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SCIENTIFIC HIGHLIGHTS

Cool magnetite: Frozen electrons below the Verwey temperature

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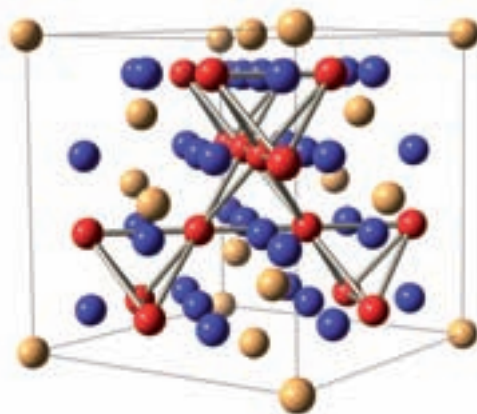3
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**Fig. 1:
Magnetite room temperature crystal structure. Blue balls denote oxygen sites, yellow balls iron A-sites and red balls iron B-sites.**

References:

[1] E. J. W. Verwey, Nature **144**, 327 (1939).

[2] J. P. Wright, et al., Phys. Rev. Lett. **87**, 266401 (2001).

[3] J. Schlappa, et al., Phys. Rev. Lett. **100**, 026406 (2008).

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[5] C. W. M. Castleton and M. Altarelli, Phys. Rev. B **62**, 1033 (2000).

Magnetite (Fe_3O_4) is known to the humanity for more than 2,000 years and still keeps intriguing and suprising us with its unusual properties. As a natural magnet it not only has been already used by ancient Chinese navigatiors as a compass, it also turns out that small magnetite particles inside migratory bird's beaks allow these animals to use the earth's magnetic field to find their way. In these days magnetite is considered for spintronic applications, because all electrons carrying electrical current in this material have the same spin orientation.

In 1939 the Dutch physicist E. J. W. Verwey found that when magnetite is cooled to temperatures below 120 K, its properties change quite drastically (Verwey transition). Its crystalline structure turns from highly symmetric to a complex low-symmetry phase and the electrical resistivity grows by a factor of hundred [1]. What exactly happens at this transition has been debated now for almost 70 years and it requires modern structural and spectroscopic tools to find the well-hidden order in the low-temperature phase [2,3].

At room temperature magnetite crystallizes in the cubic inverse-spinell structure. One-third of the iron-atoms are surrounded by 4 oxygen ions (the so-called A-sites, blue balls in Fig. 1), whereas two-thirds are surrounded by 6 oxygen ions (B-sites, red balls in Fig. 1). The B-site irons are mixed valen,t which means that on average two iron sites share one extra electron. Verwey suggested that below 120 K these extra electrons freeze to an ordered arrangement of half divalent (2+) and half tri-valent (3+) sites and therefore can no longer transport current. Such a kind of charge order has in the meantime been found in various compounds, but the Verwey transition in magnetite and especially the interplay between the crystalline and electronic structure is still not understood.

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 t_{2g} 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 at the Fe $L_{2,3}$ resonance, where 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 intensity from the (001) reflection, which cannot be reached at the iron $L_{2,3}$ 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.
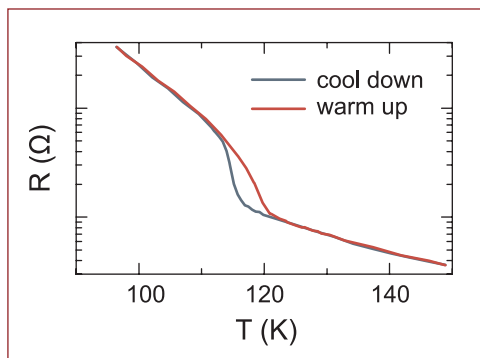
Fig. 2:
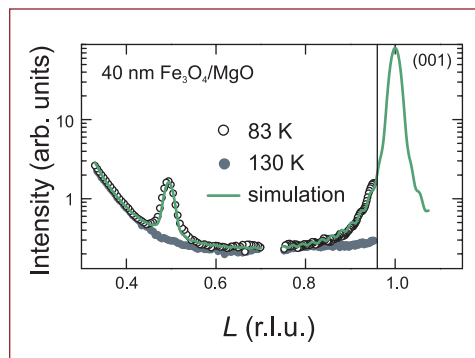**Electrical resistivity of a 40-nm magnetite thin film as a function of temperature.**

Fig. 3:
Scans along [001] (L): Open (filled) symbols are experimental data taken below (above) the Verwey temperature, the green line is a simulation.

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: $(00\frac{1}{2})$ 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 $L_{2,3}$ 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^{2+} (red solid line), A-site Fe^{2+} (orange dotted line) and B-site Fe^{3+} (red dashed line) irons, together with the $(00\frac{1}{2})$ and (001) diffraction spectra.

The $(00\frac{1}{2})$ reflection shows a strong resonance coinciding with the position of the absorption signal of B-site Fe^{2+} Ion. The $(00\frac{1}{2})$ reflection is hence a result of order involving only these B-site Fe^{2+} ions. The only degree of freedom, which can make one 2+ site different from another, is the orientation of the t_{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
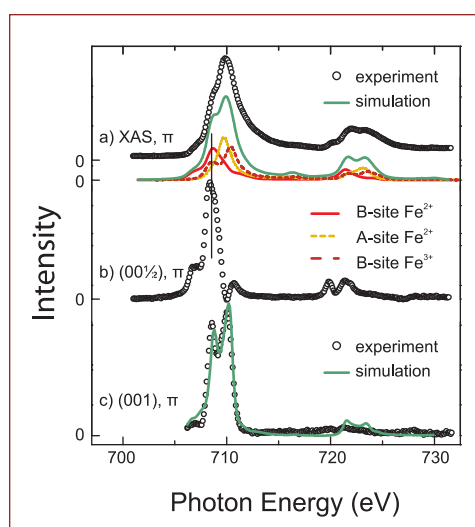

Fig. 4:
XAS and RSXD spectra around the Fe $L_{2,3}$ resonance: (a) experimental XAS spectrum (symbols) with a simulation (green line) showing the separate contribution of the different Fe sites. (b) $(00\frac{1}{2})$ RSXD spectrum and (c) (001) RSXD spectrum with a B-site charge-order simulation (green line).

Fe^{2+} and the second peak to Fe^{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.

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