Nanomagnetics

The Low-Temperature Magnetic State and Magnetic Ordering Temperature of ε-Fe_2O_3 Iron Oxide Nanoparticles

Andrey A. Dubrovskiy[1], Sergey V. Semenov[1], Yuri V. Knyazev[1], Sergey I. Popkov[1], Stas S. Yakushkin[2], Viktor L. Kirillov[2], Oleg N. Martyanov[2], and Dmitry A. Balaev[1]

[1]*Kirensky Institute of Physics, Krasnoyarsk Scientific Center, Siberian Branch, Russian Academy of Sciences, Krasnoyarsk 660036, Russia*

[2]*Boreskov Institute of Catalysis, Siberian Branch, Russian Academy of Sciences, Novosibirsk 630090, Russia*

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Abstract—The ε-Fe_2O_3 iron oxide polymorph is a well-known magnetic material with a complex magnetic structure, which undergoes a series of magnetic transitions in different temperature ranges. However, the ε-Fe_2O_3 phase diagram is still unclear. We report on the magnetic properties of a sample consisting of ε-Fe_2O_3 nanoparticles with an average size of 8 nm embedded in a SiO_2 xerogel matrix without an admixture of foreign phases. Along with the features typical of the well-known ε-Fe_2O_3 magnetic transition in the temperature range 80–150 K, the temperature dependence of magnetization $M(T)$ of ε-Fe_2O_3 includes other low-temperature anomalies. In an external field of $H = 70$ kOe, there is a noticeable temperature hysteresis of magnetization at 50–90 K, and near $T \approx 50$ K, the $M(T)$ curves have a characteristic bending, which may be indicative of an additional magnetic transition. The ferromagnetic resonance spectra shows that, near 500 K, a magnetic phase transition occurs, which was previously thought to be a transition to the paramagnetic state. An analysis of the temperature dependence of the ferromagnetic resonance spectra shows that the magnetically ordered phase in ε-Fe_2O_3 exists up to about 800 K.

Index Terms—Nanomagnetics, ε-Fe_2O_3 nanoparticles, magnetic transition, FMR spectra.

I. INTRODUCTION

The ε-Fe_2O_3 phase is a polymorphic iron(III) oxide modification with the unique magnetic properties that has been in focus for the last two decades [Tronc 1998, Gich 2005, Ohkoshi 2007, 2016, Tućek 2010, Machala 2011, Yakushkin 2012, Ivanova 2016, Edelman 2019]. In terms of application, the interest in this material is due to its high coercivity, which attains 20 kOe at room temperature [Gich 2005, Tućek 2010, Machala 2011, Ohkoshi 2016], and the related effective absorption of electromagnetic waves in the millimeter range [Ohkoshi 2007, 2016]. However, the ε-Fe_2O_3 magnetic structure still has been understudied. It is considered to be established that, at room temperature, the ε-Fe_2O_3 magnetic structure is collinear ferrimagnetic [Gich 2006]. The structural distortions in the range of 80–150 K lead to the multistage magnetic transition to the incommensurate magnetic structure [Gich 2006], which is accompanied by a sharp coercivity drop. There exists, however, a different point of view [Kurmoo 2005], according to which the material undergoes, in this temperature range, a transition from one canted antiferromagnetic structure to another and, in the low-temperature region, a metamagnetic transition is not excluded [Kurmoo 2005]. In addition, it has been long believed that the temperature of magnetic ordering (the transition to the paramagnetic state) for ε-Fe_2O_3 is ~500 K [Tućek 2010, Machala 2011]. As was shown lately in García-Muñoz [2017], the magnetic order in ε-Fe_2O_3 is retained up to ~850 K, i.e., to the temperature of the transition to the paramagnetic state and, at 500–850 K, only two iron sublattices are ordered, whereas around 500 K, all the four sublattices are arranged in the collinear ferrimagnetic structure. Obviously, further investigations are needed to elucidate the magnetic state and magnetic phase diagram of the ε-Fe_2O_3 oxide in different temperature ranges.

There are two important circumstances that essentially complicate the interpretation of the experimental data on ε-Fe_2O_3. First, the ε-Fe_2O_3 oxide only exists in the form of nanoparticles no larger than 20–40 nm in size, and, as is known, the magnetic behavior of even smaller particles is strongly influenced by the surface effects [Balaev 2013, Dubrovskiy 2015]. Second, a challenging problem is the synthesis of ε-Fe_2O_3 without admixture of other iron oxide polymorphs [Gich 2005, Tućek 2010, Yakushkin 2017], which can affect, even in minor amounts, the interpretation of the data obtained. Here, we report on the results obtained by us on the previously well-characterized single-phase ε-Fe_2O_3 nanoparticle samples, which are indicative of the occurrence of an additional magnetic transition in the low-temperature phase (at ~50 K) in strong magnetic fields and confirm the magnetic ordering of ε-Fe_2O_3 up to high (~800 K) temperatures.

II. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUES

The material under study was synthesized by embedding Fe(II) salts into the SiO_2 hydrogel via diffusion exchange with subsequent drying and calcination in air (see the detailed description of the hydrogel synthesis technique and thorough characterization of the obtained samples in Yakushkin [2018]). The sample under study consisted

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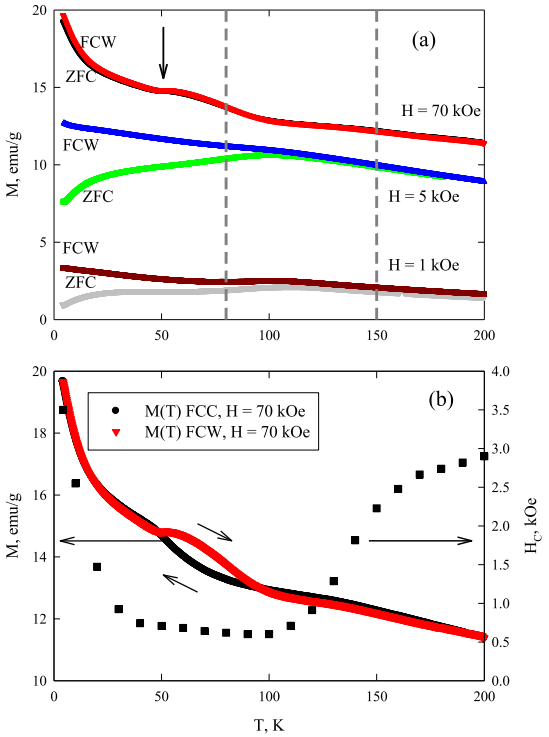

Fig. 1. $M(T)$ dependences of the investigated ε-Fe_2O_3 nanoparticle sample in different magnetic fields at different thermomagnetic prehistories. (b) $H_C(T)$ dependence (H_C is plotted along the right-hand scale), together with the $M(T)$ dependences, at $H = 70$ kOe (M is plotted along the left-hand scale).

of 20.5 weight % of ε-Fe_2O_3 in the SiO_2 xerogel matrix. According to the X-ray diffraction data, all the observed diffraction peaks belong to ε-Fe_2O_3 structure. The high-resolution transmission electron microscopy study revealed an average particle size of 8 nm [Yakushkin 2018]. The thorough analysis of the Mössbauer spectra disclosed no iron oxide polymorphic modifications except for ε-Fe_2O_3 in the sample [Knyazev 2018, Yakushkin 2018].

The magnetic characteristics were measured on a PPMS-6000 physical property measurement system. The temperature dependences of magnetization $M(T)$ were obtained in three different measurement protocols, including zero field cooling (**ZFC**) from 300 K, field cooling, and field cooled warming (**FCW**). The magnetization was normalized to the iron oxide mass in the sample.

The ferromagnetic resonance (**FMR**) spectra were recorded on a Bruker ELEXSYS 500 3 cm spectrometer operating in the X range.

III. RESULTS AND DISCUSSION

Fig. 1(a) shows the ZFC and FCW $M(T)$ dependences for the sample in different magnetic fields. Vertical dashed lines show the temperature range of 80–150 K corresponding to the well-known magnetic transition in ε-Fe_2O_3 [Gich 2005, Tuček 2010, Machala 2011]. The $M(T)$ behavior in this temperature range agrees well with the data of other authors [Kurmoo 2005, Gich 2006]: in the range of 80–150 K in relatively weak fields, the magnetization decreases with temperature, whereas in sufficiently strong fields, the difference between the $M(T)$ ZFC and $M(T)$ FCW dependences becomes insignificant. The abrupt drop of the coercivity H_C in this temperature region [H_C is plotted along the right-hand scale in Fig. 1(b)] also convincingly demonstrates the occurrence of a magnetic transition at 80–150 K. In the strong field, however, another $M(T)$ anomaly is observed, already at 50–90 K. In Fig. 1(b) (M is plotted along the left-hand scale), the $M(T)$ behavior in a field of 70 kOe at different magnetic prehistories is enlarged. It can be seen that the characteristic $M(T)$ curve bending starts with 50 K and finishes at ~90 K. In the range of 50–90 K, there is a significant temperature hysteresis: the magnetization upon cooling is lower than upon heating the sample.

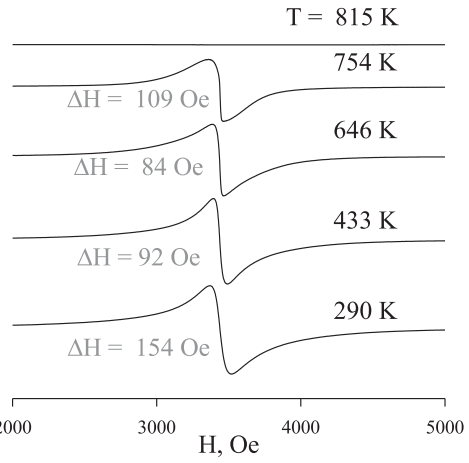

Fig. 2. FMR spectra of the ε-Fe_2O_3 nanoparticle sample at different temperatures.

