

Role of Oxygen Coordination on the Ultrafast Demagnetization in Ferrite Nanoparticles

E. TERRIER*, Y. LIU, S. BEGIN, B. PICHON, J.-Y. BIGOT AND V. HALTE

Institut de Physique et de Chimie des Matériaux de Strasbourg, UMR7504, CNRS et Université de Strasbourg,
23 rue du Loess, 67034 Strasbourg, France

In this work, we have studied the ultrafast dynamics of charges and spins in assemblies of magnetite (Fe_3O_4) and maghemite ($\gamma\text{-Fe}_2\text{O}_3$) nanoparticles. We demonstrate that using time-resolved magneto-optics one is able to disentangle those very similar iron oxide structures. The Fe_3O_4 nanoparticles are elaborated by hydrothermal decomposition and deposited by drop on a glass substrate. $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles assemblies have been obtained by annealing the Fe_3O_4 nanoparticles. Comparing time resolved transmission and Faraday rotation, our measurements show that in case of Fe_3O_4 the demagnetization occurs after the thermalization of the charges, as expected from previous works on ultrafast quenching of magnetization in ferromagnetic nanostructures. On the contrary, in the case of maghemite nanoparticles, an acceleration of the demagnetizing occurs, leading to a simultaneous charges and spins dynamics. We attribute this behavior to the rearrangement of vacancies and annealing of crystal defects in maghemite.

DOI: [10.12693/APhysPolA.127.345](https://doi.org/10.12693/APhysPolA.127.345)

PACS: 78.47.J-, 78.20.Ls, 75.30.Et, 75.75.Fk

1. Introduction

For several years oxidized states of iron have been subject to a great scientific interest particularly in the development of high density storage media. Moreover the size reduction of the particles has opened new perspectives notably in for biomedical applications: magnetic nanoparticles are already used as contrast agent for MRI, hyperthermia cancer treatment, enzyme immobilization [1]. Magnetite (Fe_3O_4) and maghemite ($\gamma\text{-Fe}_2\text{O}_3$) nanoparticles were found to be very relevant candidates for these applications [2–3]. Basic properties of these two forms of iron oxides are well known: maghemite and magnetite share the same inverse spinel structure, however all the iron cations are in trivalent state in $\gamma\text{-Fe}_2\text{O}_3$, which ensures the presence of cations vacancies in octahedral sites. In spite of these differences, the crystal structures of these iron oxides are very similar and remain hardly distinguishable with static methods such as Mössbauer spectroscopy [4].

It has been already demonstrated that time-resolved magneto-optical Kerr effect (TR-MOKE) spectroscopy is a very reliable method to study the evolution of the chemical structure of nanoparticles [5]. Following this way, we show in this present study the possibility of distinguishing magnetite and maghemite using time-resolved magneto-optical Faraday spectroscopy.

2. Experiment

Measurements were performed with a 50 fs Ti:sapphire amplifier system cadenced at 5 kHz. The output beam

is divided into two parts. The pump beam (400 nm) is generated by SHG in a BBO crystal. The probe beam (800 nm) is focused on the sample with an incidence angle of 50° with respect to the normal of the sample. The signal is measured in the polar geometry with a permanent magnetic field ≈ 0.35 T. The analysis of the polarization state of the transmitted beam is done using a polarization bridge. The detection is performed by lock-in amplifiers and photodiodes. This pump-probe configuration allows us to measure differential Faraday rotation signal $\Delta S(t)/S_0$ where $\Delta S(t) = S(\text{with pump}) - S_0(\text{without pump})$ and the transmitted signal providing information about spins and charges dynamics respectively [6].

The samples are prepared via thermal decomposition of Fe(stearate) in the presence of oleic acid as stabilizing agent and docosene as solid solvent at room temperature. It results in Fe_3O_4 nanoparticles surrounded by polymer chains with a mean diameter of 20 nm. A concentrated solution of these nanoparticles is deposited on a glass substrate. Two kinds of samples have been studied: a native one and an annealed one. The annealing is made at 300°C during two hours under argon atmosphere. The heat treatment of the native sample leads to a change of the chemical nature of the sample. Indeed, it has been shown that a complete $\text{Fe}_3\text{O}_4 \rightarrow \gamma\text{-Fe}_2\text{O}_3$ transformation occurs under annealing between 250°C and 390°C [7–8]. Thus magnetite has turned into maghemite after annealing. As one can see in both insets of Fig. 1, the thermal process did induce neither a change of the size nor aggregation phenomenon.

3. Results

The measured magnetization $\Delta M/M$ (proportional to $\Delta S/S_0$) and transmission $\Delta T/T$ dynamics of the native and annealed samples for a pump energy density of 1.67 mJ/cm^2 are shown in Fig. 1a, b respectively. All measurements were performed on a time range

