AC SUSCEPTIBILITY STUDIES OF Zn-DOPED MAGNETITE SINGLE CRYSTALS*

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(Received July 10, 2002)

We present selected results of systematic studies of AC susceptibility in the series of single crystalline $Fe_{3-x}Zn_xO_4$ ($x < 0.04$) and $Fe_{3(1-\delta)}O_4$ samples. Two sets of anomalies were found: the first one connected with the Verwey transition and the second consisting of two different effects, one at 26 K, visible only for stoichiometric samples, and the other at 50 K. While the temperature position of the first anomaly (26 K) does not depend on f, the effect at 50 K shifts to higher temperatures with increasing frequency. Both effects gradually move to lower temperatures and finally disappear with increasing x and δ. Qualitatively similar results were reported from Magnetic After Effect (MAE) technique, that records effects with the relaxation time 10^4 higher than that characteristic for our technique.

PACS numbers: 75.30.Cr, 75.50.Dd, 75.30.Gw

* Presented at the International Conference on Strongly Correlated Electron Systems, (SCES 02), Cracow, Poland, July 10–13, 2002.

1. Introduction

The aim of the present report is to study the effect of Zn doping and nonstoichiometry on the low temperature (mainly $T < 70$ K) magnetic properties of magnetite single crystals as visualised by χ_{AC}. By this means we intend to complement earlier literature reports [1] devoted only to pure magnetite.

Apart from its technological importance magnetite, Fe_3O_4, is known due to the Verwey transition at $T_{\mathrm{V}} \approx 120$ K. At high T magnetite is a disordered electron system in which "additional" (beyond Fe^{3+} ion core) electrons transfer between adjacent octahedral Fe. Although, recently, the common picture of the transition as the freezing out of mobile strongly correlated electrons have been questioned [2, 3], the ionic ordering is rather well experimentally evidenced (see the discussion in [4]). With still existing controversies over $Fe^{+3} - Fe^{+2}$ exchange we have decided to study χ_{AC}, the technique reported to have a close link with the electron exchange phenomenon [4].

2. Results and discussion

The in-phase component χ' measured at $f = 125$ Hz and $H_{\mathrm{AC}} = 1$ Oe for all studied samples (see Fig. 1) falls considerably while T approaches $T < T_{\mathrm{V}}$ region, with the simultaneous increase in the loss χ'' contribution as already reported [1]. Additionally there is the anomaly in χ below 60 K in all

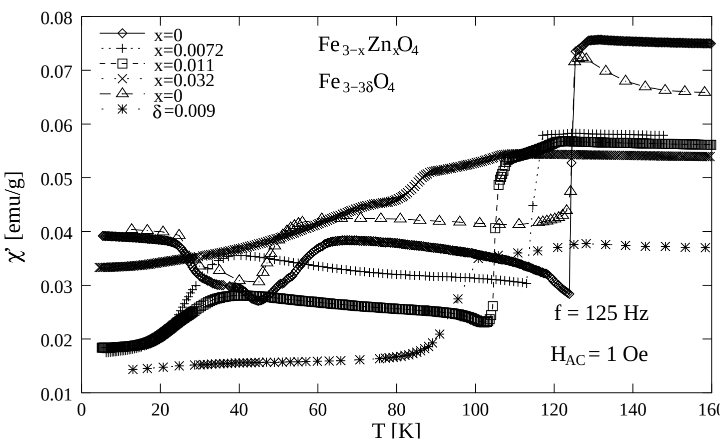

Fig. 1. Dispersive part χ' of AC susceptibility for $Fe_{3-x}Zn_xO_4$ and $Fe_{3(1-\delta)}O_4$ single crystals.

samples: χ' drops with the simultaneous peak in χ'' (see Fig. 2), proving that the domain walls can not follow H_{AC} changes. This effect is virtually the same for field cooled samples, and similar, although smaller, for field cooled and subsequently in-field measured stoichiometric magnetite. As presented in Fig. 2 linear relation $\log(f)$ *vs.* $1/T$ holds, indicating thermally activated relaxation process.

