17, 18] (Figure 3). As a result, the material breaks into several structural domains unless the external magnetic field $B > 0.2$ T along one of <100> is applied while cooling through the transition [17, 19]. This particular direction will then become both the unique c_m axis and also the magnetically easy axis [19] with some charge and orbital arrangement.

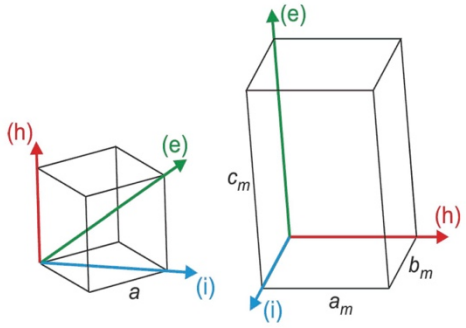

Figure 3 Magnetic easy (e), intermediate (i) and hard (h) axes above (left) and below T_V transition temperature.

Furthermore, anisotropy energy is changing at the transition by one order of magnitude as shown in Figure 4 where temperature dependencies of the dominant anisotropy constant K_1 and K_a are presented. It is worth to note, that K_1 vanishes near 130 K (isotropy point) and that magnetization remains unchanged through the transition within 0.1% accuracy.

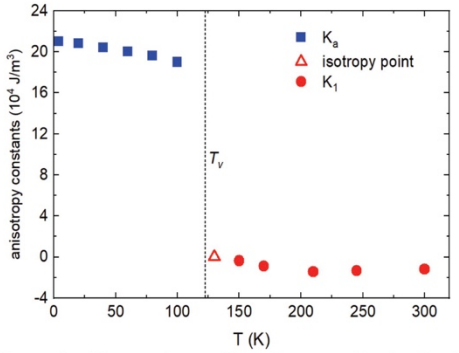

Figure 4 Temperature dependence of dominant anisotropy constants K_1 (above T_V) and K_a (below T_V). The isotropy point, $K_1 = 0$, is marked by the open triangle.

6. AXIS SWITCHING

6.1 AS OBSERVATION BY MAGNETIZATION MEASUREMENTS

Already in the early fifties Calhoun [19] has noticed that magnetic easy axis can be switched at temperatures slightly lower than T_V. Namely, when the external magnetic field is applied along one of the other <100> directions as that along c_m, then a reorientation of easy magnetic and monoclinic c_m axes takes place and this <100> direction becomes a new easy and monoclinic c_m axis [19, 20].

This magnetic manipulation of magnetic easy axis is shown in Figure 5. If the magnetic field is applied along an easy direction, the typical magnetization curve is measured (shaded triangles). If now the field is applied along other <100> cubic direction, the initial magnetization is completely different (line, 4K). At higher temperatures (60K in Fig. 5), at a certain field, the moment changes and crawls to the $M(B)$ curve characteristic for easy magnetization. And now if the field is decreased, the magnetization follows the curve, typical for an easy direction.

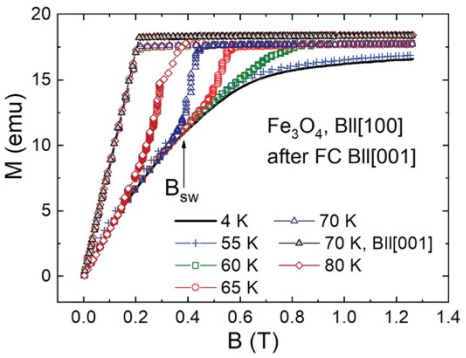

Figure 5 $M(B)$ measured along cubic axis [100] after field cooling in B=1T along other cubic axis [001] across T_V (easy axis establishing) showing AS effect [21]. Note that shaded triangles, 70K, B||[001], show a typical M(B) curve measured along an easy axis.

Clearly, switching field B_{sw} depends on temperature. Since the axis switching has a relaxation character, it was proposed [19] that B_{sw} can be described by the relation:

$$B_{sw} = cT \exp(U / kT)$$

where U is the energy barrier that must be jumped over, or tunneled through. This dependence is supported by experiment as shown in Figure 6.

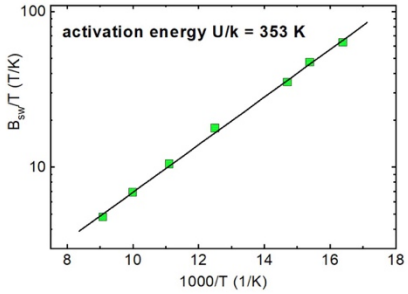

Figure 6 Temperature dependence of switching field, supporting Calhoun's [19] prediction.

