Magnetite at low temperature: Resonant Inelastic X-ray Scattering (RIXS) at the Fe K-edge

M Wilke¹, W A Caliebe², P Machek³
¹ Helmholtzzentrum Potsdam Deutsches GeoForschungsZentrum, Telegrafenberg, D-14473 Potsdam
² Hamburger Synchrotronstrahlungslabor at DESY, Notkestr. 85, D-22603 Hamburg
³ Institute of Physics of the AS CR, Cukrovarnicka 10, CZ-16253 Prague
E-mail: max@gfz-potsdam.de

Abstract. At room temperature, magnetite (cubic inverse spinel structure, Fd-3m s.g.) shows metal-like electrical conductivity, which discontinuously drops by two orders of magnitude below ca. 120 K (Tᵥ). This is due to a first-order phase transition, where the cubic structure is distorted to monoclinic symmetry (Cc s.g.). Models for this metal-insulator transition are still highly debated. We performed 1s3p as well as 1s2p RIXS measurements well below and above Tᵥ on a sample of synthetic magnetite powder to probe any difference present in the electronic states. Neither 1s3p nor 1s2p RIXS spectra reveal any differences between the two phases. Our observations are consistent with earlier EXAFS data and indicate no changes in the local structural geometry around Fe.

1. Introduction
Magnetite (Fe₃O₄, cubic inverse spinel structure, Fd-3m s.g.) is the oldest known magnetic material. At room temperature, magnetite shows metal-like electrical conductivity, which discontinuously drops by two orders of magnitude below ca. 120 K (Tᵥ, [1]). This is due to a first-order phase transition, where the cubic structure is distorted to monoclinic symmetry (Cc s.g.). In magnetite, Fe³⁺ occupies the tetrahedral position on the A-sublattice, while both Fe²⁺ and Fe³⁺ share the octahedral position on the B-sublattice. Proposed models for this metal-insulator transition (MIT) are: charge ordering on the B-sublattice at the transition or a conductivity mechanism involving electron-phonon coupled states, which are not present below Tᵥ (e.g. [2], [3], [4], [5]). Lately, a combination of weak charge order and orbital order of the t₂g states invoked by local electron interactions, that affect the electron-phonon interactions were used to explain the MIT [6].

We performed 1s3p as well as 1s2p RIXS measurements well below and above Tᵥ on a sample of synthetic magnetite powder with a view to probe any difference present in the electronic states and as a in order to support one of the mentioned models.

In RIXS experiments, X-ray emission spectra are measured with high energy resolution while scanning the excitation energy through the absorption edge of the element studied. RIXS spectra provide more detailed information about unoccupied states compared to XAFS measurements, particularly allowing separating weak quadrupolar and strong dipolar transitions. Absorption spectra acquired by partial-fluorescence yield, especially of the Kβ₁,₂-line, provide the possibility to acquire...
core-hole lifetime broadening removed XAFS spectra as the intrinsic spectral resolution in this way is governed by the lifetime of the final state [7], [8].

2. Experimental

The RIXS experiments were performed at HASYLAB, at the wiggler beamline W1. The beam is focused by a Au-coated toroidal mirror. A Si(111) double-crystal monochromator was used with an energy resolution of about 2 eV at 7 keV. The emission spectra were measured using an in-vacuo Johann spectrometer in dispersive geometry with large analyzing crystals [9]. In this arrangement, the sample is placed inside of the Rowland circle and fluorescence signal is acquired by means of position sensitive CCD. This setup gives the possibility to obtain a range of emission energies at one shot without performing time-consuming theta/2theta scans with analyzer and detector. In our experiment we used Si(531) and Si(440) spherically bent crystals as analyzers for the measurements of Kβ1,3 emission line and Si(333) spherically bent crystal for the measurement of the Kα1,2 emission lines, respectively. These reflections correspond to Bragg angles θB=73.1° and θB=66.2° (for Kβ1,3) and θB=67.8° for Kα1,2. The employed Bragg angles are optimal for the measurements in dispersive geometry, because the high energy dispersion enables us to measure a broad range of the emission spectrum and at the same time the energy resolution of the measurement is still reasonable (about 3 eV [9]). During low temperature measurements the sample was cooled using a closed-cycle He cryostat.

