Soft resonant x-ray scattering in highly stoichiometric magnetite.

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Abstract. We report here soft resonant x-ray scattering (SRXS) measurements on a single crystal of highly stoichiometric Fe3O4 (Verwey transition at TV = 123.5 K). Resonant intensity was observed at the Fe L2,3 and the O K edges for the (0,0,1/2) reflection and at the Fe L1-edge for the (001) reflection in the low temperature phase. The energy, azimuthal angle and temperature dependence was explored using either σ− or π−incidence. The (001) reflection is active in the σ−σ′ polarization channel whereas the (0,0,1/2) reflection is in the σ−π′ polarization one. The (0,0,1) reflection is also observed at energies below the Fe L1-edge, confirming that this reflection is permitted by the crystal symmetry of the low temperature phase. On the other hand, the (0,0,1/2) reflection is strictly forbidden and scattered intensity is only observed on resonance. The resonant and non-resonant signals simultaneously disappear at TV for the two studied reflections at both the Fe L-edges and the O K-edge. This result indicates that the resonant reflections and the associated electronic anisotropy of the Fe d, Fe p and O p-states are explained by the lattice distortions.

1. Introduction.

Magnetite, Fe3O4, is the first example for an oxide to show a metal-insulator phase transition, the Verwey transition [1]. This is a structural phase transition where the cubic inverse spinel structure distorts to a monoclinic unit cell. This transition was believed since its discovering as due to charge ordering of the Fe2+ and Fe3+ ions on the octahedral coordinated B sites. Resonant x-ray scattering (RXS) has developed in recent years into a powerful technique for investigations of charge and orbital ordering phenomena. RXS studies at the Fe K edge found that the charge disproportionation between the formal valences in the low-temperature phase is far from one electron disproportionation [2]. Magnetite displays a highly complex low temperature crystal structure with the appearance of superstructure diffraction peaks with wave vectors (0,0,l) and (0,0,l/2). Recently, it has been reported soft resonant x-ray scattering SRXS on a thin layer of magnetite at the L_{1,2} edge of the (0,0,1/2) and (0,0,1) reflections [3] and at the O K edge of the (0,0,1/2) reflection [4]. Both papers interpret their results as due to t_{2g} orbital and Fe^{3+}/Fe^{2+} charge ordering.

In this communication we report new SRXS experiments in a high stoichiometric magnetite (TV = 123.5 K). We note that magnetite is a very difficult system either for the unknown low temperature structure or for other experimental difficulties such as the existence of twinning, strong self-absorption, etc. We report SRXS at the Fe L_{2,3} and O K edges for the (0,0,1/2) reflection and at
the Fe L_{1}-edge for the (001) reflection. The energy, azimuthal angle and temperature dependence was studied with either σ- or π-incidence to determine the active polarization channel of the scattering process. The (0,0,1) reflection is also observed at energies below the Fe L_{1}-edge, confirming that this reflection is permitted by the crystal symmetry of the low temperature phase. The resonant and non-resonant signals simultaneously disappear at T_V at both the Fe L-edges and the O K-edge, indicating that lattice distortions and electronic anisotropy are intimately joined.

2. Experimental section.

High purity Fe_2O_3 (99.999%) was fired at 1200 °C for 24 h in a CO_2/CO (96/4) atmosphere. The powders were ground pressed into rods and sintered at 1400 °C for 24 h. Magnetite single crystals were grown from the rods in the same atmosphere by using a halogen lamp floating zone furnace. The phase purity was controlled by means of x-ray powder diffraction of the crushed crystals using a Rigaku RINT 2000 diffractometer. Magnetization at 5 K is 4,11μB and T_B measured by magnetic susceptibility was 123.5 K with a narrow transition width, indicating that the sample is homogeneous and nearly ideal oxygen stoichiometry. A large crystal was cut with the [001] cubic direction as the surface normal and polished to a flat, shiny surface.

SRXS experiments were performed on the ID08 beam line of ESRF (Grenoble, France). The experimental set-up allows to carry out azimuth-dependent scattering but no-polarization analyzer was available. The energy resolution was 800 meV at 710 eV.

3. Results and discussion.

Figure 1 shows the energy dependence of the resonant intensity at the (0,0,1/2) reflection over the Fe L_{2,3} edges. The scattered intensity was corrected by subtracting the background obtained by recording the intensity out of the Bragg condition. The absorption spectra is also plotted as reference for the energy scale. No scattered intensity was observed at energies out of the absorption edge, showing the absence of Thomson scattering. The inset of fig. 1 shows the θ-2θ scan of the (0,0,1/2) reflection at the energy of the first resonance. The spectrum shows a sharp resonance at 708.4 eV with a shoulder (706.8 eV) at the L_3 threshold and two maxima at 720 and 721.4 eV at the L_2 one. This behaviour agrees with that found on a magnetite thin film measured by Schlappa et al. [3], except for the relative intensity between the two peaks. The self-absorption effect in the bulk single crystal strongly reduces the intensity of the peak at 708.4 eV.

![Figure 1](image1.jpg)

**Figure 1.** The energy dependence of the (001/2) reflection (σ-incidence) recorded over the Fe L_{2,3} edges at 30 K. The total electron yield absorption spectrum is compared in the same energy scale. The inset shows a θ-2θ at 706.8 eV.

