

# AC magnetic susceptibility under pressure and Mössbauer effect studies of the isotropy point $T_{IP}$ in magnetite

J. Żukrowski<sup>a,\*</sup>, A. Wiecheć<sup>a</sup>, R. Zach<sup>b</sup>, W. Tabiś<sup>a</sup>, Z. Tarnawski<sup>a</sup>, G. Król<sup>a</sup>,  
N.-T. H. Kim-Ngan<sup>c</sup>, Z. Kąkol<sup>a</sup>, A. Kozłowski<sup>a</sup>

<sup>a</sup> Department of Solid State Physics, Faculty of Physics and Applied Computer Science, AGH University of Science and Technology, Kraków, Poland

<sup>b</sup> Institute of Physics, Cracow University of Technology, Kraków, Poland

<sup>c</sup> Institut of Physics, Pedagogical University, Kraków, Poland

Received 19 May 2006; received in revised form 19 May 2006; accepted 9 June 2006

Available online 30 January 2007

## Abstract

The results of AC magnetic susceptibility measurements of zinc ferrite ( $\text{Fe}_{3-x}\text{Zn}_x\text{O}_4$ ,  $x=0, 0.0072, 0.0174, 0.049$ ) single crystalline samples under pressure up to 1.2 GPa in the temperature range close to the Verwey transition temperature ( $T_V$ ) are reported. The isotropy point  $T_{IP}$  increases with pressure for each  $x$  but the disappearance of primary anisotropy constant at  $T_{IP}$  has no effect on Mössbauer spectrum at ambient pressure. Finally, Mössbauer effect data in the vicinity of the Verwey transition does not support the recent claim of the inverse to normal spinel crossover at the transition.

© 2007 Elsevier B.V. All rights reserved.

PACS: 71.30.+h; 64.70.Kb; 61.50.Ks; 76.80.+y

Keywords: Magnetite; Magnetic properties; High pressure; Mössbauer spectroscopy; Verwey transition

## 1. Introduction

Magnetite has been the subject of many extensive studies, mostly concerning the nature of the Verwey transition, which precise origin is still unknown. The most recent papers [1–3] clearly indicate that the problem what actually orders at  $T_V$  and what are the intervening interactions causing this ordering is still open and interesting for condense matter community despite over 60 years of studies.

At high temperatures magnetite crystallizes in cubic  $Fd\bar{3}m$  inverse spinel structure. Iron  $3+$  cations reside on tetrahedral positions, while both  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  are present on octahedral sites. The traditional, commonly accepted up to middle 90th, picture is that one electron from each two octahedral Fe ions may be treated as traveling across all octahedral positions, setting the mean Fe octahedral valence as 2.5. Due to strong nearest-neighbor Coulomb interactions of those mobile electrons, they

freeze out below  $T_V$  on specified positions, thus establishing well-defined  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  cations. This electronic charge ordering occurs simultaneously with the change of crystal symmetry to low temperature monoclinic. This strictly ionic model has been largely questioned [2] by the experiments performed within last 5 years and either some form of more complicated atomic order [1,4,5] (including iron dimer ordering [6]), or the lack of any charge ordering [2,3] were proposed. On the other hand, some ordering certainly develops below  $T_V$ , what can easily be observed by, e.g. AC magnetic susceptibility studies [7] at  $T_V$ , or by the axis switching [8] at temperatures below  $T_V$ , the phenomenon strictly related to the transition.

A few years ago it was found [9], based on Mössbauer studies under pressure, that apart from the Verwey transition there is also a crossover to normal spinel lattice that proceeds at the same temperature  $T_{CC} = T_V$  as the Verwey transition under ambient pressure, but where  $T_{CC}$  grows when pressure is increased (contrary to  $T_V$ , which lowers with pressure). Quite recently [3], these studies were complemented with the structure under pressure measurements and the structural transition was found at  $T_V$  even though, for elevated pressure, the Verwey transition

\* Corresponding author.

