X-RAY DIFFRACTION STUDIES OF Zn-DOPED MAGNETITE*

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X-ray powder diffraction studies were performed on $Fe_{3-x}Zn_xO_4$ (x = 0, 0.0046, 0.0072, 0.015, 0.0185, 0.0249, 0.036) in the temperature range 70 K-300 K. We intended to check if structural characteristics distinguish between the samples exhibiting the Verwey transition of discontinuous and continuous character, as found *e.g.* for resistivity and heat capacity results. We have found that within experimental error range no clear distinction between those two regimes of the Verwey transition can be deduced from the compositional dependence of lattice constants and monoclinic angle.

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The aim of the report is to present the introductory results of the planed systematic measurements of the dopant contents influence on the structural properties of magnetite based materials. Here the structural parameters for $Fe_{3-x}Zn_xO_4$ ($x < 0.04$) are presented.

Magnetite, Fe_3O_4, reveals the spectacular phase transformation at $T_V \approx 120$ K (known as the Verwey transition) at which anomalies in many physical properties were found. The common belief is that the transition is related to the iron cation valence instability at the octahedral positions of the spinel lattice. Above T_V the valence of 2.5 may be attributed to all of the octahedrally coordinated Fe, whereas below the transition temperature some charge segregation on the octahedral positions occurs. Even very small substitutions for iron (as with Zn or Ti), or departure from ideal stoichiometry greatly disturbs this strongly correlated electron-phonon system. Ultimately, the lowering number of Fe can change the order of the transition: high temperature phase transforms discontinuously into low temperature long range

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charge-ordered phase for low dopant concentration, whereas for the concentration exceeding certain level the low- temperature short range ordered phase develops continuously ("second order" Verwey transition). These two regimes can also be seen in compositional dependence of several physical properties, *e.g.* resistivity and heat capacity [1]. Since the transition is reflected in the change of the crystal structure from high temperature cubic (Fd3m) to presumably low temperature monoclinic (Cc; although both the symmetry as well as the actual atomic arrangement are the subject of controversy, see *e.g.* [2]), it is interesting to check if the first and second order regimes are also distinguished by the structural characteristics. The preliminary studies of powder neutron diffraction on zinc ferrites were already completed. Here, the same problem has been addressed by X-ray diffraction measurements.

Single crystalline zinc ferrites $Fe_{3-x}Zn_xO_4$, were grown from the melt by the cold crucible technique (skull melter) [3], and then subjected to subsolidus annealing under CO/CO_2 gas mixtures to establish the appropriate metal/oxygen ratio [4]. After quenching the samples were trimmed and finely powdered, and the transition temperature (*i.e.* sample quality) was checked by AC susceptibility. The composition x was read from the universal T_V *vs* x relation [5].

Temperature dependent X-ray diffraction (XRD) measurements in the temperature range 70–300 K were performed on a Siemens D5000 diffractometer equipped with the OXFORD continuous flow cryostat, and a rear graphite monochromator using CuK_α radiation. The $Fe_{3-x}Zn_xO_4$ samples were mixed with high purity tungsten powder (Puratronic, 99.999%) in weight ratio 3:1 and loaded in the cavity holder, which was mounted on the cold finger of the cryostat. Tungsten powder was used in temperature dependent measurements as an internal standard. The complete XRD scans ($16\,\mathrm{deg} \leq 2\theta \leq 114\,\mathrm{deg}$) were generally collected at 300 K, 70 K and, in selected cases, at some other temperatures to clarify structural problem. To follow the temperature behavior of the lattice parameters of $Fe_{3-x}Zn_xO_4$ compounds only restricted 2θ ranges, comprising 10 or 12 selected Bragg peaks, were collected at temperatures in the vicinity of the transition with a step of 0.02 deg in 2θ. Prior to each 2θ scan the temperature of the sample was stabilized for 30 min. The XRD patterns were fitted using FULLPROF [6] program assuming the pseudo-Voight function for peak shape and polynomial function for the background intensity.

