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Magnetic and structural studies of magnetite at the Verwey transition

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Abstract

Studies of the Verwey transition in zinc doped magnetite ($Fe_{3-x}Zn_xO_4$, $x = 0, 0.0097, 0.011, 0.036$) by simultaneous ac magnetic susceptibility (χ) and electric resistance measurements are presented. The temperature hysteresis of the Verwey transition increases from 0.03 K for stoichiometric magnetite to 0.5 K for Zn doped samples, despite the continuous character of the transition. The results of introductory observations of structural changes are also presented.

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Keywords: Metal–insulator phase transition; Magnetite; Photon correlation spectroscopy

1. Introduction

The Verwey transition in magnetite at ca. $T_V = 125$ K is mainly known for its rise of resistivity ρ by two orders of magnitude on cooling below T_V. The transition is also reflected in alterations in magnetic ac susceptibility χ_{ac} and the crystal symmetry that changes from cubic to monoclinic below T_V. It was generally believed to be related to the presence of Fe^{3+} and Fe^{2+} ions on octahedral positions in the lattice that lack their individuality at elevated temperatures. The electrons are frozen on particular positions at low T, forming individuated Fe^{2+} and Fe^{3+} cations, whereas they are spread across all octahedral Fe positions above T_V, undergoing thus an order disorder electronic transition. However, neither the notion of iron of exact +2 and +3 valence [1,2,3], nor the mixed valence above T_V [2] are now accepted and the dominant role of electronic correlations is now increasingly criticized (the Anderson criterion is not fulfilled [1]). Finally, some recent results [4] show that no charge ordering is justified since at T_V (at higher pressures) magnetite is a normal spinel and Fe^{3+} ions only reside on octahedral sites where the charge ordering was postulated. Whatever the reason for the transition is, it is a very spectacular first order phase transformation; bearing in mind the long time lapse from its first discovery, it should be well characterized by now. However, the thermodynamic documentation of the Verwey transition is not as complete as other spectacular phase transformations, e.g. the ice to water transition (see e.g. [5]). In view of all these facts we have initiated a project to observe how the system reacts when the heat of transition is delivered to the sample exactly at the transition temperature. In other words, we wanted to trace the transition during the process and to simultaneously measure the temporal dependence of as many physical characteristics as possible. The simultaneous measurements of the electrical resistance R, magnetic susceptibility χ as well as the temporal temperature profile $T(t)$ for stoichiometric magnetite have already been presented [6]. Here we provide results for magnetite samples low doped with zinc, exhibiting the Verwey transition of first and second order and we show some preliminary results on the structural changes during the Verwey transition in stoichiometric magnetite.

2. Experimental results and discussions

The single crystalline samples of $Fe_{3-z}Zn_xO_4$ (typical mass of 0.25 g in order to increase the heat capacity and to allow for slow heat delivery) were prepared from 99.99% pure Fe_2O_3 and 99.999% ZnO powders by the skull

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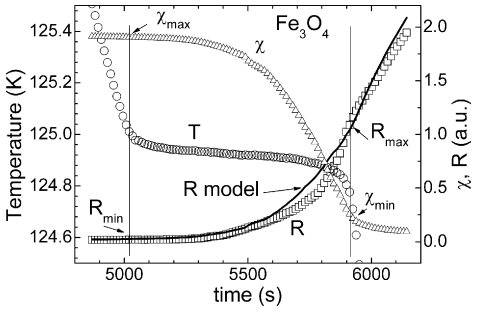

Fig. 1. The results of simultaneous measurements of dynamic susceptibility χ, resistance R and the temperature profile T, while the stoichiometric magnetite sample was cooled to the stable temperature just below T_V. The vertical lines bracket the transition. The line describes the time dependence of sample resistance simulated by low- and high-value resistance series connections.

melter technique and subsequently annealed for stoichiometry. ac susceptibility (f = 188.88Hz, H_{ac} = 0.5 Oe) and the electrical resistance (4-point method, ultrasonic bonded contacts) were measured on the home-made equipment. The miniature Pt1000 thermometer was glued to the sample surface to monitor the sample temperature (see the inset of Fig. 2).