*corresponding author; e-mail:
erwan.terrier@ipcms.unistra.fr

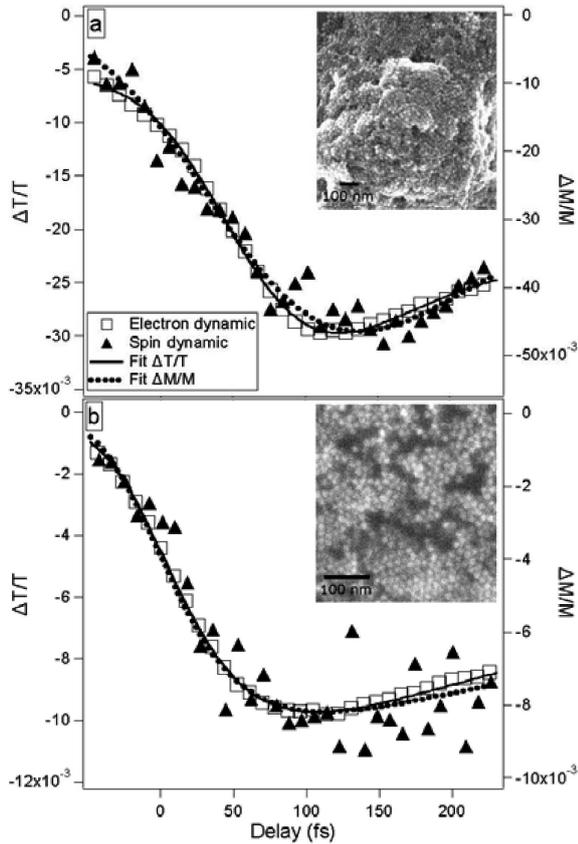


Fig. 1. Time resolved thermalization dynamics of magnetization $\Delta M/M$ and transmission $\Delta T/T$ with their corresponding fit and Scanning Electron Microscope images in insets for (a) Fe_3O_4 nanoparticles and (b) $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles.

of 20 ps, but for a sake of clarity, we only display the very short timescale (~ 50 fs to 230 fs). For each curve, we observe the classical steps of spins and charges dynamics: first, electrons acquire a large energy above the Fermi level leading to a nonthermal electronic distribution. These populations then thermalize to a hot Fermi distribution via electron-electron scattering. During this thermalization process ($\tau_{\text{eth}} = 37$ fs), we observe a fast demagnetization of the nanoparticles with time constant $\tau_{\text{sth}} = 105$ fs in case of the native sample. In case of the annealed one, the corresponding time constants are $\tau_{\text{eth}} = 42$ fs, $\tau_{\text{sth}} = 33$ fs. This step is followed by a cooling of electrons due to the electron-phonon interaction, the magnetic moments return then to an equilibrium state leading to a re-magnetization of the nanoparticles. The time constants for this relaxation process are $\tau_{\text{erelax}} = 198$ fs, $\tau_{\text{srelax}} = 190$ fs and $\tau_{\text{erelax}} = 283$ fs, $\tau_{\text{srelax}} = 293$ fs for the native and annealed samples respectively. All values are obtained by fitting experimental data using a convolution of the pump with an exponential function [9]. For each fitted curve, the error bar is estimated at ± 10 fs.

Let us focus on the thermalization times. First, the invariance of τ_{eth} with the thermal process is clear within

our temporal resolution. Surprisingly, the fits reveal different behaviours of τ_{sth} between both samples: after heat treatment, τ_{sth} become as short as τ_{eth} .

Magnetic order in maghemite and magnetite is mainly governed by superexchange between iron cations from the tetrahedral (A) and octahedral (B) sites via oxygen atom. Thus the strength of coupling depends on the bonds length and the bond angle Fe-O-Fe: the shorter and the closer to 180° the bonds are, the stronger the coupling is.

It has been suggested that the annealing process of Fe_3O_4 nanoparticles causes a vacancy ordering and annealing of volume defects inducing an enhancement of the antiferromagnetic interactions [8]. Our results tend to confirm these hypotheses: the acceleration of τ_{sth} would be associated with the reinforcement of the antiferromagnetic interactions due to a rearrangement of the crystal structure (notably on the length and the angle of bonds between irons cations and oxygen atom).

4. Conclusions

Performing time-resolved Faraday measurements in magnetite and maghemite nanoparticles, allowed us determining the thermalization times of the charges and spins dynamics. τ_{sth} is larger than τ_{eth} for magnetite (105 fs vs. 37 fs respectively) whereas they are similar (35 fs) for the maghemite, within our time resolution. We interpret this acceleration of τ_{sth} by considering an enhancement of the antiferromagnetic interactions. It shows that the valence of oxygen has a strong impact on the ultrafast dynamics of the charges and spins in ferrite nanoparticles.

Acknowledgments

The authors thank the ‘‘Agence Nationale de la Recherche’’ in France via the project EQUIPEX UNION: # ANR-10-EQPX-52 and the LABEX NIE: ANR-11-LABX-0058_NIE.

References

- [1] T.F. Daou, Ph.D Thesis, Strasbourg University, Strasbourg 2007.
- [2] B. Hillebrands, K. Ounadjela, *Spin Dynamics in Confined Magnetic Structures II, Topics in Applied Physics*, **87**, Springer-Verlag Berlin Heidelberg, 2003.
- [3] S. Mornet, Ph.D Thesis, Bordeaux I University, Bordeaux 2002.
- [4] R.E. Vandenberghe, C.A. Barrero, G.M. da Costa, E. Van San, E. De Grave, *Hyperfine Interactions*, **126**, 247 (2000).
- [5] J.-Y. Bigot, H. Kesserwan, V. Halté, O. Ersen, M.S. Moldovan, T.H. Kim, J. Jang, J. Cheon, *NanoLett.* **12**, 1189 (2012).
- [6] J.-Y. Bigot, L. Guidoni, E. Beaupaire, P.N. Saeta, *Phys. Rev. Lett.* **93**, 077401 (2004).
- [7] M.M. Can, M. Coskun, T. Firat, *J. Alloys Comp.*, **542**, 241 (2012).
- [8] C. Vichery, I. Maurin, P. Bonville, J.P. Boilot, T. Gacoin, *J. Phys. Chem. C* **116**, 16311 (2012).
- [9] L. Guidoni, E. Beaupaire, J.-Y. Bigot, *Phys. Rev. Lett.* **89**, 017401 (2002).