E-mail address: zukrow@uci.agh.edu.pl (J. Żukrowski).

proceeded within normal spinel phase. Since in normal spinel only  $\text{Fe}^{3+}$  are present on octahedral positions, i.e. any possible charge ordering cannot be related to frozen-in high  $T$  mixed valence, the Verwey transition was suggested to be caused by lattice deformation related gap opening. The main task of our paper is to verify this conjecture by the precise Mössbauer effect studies at ambient pressure of well characterized, stoichiometric single crystalline magnetite (previous measurements were done on, possibly nonstoichiometric, powder). We will also augment our previous [10] ac susceptibility studies under pressure of zinc ferrites to show that the isotropy point temperature  $T_{\text{IP}}$  (close to 130 K for stoichiometric magnetite and lower for doped zinc ferrites) rises with pressure. Since  $T_{\text{CC}}$  also rises with pressure and, for  $p < 0.1$  GPa as in our experiment, is close to  $T_{\text{IP}}$ , we will try to verify suggestion that in [9] the isotropy point is seen, instead of the crossover from inverse to the normal spinel.

## 2. Experimental

AC susceptibility was measured on single crystalline zinc ferrite samples  $\text{Fe}_{3-x}\text{Zn}_x\text{O}_4$ ,  $x=0, 0.0072, 0.0149$  and  $0.049$ , skull melter grown and annealed for stoichiometry. The samples, with (100) direction set parallel to the AC magnetic field, were in the He gas operated beryllium pressure cell capable of supplying  $0.01 \text{ GPa} < p < 1.2 \text{ GPa}$ . The temperature dependence of AC susceptibility under different pressures for  $x=0$  is shown in Fig. 1. The arrows mark the temperature  $T_{\text{IP}}$  (clear kink in the  $\chi_{\text{AC}}(T)$  relation shown in detail in the inset of Fig. 2) where the first order anisotropy constant vanishes (isotropy point). The  $T_{\text{IP}}$  dependence upon pressure for all studied samples is shown in Fig. 2. In the inset of Fig. 1 the coordination crossover temperature  $T_{\text{CC}}$  versus pressure, inferred from [9] is drawn on top of pressure dependence of the compensation point  $T_{\text{IP}}$  for our stoichiometric magnetite. Since the data from [9] were collected for powder sample and  $T_{\text{CC}}$  was not very well defined [3,9] the idea after this comparison was that both temperatures actually refer to the same effect. Mössbauer effect experiments to check this conjecture were performed at ambient pressure both on powdered stoichiometric single crystal of magnetite and on the bulk stoichiometric single crystal in the form of  $100 \mu\text{m}$  thick platelet. The  $^{57}\text{Fe}$  measurements were performed in the transmission geometry using a constant acceleration type spectrometer with a  $^{57}\text{Co}$  in Rh source kept at room temperature and the absorber placed in a closed cycle refrigeration system.

While very sharp change of Mössbauer spectrum at  $T_{\text{V}}$  was obtained for single crystal (typical spectra for high and low temperatures are presented in Fig. 3a) only a wide transition was found for powder sample (not shown). The

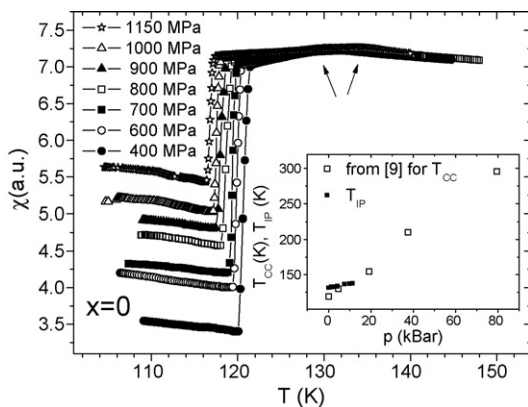


Fig. 1. Pressure dependence of the ac susceptibility around  $T_{\text{V}}$  for stoichiometric magnetite sample. The arrows bracket the region where peaks at  $T_{\text{IP}}$  due to the primary magnetic anisotropy constant vanishing are situated. In the inset those peaks positions vs. pressure are plotted (bulk symbols) on top of configuration crossover temperature  $T_{\text{CC}}$  from Ref. [9].

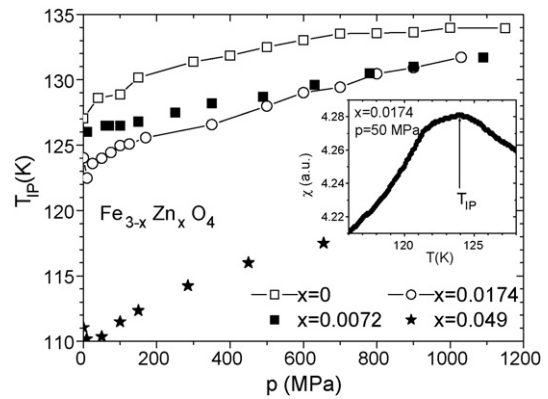


Fig. 2. Pressure dependence of the isotropy point  $T_{\text{IP}}$  for studied zinc ferrites. The inset shows the vicinity of peak at  $T_{\text{IP}}$  for  $x=0.0174$ .