Results of the typical simultaneous χ, R and T versus time measurements illustrating how the low T phase sets up are shown in Fig. 1 for stoichiometric sample. For each experiment the sample was cooled (heated) to the well established surrounding temperature across the transition. The low temperature drop in susceptibility is linked to the diminished size of structural domains in the low temperature phase of magnetite [7]. Magnetic domain walls movement, mainly responsible for susceptibility signal, is then highly curtailed, resulting in a drop in $\chi(T)$. We can thus assume that the quantity $C(T) = (\chi_{max} - \chi(T))/(\chi_{max} - \chi_{min})$, where χ_{max} and χ_{min} are susceptibility values marking the beginning and the end of the transition (see Fig. 1), is a rough measure of the low temperature phase (that this is the realistic assumption may be seen from the right inset of Fig. 2, where the scaled resistance for x = 0.011 versus scaled χ is presented: the electrical state of the sample is a unique function of the susceptibility). Assuming further that both low-T and high-T magnetite phases may be modeled by high- and low-value resistors (with their relative number $C(T)$), an electrical model of magnetite in the vicinity of transition may be constructed using a mixed series and parallel connection of resistors. Since the resistors number is naturally large, the model breaks into two well defined options: series and parallel connection of resistors. The results of the series connection (where, additionally, the low-T resistance was assumed to depend on temperature) are shown in Fig. 1. Although the agreement with the experimental data is only qualitative, the alternative parallel connection of the resistors leads to a model that is completely at odds with the experiment. Naturally, the model is an oversimplification, but we can consider several current paths (i.e. sort of parallel connections) each one composed of "series connection" of low and high-temperature clusters. According to our model each path is composed of, statistically, the same number of high and low temperature clusters. In any case, our results suggest that the new low temperature phase, of much higher resistance than at high temperatures, renders the current conduction through the sample more difficult already of the very beginning of the transition.

To measure the temperature hysteresis of the transition, very precise heat capacity studies were performed on the stoichiometric sample [6]; we are certain that the hysteresis of the Verwey transition exist and it does not exceed 0.03 K. Several artifact reports in the literature claiming larger hysteresis for stoichiometric magnetite may easily be caused by not properly taking into account the huge heat capacity at the transition (and the large anomaly in heat conduction [8]): the thermometer reflects the probe properties of the heater rather than the sample temperature. To estimate the hysteresis in zinc doped magnetite, where the heat capacity is much lower and the anomaly in heat transfer is not so pronounced, the samples were heated with the current passing through them (as opposed to heating with the probe heater that could bring about erroneous temperature reading) in several stages of the transition. The results, for one sample x = 0.011, are shown in Fig. 2. It is clear that the hysteresis is close to $\Delta T_V \sim 0.5$ K. Similar values for the hysteresis were obtained by the same method for a sample with x = 0.0097, while no such studies were performed for a sample with x = 0.036. The same values of the hysteresis were found by the observation of the thermometer readouts during normal (i.e. by external heater) heating. Even with the most inconvenient case of stoichiometric sample (due to already mentioned anomalies) the on-sample thermometer observation corresponded to an error not exceeding 0.05 K. We can thus conclude that with our experimental setup we can estimate the hysteresis with uncertainty ±0.05 K.

Since the changes of the electronic pattern monitored by χ and R are linked to the lattice, the direct observation of the generation of the new symmetry phase at the transition (e.g. by the observation of (4 4 1/2) [9] superlattice reflections) was the next logical experimental step. Here we report on the preliminary experiment performed on ID10A setup (on Troika 1) at the ESRF, with an E = 8 keV monochromatic X-ray beam. By using a partially coherent beam, we were able to access both static (ensemble averaged) and the dynamic structural information.

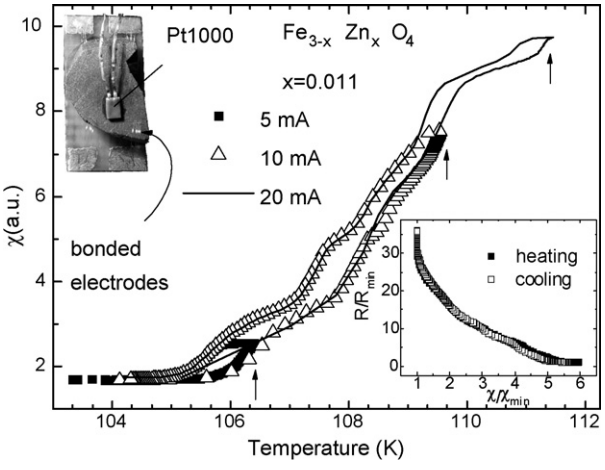

Fig. 2. Hysteretic behavior of susceptibility for x = 0.011 zinc ferrite sample. The results of heating with three currents flowing through the sample are shown. The arrows indicate the point where the heating current were set to zero. The wavy line of $\chi(T)$ profile results from sample inhomogeneity. In the right inset the scaled resistance is plotted vs. the scaled susceptibility, suggesting the universal behavior. The left inset shows the sample experimental arrangement. The length of the Pt1000 thermometer is ca. 1.5 mm.

