Available online at www.sciencedirect.com
ScienceDirect
Journal of Magnetism and Magnetic Materials 316 (2007) e738–e740
Journal of magnetism and magnetic materials
www.elsevier.com/locate/jmmm

Study of the Verwey transition in magnetite by low field and magnetically modulated non-resonant microwave absorption

M.P. Gutiérrez[a,*], G. Alvarez[b], H. Montiel[c], R. Zamorano[a], R. Valenzuela[b]

[a]Escuela Superior de Física y Matemáticas del Instituto Politécnico Nacional, México, D.F. 07738, Mexico
[b]Instituto de Investigaciones en Materiales de la Universidad Nacional Autónoma de México, México, D.F. 04510, México
[c]Centro de Ciencias Aplicadas y Desarrollo Tecnológico de la Universidad Nacional Autónoma de México, México, D.F. 04510, México

Available online 13 March 2007

Abstract

We have investigated the Verwey phase transition (VPT) by two novel non-resonant microwave absorption techniques: low-field absorption (LFA) and magnetically modulated microwave absorption spectroscopy (MAMMAS). Measurements were carried out on sintered polycrystalline samples of Fe_3O_4, in the 77–300 K temperature range. LFA refers to the microwave absorption around the zero DC field range ($-1000 < H_{DC} < +1000$ G). LFA measurements showed an hysteretic behavior; a minimum in the hysteresis loop width was observed at 126 K, which can be associated with a minimum in magnetic anisotropy, as a consequence of charge localization below the VPT. MAMMAS experiments are based on the variations in microwave absorption (at constant H_{DC}), as a function of temperature, and seem particularly well adapted to detect a wide range of phase transitions. In the magnetite case, a continuous increase in the microwave power absorption level was observed as temperature decreased, reaching a strong maximum at 130 K and a minimum at 100 K. An inflection point at 126 K was found, in very good agreement with LFA measurements. These results are discussed in detail.

PACS: 75.30.Gw; 75.50.Gg; 78.70.Gq

Keywords: Verwey phase transition; Non-resonant absorption technique; Magnetite

1. Introduction

Magnetite is the oldest magnetic material known, and it is still intensely studied. It is a mixed-valence iron oxide that exhibits a complex transition, first described by Verwey [1], as a discontinuous drop in electrical conductivity upon cooling below 122 K. This became the Verwey temperature, T_v. Many studies and reviews on the Verwey transition are collected in some special issues [2–6].

In this paper, we present a study of the Verwey transition by using two novel non-resonant microwave absorption techniques: low-field absorption (LFA) and magnetically modulated microwave absorption spectroscopy (MAMMAS).

LFA refers to the non-resonant microwave absorption around the zero DC field range ($-1000 < H_{DC} < +1000$ G), in otherwise typical electron paramagnetic resonance setup. It has been observed in a wide variety of materials such as high-temperature superconductors [7], silicate glasses [8], amorphous ferromagnetic ribbons [9], and ferrites [10]. The source of the absorption signal can therefore be a reflection of the fluxoid tubes characteristic of the mixed state in superconductors, or the interaction of microwaves with the electric and/or magnetic dipoles, or also the magnetization processes of the domain structure in ordered materials.

MAMMAS consists in the study of the derivative of microwave absorption during a temperature scan of the sample, which is subjected to a constant DC field [11]. This technique monitors any change in the microwave absorption regime and is therefore particularly well adapted for the study of phase transitions.

To our knowledge this is the first time both methods are applied to the investigation of the Verwey transition; the obtained results are discussed in detail.

*Corresponding author. Tel.: +52 55 57296000x55 055.
E-mail address: mpga@servidor.unam.mx (M.P. Gutiérrez).

0304-8853/$ - see front matter
doi:10.1016/j.jmmm.2007.03.080

2. Experimental

A polycrystalline sintered sample of magnetite, Fe_3O_4 was prepared by reducing α-Fe_2O_3 (Aldrich, 98%) under hydrogen atmosphere [12]. X-rays diffraction pattern showed a single phase corresponding to magnetite. Measurements of LFA and MAMMAS responses were carried out at 9.4 GHz in the 77–300 K temperature range. The temperature of the sample was controlled by flowing cold N_2 gas through a double walled quartz tube, placed at the center of the microwave cavity.

