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Magnetic clusters in ilmenite-hematite solid solutions

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We report the use of high-field $^{57}$Fe Mössbauer spectroscopy to resolve the magnetic ordering of ilmenite-hematite [$x$FeTiO$_3$–$(1-x)$Fe$_2$O$_3$] solid solutions with $x > 0.5$. We find that nanometer-sized hematite clusters exist within an ilmenite-like matrix. Although both phases are antiferromagnetically ordered, the hematite clusters show ferrimagnetic behavior due to superexchange coupling with Fe$^{3+}$ in ilmenite. For ilmenite-rich samples ($x=0.95$), the clusters are isolated and superparamagnetic. For more hematite-rich samples with $x=0.80$ and $x=0.70$, the clusters interact to form a cluster glass.

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I. INTRODUCTION

The ilmenite-hematite [$x$FeTiO$_3$–$(1-x)$Fe$_2$O$_3$] solid solution series has attracted significant attention because of its complex magnetic and electronic properties. Both ilmenite (FeTiO$_3$) and hematite ($\alpha$-Fe$_2$O$_3$) are antiferromagnetic and insulating but intermediate compositions can be ferrimagnetic and semiconducting. The system is of significant interest as a source of natural remnant magnetism on the earth, the moon, and the planet Mars. It is also considered promising for spintronics applications. The semiconducting properties can be controlled as a function of size and morphology of the magnetic clusters exist, with long-range magnetic correlations that are resolved by high-field $^{57}$Fe Mössbauer studies of ilmenite-hematite [$x$FeTiO$_3$–$(1-x)$Fe$_2$O$_3$] solid solutions with $x > 0.5$. We find that nanometer-sized hematite clusters exist within an ilmenite-like matrix. Although both phases are antiferromagnetically ordered, the hematite clusters show ferrimagnetic behavior due to superexchange coupling with Fe$^{3+}$ in ilmenite.

A detailed understanding of the magnetic and Fe$^{2+}$/Fe$^{3+}$ charge ordering in ilmenite-hematite is therefore of great importance.

Ilmenite and hematite both have rhombohedral crystal structures. The complex magnetic properties of their solid solutions derive from incompatibilities between their different modes of cation and magnetic ordering. In ilmenite, Fe$^{3+}$ A layers alternate with Ti$^{4+}$ B layers along the rhombohedral [111] axis. Adjacent Fe$^{3+}$ A layers have opposite magnetization directions parallel to [111], and the Néel temperature of ilmenite is around 55 K. In hematite, Fe$^{3+}$ occupies both A and B layers with antiferromagnetic coupling between adjacent layers. Hence the antiferromagnetic modulation length of hematite is about half that of ilmenite. The Néel temperature of hematite is about 955 K. Above 263 K (the Morin transition temperature), or in samples with small grain size (<20 nm), or with (1%) Ti$^{4+}$ substitution, the sublattice magnetization directions of hematite are perpendicular to [111] with a small canting of the two sublattices. This results in weak ferromagnetism (canted antiferromagnetism) of ~0.4 A m$^2$/kg, with the net magnetization nearly perpendicular to the sublattice magnetization directions. In pure bulk hematite below 263 K the sublattice magnetization is along [111]. Owing to immiscibility of ilmenite and hematite below ~1000 K, exsolution of near-end-member phases occurs upon slow cooling. Rapid cooling quenches metastable solid solutions.

Previous measurements have revealed the overall magnetic properties of the ilmenite-hematite system (for phase diagrams see Refs. 6 and 7) but at the atomic scale, the magnetic ordering remains largely unresolved. For 0.5 ≤ $x$ ≤ 1.0 magnetization measurements show that solid solutions are significantly magnetic, up to more than ~30 A m$^2$/kg for compositions of $x$=0.6–0.7, due to Fe$^{3+}$ ions substituting for Ti$^{4+}$ in the B layers, resulting in a ferrimagnetic structure. Neutron diffraction has shown that for 0.5 ≤ $x$ ≤ 1.0 essentially all Ti$^{4+}$ is in the B layers but the cation distribution within layers is inhomogenous. Magnetization measurements suggest that small magnetic clusters exist, with long-range magnetic correlations beyond a percolation threshold of $x = 0.87$. However, the details of Fe$^{2+}$/Fe$^{3+}$ charge-ordered cation distribution and their implications for magnetic ordering are yet to be clarified.

To determine the local structure and magnetic properties, we performed high-field $^{57}$Fe Mössbauer studies of ilmenite-rich solid solutions with $x=0.95$, $x=0.80$, and $x=0.70$. High-field Mössbauer studies can elucidate both cation distributions in ferrimagnets and superparamagnetic relaxation phenomena.

