ESRF	**Experiment title: Vibrational density of states of Fe atoms in Fe_3O_4 above and below the Verwey transition.**	**Experiment number**: HS-1470
Beamline: ID18	**Date of experiment**: from: 03 July 2001 to: 08 July 2001	**Date of report**: 08 October 2001
Shifts: 15	**Local contact(s)**: Dr. Aleksander CHUMAKOV	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

*Jozef KORECKI[1], ***Bartosz HANDKE[1], *Andrzej KOZLOWSKI[1], *Bert NIESEN[2]

[1]Dep. of Solid State Physics, Univ. of Mining and Metallurgy, PL-30069 Cracow, Poland

[2]Nuclear Solid State Physics, University of Groningen, 9747 AG, Groningen, Netherlands

Report:

Magnetite (Fe_3O_4) is a mixed valence compound with the tetrahedral (A) sublattice occupied by ferric ions, while octahedral (B) sublattice equally occupied by Fe^{2+} and Fe^{3+} ions. The distribution of iron ions at the octahedral sites changes from dynamic disorder to long range order when lowering temperature to T_V=120K. Also, crystal symmetry changes from cubic spinel type to unit cell which is monoclinic but close to orthorhombic. This transition (the Verwey transition) is accompanied by the sudden change in latent heat and drastic drop of the dc conductivity. Despite the large number of previous studies, there is no evidence of association lattice dynamic with charge ordering. Moreover, quite recently, the generally accepted ionic model of the Fe^{2+} and Fe^{3+} ordering on the B sites have been questioned [1,2].

The access to X-ray produced by third generation synchrotron radiation sources enable studies to measure the vibrational density of states of Fe atoms as a function of temperature or pressure [3,4]. The inelastic nuclear resonant scattering/absorption become powerful tool to investigate changes in phonon spectrum of thin films with remarkable energy resolution down to 1 meV.

To investigate lattice dynamic of in the Verwey transition region, we have grown an epitaxial $^{57}Fe_3O_4$ layer on top of a MgO(001) substrate with a thickness of 500 nm. Mössbauer investigations have shown that the spectrum of this layer is identical to that of single crystal magnetite [5]. The Verwey transition have been clearly observed in this sample by looking at the accompanying change in the Mössbauer spectrum and in the XRD diffractograms, which occurred at 122K, indicating nearly perfect stoichiometry. The sample was mounted on the tail of a closed-cycle refrigerator placed on a goniometer head. Additionally, we have applied magnetic field (0.3 T) during cooling through T_V provided by permanent magnets. This was necessary in order to avoid twinning of a c-axis and achieving possible single domain structure. To optimize the count rate we have chosen grazing incidence regime, in which the beam enters the sample at an angle of 1^o with the surface plane. Off-resonance events associated with phonon creation and annihilation were detected by avalanche photodiode placed 2-3 mm from the sample. In order to measure instrumental function at the same time the elastic nuclear forward scattering signal was measured by another photodiode. The average count rate of 50 cps at 18 meV, gave us very good statistic for density of state (DOS) calculations, which were evaluated by the DOS22 program [6].

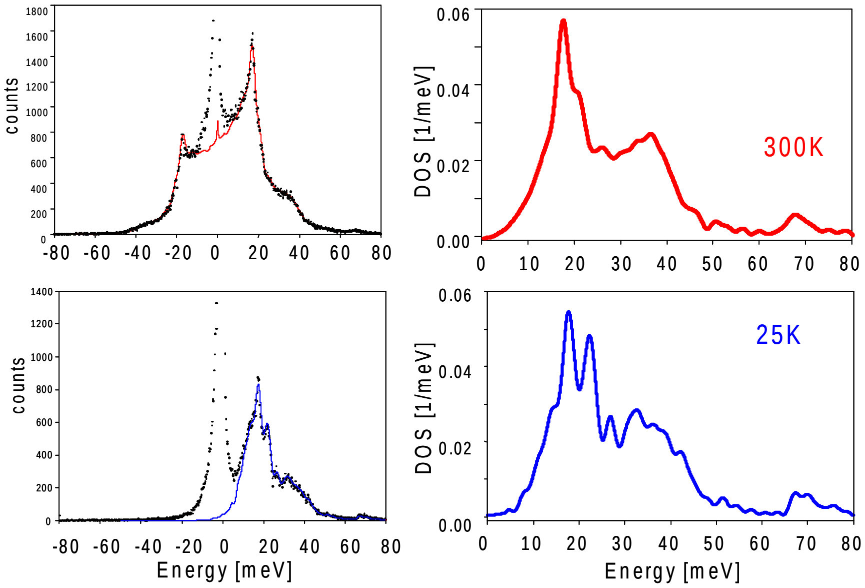

Fig. 1
Inelastic nuclear resonance spectra for 300K and 25K togather with calculated DOS.