3. Results and Discussion

3.1. RIXS and XANES of magnetite at room temperature

The intensity around energies of the Kβ1,3-emission line of magnetite as a function of the excitation energy across the Fe K-edge is plotted in Figure 1a. The XANES spectrum based on the partial fluorescence-yield around the maximum of emission spectra and a high-resolution absorption spectrum are compared in Figure 1b. Both spectra reveal the same spectral features, i.e. a pre-edge several eV below the edge, a resonance in the main edge and at least three features at the white line and slightly higher energies (7130–7150 eV), which can be attributed to 1s-3d-like, 1s-4p transitions and multiple scattering of the photo electron. Finally the first EXAFS maximum is visible at ~7190 eV. The spectrum taken by fluorescence yield shows a much better separation of the pre-edge from the tail of main absorption edge and highlights the removal of the core-hole lifetime broadening (1.25 eV [10]) by the use of the partial fluorescence yield. However, the energy resolution of this spectrum is certainly still dominated by the relatively large bandwidth of the Si(111) monochromator (2 eV).

In Figure 2a, the corresponding RIXS plane, which represents the same data as shown in Fig. 1a, is plotted as a function of excitation energy and energy transfer (final state energy) in the the pre-edge and main edge energy region. Cross-sections through the pre-edge structure at constant excitation energy and energy transfer are shown in Fig. 2b and 2c, respectively. The pre-edge is assigned to 1s-3d-like transitions that are quadrupolar in nature in the case of centro-symmetric sites (e.g. O₆) and become dipolar through p-d mixing in the case of non-centrosymmetric sites (e.g. T₄) [8]. For magnetite the contributions from the three different Fe sites strongly overlap and cannot be clearly separated in the spectra. The tail of the pre-edge at final state energies of 55-57 eV and an excitation energy of ~7115 eV indicate an additional weak contribution off the line of constant emission energy (diagonal in Fig. 2a).
3.2. RIXS and Verwey transition
Cross-sections through the 1s3p and 1s2p RIXS plane acquired at room temperature and at low temperature, far below the Verwey transition, are shown in Fig. 3 & 4. The spectra reveal no energy shifts in the features of the pre-edge. The small differences in normalized intensity can be attributed to uncertainties of the background correction and normalization procedure or to slight instabilities of the beamline optics over the relatively large time period necessary to acquire the two RIXS spectra. This can be verified by X-ray emission spectra excited in the pre-edge that were taken with a much smaller time interval, i.e. they are only separated by the time needed to heat or cool the sample. This comparison (Fig. 5) reveals no differences for the two temperatures, either, which can be also observed at other energies in the pre-edge.

The observations found here for the RIXS indicate no changes in the in the unoccupied electronic states probed by this method, which imply that the average local structural geometry around Fe is preserved across the phase transition at T_v. Our observations are consistent with earlier EXAFS data [3], where the phase transition was only discernible in anomalous variations of the fitted Debye-Waller parameter in the temperature range of the transition. Both results are consistent with the model proposed by [6] and it seems unlikely that this transition is detectable by XAFS techniques even if better resolved data can be acquired.
Fig. 3: Comparison of cross-sections through the 1s3p RIXS at temperatures below and above $T_V$ as indicated at constant excitation energy (left) and at constant energy transfer (right).

Fig. 4: Comparison of cross-sections through the 1s2p RIXS at temperatures below and above $T_V$ as indicated at constant excitation energy (left) and at constant energy transfer (right).

Fig. 5: Comparison of normalized $K\beta_{1,3}$ (left) and $K\alpha_{1,2}$ (right) emission lines acquired at the maximum of the pre-edge and at temperatures indicated.

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