II. EXPERIMENTAL DETAILS

Samples with nominal compositions of $x=0.95$, $x=0.80$, and $x=0.70$ were prepared by heating mixtures of Fe$_2$O$_3$ and TiO$_2$ in Ag foils, sealed into silica tubes, at 900–920 °C followed by rapid cooling (for details see Refs. 7 and 22). The samples are referred to as Ilm95, Ilm80, and Ilm70. The x-ray diffraction analysis given in Ref. 7 shows that Ilm95 is a pure rhombohedral phase of ilmenite-hematite while Ilm70 is almost purely rhombohedral with a small impurity of an unidentified phase. Unpublished data of Ilm80 indicates a pure ilmenite-hematite sample. In Ref. 7, Ilm95 and Ilm70 compositions have been redetermined by use of x-ray diffraction and corresponding samples are listed as Ilm97.4 and Ilm71.0.

Mössbauer spectra were obtained using a conventional constant acceleration spectrometer with a source of $^{57}$Co in rhodium. Isomer shifts are given relative to $^{57}$Fe at 295 K. Spectra with and without a magnetic field of 6 T, applied parallel to the gamma-ray propagation direction, were ob-
tained using a liquid-helium cryostat with a superconducting coil.

III. RESULTS AND DISCUSSION

Figure 1 shows Mössbauer spectra of Ilm95, Ilm80, and Ilm70. Zero-field spectra obtained at 6 K [Figs. 1(a), 1(e), and 1(i)] show the presence of a magnetic (six-line) component (red fit) with a magnetic hyperfine field of 50.0 T in Ilm95, 51.0 T in Ilm80, and 51.2 T in Ilm70. In Ilm80 and Ilm70 the isomer shifts of this sextet are 0.53 mm s⁻¹ and the quadrupole shifts are −0.11 mm s⁻¹, which are very close to the values for Fe³⁺ in pure hematite with the sublattice magnetization perpendicular to [111]. The hyperfine fields are slightly smaller than that of pure hematite ($B_{hf} \sim 53$ T). This may be explained by the presence of Ti⁴⁺ in the hematite or by magnetic relaxation effects. It is reasonable to assume that these components in Figs. 1(a), 1(e), and 1(i) are all due to Fe³⁺ in hematite-like environments, and hence that their isomer shifts are nearly identical. By comparing the line positions of lines 1 and 6 of the hematite sextets in Figs. 1(a), 1(e), and 1(i) we can estimate the quadrupole shift in Ilm95 as $\epsilon = +0.2 \pm 0.02$ mm s⁻¹. This shows that the sublattice magnetization of the hematite-like component in Ilm95 is actually parallel to [111] at low temperature, in agreement with neutron studies on a sample with $x = 0.90$. The 6 T spectra [Figs. 1(b), 1(f), and 1(j)] were obtained at 6 K with the magnetic field applied parallel to the gamma-ray direction. Remarkably, the hematite sextets seen in the zero-field spectra have transformed into two sextets. This is surprising because application of large applied fields to antiferromagnetic hematite at temperatures below $T_M$ results only in some line broadening in the Mössbauer spectra. Moreover, high-field Mössbauer studies of canted antiferromagnetic hematite nanoparticles have shown that the small net magnetic moment due to canting was aligned with the applied field, such that the sublattice magnetization directions become nearly perpendicular to the field, and the spectra therefore consist of a single sextet with relatively narrow lines and a magnetic splitting close to that of the zero-field spectra. Thus, the behavior of the hematite components in the high-field spectra in Figs. 1(b), 1(f), and 1(j) is clearly different from that of antiferromagnetic and canted antiferromagnetic hematite, and it indicates that the hematite in the three samples responds ferrimagnetically to an applied field. In Ilm95 the magnetic hyperfine fields of these sextets are 56.3 and 44.7 T, in Ilm80 they are 56.6 and 44.3 T, and in Ilm70, 56.8 and 44.6 T. Within uncertainty ($\sim 0.5$ T) these magnetic hyperfine fields correspond to the values in the zero-field spectra $\pm 6$ T. Also, lines 2 and 5 of the zero-field spectra are much less intense in the 6 T spectra [Figs. 1(b), 1(f), and 1(j)]. This shows that the sublattice magnetizations of the hematite components are either nearly parallel or antiparallel to the applied field.

