BERLINER ELEKTRONEN-SPICHERING-GESellschaft fUR SYNCHROTRONSTRAHLUNG M.B.H.

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Cool magnetite: Frozen electrons below the Verwey temperature


Magnetite (Fe₃O₄) is known to the humanity for more than 2,000 years and still keeps intriguing and surprising us with its unusual properties. As a natural magnet it not only has been already used by ancient Chinese navigators as a compass, but also the birds use the earth’s magnetic field to find their way. At room temperature magnetite crystallizes in the cubic inverse-spinell structure. One-third of the iron-atoms are surrounded by 4 oxygen neighbours. The aim of our work was to investe the connection between the formation of low-temperature superstructure in magnetite and the electronic state of the Fe ions. For this purpose we used the technique of resonant soft X-ray diffraction (RSXD) [5], which directly combines spectroscopy with diffraction. We applied photons with energies that the scattered signal is most sensitive to the electronic states of the Fe ions.

For the experiment we chose magnetite thin films rather than bulk crystal, because films allow us to pick up intensities from the (001) reflection, which cannot be reached at the Fe L₂,₃ resonance, where the scattered signal is most sensitive to the electronic states of the Fe ions.

In a recent powder-diffractometry experiment the crystalline structure of magnetite at low temperatures could mostly be solved and signatures of charge order were indeed found [2]. Based on this crystal structure, band structure calculations predict an additional ordering of orbitals (i.e. ordering in the arrangement of charge around the ions) for the low-temperature phase [4]. Typically charge and/or orbital order lead to a displacement of neighbouring oxygen ions and to the appearance of superstructure reflections, which can be probed by e.g. neutron diffraction. In the case of magnetite, though, the orbital order is well hidden, because it involves only the t₂g orbitals, which interact very little with oxygen neighbours. The aim of our work was to investe the connection between the formation of low-temperature superstructure in magnetite and the electronic state of the Fe ions. For this purpose we used the technique of resonant soft X-ray diffraction (RSXD) [5], which directly combines spectroscopy with diffraction. We applied photons with energies that the scattered signal is most sensitive to the electronic states of the Fe ions.

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For the experiment we chose magnetite thin films rather than bulk crystal, because films allow us to pick up intensities from the (001) reflection, which cannot be reached at the iron L₂,₃ resonance, directly, as the wavelength is too large. The broadening of reflections in thin films transfers enough intensity into the reachable momentum space such that the diffraction signal can be still picked up. Our magnetite films had a thickness of 40 nm and showed a sharp Verwey transition at 115 K (see Fig. 2). RSXD experiments were carried out at beamline UE52-SGM, using the UHV diffractometer built at the Freie Universität Berlin.
Fig. 3 shows the diffraction scan at a photon energy of 708.5 eV along the L-direction. Below the Verwey temperature we see two diffraction peaks: (00½) and (001), the second one visible as an onset. Both reflections disappear above the Verwey temperature, demonstrating their relation to the low-temperature phase. To investigate the origin of these reflections we studied their intensity across the Fe L\textsubscript{2,3} resonance and compared it with X-ray absorption (XAS) data. For this study we decomposed the XAS signal into the contributions of the three different Fe sites, making use of cluster model calculations. Fig. 4(a) displays XAS with the single contributions, from B-site Fe\textsuperscript{2+} (red solid line), A-site Fe\textsuperscript{2+} (orange dotted line) and B-site Fe\textsuperscript{3+} (red dashed line) irons, together with the (00½) and (001) diffraction spectra.

The (00½) reflection shows a strong resonance coinciding with the position of the absorption signal of B-site Fe\textsuperscript{2+} ion. The (00½) reflection is hence a result of order involving only these B-site Fe\textsuperscript{2+} ions. The only degree of freedom, which can make one 2+ site different from another, is the orientation of the T\textsubscript{2g} orbitals, implying an orbital order in the system. This result is in fact the first direct observation of orbital order in magnetite.

In contrast, the (001) reflection shows a double-peak structure, which decreases sharply toward low and high-energy sides. The two maxima are well-separated and their position coincides with the position of the maxima of the absorptions signals belonging to the two B-site irons, the first peak to the maximum of Fe\textsuperscript{2+} and the second peak to Fe\textsuperscript{3+}. A simulation using the charge order scenario proposed in Ref. [3] gives a very good agreement with the experimental findings. From this result we can safely conclude that the (001) reflection is indeed a result of the charge order of the B-site iron ions.

In conclusion, using resonant soft X-ray diffraction from a magnetite thin film we find clear spectroscopic evidence for charge and orbital order.

Fig. 2: Electrical resistivity of a 40-nm magnetite thin film as a function of temperature.

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