We have collected ±80 meV high quality inelastic nuclear resonant data for temperatures above and below Verwey transition at 295K, 140K, 120K, 100K, 25K. Fig.1 represents two of them together with calculated DOS. Because of probable difference between real and measured temperature we have also carried out elastic forward scattering measurements. From time-domain spectra we were able to point exact transition region which occurred 115K and 120K. We have observed that pronounced changes in inelastic spectra took place up to 30 meV. So, we have decided to performed additional measurements for a narrower energy range from -5 meV to +30 meV for 80K, 95K, 105K, 110K, 115K and 130K. All the measurements described above were carried out with the beam along [100] crystal direction. Additionally, we have done measurements along [110] direction at 25K (±80 meV scan), to find any anisotropy of inelastic nuclear resonance scattering.

Preliminary analysis indicates a rather monotonic change in the calculated DOS [Fig.2] with temperature. The intensity 22 meV peak lowers with increasing of temperature and almost disappears at 295 K while the intensity of 18 meV peak remains unchanged. One can observe change of the DOS peak structure between 30 and 40 meV. There is also strong modification of DOS at low energies which has more abrupt character. It is best visualized plotting row data normalized to the maximum inelastic intensities [Fig. 3], where the data are grouped in to sets corresponding to temperatures below and above Verwey transition. It might be indication of phonon softening occurring above $T_{V.}$

The only weak point in the successful experiment was fault in heater cryostat which hindered measurements at temperatures between 140K and 200K.

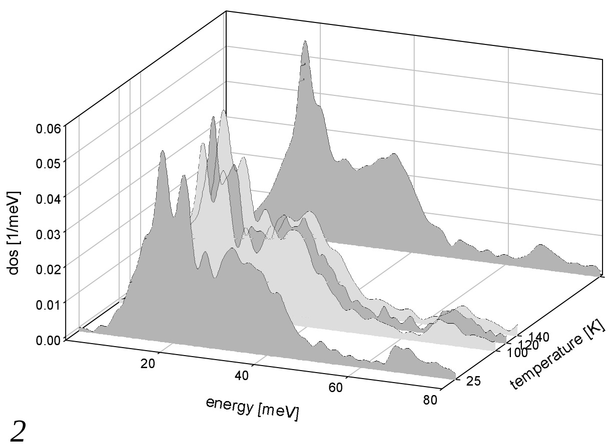

Fig. 2
Calculated DOS from ±80 meV data scans.

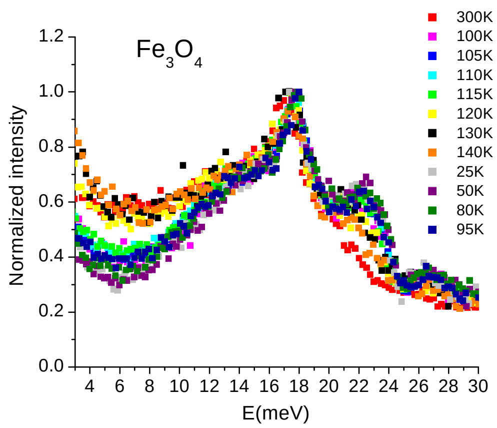

Fig. 3
Raw data normalized to highest inelastic peak.

[1] P. Novak et al., Phys. Rev., **B61** (2000) 1256
[2] J. Garcia et al., Phys. Rev. Lett., **85** (2000) 578
[3] A.I. Chumakov et al., Phys. Rev.**, B54** (1996) R9596
[4] R. Lübbers et al., Science, **287** (2000) 1250
[5] B. Handke et al., J. Radioanal. Nucl. Chem., **246** (2000)
[6] V.G. Kohn et al., Hyp. Int., **125** (2000) 205