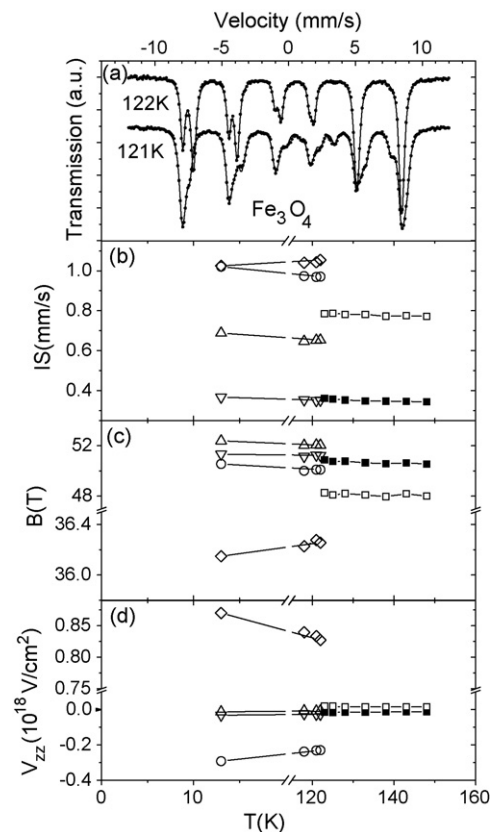


Fig. 3. Results of Mössbauer effect studies on stoichiometric magnetite single crystal. In (a) both experimental (dots) and fitted (line) spectra, just above and just below the Verwey transition, are shown.

spectra were analyzed within the transmission integral approximation assuming two components ( $T > T_{\text{V}}$ ) and four components ( $T < T_{\text{V}}$ ). The temperature dependence of the isomer shift, hyperfine field and electric field gradient are shown in Fig. 3(b)–(d). The isomer shift parameters are reported versus shift of  $\alpha\text{-Fe}$  kept at room temperature.

## 3. Discussion and conclusions

For all studied compounds the temperature  $T_{\text{IP}}$  of the isotropy point, increases with pressure. Since  $T_{\text{V}}$  decreases with pressure, as was proved from both these studies and the vast literature data,

including [10], the positive scaling of  $T_V$  versus  $T_{IP}$  suggested in [11] as a proof of a possible magnetic origin of the Verwey transition, does not exist.

Since the  $T_{IP}$  rises with pressure, as the changeover temperature  $T_{CC}$  in [9] and since the idea that magnetite transforms from inverse to normal spinel at  $T_{CC}$  is highly controversial, we decided to check if  $T_{CC}$  and  $T_{IP}$  might refer to the same physical phenomenon, erroneously interpreted in [9], and recently also in [3]. This is the reason why the Mössbauer effect studies were commenced.

Since the discovery of the phenomenon by Rudolf Mössbauer, tremendous number of Mössbauer effect studies of magnetite were reported. Highly different spectra were observed for high and low temperatures and their interpretation was by no means simple. Two components, with the intensity factor of two, were usually resolved at high temperatures and were attributed to tetrahedral  $Fe^{3+}$  cations ( $IS = 0.36$  mm/s,  $B = 50.8$  T,  $V_{zz} = -1.6 \times 10^{16}$  V/cm<sup>2</sup>) and mixed valence octahedral positions ( $IS = 0.78$  mm/s,  $B = 48.3$  T,  $V_{zz} = +1.8 \times 10^{16}$  V/cm<sup>2</sup>). Our high temperature data, Fig. 3a, are very close to those reported previously. It is also clear that no anomaly is seen close to the isotropy point (at ca. 130 K) even though the experiment was dedicated for this issue (i.e. the temperature region around compensation point was carefully scanned) and despite the fact that the isotropy point is clearly observed in NMR results [12]. In other words, our conjecture that in [9] the Mössbauer spectra reflect the changing of magnetic easy axis direction at  $T_{CC}$  not a transition from inverse to normal spinel must be rejected.

