ESRF	Experiment title: **NUCLEAR INELASTIC SCATTERING STUDIES OF STRONG ELECTRON-PHONON COUPLING IN MAGNETITE WITH FIRST AND SECOND ORDER VERWEY TRANSITION**	**Experiment number**: **HE3473**
Beamline: ID20	**Date of experiment**: from: 22 September 2010 to: 28 September 2010	**Date of report**: 20 March 2011
Shifts:	**Local contact(s)**: Dr Marcin Zając	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Przemysław PIEKARZ, Andrzej KOZŁOWSKI, *Wojciech TABIŚ, *Tomasz KOŁODZIEJ, Zbigniew KĄKOL

The exact mechanism of the Verwey transition in magnetite is still an open question despite 70 years of efforts to explain it. The fact that the electrical transition is simultaneous with the structural one suggests that coupling between electronic states and crystal lattice may play an important role and this idea was supported already 30 years ago by neutron studies [Fuj75, Sha76]. Recent theoretical analysis [Pie0607] have confirmed a crucial role of electron-phonon and electron-electron correlations in the mechanism of the transition pointing out to at least three phonon modes that are at the origin of the observed low temperature structure and are coupled to electrons. It was also suggested [Koz9697] that the changing of electron-phonon coupling could explain the second, still unresolved phenomenon of magnetite: the Verwey transition of first and second order.

Indeed, if nonstoichiometry parameter 3δ in $Fe_{3(1-\delta)}O_4$ or doping x in $Fe_{3-x}(Zn,Ti)_xO_4$ exceeds the universal value $3\delta=x=0.012$, the originally first order Verwey transition (type I samples) turns to continuous one (type II) that disappears altogether for $3\delta=x>0.04$. In other words, electron-electron and electron-phonon interactions can be finely tuned by doping or nonstoichiometry triggering dramatic changes in material properties: not only the transition character is altered, but also T_V vs $x=3\delta$ (see Fig. 1) have two different slopes and a diffuse scattering observed for X_3 phonon mode [Ara93] is distinct. We have, finally, found that the heat capacity [Koz9697] is also strikingly different, as shown on Fig. 2. Note that the temperature dependence of the Debye temperature (inset of Fig. 2) suggests a drastic change of properties at T_V for type I materials and a continuous evolution for type II samples rather than a low T excess of heat capacity for type II samples due to thermal fluctuations. In any case and together with previously mentioned strong electron-phonon coupling, the heat capacity results suggested that either the change of this coupling, or the alteration of lattice dynamics triggers the different characters of the Verwey transition. We have spend quite a time trying to show experimentally that the lattice dynamics is indeed different for both classes; in particular, our previous experiment on ID18 was partially aimed to show it. The present experiment, where partial phonon density of states (DOS=g(E)) for

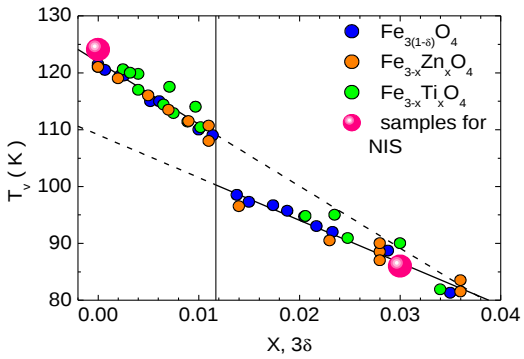

Fig. 1. Universal T_V vs. $3\delta=x$ relation with the clear step dividing discontinuous (type I) and continuous (type II) Verwey transition. Composition of samples used in present experiment is marked.

