ESRF	**Experiment title:** RESONANT X RAY SCATTERING STUDIES OF THE AXIS SWITCHING IN LOW T ($T<T_V$) MAGNETITE SINGLE CRYSTAL	**Experiment number**: HS3981
Beamline: ID20	**Date of experiment**: from: 10 November 2009 to: 17 November 2009	**Date of report**: 20 February 2010
Shifts: 19	**Local contact(s)**: Dr Claudio MAZZOLI	*Received at ESRF:*

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It was recently found [1] that the Verwey transition in magnetite at T_V=124K is actually composed of three partially decoupled ordering phenomena: crystal lattice distortion (LD) from high T Fd3m symmetry, charge (CO) and orbital (OO) ordering, all of them taking place at different T (LD at 124K, CO and OO a few K above T_V). This different way the lattice and the electronic states are organized could be independently observed by measuring particular reflections at the Fe K-edge: the change of structure could be observed by T dependence of e.g. (003), or (2 0 11/2) peaks, the orbital order by e.g. (007/2) peak (measured at resonance) and the charge order by e.g. (0 0 1) (again at resonance). Thus, those peaks reflect how the different subsystems of the material behave as the material crosses the transition temperature, but also may be used to observe how these systems react when particular perturbations are applied. It is well known [2] that if a magnetic field is applied at temperatures lower than T_V, magnetic easy axis switching (AS) occurs (monoclinic c axis, the one doubled, switches simultaneously), the phenomenon very likely in close relation to the Verwey transition. Our very extensive measurements (both using bulk methods, as M(H) [2], or microscopic NMR [3]) showed also that AS is permanent: once the axis is changed, it does not go back when the field is removed. The main goal of HS3981 experiment was to see if AS is also linked with the switching of charge ordering (measured by (001) peak) and OO (measured by (007/2)).

The experiment was conducted on ID20 beamline, tuned to work at the iron K-edge. The sample was a magnetite single crystal, grown by the skull melter technique and subsequently annealed for stoichiometry. The crystal was cut parallel to (001) plane and glued to the vertical sample holder. The whole ensemble was placed on the sample stick of the vertical split superconducting coil cryostat (see Fig.1, where several aspects of experiment geometry, crystal lattice (cubic) directions, monoclinic c axes directions -bold arrows- and sample orientation are marked). Upon field cooled through the Verwey transition the sample was basically crystallographically and magnetically single domain (only the „domain [010]" is left, as shown on the right panel of Fig.1); ZFC resulted in breaking into domains, with monoclinic c-axis pointing along all <100> directions (left panel of Fig.1). Additionally, 4 electrical contacts were attached to the sample (Fig.1, left panel) and connected to a lock-in nanovoltmeter for simultaneous measurement of the resistance (see [4] for the description how AS may be observed through changes in the resistance). In most cases, (2 0 11/2), (003) and (3/2 0 5) peaks (off-resonance) and (001), and (007/2) (at resonance) were measured and treated as the indication of lattice distortion, charge order and orbital order respectively. The results presented below comprise only ca 20% of all collected data. Three experiments were performed :

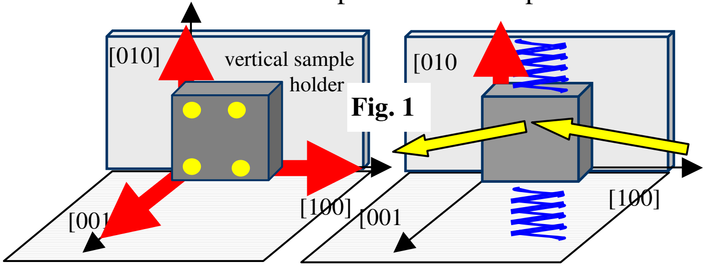

Fig. 1

1. Field cooling (FC) to 5K. This treatment leaves only one c-axis along [010] cubic axis with no magnetic domain structure. No c axis doubling along [001] was found, as expected, which was confirmed by the almost complete annihilation of (3/2 0 5) and (2 0 11/2) peaks and the presence of strong (0 1/2 6) peak. Also, the OO peak (0 0 7/2) was extinct, contrary to CO peak (0 0 1). Removing field did not cause any significant changes (in particular, the (001) reflection did not change): occurrence of magnetic domain structure does not affect either LD or OO and CO.

2. ZFC to 8K. Based on our previous bulk measurements, this experiment should result in domain (both magnetic and structural) rich state that, however, does not change once a magnetic field (lower than 1T) is applied. In fact, only very small changes of peaks shape before and after magnetic field along [010] was applied, were found, as expected.

3. AS at 110K: this is the main part of the experiment. We were expecting that the AS proceeds immediately once the field of 0.5T is applied and, once switched, the system stays at this "new" state. Also, if the axis in the domain [001] is switched to [010] (i.e when domain [001] converts to the domain [010]), as in our case, then all (h k n/2) peaks should get lower while those of (h n/2 l) should increase.