The described behavior is only observed in sufficiently strong (above ~50 kOe) external fields, so one can attribute it to the magnetic transition starting around 50 K with increasing temperature. García-Muñoz [2017] suggested the occurrence of a metamagnetic transition in ε-Fe_2O_3 at 50 K. At the same temperature, the maximum in the temperature dependence of the permittivity of ε-Fe_2O_3 was observed [Dubrovskiy 2019]. In addition, at a temperature of 50 K, the coercivity starts noticeably growing with a decrease in temperature.

To obtain data on the ε-Fe_2O_3 magnetic order at high (up to ~800 K) temperatures, we used the FMR technique. Considering an FMR spectrum as applied to an ensemble of single-domain particles of similar sizes, one may approximately assume the integral intensity I_{FMR} of the absorption signal to be proportional to the saturation magnetization. In this case, the absorption line width ΔH depends on many parameters for an individual particle, including the crystallographic anisotropy and saturation magnetization of the magnetic phase [de Biasi 1978, Raikher 1994, Berger 2000]. Typical FMR spectra of the investigated sample recorded at different temperatures are presented in Fig. 2. The FMR spectra are observed up to the high temperatures, which evidences for the presence of magnetic ordering of the sample at high temperatures.

Fig. 3 shows the $I_{FMR}(T)$ dependences (I_{FMR} is plotted along the left-hand scale) obtained upon heating the sample above 800 K and upon cooling from this temperature. The temperature at which the integral intensity becomes vanishingly small is ~800 K. This is consistent with the data on the ε-Fe_2O_3 nanoparticle samples synthesized using the technique proposed in Balaev [2019]. In addition, one can see in Fig. 3(a) that the $I_{FMR}(T)$ dependences obtained upon heating and cooling the sample are different below 500 K. It would be reasonable to attribute this fact to the magnetic transition at 500 K. The qualitative

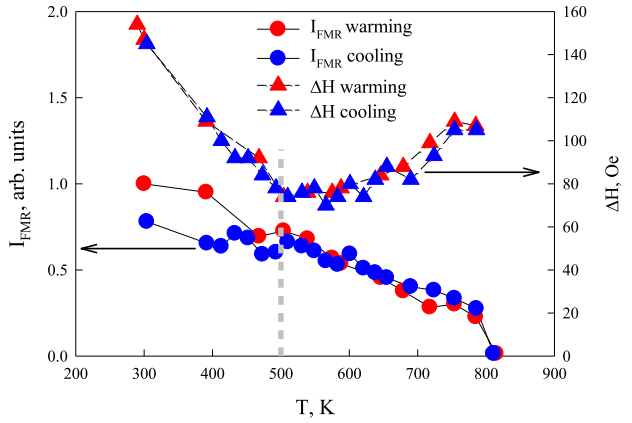

Fig. 3. $I_{FMR}(T)$ dependences (I_{FMR} is plotted along the left-hand scale) and $\Delta H(T)$ (ΔH is plotted along the right-hand scale) of the FMR spectra of the ε-Fe_2O_3 nanoparticle sample.

change in the $\Delta H(T)$ behavior (ΔH is plotted along the right-hand scale) around 500 K (see Fig. 3) also indirectly suggests the change of the ε-Fe_2O_3magnetic order. These data point out the existence of the magnetic order in the high-temperature (up to ~800 K) region, whereas at 500 K, the magnetic transition occurs, which confirms the conclusions made in García-Muñoz [2017].

IV. CONCLUSION

The magnetic investigations of the ε-Fe_2O_3 nanoparticles revealed the $M(T)$ anomaly in a field of $H = 70$ kOe in the vicinity of 50 K, which is accompanied by the temperature hysteresis of magnetization at 50–90 K. This suggests the occurrence of another magnetic transition in ε-Fe_2O_3, along with the well-known transition in the range of 80–150 K, which only occurs in sufficiently strong external magnetic fields. The nature of this magnetic transition is not clear by now and additional experiments are needed to clarify the changes in the magnetic structure in ε-Fe_2O_3 in the vicinity of 50 K and relatively high magnetic fields.

The analysis of the temperature evolution of the FMR spectra allows us to speak about the existence of a high-temperature magnetically ordered phase in the ε-Fe_2O_3 oxide. In addition, the behavior of the parameters of the FMR spectra clearly reflects the well-known magnetic transition near 500 K, and the presence of magnetic order up to a temperature of ~800 K above which the system passes to the paramagnetic state.

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