Dr hab. Inż. Andrzej Kozłowski
Katedra Fizyki Ciała Stałego
Wydział Fizyki i Informatyki Stosowanej AGH
Al. Mickiewicza 30, 30-059 Krakow

Kraków, 21 kwietnia 2011

Eksperyment HE3480:

RESONANT X RAY SCATTERING STUDIES OF THE AXIS SWITCHING IN LOW T ($T<T_V$) MAGNETITE SINGLE CRYSTAL

Wykonany w dniach: 17.11. 2010 do 23.11. 2010 na stanowisku ID18 w ESRF

*Andrzej KOZŁOWSKI, *Emilio LORENZO-DIAZ, Zbigniew TARNAWSKI, Wojciech TABIŚ, *Tomasz KOŁODZIEJ, Zbigniew KĄKOL, *Maciej ZUBKO

*osoby obecne przy eksperymencie

When cooled below T_V=124K, magnetite undergoes the Verwey transition, where many physical properties have spectacular anomalies. Since also the structure changes at T_V, from cubic to monoclinic (anisotropic), each of the high temperature cubic <100> directions may become the low temperature monoclinic *c*-axis. As a result, the material breaks into structural domains unless the external magnetic field along particular <001> is applied while cooling through the transition: this particular direction will then become the unique *c*-axis. If now the sample is magnetized along other <100> direction below T_V, the axis switching (AS), the phenomenon intimately linked to the Verwey transition, takes place, i.e. this axis becomes monoclinc *c* direction [1]. Since the Verwey transition actually consists [2] of three phenomena (lattice distortion LD linked to *c* axis; charge, CO, and orbital ordering, OO), all of them taking place at different *T* (LD at 124K, CO and OO a few K above T_V), then the question was naturally raised if all those subsystems change due to AS. The tool to check it was to observe different reflections: LD could be observed by T dependence of (003), or (2 0 5.5) peaks, the orbital order by e.g. (007/2) peak and the charge order by e.g. (0 0 1) (last two measured at resonance) [2]. We have proved, in HS3981, that LD and OO was changed in AS, but the results for CO were not clear. Thus, the main purpose of the present experiment was to check, by the RXS technique on ID20 beamline, if charge order, formed just above T_V is susceptible to the magnetic easy axis switching by magnetic field; in the present experiment, Zn doped sample, where all three subsystems are most clearly separated, was measured [rep].

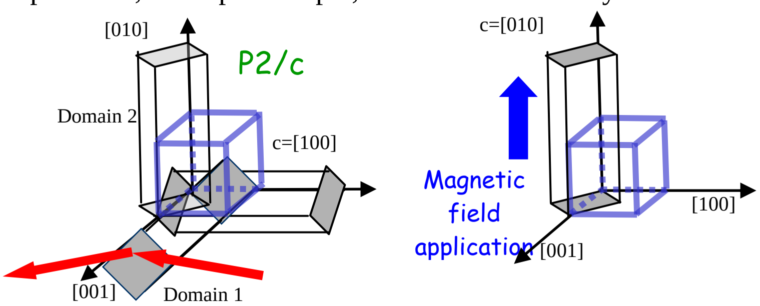

Fig. 1. Experimental layout showing magnetite single crystal (cube) with 3 possible monoclinic domains and the domain 1 inspected by X ray beam. Under external magnetic field only the domain 2 survives, causing essentially no reflections.

The experiment layout is presented on Fig. 1. Single crystal of $Fe_{3-x}Zn_xO_4$, with x=0.0085 (magnetite of the first order Verwey transition) was placed on the cold finger of the cryostat with cubic (001) plane facing the incoming radiation. When cooled below T_V, at least 3 monoclinic domains with c axes pointing along [001], [010] and [100] were formed. Since we have observed (003), (2 0 11/2), (007/2) and (0 0 1) reflections, only the domain 1 was monitored ((300), and (030) are extinct and so is with other relevant reflections from remaining domains). Vertical magnetic field (B<8T), supplied by the supercondicting magnet, could trigger AS, if the experiment were performed at *T* sufficiently close to T_V; in such a case, only the domain 2 should sustain and grow at the expense of others. This should cause the major diminishing of the observed reflections in case all subsystems underwent the change.

