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Goethite (α-FeOOH) magnetic transition by ESR, Magnetometry and Mössbauer

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HIGHLIGHTS

- We studied a magnetic transition of a natural goethite sample.
- It was observed by ESR the spin flop effect and the transition to the PM state.
- Spectra simulations showed ESR lines of different spins interactions with vicinity.
- T_N was determined as 372 and 370 K by ESR and Magnetometry respectively.

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ABSTRACT

A natural sample of the mineral goethite was characterized by X-band Electron Spin Resonance (ESR), vibrating sample Magnetometry and Mössbauer spectroscopy techniques, with the main objective of studying the magnetic transition from the antiferromagnetic to the paramagnetic state that this mineral undergoes upon reaching a certain critical temperature (Néel temperature). Although an ESR signal was not expected in goethite samples at room temperature, due to its antiferromagnetic arrangement, a resonance line was observed. This behavior was attributed to the existence of vacancies in the mineral structure. Increasing the temperature from RT to 352 K no significant change occurred in the ESR spectra. From 352 K, the goethite spectrum showed an additional ESR line, the intensity of this line grew until it stabilized at around 444 K. The appearance of this new resonance line, and its evolution with temperature, was attributed to two subsequent effects: firstly the spin flop effect from 352 to 372 K; and secondly, the transition to the paramagnetic state at $T_N = 372$ K. Magnetometry and Mössbauer measurements corroborated this assumption and the transition temperature was identified by magnetometry as $T_N = 370$ K. Simulations of the goethite ESR spectra in both antiferromagnetic and paramagnetic states were performed by deconvolution of the resonance lines into two contributions, one from species with vacancies in their vicinity, and another with complete vicinity.

1. Introduction

The mineral Goethite is an iron oxyhydroxide, whose chemical formula is α-FeOOH. This mineral is one of the most abundant iron compounds in nature and it is part of various types of soils [1], as well as hematite, kaolinite and ferrihydrite [2]. Goethite is also contained in sediments, rock erosion and steel corrosion products. In massive aggregate in the crystal form, goethite is dark brown or black, while the powder is yellow and is responsible for the coloration of many rocks and soils. This mineral has been used as yellow pigment for the production of inks and printer toners, as

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precursor for producing magnetic particles in magnetic memory materials [1]. In the last decade, it was found, and analyzed by Mössbauer spectroscopy, goethite traces on the surface of the Columbia Hills on Mars. This is mineralogical evidence for aqueous processes, considering that goethite requires an aqueous environment for its formation [3].

Goethite consists of an arrangement of anions with a hexagonal compact structure (HPC-Hexagonal Close Packed) (O^{2-} and OH^-), with Fe^{3+} ions occupying half of the octahedral interstices within a layer. The iron ions are distributed in two rows and separated by two rows of empty sites. Each iron ion is surrounded by three O^{2-} and three OH^- resulting in the FeO_3OH_3 octahedral structure. This distribution shows orthorhombic symmetry (Pnma space group) with $a = 0.9956$ nm, $b = 0.30215$ nm and $c = 0.4608$ nm [1,4–6].

Among the physical properties of goethite, its magnetic property have been the most difficult to interpret and is not yet fully understood. At room temperature, goethite commonly shows antiferromagnetic behavior [1]. This mineral also shows a weak ferromagnetism [7]. In the antiferromagnetic state (below the Néel temperature), the spins in goethite are oriented with spin “up” or “down” in alternating layers of the octahedra [1]. No general consensus has been reached concerning the origin of the weak ferromagnetic effect in goethite at room temperature. Several authors have proposed, and most of agree, that the effect has its origin in a not fully balanced number of spins, caused by the presence of vacancies and defects [8–10].