For low temperatures, from three up to nine magnetic components were found [13]. In very precise studies on oriented, detwinned single crystal [14] the low  $T$  spectrum was fit with five components, the one corresponding to tetrahedral site of  $Fe^{3+}$  and two components for each octahedral  $Fe^{3+}$  and  $Fe^{2+}$  sites; similar results were found for [15]. In our studies, only four low temperature components were needed to obtain a reasonably good fit and the relative intensities were: 4 ( $IS = 0.35$  mm/s):2 ( $IS = 0.63$  mm/s):2 ( $IS = 0.96$  mm/s):1 ( $IS = 1.03$  mm/s). Although the intensity of the first component is higher than 1/3 of the integrated intensity of all components, its IS almost coincides with that for  $Fe^{3+}$  at higher temperatures. Since also the hyperfine field is compara-

ble (Fig. 3c) to the relevant component at high temperatures and the same is true for  $V_{zz}$  (Fig. 3d), we see no arguments to claim that the tetrahedral iron cations change their valence at  $T_V$ .

In conclusion, we have shown that no direct indications of the change of a spinel structure from inverse to normal can be drawn from Mössbauer measurements results. We have also shown that Mössbauer effect parameters do not show any anomaly at the isotropy point.

## Acknowledgement

This project is financially supported by Polish Ministry of Education and Science Grant for the years 2006–2008.

## References

- [1] J.P. Wright, J.P. Attfield, P.G. Radaelli, Phys. Rev. B 66 (2002) 214422.
- [2] J. Garcia, G. Subias, M.G. Pgoietti, J. Blasco, H. Renevier, J.L. Hodeau, Y. Joly, Phys. Rev. B 63 (2001) 054110;  
G. Subias, J. Garcia, J. Blasco, Phys. Rev. B 71 (2005) 155103.
- [3] Kh.G. Rozenberg, M.P. Pasternak, W.M. Xu, Y. Amiel, M. Hanfland, M. Amboage, R.D. Taylor, R. Jeanloz, Phys. Rev. Lett. 96 (2006) 045705.
- [4] I. Leonov, A.N. Yaresko, V.N. Antonov, M.A. Korotin, V.I. Anisimov, Phys. Rev. Lett. 93 (2004) 146404.
- [5] H.-T. Jeng, G.Y. Guo, Huang D.J., Phys. Rev. Lett. 93 (2004) 156403.
- [6] H. Seo, M. Ogata, H. Fukuyama, Phys. Rev. B 65 (2002) 085107.
- [7] Z. Tarnawski, A. Wiecheć, M. Madej, D. Nowak, D. Owoc, G. Król, Z. Kąkol, L. Kolwicz-Chodak, A. Kozłowski, T. Dawid, Acta Phys. Pol. A 106 (2004) 771.
- [8] B.A. Calhoun, Phys. Rev. 94 (1954) 1577.
- [9] M.P. Pasternak, W.M. Xu, G.Kh. Rozenberg, R.D. Taylor, R. Jeanloz, J. Magn. Mater. 265 (2003) L107;  
M.P. Pasternak, W.M. Xu, G.Kh. Rozenberg, R.D. Taylor, R. Jeanloz, J. Phys. Chem. Sol. 65 (2004) 1531.
- [10] A. Wiecheć, R. Zach, Z. Kąkol, Z. Tarnawski, A. Kozłowski, J.M. Honig, Physica B 359–361 (2005) 1342.
- [11] Z. Kąkol, A. Kozłowski, M. Bałanda, H. Schwenk, B. Luthi, J.M. Hong, in: M. Abe, Y. Yamazaki (Eds.), Proc. ICF8, The Japan Society of Powder and Powder Metallurgy, Japan, 2000, pp. 126–130.
- [12] P. Novak, H. Stepankova, J. English, J. Kohout, V.A.M. Brabers, Phys. Rev. B 61 (2000) 1256.
- [13] R.E. Vanderberghe, E. De Grave, in: G. Long, F. Grandjean (Eds.), Mössbauer Effect Studies of Oxide Spinel, Mössbauer spectroscopy Applied to Inorganic Chemistry, vol. 3, Plenum Press, New York, 1989.
- [14] R.S. Hargrove, W. Kundig, Solid State Commun. 8 (1970) 303.
- [15] F.J. Berry, S. Skinner, M.F. Thomas, J. Phys.: Condens. Mat. 10 (1998) 215.