Measurements were done in a Jeol JES-RES3X spectrometer. For LFA experiments, this system was implemented with a Jeol ES-ZCS2 zero cross sweep unit, which compensates digitally for any remanence in the electromagnet, thus allowing measurements by cycling the DC magnetic field, H_{DC} about its zero value. LFA measurements were performed as a function of H_{DC} in symmetric field-sweeps in the $-1000\,G \leqslant H_{DC} \leqslant +1000\,G$ range. In this technique the sample is zero-field cooled to the desired temperature, and then it is maintained at a fixed temperature with a maximum deviation of 1 K during the whole LFA measurement (~4 min of sweep). For the MAMMAS experiments, the sample was subjected to a constant magnetic field ($H_{DC} = 600\,G$), and a weak AC magnetic field ($H_{mod} = 4\,G$). A modulation frequency of 100 kHz was superimposed to the H_{DC}. An incident microwave power of 7 mW was used.

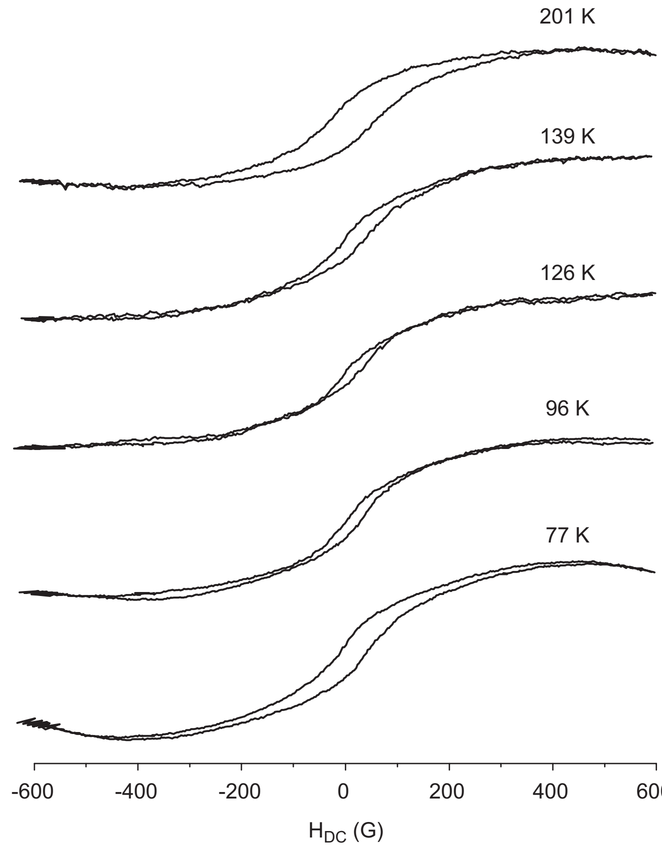

Fig. 1. Hysteresis loop behavior of LFA signal as a function of temperature, for selected temperatures.

3. Results

Fig. 1 presents the LFA signal behavior for selected temperatures which showed hysteresis on cycling the DC field around zero. This feature has been associated with low-field magnetization processes in soft ferromagnetic materials [9]. The area inside of the hysteresis loop (HLA) shows a clear dependence on temperature as can be seen in Fig. 2. As temperature decreases from room temperature, this area remains approximately constant up to 160 K where it abruptly diminishes, reaching a minimum value at 126 K. This temperature is very close to the Verwey temperature reported in literature (122 K).

For lower temperatures this area increases again. The peak to peak width of LFA signal (the difference in H_{DC} field between maximum and minimum of the signal), ΔH_{LFA}, exhibits a similar behavior. ΔH_{LFA} has been observed to be in agreement with anisotropy field of ferromagnetic systems [9].

The MAMMAS profile is presented in Fig. 3. The derivative of microwave absorption increases continuously as temperature diminishes from room temperature and a maximum value is observed at 130 K, where it suddenly decreases down to 100 K. An inflection point is observed at 126 K, which is coincident with Verwey phase transition (VPT) temperature.

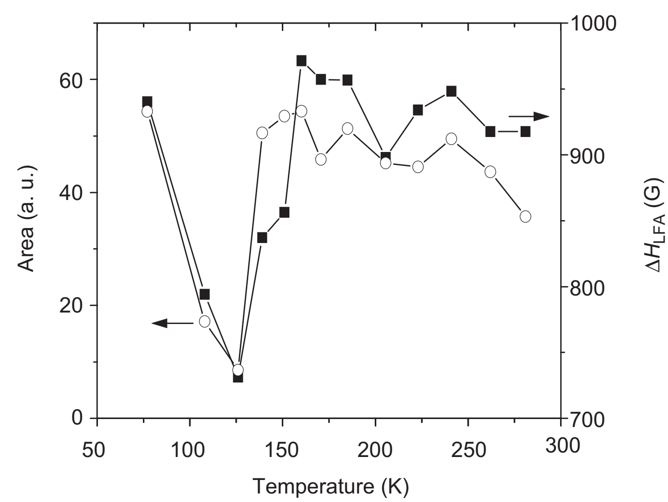

Fig. 2. Behavior of the area inside of the hysteresis loop and ΔH_{LFA} as a function of temperature.

