



Origin of unusual thermomagnetic behaviors in maghemite



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ARTICLE INFO

Keywords:
Maghemite
Thermomagnetic
Magnetization
Magnetic interaction

ABSTRACT

Usually, in any magnetic system, the saturation magnetization increases as decreasing ambient temperature and the field-cooled magnetization is no less than that in zero field-cooled procedure. However, in this work, we observed diametrically opposite experimental phenomena in γ -Fe₂O₃ microspheres. And we found that the presence of Fe³⁺ spin chaos provoked by the competition of strong Fe³⁺(A)—O²⁻—Fe³⁺(A) and Fe³⁺(B)—O²⁻—Fe³⁺(B) interactions was the root cause for all of these thermomagnetic anomalies. Our findings were supported by exploring the physical significance of Boltzmann *H*-theorem through quantum mechanics analyses and estimating entropy changes on the basis of Clausius-Clapeyron type equation. It is anticipated that this article will shed new light on the understanding of thermomagnetic behaviors in ferrimagnetic materials.

1. Introduction

Maghemite is the red-brown γ polymorph of Fe₂O₃ and belongs to the wide range of naturally occurring iron oxides [1]. It is normally found in tropical and subtropical soils, and is commonly formed from the oxidation of lithogenic magnetite [2–5]. Also it can be formed by dehydroxylating of lepidocrocite or heating of goethite in the presence of organic matter [2]. It is also identified as a corrosion product of steel waste canisters [6] and iron archaeological analogues [7–9].

Owing to its excellent electromagnetic properties and chemical stability, interest in γ -Fe₂O₃ has been steadily increasing in recent years catalysed by their rapidly expanding areas of potential application, ranging from ultrahigh density recording media to medicine [10–16]. In any case, the magnetic properties of γ -Fe₂O₃ are of fundamental importance and hence lay the basis for its magnetically-relevant applications. Therefore, considerable effort has been devoted to working on a blueprint for understanding every aspect of its magnetic properties, such as magnetocrystalline constant [17–20], magnetic viscosity [21–25] and a variety of thermomagnetic behaviors [26,27]. Despite the progress achieved to date, research on basic thermomagnetic performance of γ -Fe₂O₃ is still in its early stage, and many phenomenological results reported in the above studies are not sufficiently discussed.

Herein, we focus our attention on abnormal thermomagnetic behaviors found in spherical γ -Fe₂O₃ product, which are obtained from the low-temperature oxidation of magnetite microspheres. The origin of these magnetic anomalies is thoroughly investigated on the basis of both experimental analyses and theoretical demonstration.

2. Experimental

2.1. Chemicals used and procedure

Fe₃O₄ microspheres were firstly synthesized following the procedure described by Li [28] with little modification. Typically, FeCl₃·6H₂O (2 mmol) was dissolved in ethylene glycol (50 mL) to form a clear solution, followed by the addition of sodium acetate (1.8 g) and polyethylene glycol (0.1 g, M = 1000). The mixture was stirred vigorously for 20 min and then sealed in a teflon lined stainless-steel autoclave (70 mL capacity). The autoclave was heated to and maintained at 180 °C for 48 h, and allowed to cool to room temperature spontaneously. The product was washed several times with deionized water and ethanol and dried at 60 °C for 4 h. Then the as-synthesized black powder was put into the high-temperature tubular furnace at 300 °C for 2 h and finally red-brown γ -Fe₂O₃ product was obtained.

2.2. Characterization of samples

The chemical composition of the resultant product is characterized by the powder X-ray diffractometer (Rigaku D/max-rA) equipped with a rotating anode and a Cu K_{α1} radiation source ($\lambda = 1.5406 \text{ \AA}$) at a step width of 0.02°. The product morphologies were investigated by using field-emission scanning electron microscopy (JEOL JSM-6700F). The high-resolution transmission electron microscopy (HRTEM) experiments were conducted using a Field Emission Gun (FEG) JEOL 2010F microscope with a point resolution of 0.19 nm. The Raman spectrum was