Activation energy U, similarly as the Verwey transition is sensitive to a doping or nonstoichiometry. The results of activation energy in doped or nonstoichiometric samples are presented in Figure 7. For each case, the activation energy increases with the lowering Verwey temperature i.e. higher level of defects.

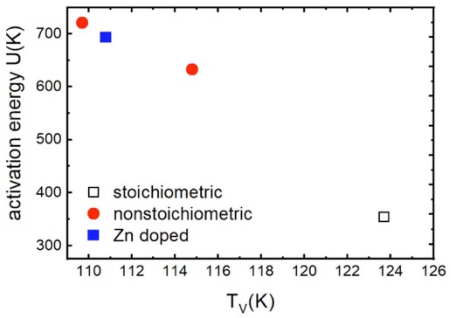

Figure 7 Activation energy vs. Verwey temperature changed either by doping or nonstoichiometry [24].

AS phenomenon was confirm by resistivity experiments [22] and it has also an impact on macroscopic size. Changes of sample size in magnetic field were observed by the strain gauge technique [23]. This result was interpreted as caused by the specific electronic structure of magnetite (trimerons).

Direct observation of the crystalline structure proved that magnetic easy axis switching is strictly related to the crystallographic structure relaxation [25]. So, we see, that the manipulation of the structure by the magnetic field is possible.

Our attempts to prove this fact microscopically by the NMR studies are described below.

6.2 NMR OBSERVATION OF AXIS SWITCHING

The NMR spectroscopy is the experimental method that can detect separate iron atoms in all different positions, thus low-temperature magnetite NMR spectrum consists of eight lines assigned to eight crystallographically nonequivalent tetrahedral A sites and sixteen lines from sixteen crystallographically nonequivalent octahedral B sites.

The experiments detecting the axis switching by NMR spectroscopy were performed by comparing the spectra before and after the axis switching. Since tetrahedral Fe atoms are nearest neighbours of octahedral Fe sites where we expect the changing arrangements, so Fe tetrahedral atoms act here as probes observing AS processes.

The results of measurements are presented in Figure 8, together with the schematic representation of c_m axis arrangement.

The experiment was carried out in three steps [26]. First, the sample was cooled in a magnetic field of 1.3 T through the Verwey transition to establish unique magnetic easy axis and in the same time unique monoclinic c_m axis with accompanying charge and orbital order in the sample. Then, NMR spectrum was recorded in the magnetic field 0.3 T at 20 K (Figure 8a). In the second step magnetic field was applied perpendicularly to the easy direction of magnetization, and another The NMR spectrum was recorded (Figure 8b). NMR spectrum is now significantly different than before. It results from the different surrounding of the probe due to different B direction, without, however, affecting charge order since the temperature and magnetic field are too low to cause the axis switching to occur.

In the third step, to enable axis switching, the temperature was raised to 80 K and the field was increased to 1.3 T. After AS occurred, sample was cooled down to 20 K and NMR spectrum was again collected in 0.3 T magnetic field (Figure 8c).

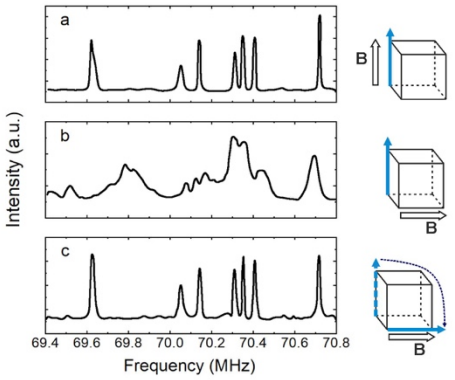

Figure 8 Axis switching detection by NMR – three steps of experiment: (a) and (c) spectra with B along the easy axis before and after AS respectively, (b) second step: spectrum with field perpendicular to the easy axis (see text for details).

The dynamics of the process was also captured by NMR measurements [26] as shown in Figure 9.

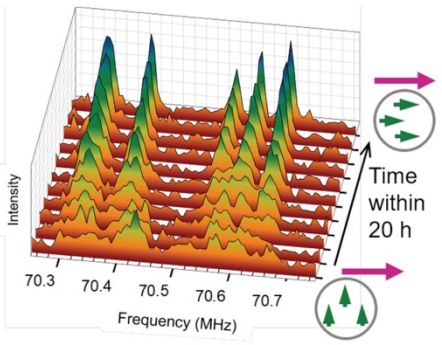

Figure 9 Axis switching dynamics observed by NMR; $T = 57$ K, B=0.5 T (see text for details).