The Néel temperature of goethite is around $T_N = 400$ K, but this value can vary [1,11]. This difference in the values for each sample type can range from 261 to 398 K [12], depending on several characteristic factors of goethite as particle size, crystallinity and ions substitutions, like Al [1]. It is also possible that particles of goethite themselves may exhibit a Néel temperature different than that of bulk goethite [13]. Regarding vacancies, removal of ions from the goethite structure (increase in vacancy concentration), for example, it has a strong influence on the Néel temperature. The removal of Fe^{3+} ions is more effective at decreasing the Néel temperature than the removal of oxygen ions. Experiments reported in the literature showed that for a given goethite sample, a reduction in Néel temperature from 400 to 358 K requires an increase of 8% iron vacancy concentration. In addition, small particle sizes results in an increase in vacancy concentration and therefore a decrease in Néel temperature [14]. Other factors may influence the Néel temperature of goethite. The Néel temperature is reduced with a decrease in the crystallinity and/or increasing in the Al concentration (or other cations) in the goethite structure [15]. Barrero et al. (1999) [15] tried to classify the magnetic behavior of goethite in function of the particle size. In a later work, Barrero et al. (2006) [16] showed that this behavior depends on structural and chemical characteristics, moreover proposed a diagram, which shows different magnetic behaviors of goethite before the Néel temperature, depending on the water content and surface area.

This research aimed to study the magnetic behavior of goethite with increasing temperature, more specifically, the magnetic transition that this mineral undergoes from the antiferromagnetic to the paramagnetic state. It is important to highlight that even though there are a considerable number of papers about the Néel temperature behavior of goethite [9], few studies on this subject involve the electron spin resonance (ESR) technique, particularly concerning its magnetic transition. Thus, this research was focused on the ESR technique, producing results shown for the first time, such as the ESR spectra simulations of goethite below and above T_N that separately showed the resonance lines corresponding to the different species. Magnetometry and Mössbauer spectroscopy were also used in the temperature range where the magnetic transition takes place to confirm the results obtained; X-ray diffraction was used to characterize the goethite samples before and after the transition.

This work was conducted with a sample of natural goethite. However, care was taken to synthesize a goethite sample in the laboratory to certify that the behavior of the natural sample was similar to the synthetic, to exclude the possibility of the presence of impurities. Both samples showed similar behavior in tests with all the techniques used in this work. One possibility for a future work would be to repeat the measurements on the magnetic transition with a synthetic sample.

2. Experimental details

2.1. Samples

The natural goethite sample was removed from the municipal quarry of the village of Antônio Pereira, Minas Gerais, Brazil.

The synthetic goethite sample was prepared according to the method described by Cornell and Schwertmann [1]. A mixture of 400 ml of KOH at 2.5 mol L^{-1} to 1659 mL of $Fe(NO_3)_3$ at 0.15 mol L^{-1} was prepared in plastic container. The mixture was vigorously stirred until complete homogenization. The solution was left for 48 h at 353 K. The precipitate formed was filtered and dispersed in HNO_3 0.01 mol L^{-1} to wash the material; this procedure was repeated five times. After washing with HNO_3, the material was rinsed three times in ultrapure water and then lyophilized. Lyophilization was the preferred method to remove water because it is less aggressive than heating the sample and the structure of the products formed in solution is maintained. The solutions were frozen at 253 K, after vials were connected to pump lyophilizer (high vacuum, 200 mmHg).

2.2. XRD

X-ray diffraction (XRD) measurements were performed at room temperature in a PANalytical diffractometer, model X'Pert PRO MPD, with Cu-Kα radiation, using the technique known as θ-2θ (*i.e.* Bragg-Brentano geometry). The 2θ scan range used was 5–80°, with an angular step of 0.030°. The counting time per point was 4.0 s. In order to minimize possible preferential orientations effect in the diffractogram of powder samples, these were cyclically rotated during the measurement process with a period of 2 s. Both samples, synthetic and natural, were measured before and after any eventual temperature excursion above RT.

2.3. ESR

The ESR experiments were performed on a JEOL spectrometer (JES-PE-3X) operating at X-band (~9.5 GHz) and magnetic field modulation of 100 KHz. The measurements with the synthetic goethite samples were performed in powder form, while measurements of natural goethite samples were performed in powder and in the form of small flakes of about 5 mm in length and 2 mm in thickness. For the natural sample, the flake form was chosen since it exhibited a more intense ESR signal, because has higher density than the powder sample. The samples were measured in quartz tubes 4 mm in diameter at room temperature, and in tubes 3 mm in diameter in the case of measurements involving temperature variation. Some measurements were performed with a magnetic field marker MgO:Mn^{2+}, that was maintained in the cavity of the ESR spectrometer, whose signals were obtained simultaneously with the signals of the samples.

The experiments with temperature variation were performed with a variable temperature controller (JES-VT), in the region from 300 to 500 K, by varying the temperature at short intervals and