Very similar results were observed: indeed, LD peaks (2 0 11/2) and (3/2 0 5) almost vanished as well as OO peak (0 0 7/2), what proves that AS is not only connected to the c-direction changes but is also linked to the change of existing orbital ordering. Also, the (003) peak, related to lattice distortion of the cubic lattice periodicity, changed; in particular, both peak height and the width lowered, which means that correlation length has increased (the structure became less perturbed). This is in strong contrast to (001) peak, linked to charge order of the same periodicity (Fig.2), that does not change at all. Although other experiments, performed in similar conditions, showed partially changing also of the (001) reflection, the result that CO and lattice distortion may react independently appears to be completely counterintuitive and is probably the most astonishing result of our experiment. It was clear to us (and to Calhoun, the first investigator of AS [5]) that magnetic field switches the easy magnetic axis, the monoclinic c-axis, and all electronic arrangements that define this axis; since our results show that CO may not be one of those electronic arrangements, the problem of charge ordering and its change under magnetic field needs immediate further investigation. In strong contrast to our previous experience, all the subsystems observed here (LD, CO and OO) partially relax once the field is removed, but the new domain state is different than the original one (before field application), as is most clearly seen by the comparison of almost completely not regained (3/2 0 5) peak, partially regained (2 0 11/2) and almost totally regained (0 0 7/2) reflection (Fig. 4).

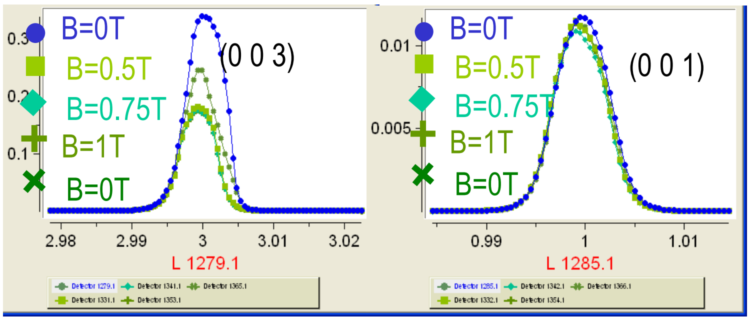

Fig. 2. Field influence on LD and CO peaks. Note decreasing heights and width of (003) with almost no change of (001).

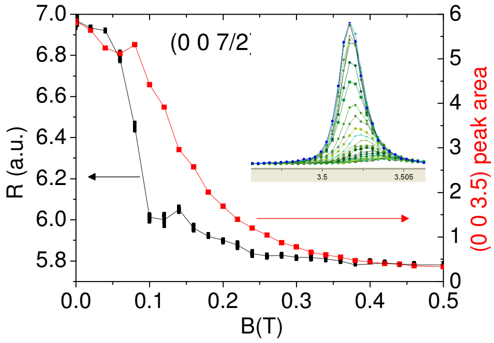

Fig. 3. Change of OO peak and sample resistance R with increasing field; abrupt jump in R marks the AS, reflected by a small peak in peak area. Peak shape is shown in the inset

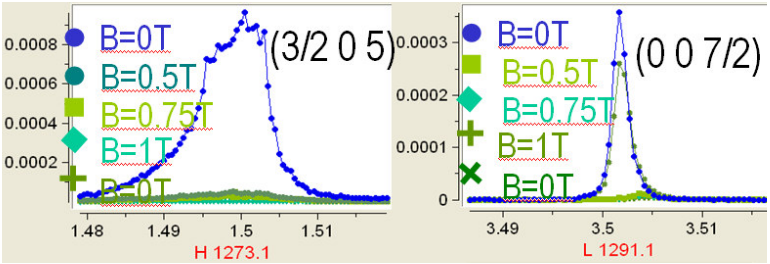

Fig. 4. Field influence on lattice doubling peaks ((007/2) is due to OO) and diverse peaks relaxation once the field was removed

More systematic observation of orbital ordering (0 0 7/2) peak was performed once the slowly increasing field was applied. We have also simultaneously measured electrical resistivity across the sample. The usual sudden break in R(B) plot marking AS [4] is observed (Fig.3), which is reflected in sudden change of (0 0 7/2) peak intensity. Note, however, that the change of (0 0 7/2) peak is gradual and smooth suggesting again some decoupling between; the electrical response and the orbital ordering.

In conclusion, the data consistently show that axis switching occurs when the magnetic field is applied: the monoclinic c-axis direction changes according to the field direction, which is reflected in lattice distortion peak change. Orbital ordering follows lattice distortion (. Charge ordering may be partly decoupled from the lattice, as suggested by the different behavior of the (001) peak. Since this is in strong conflict with the predicted behavior, we would like to repeat the experiment and trace the (001) peak under a slowly increasing magnetic field (as it was done with OO reflection). We have also noticed different changes of the (0 0 7/2) peak after a gradual field increasing as compared to resistance (and magnetization) changes (that are rather rapid). Again, it suggests that the partially decoupled electronic systems, all engaged in the Verwey transition, may behave differently once the external force (like B here) is applied.

Finally, we have found unexpected differences between these and our other experimental data from the past; especially, the observed effect of magnetic field is faster here and proceeds down to much lower T than was observed in bulk measurements. Experiment aimed to prove that this may be peculiar to the surface effects is now in progress.

The HS3981 experiment was successful and almost all planned issues were addressed, and we have found unexpected phenomena that required more work. Finally we highly appreciate the help of dr Claudio Mazzoli, our local contact.

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