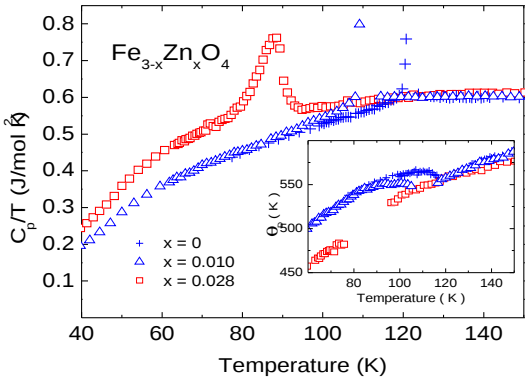

Fig. 2. T dependence of heat capacity in $Fe_{3-x}Zn_xO_4$. The baseline for $x=0.028$ (II order transition) at $T<T_V$ is larger than for I order samples, as better seen in T dependence of Debye θ (the inset; the peak is removed for clarity). For $T>T_V$ the backgrounds are identical.

iron atoms were observed directly, was aimed to compare the lattice dynamics for sample with first order transition with that exhibiting continuous one.

Two single crystalline samples, with natural abundance of ^{57}Fe isotope, were measured: stoichiometric magnetite and $Fe_{3-x}Zn_xO_4$ with x=0.03, displaying Verwey transition of second order. Samples (of the thickness < 0.1

mm, with exposed (001) plane) were glued to thin sapphire plates (ca. 0.16 mm) and placed on specially made sample holders that allowed to control sample inclination vs. incoming radiation; the best results, i.e. strongest NIS signal and instrumental function, were obtained at ca 45^0 inclination. Sample temperature was monitored both by system thermometer placed on the cold finger and by Pt thin film thermometer glued directly to the sample. NIS measurements were performed at 50K, 150K (in energy range -40meV-100meV), 65K and 135K (in energy range -20meV-50meV). To improve the signal-to-noise ratio, the data were collected in energy scans lasting approximately 40 min each. The average count rate in the intensity maximum of the inelastic part was around 4 and dozens of scans were required to obtain reasonable statistic.