The main experiments were performed at 3 characteristic temperatures, shown symbolically on Fig.2d, on top of temperature dependence of all peaks intensities. At low *T*=25K, AS should not occur, i.e. no change was expected, while at *T*=90K, all essential features should be observed. Finally, at *T*=116K, the system is above T_V, but both the charge and orbitals already started to organize. The representative results are presented on Fig.2a-c; here only (001) peak, sensitive to CO and (2 0 5.5), sensitive to monoclinic axis doubling, are shown. In accord with our prediction, at 25K the system barely changes, although some changes are observed that are beyond the experimental error. At 90K the superlattice peak diminishes signalling the drastic reduction of domain 1 population, with almost no change of (001) reflection. The same situation is observed at 116K despite the fact that in this *T* region charge ordering is not amplified by lattice distortion [3]; at this T, (2 0 5.5) peak is practically non existing, but the fluctuations at this reciprocal lattice

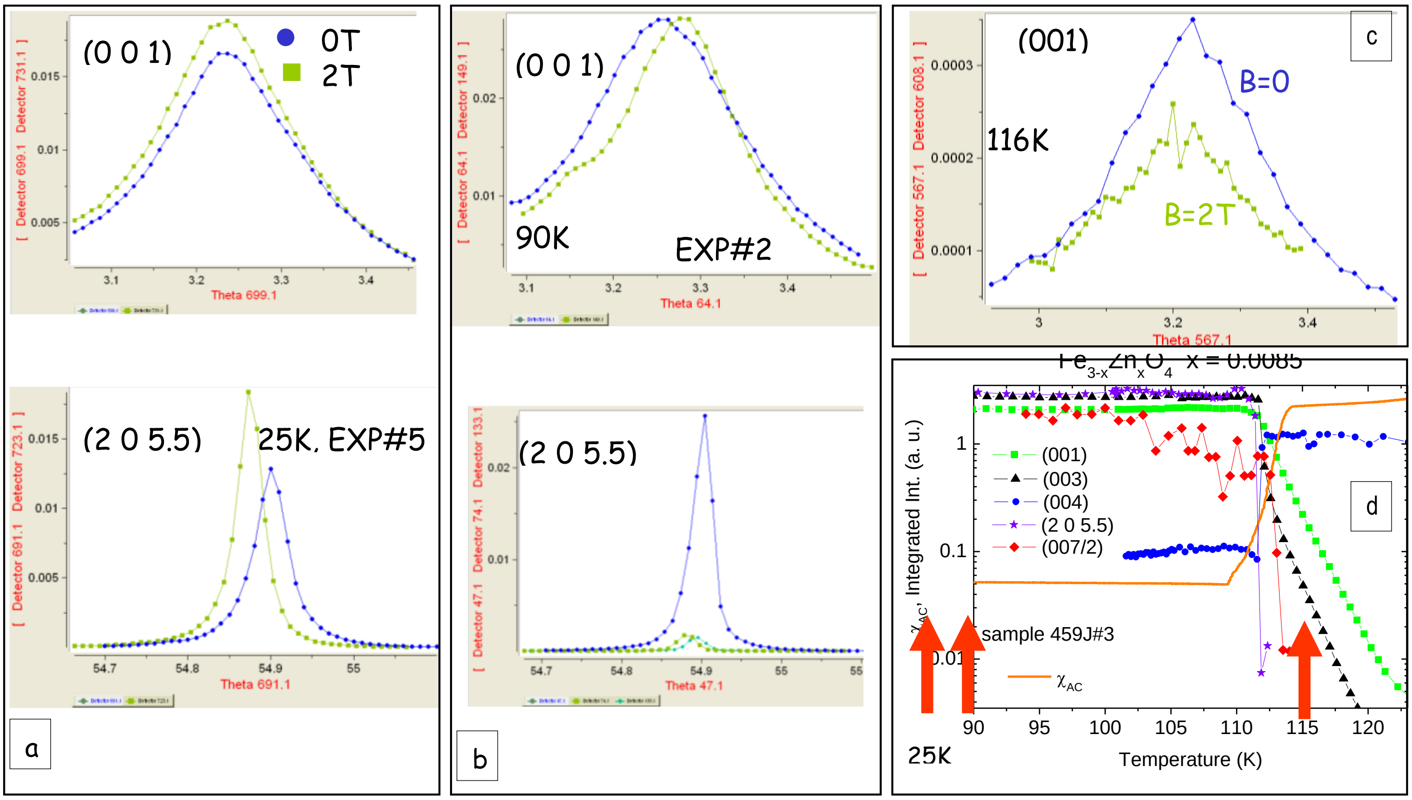

Fig. 2. In d the 3 temperatures where the measurements were performed are marked, on top of several peaks temperature behavior [4] and the T dependence of magnetic susceptibility. In a and b the peak (001), due to CO, and the one resulting from lattice doubling (2 0 11/2) are shown at T=25K (virtually no change) and at T=90K; in this last case, diminishing (2 0 11/5) proves the lowering domain 1 volume, with no change in CO arrangement (no change in (001)). Essentially similar result is observed at 116K, where the superlattice reflection (2 0 11/5) is too small to be analyzed.

positions are observed. In any case, all those results prove that while three subsystems (lattice symmetry, orbital order and charge order that makes some pattern on top of distorted cubic lattice) order at $T<T_V$, one of those, the charge order, is robust against any magnetic field manipulation, contrary to direction of lattice distrortion and