Vol. 91 (1997) *ACTA PHYSICA POLONICA A* No. 2

Proceedings of the European Conference "Physics of Magnetism 96", Poznań 1996

RHOMBOHEDRAL DISTORTION IN $Fe_{3-y}Zn_yO_4$ AT VERWEY TRANSITION

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The time-of-flight neutron diffraction data were collected for two $Fe_{3-y}Zn_yO_4$ powder samples showing different order of the Verwey transition: $y = 0.0072$ — first order, $y = 0.0249$ — second order. Measurements were performed on spallation neutron source in ISIS Rutherford Appleton Laboratory. At low temperatures (below Verwey transition temperature T_V) clear splitting of certain reflections characteristic of rhombohedral distortion was observed for both samples. We found that this distortion is much bigger for the sample exhibiting first-order than for the sample showing second-order transition.

PACS numbers: 61.12.–q, 64.70.Kb, 75.50.Gg

1. Introduction

Magnetite has been the object of many extensive studies which were linked firstly with the existence of the phase transition near 120 K (Verwey transition). At this point electrical phase transition is observed which is accompanied by the crystal symmetry change and heat capacity anomaly. Results on heat capacity measurements [1] performed on nonstoichiometric $Fe_{3(1-\delta)}O_4$ single crystals demonstrate that in the range $-0.0005 \leq \delta \leq \delta_c \approx 0.0039$ the Verwey transition is of first order, whereas in the range $\delta_c \leq \delta \leq 3\delta_c$ the transformation is of second order. This feature was independently verified by resistivity and Seebeck coefficient measurements. Our measurements performed on low doped $Fe_{3-y}M_yO_4$, where M = Zn or Ti show the remarkable similarity with the above observations [2,3] in the dependence of their physical properties on dopant concentration y and 3δ, as well as on the temperature.

All the above efforts were aimed to elucidate the origin of interactions leading to the Verwey transition. This is still an unresolved problem partially because the low temperature structure of magnetite is not yet fully determined.

It is well established that above the Verwey transition magnetite crystallizes in the cubic inverse spinel structure. This structure holds also for the high-temperature phase of Zn doped ($y > 0.1$) magnetite. The neutron [4] and electron diffraction [5] experiments established a monoclinic Cc crystal structure of magnetite below the Verwey transition. The monoclinic c_M-axis is actually tilted by angle $\beta_M \approx 0.20°$ away from the vertical towards the $-a_M$ direction due to rhombohedral elongation along the $[\bar{1}11]$ or $[\bar{1}1\bar{1}]$ axes [4].

There are no available data concerning the crystal structure of $Fe_{3(1-\delta)}O_4$ and $Fe_{3-y}Zn_yO_4$ ($y < 0.04$) below T_V. Yet the knowledge of exact structure is critical for the interpretation of experimental data as well as for the characterization of the Verwey transition. In fact, some models [6] suggest an intimate connection between the Verwey transition and crystal lattice properties. For this reason we undertook systematic powder neutron diffraction measurements of the crystal structure and the lattice parameters for $Fe_{3-y}Zn_yO_4$.

2. Experiment

Single crystalline zinc ferrites, $Fe_{3-y}Zn_yO_4$ of small doping level y are grown from the melt by the cold crucible technique (skull melter) [7]. These crystals are then subjected to subsolidus annealing under appropriate CO/CO_2 gas mixtures to establish appropriate metal/oxygen ratio [8]. Actual composition and sample uniformity are checked using a microprobe electron analyzer.

The samples we used were two 1 cm^3 $Fe_{3-y}Zn_yO_4$ powder (grain size 10–30 μm). First sample, SM448, with the mean composition $y = 0.0072 \pm 0.0025$ falls within first-order transition range, while SM341 with $y = 0.0249 \pm 0.0035$ shows transition of the second order.