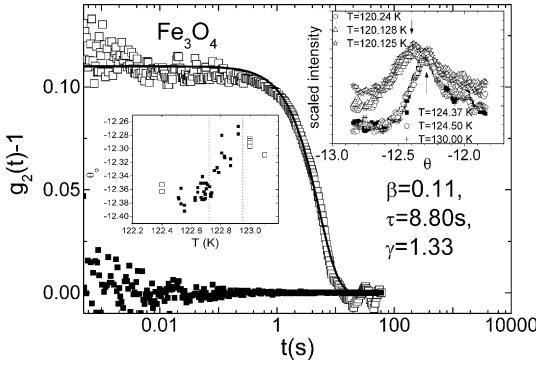

Fig. 3. Second order correlation function $g_2(t)$ for the stoichiometric magnetite sample measured around the center of the fundamental (4 4 0) Bragg reflexion (open symbols). The correlations of the monitor readings are shown in full symbols. The $g_2(t)$ function is fit with a stretched exponential (solid line): $g_2(t) = \beta \exp(-2(t/\tau)^{\gamma})$. The left inset shows the temperature dependence of the primary peak shoulder position θ_0 in the transition region, bracketed by vertical lines (full symbols; open squares indicate typical positions of the peak at low and high T (not in scale)). Only the representative scans from a total of 100 are presented. The peak shoulder is in the right inset and its position θ_0 is defined by the arrows.

Fluctuations of the speckle pattern around superlattice reflections are a measure of structural fluctuations near the transition region.

The same sample with $x = 0$ as reported above, cut approximately parallel to (1 1 0) plane, was measured and again the miniature Pt1000 thermometer was glued to the surface. Due to technical problems, we could only observe the temperature variation of the cubic phase peak shoulder (see the right inset of Fig. 3). We have carefully scanned the transition region (with ca. 5 mK T steps) and the corresponding T dependence of the peak shoulder position θ_0 is shown in the left inset in Fig. 3. Those results suggest that the structural changes proceed gradually across the transition (bracketed by vertical lines), in agreement with the R and χ behavior.

Photon correlation spectroscopy with coherent radiation was carried out at temperatures just below T_V. The results are shown in Fig. 3 as the second order correlation function $g_2(q,t)$ [10]. Although a precise analysis was not possible the data clearly show that lattice dynamics, with a characteristic time τ of tens of seconds, can be observed in Fe_3O_4 by this technique.

In conclusion, the direct observation of the emergence of a second phase (the low-T phase in case of results shown in Fig. 1) at the Verwey transition was performed by means of simultaneous magnetic susceptibility and resistance for four single crystalline zinc doped magnetite samples. The results suggest that the new low temperature phase efficiently blocks current conduction through the sample already at the very beginning of the transition. We have also found that the hysteresis of the transition grows from ca. 0.03 K for stoichiometric magnetite (exhibiting the transition of the first order) to 0.5 K for higher Zn concentration, despite the continuous character of the transition in this case. Finally, the results of preliminary studies at ESRF of the proliferation of a new crystallographic phase were presented and the characteristic life time of structural fluctuations below the transition was estimated to be of the order of tens of seconds.

Acknowledgements

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References

[1] J.P. Wright, J.P. Attfield, P.G. Radealli, Phys. Rev. B 66 (2002) 214422.
[2] J. Garcia, G. Subias, J. Phys. Condens. Matter 16 (2004) R145.
[3] P. Novak, H. Stepankova, J. English, J. Kohout, V.A.M. Brabers, Phys. Rev. B 61 (2000) 1256.
[4] M.P. Pasternak, W.M. Xu, G.Kh. Rozenberg, R.D. Taylor, R. Jeanloz, J. Magn. 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;
G.Kh. Rozenberg, M.P. Pasternak, W.M. Xu, Y. Amiel, M. Hanfland, M. Amboage, R.D. Taylor, R. Jeanloz, Phys. Rev. Lett. 96 (2006) 045705.
[5] M. Grimsditch, V.G. Karpov, J. Phys. Cond. Matter. 8 (1996) L439.
[6] 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.
[7] M. Bałanda, A. Wiecheć, D. Kim, Z. Kąkol, A. Kozłowski, et al., Eur. Phys. J. B 43 (2005) 201–212.
[8] A. Salazar, A. Oleaga, A. Wiecheć, Z. Tarnawski, A. Kozłowski, IEEE Trans. Magn. 40 (2004) 2820–2822.
[9] G. Król, J. Kusz, Z. Tarnawski, Z. Kąkol, W. Tabiś, A. Kozłowski, Acta Phys. Pol. A109 (2006) 601–605.
[10] B. Lengeler, Naturwissenschaften 88 (2001) 249–260.