4. Discussion

Hysteresis in LFA can be explained in terms of the magnetization processes, because of the existence of magnetic domains in the whole range of temperature (the Curie point of magnetite is ~860 K). These results suggest

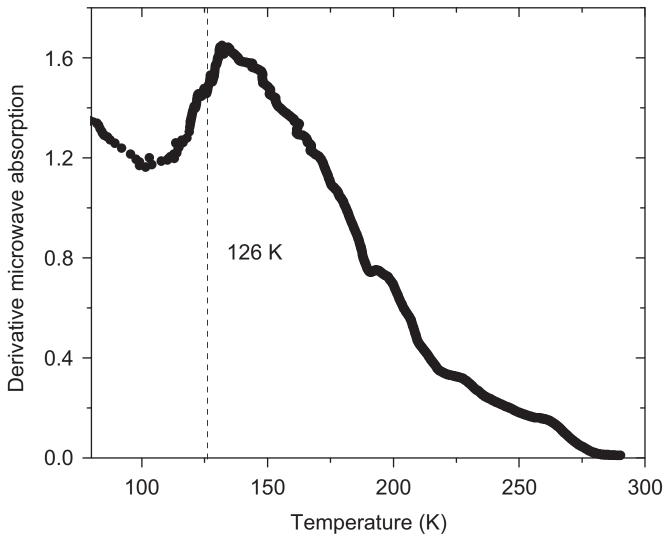

Fig. 3. MAMMAS profile of magnetite as a function of the temperature.

that the magnetization dynamics is influenced by the electronic nature of the metal–insulator transition mechanism and the structural transition at VPT. By comparing the HLA and ΔH_{LFA} temperature dependence, it seems that this phenomenon is also related with an anisotropy decrease in the neighborhood of the VPT, due to a charge rearrangement. Below the transition temperature, the anisotropy increases due to an additional contribution to magnetostriction that appears as a consequence of a distorted cubic phase [13]; therefore, the hysteresis becomes wider.

The energy absorption observed in MAMMAS has shown to be very sensitive to the changes in the conductivity. The response follows an approximate exponential growth as temperature diminishes from 300 to 130 K, suggesting a direct correlation with the conductivity mechanism, which is thermally activated. The sudden drop at 130 K remains until VPT is completed (100 K), indicating a clear change in the energy absorption as a result of the drop in conductivity. This kind of correlation has been also observed by other researchers [8,14].

5. Conclusion

The evolution of LFA signal with temperature clearly allowed to detect changes in the anisotropy of the system, and MAMMAS profile gave information about the changes in conductivity process associated with the Verwey phase transition. We have showed that non-resonant microwave absorption techniques LFA and MAMMAS are also powerful tools in investigating the metal–insulator and structural transitions in magnetite.

References

[1] E.J.W. Verwey, Nature (London) 144 (1939) 327.
[2] N.F. Mott, Philos. Mag. B 42 (1980) 325.
[3] H. Seo, M. Ogata, H. Fukuyama, Phys. Rev. B 65 (2002) 085107.
[4] J. García, G. Subías, J. Phys.: Condens. Matter. 16 (2004) R145.
[5] J.B. Goodenough, MRS Bull. 30 (2006) 849.
[6] G.Kh. Rozenberg, M.P. Pasternak, V.M. Xu, Y. Amiel, M. Hanfland, M. Amboage, R.D. Taylor, R. Jeanloz, Phys. Rev. Lett. 96 (2006) 045705.
[7] G.K. Padam, S.N. Ekbote, M.R. Tripathy, G.P. Srivastava, B.K. Das, Physica C 315 (1999) 45.
[8] R.R. Rakhimor, H.R. Ries, D.E. Jones, L.B. Glebov, L.N. Glebova, Appl. Phys. Lett. 76 (2000) 751.
[9] H. Montiel, G. Alvarez, I. Betancourt, R. Zamorano, R. Valenzuela, Appl. Phys. Lett. 86 (2005) 072503.
[10] H. Montiel, G. Alvarez, M.P. Gutiérrez, R. Zamorano, R. Valenzuela, J. Alloys Compounds 369 (2004) 141.
[11] G. Alvarez, R. Zamorano, J. Alloys Compounds 369 (2004) 231.
[12] H. Sesigur, E. Acma, O. Addemir, A. Tekin, Mat. Res. Bull. 31 (1996) 1573.
[13] J.P. Wrigth, J.P. Attfield, P. Radaelli, Phys. Rev. B 66 (2002) 214422.
[14] P.S. Neelakanta, J.C. Park, IEEE Trans. Microwave Theory Techniques 43 (1995) 1381.