ESRF	**Experiment title:** Study of the Verwey transition by DAFS and X-Ray Anomalous Scattering.	**Experiment number:** HS-483
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Report:

Magnetite (Fe_3O_4) undergoes a metal-insulator transition (the so-called Verwey transition) near T_V= 120 K, associated to a change in the lattice symmetry. Verwey [Nature 144, 327 (1939)], first proposed that this transition is due to the ordering of the Fe^{2+} and Fe^{3+} ions on the octahedral sites of magnetite's inverse spine1 structure, giving rise to the forbidden $(002)_c$ reflection. New charge-ordering models, based on recent experimental results, have also been proposed but the nature of the transition is still not completely understood [Mizoguchi, J. Phys. soc. Jpn. 44, 1512 (1978); Zuo et al. Phys. Rev. B 42, 8451 (1990)].

We have investigated the charge-ordering of magnetite below T_V by means of X-Ray Anomalous Diffraction. A single crystal of Fe304 was grown by the floating-zone method with its axis parallel to cubic [00l]. A magnetic field of about 1 T was applied along [00l] to establish the c-axis along that direction. DAFS spectra of the forbidden $(002)_c$ and fundamental $(004)_c$ reflections were recorded at 20 K, under this magnetic field. The energy dependence of the intensity of (002) reflection near the iron K-edge is shown in Figure 1. There is a stricking enhancement of the intensity at E=7.11 KeV and E=7.125 KeV, which correspond to the prepeak and about 8 eV above the edge

respectively, in the fluorescence spectra. Besides, EXAFS oscillations were observed in an extensive range of energy.

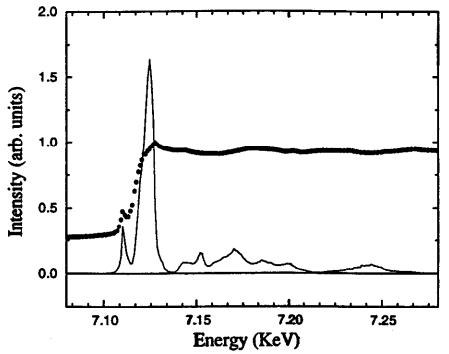

Figure 1. Energy dependence of the intensity of $(002)_c$ reflection near the iron K-absorption edge at T=20 K. Closed circles represent the measured fluorescence.

In order to investigate the nature of this superlattice reflection, we have measured the intensity of the (002) reflection as a function of the azimuthal angle. The experimental results, at E=7.125 KeV, are shown in Figure 2. In contrast to a normal charge-ordering reflection, a characteristic oscillation of 90° period, typical of an orbital ordering, is observed. Similar angular dependence is observed at the prepeak (E=7.11 KeV) and at the fine structure (E=7.17 KeV). We have also observed that the intensity of this reflection at E=7.125 KeV, does not decrease, by increasing the temperature up to RT. In any case, the structural phase transition takes place around 107 K, as expected, since the superlattice reflection (l/2 0 4) disappears at this temperature. In conclusion, we have observed for the first time, orbital ordering in magnetite at RT. A detailed interpretation of this result is still in progress.

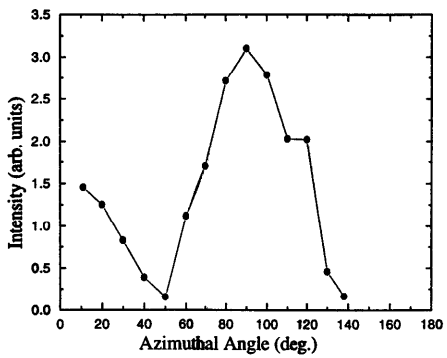

Figure 2. Azimuthal-angle dependence of the intensity of $(002)_c$ reflection at E=7.125 KeV and T=20 K.