The time-of-flight (t-o-f) neutron diffraction data were collected on spallation neutron source at Rutherford Appleton Laboratory in England by the fixed angle backscattering detectors. The t-o-f range used was 20–130 ms corresponding to d-spacing 0.6–2.6 Å. Under these experimental settings the diffraction data have an approximately constant resolution of $\Delta d/d = 8 \times 10^{-4}$. The normal counting time of 10 min was proved to be long enough for the evaluation of lattice parameters, while time of 3 h (at $T = 4.2$, 100 and 150 K in the case of SM448 and $T = 4.2$, 70 and 150 K for SM341) was designed for the precise structure refinement. The temperature was scanned at intervals of 10 K (2 K in the region close to the transition).

3. Experimental results and discussion

For both samples at highest T the best fit was obtained assuming cubic $Fd3m$ symmetry, in full agreement with the reported data for pure magnetite. Low temperature (below $T = 110$ K) diffraction pattern for first-order SM448 sample showed clear splitting of $\langle hh0 \rangle$ (with the intensity ratio 3:1) and $\langle hhh \rangle$ (intensity ratio 1:1) cubic reflection which rapidly coalesce into one at the transition. This is in agreement with literature reports (e.g. [4]) about rhombohedral elongation

of the original cubic cell along ⟨111⟩ direction. The low temperature splitting of the relevant ⟨*hhh*⟩ and ⟨*hh*0⟩ reflections for SM341 is much smaller and only broadening of these peaks is visible. The comparison between both samples may best be inferred from Fig. 1, where rhombohedral and cubic lattice constants a for both samples are shown on the same scale. Monoclinic angles β_M for both samples are shown in Fig. 2. We found that below transition our data are well fitted to a power law in the vicinity of the transition (see Fig. 2). Clearly, SM341 undergoes much smaller structure change than the first-order sample SM448.

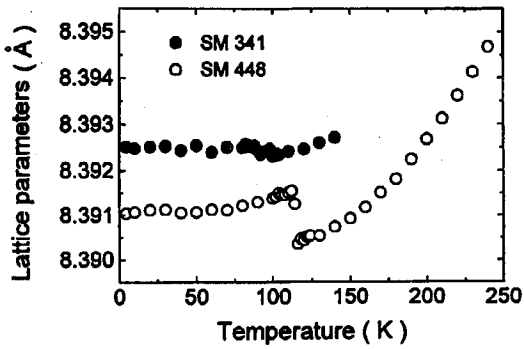

Fig. 1. Lattice parameters: cubic for $T > T_V$, rhombohedral for $T < T_V$.

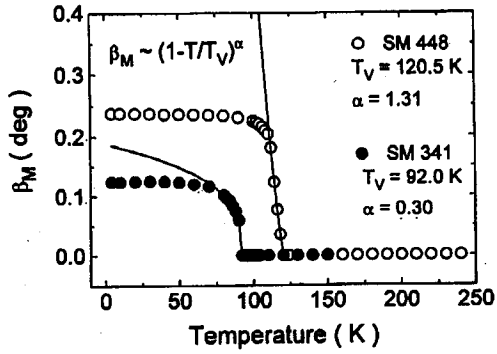

Fig. 2. Calculated monoclinic angle β_M for $Fe_{3-y}Zn_yO_4$.

In conclusion, the powder neutron diffraction scattering experiment on $Fe_{3-y}Zn_yO_4$ ($y = 0.0072$ — first-order sample, $y = 0.0249$ — second-order sample) was performed at spallation neutron source ISIS in Rutherford Appleton Laboratory in England. We found that the rhombohedral distortion for less doped sample is much bigger than the corresponding distortion of more doped sample. As a result, lattice contribution to the Verwey transition should be considered, which was suggested by our heat capacity results [9, 10].

Acknowledgment

Some of us (A.K., Z.K., and R.Z.) gratefully acknowledge support from the British Council, Rutherford Appleton Laboratory, and Faculty of Physics and Nuclear Techniques of University of Mining and Metallurgy.

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