![Figure 2](image2.jpg)

**Figure 2.** Comparison of the resonant scattered intensity of the (0,0,1/2) reflection for σ− and π−incidence at 706.8 eV as a function of the azimuth angle.
In order to determine the nature of this resonant reflection, we have measured the dependence of the intensity on the azimuth angle. This analysis was unfruitful since surface effects such as mosaicity and twinning obscured the studied azimuthal behaviour. Our results do not lead to a monotonous azimuth dependence but we conclude that the energy line shape of SRXS spectra was identical for all studied azimuth angles over a range $-90^\circ \leq \phi \leq 90^\circ$. In order to identify the active polarization channel, we have carried out experiments with either $\sigma$- or $\pi$-incidence. Figure 2 compares the intensity at 706.8 eV for different azimuth angles between $\sigma$- and $\pi$- incidence. Neither different intensity nor different spectral line shape are obtained (we note that the measured intensity is $\sigma\sigma + \sigma\pi$ for $\sigma$-incidence and $\pi\pi + \pi\sigma$ for $\pi$-incidence). Therefore, we conclude that the only active polarization channel is the $\sigma\pi$ one.

We have also measured the $(0,0,1)$ reflection at the Fe L$_1$ edge, both on resonance and out of resonance at energies below the absorption edge. We observe scattered intensity in both conditions, showing that this reflection is permitted in the low temperature phase. In this case, the active polarization channel is only the $\sigma\sigma$ one [5].

Figure 3 shows the energy scan of the $(0,0,1/2)$ reflection in the vicinity of the O K-edge. The O K-edge absorption spectrum is also reported for comparative purposes. A sharp resonance was observed corresponding with the rising edge of the pre-peak structures of the O K-edge. The textAlign measurements as a function of the azimuth angle have shown a non-monotonous behaviour similar to that observed at the L$_{3,2}$ resonance. On the other hand, the intensity of the reflection and the spectral shape is independent of the incident photon polarization. The $\sigma$- and $\pi$-incidence spectra superimpose as it is shown in figure 3. This result, similar to the L$_{3,2}$ edge, guarantees that the $(0,0,1/2)$ reflection appears only in the $\sigma\pi$ polarization channel. Moreover, the absence of scattering below the O K-edge confirms that this reflection is forbidden by symmetry.

![Figure 3](image)

**Figure 3.** The energy dependence of the $(0,0,1/2)$ reflection at the O K-edge for $\sigma$- and $\pi$- polarization incidence. The O K-edge absorption spectrum is also shown.

![Figure 4](image)

**Figure 4.** The temperature dependence of the integrated intensities of the low-temperature reflections.

We have also measured the temperature dependence of all the resonant reflections and the $(0,0,1)$ out of resonance. The results are reported in figure 4. The resonant and non-resonant scattered intensities simultaneously disappear at $T_V$ ($\pm 0.5$ K) for the three studied reflections showing that the origin of the resonances is the structural change at the Verwey transition.

From the present experimental study we can conclude that the $(0,0,1/2)$ reflection is forbidden by symmetry and the resonant scattering at the Fe L$_1$ and L$_{2,3}$ edges and at the O K edge is in the $\sigma\pi$ channel. Therefore, we can identify these resonances as anisotropy of the tensor of susceptibility (ATS reflections). The main characteristic of these Thomson-forbidden reflections...
because of a symmetry operation is that they become allowed when the incident photon energy is tuned to a resonance. On resonance, the x-ray atomic scattering factor is anisotropic and is sensitive to the anisotropic charge distribution around the resonant ion. Thus, these resonances appear because the off-diagonal elements of the atomic scattering tensor are different from zero and they do not subtract by special symmetry operations, such as a glide plane or a screw axis. That is exactly what happens in our case, if we consider the crystallographic structure (orthorhombic \textit{Pmca} structure) as described by Wright et al \cite{6}, a glide plane symmetry operation relates the atoms at \(z\) position to those at \(z+1/2\) position in the orthorhombic cell, which makes resonant intensity to be observed at the \((0,0,1/2)\) scattering vector. From the electronic point of view, the non-diagonal elements of the atomic scattering factor represent the anisotropy in the symmetry projected (p or d) electronic density of states. In this sense, the observation of these reflections probes the anisotropy and the ordering of the 2p and 3d states at the oxygen and the iron atoms, respectively.

The main problem concerning magnetite is that there are 8 and 6 different crystallographic sites for the O and Fe atoms, respectively, in the \textit{Pmca} description. Only from the SRXS experiment, we can not identify what of these atoms are anisotropic and contribute to the resonant signal. Recently, Wilkins et al. \cite{7} showed that the \((0,0,1/2)\) reflection originates from the local displacements around the resonant atoms. They propose, using theoretical simulations that the main contribution comes from the O2 atoms (O K edge resonance) and the B4 atoms (Fe L\textsubscript{2,3} edge) in the Wright description. Considering the formal charge ordering where B4 sites are nominally Fe$^{2+}$, this ordering could be associated to the $t_{2g}$ states as it was theoretically proposed \cite{8}. However, the proposed orbital order for the B4 atoms is ferro-orbital and consequently, it can not give any contribution to the \((0,0,1/2)\) reflection.

4. Conclusions.

We have detected SRXS at the \((0,0,1/2)\) and \((0,0,1)\) reflections either at the O K-edge or at the Fe L-edges. The active polarization channel is $\sigma-\sigma$ for the \((0,0,1)\) reflection and $\sigma-\pi$ for the \((0,0,1/2)\) reflection. These results conclude the existence of a charge density wave with the \((0,0,1)\) wave vector and an electronic anisotropy of the Fe d, Fe p and O p-states with the \((0,0,1/2)\) periodicity. The observation of SRXS at these two reflections agrees with the \textit{Pmca} description, where the \((0,0,1)\) periodicity comes from the existence of different crystallographic B sites and the \((0,0,1/2)\) periodicity originates from the existence of a glide plane.

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