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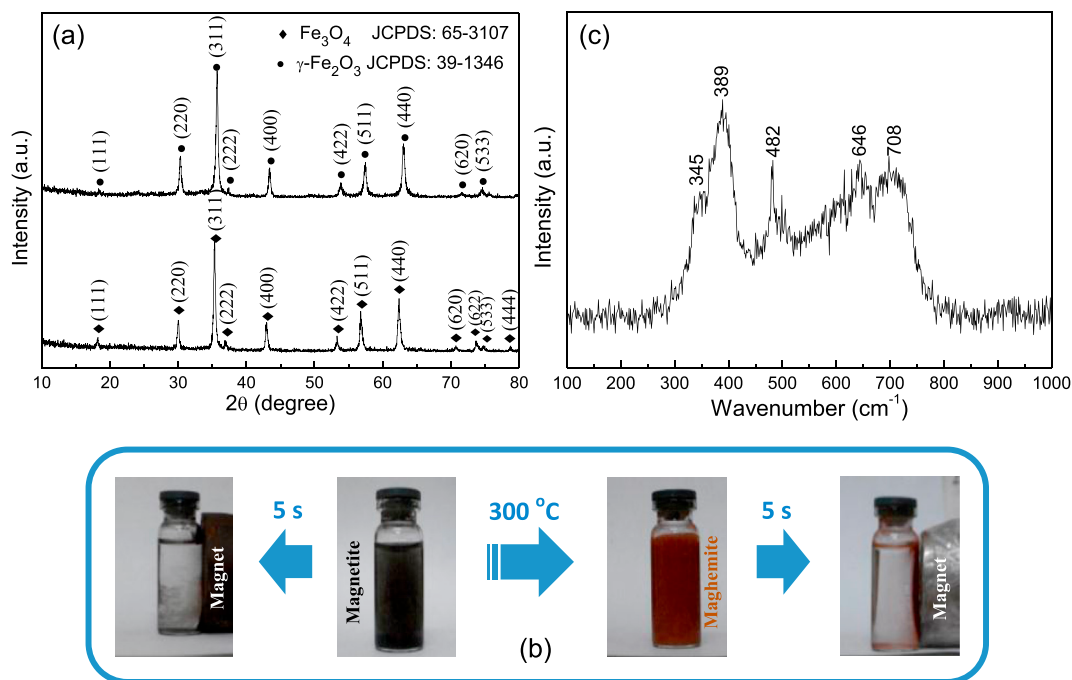


Fig. 1. (a) XRD patterns and (b) magnetic responses (digital photographs) of Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$ products. (c) Raman spectrum of the $\gamma\text{-Fe}_2\text{O}_3$ product.

recorded using a Super LabRam microscopic Raman spectrometer (Labram, Jobin Yvon, France, a He–Ne laser with an excitation wavelength of 532 nm).

The magnetic measurements were conducted on Quantum Design SQUID MPMS-XL7 magnetometer with magnetic fields up to 70 kOe and temperature range of 5–350 K.

The field-cooled (FC) magnetization curves were measured according to the following procedure: At first, the sample was cooled from 350 K in an applied field of 70 kOe down to the desired temperatures; then the field was set to be zero, and the magnetization curves were measured in the field range starting from 0 to 70 kOe. Likewise, the zero field-cooled (ZFC) magnetization curves were measured in the same way with the cooling field set to be zero all the time.

The ZFC and FC temperature-dependent magnetization [$M(T)$] curves were measured according to the following procedure: Firstly, the sample was cooled from 350 to 5 K in a zero magnetic field; then the magnetization of the sample was measured during the heat-up process from 5 to

350 K in a given magnetic field (e.g., 100 Oe or 30 kOe in our experiments); After that, the sample was cooled down again from 350 to 5 K with the applied field held constant, and the magnetization was measured during the heat-up process from 5 to 350 K in the same magnetic field.

The saturation magnetization (M_S) values of the sample were determined by the law of approach to saturation (LATS) based on the magnetization curves at different temperatures.

3. Results and discussion

The chemical composition of the as-prepared products is shown in Fig. 1(a), in which all the diffraction peaks of uncalcined product can be indexed to the cubic structure of Fe_3O_4 (JCPDS No. 65–3107). After calcination, most of the diffraction peaks appreciably shift rightward, unambiguously corresponding to $\gamma\text{-Fe}_2\text{O}_3$ (JCPDS No. 39–1346) phase. It is clearly seen from Fig. 1(b) that the colour of the product turns from

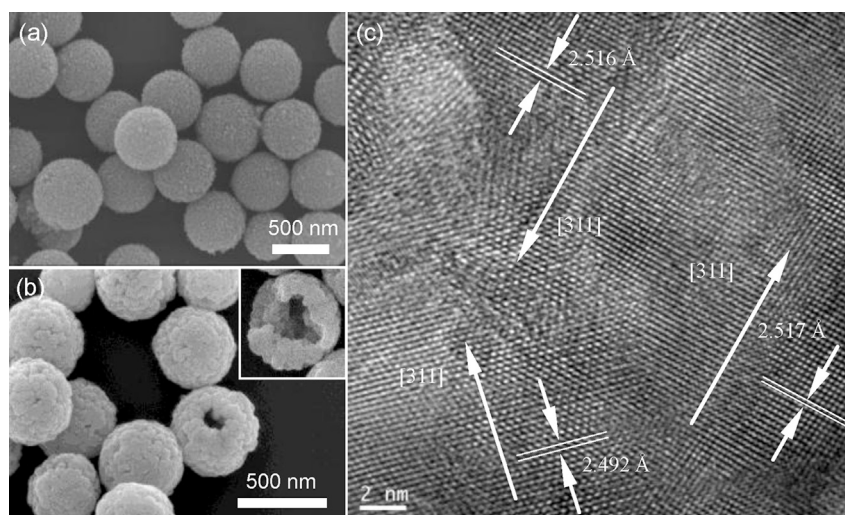


Fig. 2. SEM images of (a) Fe_3O_4 and (b) $\gamma\text{-Fe}_2\text{O}_3$ products. A broken sphere is shown as an inset in panel b. (c) A typical HRTEM image of $\gamma\text{-Fe}_2\text{O}_3$ product.

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