orbital order. This is the completely new result suggesting that the coupling between the lattice and charge is much lower than previously expected and the following scenario may be proposed. When magnetite is cooled from high temperatures, the charge on octahedral iron positions starts to organize already at high temperatures, in a similar way on magnetite exhibiting first and second order transition. This process would ultimately lead to the continuous phase transition at much lower temperature if not the stimulating action of the lattice: it changes the structure, causing orbital ordering (on different positions than CO) and an mplification of CO.

This important phenomenon, found above, should be further studied, not only for the sake of magnetite, but also due to the fact that it can be common for all transition metal oxides.

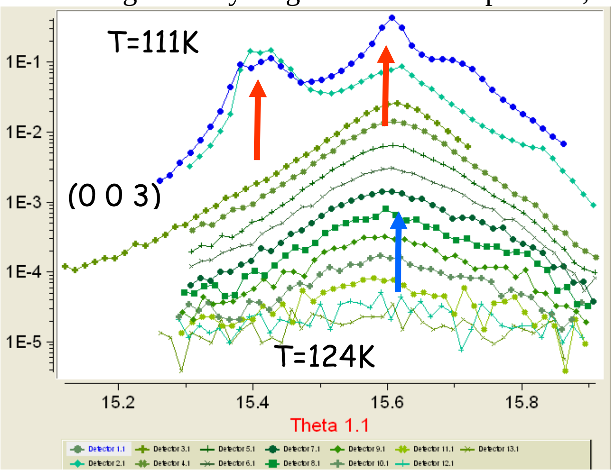

Fig. 3 Temperature dependence of (003) peak in the vicinity of the Verwey transition. Note drastic intensity reduction and two uncorrelated processes marked in red and blue.

HE3480 consisted of many experiments, the most interesting presented above. In the other experiment, we have confirmed the our previous result [3] of two-component (003) reflection. Fig. 3 suggests that (003) above T_V contains the part that gives rise to (001) reflection, i.e CO. I.e. two different processes are observed by (003), supporting our above conjecture.

In our opinion, the HE3480 experiment was successful, although we could not place the additional magnet, as we have planned; this would resolve much controversy, still present. Also, previous sample, stoichiometric magnetite, was not measured due to time constraints. We highly appreciate the help of dr Claudio Mazzoli, who, eventhough he was not our local contact this time, was with us for a long time.

References

[1] B. A. Calhoun, Phys. Rev. **94**,1577 (1954); G. Król, et al., J.All.Comp. 442, 83 (2007)
[2] J.E. Lorenzo, et al., PRL 101, 226401 (2008)
[3] W. Tabis, in preparation
[4] Experimental report from HS3981.