X-ray diffraction patterns of $Fe_{3-x}Zn_xO_4$ compounds were indexed between 300 K and T_V on the base of the $a \times a \times a$ cubic unit cell and Fd3m space group. Next, below T_V the patterns were indexed in the rhombohedral symmetry (space group $R\bar{3}m$) and on the basis of the distorted $a \times a \times a$ unit cell (a is the lattice parameter of the RT cubic unit cell), instead of the

actual monoclinic symmetry to avoid problems with strong overlap of peaks that are not observed but are permissible by much lower symmetry. Since no accurate model of the low temperature complex structure of $Fe_{3-x}Zn_xO_4$ compounds is available in the literature the pattern matching method was applied (refinement without structural model) to refine these patterns and to obtain the most reliable values of the lattice parameters. Monoclinic unit cell ($\sqrt{2}a \times \sqrt{2}a \times 2a$) parameters were then calculated from fitted rhombohedral unit cell data, and the temperature dependencies of monoclinic β_M for two representative samples undergoing first and second order type transitions are shown on Fig. 1. Compositional dependence of rhombohedral a_R and monoclinic β_M are presented on Fig. 2 and 3, together with the relevant results from powder neutron diffraction studies [7].

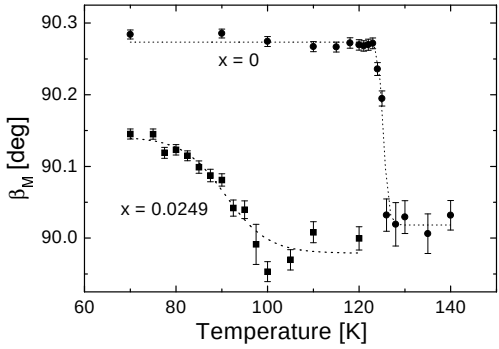

Fig. 1. Temperature dependence of monoclinic β_M angle for representative $Fe_{3-x}Zn_xO_4$ samples of different character.

The Verwey transition is manifested by the jumps in all lattice parameters (in particular those presented on Fig. 2 and 3) in their dependence upon temperature. Although these jumps diminish with the composition no clear distinction between first and second order Verwey transition can be inferred from Fig. 2 and 3: lattice parameters change continuously with concentration both below and above the Verwey transition. So, although the lattice dynamics differs for first and second order regime, as seen from heat capacity studies [1], these changes are too subtle to be observed directly by this preliminary lattice parameters characteristics and the problem requires further studies.

In conclusion, we have measured temperature dependence of X-ray powder diffraction in a series of Zn doped magnetite. Although clear anomaly in all structural characteristics is present at the Verwey transition this anomaly does not differentiate between continuous and discontinuous Verwey transition, at least within experimental error of our technique.

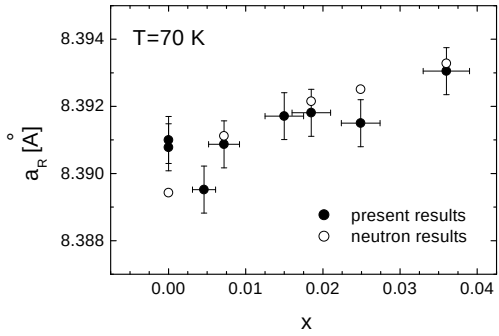

Fig. 2. Compositional dependence of rhombohedral lattice parameter a_R at $T = 70$ K.

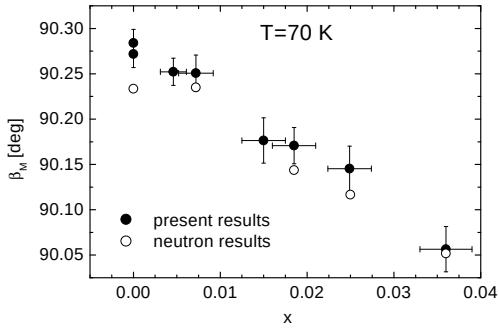

Fig. 3. Compositional dependence of monoclinic β_M angle at $T = 70$ K.

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