The hematite components with larger hyperfine fields in the 6 T spectra correspond to Fe³⁺ in the minority sublattices, i.e., the B layers in the model of Ishikawa et al. because the magnetic hyperfine field of Fe³⁺ is antiparallel to the magnetic moment. If we assume that all Ti⁴⁺ is in the B layers, and that Fe³⁺ is equally distributed between A and B layers, we can write the chemical composition as $(\text{Fe}^{2+}_x, \text{Fe}^{3+}_{1-x})_{\text{A-site}} \cdot (\text{Ti}^{4+}_x, \text{Fe}^{3+}_{1-x})_{\text{B-site}} \cdot \text{O}_3$. Hence, the number of B...
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FIG. 2. (Color online) Schematic representation of cluster formation in Ilm95 and Ilm80. (a) Fe$^{3+}$ ions in Ilm95 form isolated antiferromagnetic clusters (red - dark gray in print - arrows represent magnetic spins of Fe$^{3+}$ ions) and surrounding Fe$^{2+}$ (blue - light gray in print - arrows) couple to the Fe$^{3+}$ cluster leading to a net “ferromagnetic” moment. Mainly Fe$^{2+}$ ions at the rim of a Fe$^{3+}$ cluster contribute to the net moment. The large blue arrow to the right of the panel shows resulting magnetization. (b) Fe$^{3+}$ ions in Ilm80 form antiferromagnetic clusters. Most surrounding Fe$^{2+}$ ions couple magnetically to Fe$^{3+}$ clusters. As spin frustration may exist, especially further away from the clusters, the ferromagnetic alignments of Fe$^{3+}$ moments may not be complete in zero field. The large blue arrow below the panel indicates the net magnetization.

The results presented above support the cation distribution and magnetic properties model schematically illustrated in Fig. 2. In all samples, the Fe$^{3+}$ ions are equally distributed on A and B layers and they couple antiferromagnetically to form $\alpha$-Fe$_2$O$_3$ clusters in an ilmenite-like matrix. In Ilm95 [Fig. 2(a)] the clusters have preferred sublattice magnetization along [111]. It is likely that the magnetic anisotropy of the ilmenite matrix stabilizes the magnetization direction of the clusters below its Néel temperature. Given the exchange constants in Ref. 34, an Fe$^{3+}$ ion that has an Fe$^{2+}$ ion as a nearest neighbor in the adjacent B layer is likely to couple magnetically to that Fe$^{3+}$ cluster. Exchange energy equals about −30 K per Fe$^{2+}$-Fe$^{3+}$ atom pair. For comparison, the antiferromagnetic coupling between Fe$^{3+}$ pairs in hematite is about −50 K, and the ferromagnetic in-layer coupling between Fe$^{2+}$ pairs in ilmenite is −10 K. As the surrounding Fe$^{2+}$ ions are in the A layers, they line up with parallel moments, and this leads to a net magnetization for each cluster [see Fig. 2(a)]. The effect arises because the antiferromagnetic modulation length of ilmenite is twice that of hematite and because of the strong antiferromagnetic coupling between iron ions in adjacent A and B layers. We can estimate the cluster sizes. We find that for a cluster moment of 150$\mu_B$, corresponding to ~38 nearest-neighbor Fe$^{2+}$ ions surrounding an $\alpha$-Fe$_2$O$_3$ cluster, that cluster will, depending on its shape, have a size (diameter) of ~1–2 nm.

In Ilm80 and Ilm70, the $\alpha$-Fe$_2$O$_3$ clusters interact and they have sublattice magnetization directions perpendicular to [111]. Magnetic order may be stabilized above 200 K by larger cluster sizes, exchange interactions between clusters (mediated by Fe$^{3+}$ ions), and to lesser extent dipole interactions between clusters. In Fig. 2(b), the magnetic cluster structure for Ilm80 is illustrated schematically. Most Fe$^{2+}$ ions in the sample are coupled to the clusters. The moments of Fe$^{2+}$ ions that are nearest to a $\alpha$-Fe$_2$O$_3$ cluster are aligned in parallel due to the exchange coupling with Fe$^{3+}$ in the cluster. The magnetization of Fe$^{2+}$ ions further away from the $\alpha$-Fe$_2$O$_3$ clusters may be in a relaxed but frustrated state indicated in Fig. 2 by magnetic moments pointing at an oblique angle to [111]. If all Fe$^{2+}$ spins are approximately parallel in an applied field, this leads to saturation moments of 2.67$\mu_B$ and 2.15$\mu_B$ per Fe ion in Ilm80 and Ilm70, respectively. This agrees with previous magnetic measurements: ~2.8$\mu_B$ and ~2.2$\mu_B$ per Fe for similar compositions. 3
IV. CONCLUSIONS

Our work provides evidence for the presence of hematite clusters with net magnetic moments due to surrounding Fe$^{2+}$ in an ilmenite-like matrix. This is probably the clearest observation to date that antiferromagnetic clusters can behave perfectly ferrimagnetically because of exchange coupling to a normally antiferromagnetic matrix. Simultaneously, it shows how superparamagnetism and cluster-glass behavior can be established in ilmenite-hematite solid solutions. In comparison with the preliminary cluster description originally suggested by Ishikawa$^{16}$ based on magnetic measurements of quenched hematite-ilmenite solid solutions, and supported by subsequent work,$^{6,7,24}$ our results yield an atomic-scale explanation of the macroscopic magnetic properties observed in this system.

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