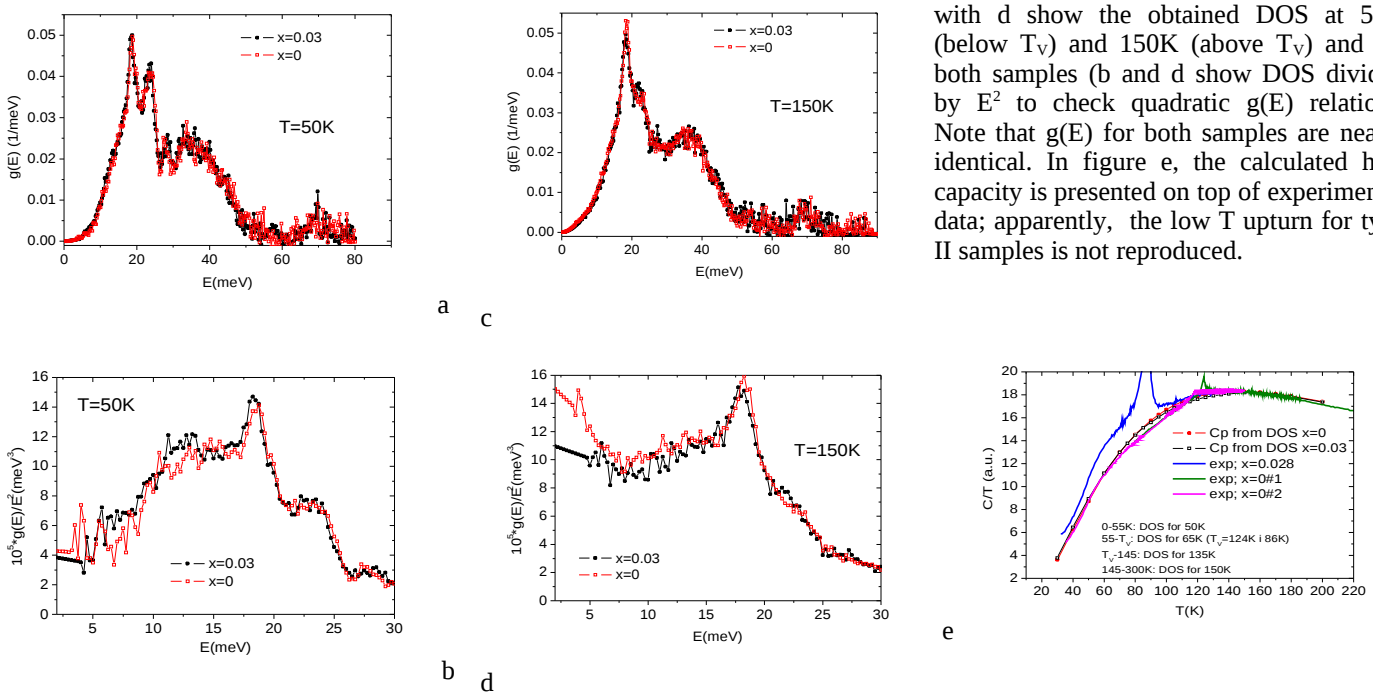

Fig.3. The coupled figures a with b and c with d show the obtained DOS at 50K (below T_V) and 150K (above T_V) and for both samples (b and d show DOS divided by E^2 to check quadratic g(E) relation). Note that g(E) for both samples are nearly identical. In figure e, the calculated heat capacity is presented on top of experimental data; apparently, the low T upturn for type II samples is not reproduced.

Data processing to extract phononic partial density of states was done following the procedure described in [Kohn9800]; we estimate that due to subtraction difficulties of the elastic central part, g(E) are reliable for E>3 meV. The comparison of DOS for two samples at temperatures below and above T_V is shown in Fig.3. It is clear that Fe DOSs are almost identical for both samples and that they are different below and above the Verwey transition, similarly to the results obtained previously [Handke05].

Based on only four temperatures at which the data were obtained, we may say that the drastic decrease of low T DOS is sudden and occurs at T_V. Contrary to that, the smearing out of the peak at ca 25 meV is continuous (this is supported by previous results, where the data were collected in many temperatures). Since partial iron DOS is very similar for samples exhibiting the Verwey transition of first and second order, the heat capacity for both samples should also be comparable, provided oxygen vibrations are similar. This assumption is reasonable since oxygen vibrations contribute mainly to high energies. Utilizing oxygen DOS presented in [Handke05] we have estimated temperature dependence of heat capacity for both our samples and compared to the real experiment. (Fig.3e). Clearly, the apparent excess of heat capacity at $T<T_V$ for doped sample with continuous Verwey transition cannot be explained by the different lattice vibrations and the other factor differentiating type I and type II materials and causing different heat capacity must be found.

References

[Fuj75]Y. Fujii, G. Shirane, Y. Yamada, Phys. Rev. **B11,** 2036 (1975)

[Sha76] S. M. Shapiro, M. Iizumi, and G. Shirane, Phys. Rev. **B14**, 200 (1976)

[Ara93] R. Aragón, et.al. , PRL. **70**, 1635 (1993)

[Pie0607] P. Piekarz et al. Phys. Rev. Lett. **97**, 156402 (2006); Phys. Rev. **B 76**, 165124 (2007)

[Sch00] H.Schwenk et al., Eur. Phys. J. **B13**, 491 (2000).

[Koz9697] A. Kozłowski et al., Phys. Rev. **B54**, 12093 (1996); Z. anorg. allg. Chem. **623**, 115 (1997).

[Handke05] B. Handke, A. Kozłowski, K. Parliński, J. Przewoźnik, T. Ślęzak, A. I. Chumakov, L. Niesen, Z. Kąkol, and J. Korecki, Phys. Rev. B **71**, 144301 (2005)

[Kohn9800]V. G. Kohn, A. I. Chumakov, and R. Rüffer, Phys. Rev. B **58**, 8437 (1998); V. G. Kohn, and A. I. Chumakov, Hyperfine Interact. **125**, 205 (2000).