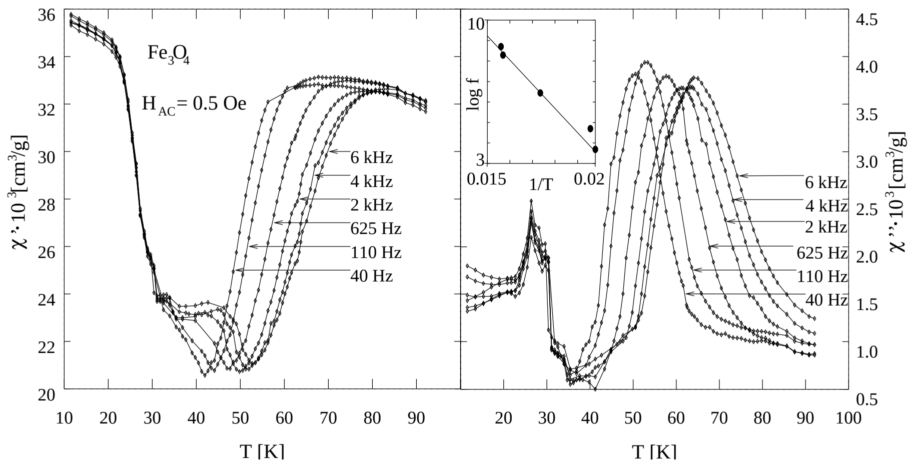

Fig. 2. AC χ' and χ'' for stoichiometric Fe_3O_4; the inset proves that the peak in χ'' at $T = 50 - 70$K is a manifestation of relaxation effects described roughly by the formula $f = (1/\tau_0)\exp(-Q/k_B T)$. Values of Q equal to 98, 26 and 42 (in meV), and τ_0 equal to 4.5×10^{-13}s, 6.7×10^{-8}s and 1.3×10^{-9}s were found for $x = 0$, 0.0072 and 0.011, respectively.

Interestingly, the qualitatively similar results have been noticed by MAE [6], the technique that records effects with the relaxation time 10^4 higher than that characteristic for our technique. In particular, the relaxation gap was observed there between 30 and 50 K, *i.e.* at the T range where our anomalies are found. Thus both our results and MAE data prove the existence of the relaxation effects at ca. 60 K for stoichiometric magnetite and at lower T for doped and nonstoichiometric samples with very wide relaxation time spectrum.

In case of stoichiometric magnetite the drop in χ' at 60 K is further followed by the increase of χ', exhibiting characteristic subtle structure until the high-T χ' value is reached, suggesting that the wall movement once more takes place at lower T. Since this anomaly is absent in the results of in-field measurements, the external magnetic field apparently curtails the processes that enable the wall movement at temperatures below 26 K. Moreover, the effect at $T = 26$ K is of different kind than that at 60 K since no f dependence was seen. The corresponding peak is again observed in the results from MAE [4,6]; there, however, the peak shows typical relaxation behaviour and is linked to intraatomic Fe^{2+} electron excitations. If the relaxation times of these processes were of the order of the characteristic observation time for MAE, *i.e.* 1 to 180 s, our technique should see the static arrangement resulting in $\chi'' = 0$. Thus, the fact that we still observe the anomaly suggests that some more complicated phenomena are taking place.

In conclusion, we have measured temperature, frequency and $H_{\rm AC}$ dependence of AC susceptibility of single magnetite based crystals. We have found the usual drop in χ' at $T_{\rm V}$ followed at lower T by the anomaly, that was explained by the slowing domain wall movement. The additional anomaly at $T = 26$K, observed only for stoichiometric magnetite, does not show the typical f dependence, suggesting that some complicated effects are taking place. Since both anomalies are probably linked to the octahedral iron energy level fluctuations, AC susceptibility studies, together with MAE, may help to clarify the still open problem of the processes causing the Verwey transition.

This research was supported by the Faculty of Physics and Nuclear Techniques, University of Mining and Metallurgy.

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