Again, the sample was cooled in magnetic field of 1.3 T through the Verwey transition to establish unique magnetic easy axis. Then, NMR spectra were recorded at $T = 57$ K in the magnetic field $B = 0.5$ T perpendicular to the easy axis. Spectra were recorded one after another for 20 hours. Selected data are displayed in Figure 9. The first measured spectrum (in front of Figure 9) displays the state at the very beginning of the switching process while the last measured spectrum (last in Figure 9) indicates that the axis switching occurred.

6.3 SIMULATION OF MAGNETITE STRUCTURE CHANGES DURING AS

The arrangement of Fe atoms in octahedral (B) positions together with electron orbitals [27] is presented in Figure 10. Trimerons are marked by the green lines.

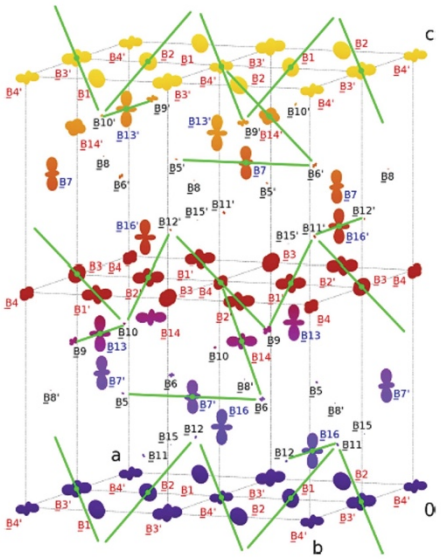

Figure 10 Octahedral Fe positions in the magnetite monoclinic cell. Trimerons are marked by the green lines.

Taking into account the results of Senn [8] and Król [24], it was possible to build models of the low-temperature magnetite structure before and after the process of switching the axis. It was then possible to compare both atomic arrangements to obtain information on iron A and B atoms position, valence and symmetry changes caused by AS.

As a result of AS, atoms change their position slightly, and, to a greater extent, their valence. Two examples illustrating possible changes are presented in Figures 11 and 12. The first one shows Fe B atoms and its surrounding before (a) and after (b) AS. Both symmetry and valence have changed.

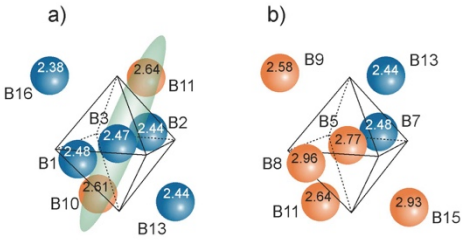

Figure 11 Fe B atoms and its surrounding before (a) and after a(b) axis switching.

The second one shows Fe B13 atom and its surrounding before (a) and after (b) AS. Note that in this case both valence of the atom in this site and the valence of neighboring Fe atoms is not affected and only their surrounding is reoriented.

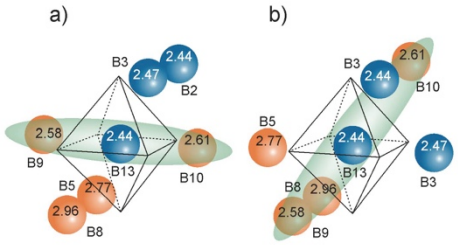

Figure 12 Fe (B) atom that does not change its symmetry (i.e. also its valence and the valence of nearest neighbors) in AS.

Thus, AS in magnetite is connected with Fe B-atoms orbitals reorganization rather than long-range electron processes, as the Verwey transition. Nevertheless, electron rearrangements occurring in AS do not only involve immediate surroundings but turn out to be a collective process.

3. SUMMARY

The easy magnetic axis switching in magnetite is clearly reflected in field dependence of magnetization but the direct structural data showed that magnetic and structural monoclinic axes are switched simultaneously. In other words, crystal structure can be modified by magnetic field as observed microscopically by NMR and RXS that also proved charge and orbital ordering alteration.

All presented experimental results suggest that trimeron change being essential for the axis switching is also a precursor of the Verwey transition although correlation is not straightforward since the activation energy rises with decreasing Verwey transition temperature, contrary to the first expectation. Nevertheless, further observation of the axis switching and the attempt to construct its microscopic mechanism may provide a simple way to simulate the phase transformation.

It might be also a key point to the understanding of majority of strongly correlated electronic behavior in magnetite, but also in transition metal oxides.

ACKNOWLEDGEMENTS

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