Origin of Self-Reversed Thermoremanent Magnetization

Richard J. Harrison,1 Takeshi Kasama,2,3 Thomas A. White,3 Edward T. Simpson,3 and Rafal E. Dunin-Borkowski1,2

1Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge CB2 3EQ, United Kingdom
2Frontier Research System, The Institute of Physical and Chemical Research, Hatsuyama, Saitama 350-0395, Japan
3Department of Materials Science and Metallurgy, University of Cambridge, Pembroke Street, Cambridge CB2 3QZ, United Kingdom

(Received 2 September 2005; published 21 December 2005)

The ability of certain magnetic minerals to acquire a remanent magnetization that opposes the direction of the Earth’s magnetic field has fascinated rock magnetists since its discovery in 1951. Here, we determine the origin of this phenomenon, which is termed self-reversed thermoremanent magnetization (SR-TRM). We present direct transmission electron microscopy observations of negative exchange coupling across antiphase domain boundaries (APBs) in ilmenite-hematite. This coupling is linked intrinsically to the origin of SR-TRM and is responsible for the formation of two new classes of magnetic domain wall at APBs. We present simulations of the chemical and magnetic structure of the APBs and show that SR-TRM is generated by coupling between strongly ferrimagnetic Ti-rich domains and weakly ferrimagnetic Fe-rich domains, which form during the transition from short- to long-range cation order.

DOI: [0.1103/PhysRevLett.95.268501]

PACS numbers: 91.60.Pn, 75.70.Cn, 75.75.+a, 91.25.Ng

In 1951, Néel’s prediction that some minerals could become magnetized antiparallel to an applied magnetic field threatened to discredit geological observations suggesting that the Earth’s magnetic field had reversed its polarity many times throughout history [1]. Examples of self-reversed thermoremanent magnetization (SR-TRM) were soon discovered in volcanic rocks from Haruna [2] and attributed to intermediate members of the ilmenite-hematite solid solution (FeTiO3-Fe2O3) [3]. The mechanism of SR-TRM is still poorly understood, but is thought to require the presence of two phases within the mineral [4]. A weakly magnetic, metastable “x phase” is thought to be the first phase to become magnetized on cooling, acquiring a normal TRM in the presence of an applied field. A strongly magnetic, stable phase then becomes magnetized at a lower temperature. This phase acquires a reversed TRM as a result of negative exchange coupling to the x phase. SR-TRM in ilmenite-hematite occurs in grains that have cooled rapidly through a high-temperature cation ordering phase transition to form nanoscale antiphase domains (APDs). An alternating sequence of Fe-rich and Ti-rich cation layers is established in each APD. The ordering of the layers is interchanged between adjacent domains, which are separated by cation-disordered antiphase boundaries (APBs). Since SR-TRM is observed only when the density of APBs is sufficiently high (i.e., when the APDs are sufficiently small), it has been proposed that Fe-enriched APBs act as the x phase and that negative magnetic exchange coupling between APBs and APDs is the most likely cause of SR-TRM [5–7].

In order to examine the nature of magnetic exchange coupling at APBs in ilmenite-hematite, a solid solution containing 70% ilmenite and 30% hematite (ilm70) was synthesized at 1573 K, quenched through the cation ordering phase transition and annealed for 10 hours at 1023 K. The sample, which contained a microstructure of APDs separated by APBs, was examined using off-axis electron holography, a technique that allows the phase shift of a high-energy electron wave to be recorded in a transmission electron microscope (TEM) [8,9]. The phase shift is used to provide a quantitative, noninvasive measurement of the magnitude and direction of the magnetic flux in the material with nanometer spatial resolution. Prior to each measurement, the sample was saturated magnetically by tilting it to an angle of +30° to the horizontal and exposing it to the 2 T vertical field of the objective lens of the Philips CM300ST TEM. It was then tilted to −30° and exposed to a chosen field, which was then removed. All holograms were recorded digitally at 300 kV, with the objective lens switched off and the sample at zero tilt. Representative results are shown in Figs. 1(a)–1(c). Each figure, which is derived from the gradient of the measured phase shift, shows a magnetic remanent state obtained at a different stage of the switching process. The direction and magnitude of the in-plane magnetic flux are defined by the hue and intensity of the color, respectively.

The magnetization in this sample is constrained by shape and magnetocrystalline anisotropy to lie parallel or antiparallel to the intersection of the specimen plane with the (001) crystallographic plane (indicated by the double black arrow in Fig. 1). As a result, regions with strong in-plane magnetization appear either blue or green. Regions that have weak in-plane magnetization appear as dark bands. Analysis (see Fig. 2) shows that the dark bands in Fig. 1 are associated with three distinct types of magnetic wall. A fingerlike region of reversed magnetization [labeled “1” in Fig. 1(a)] enlarges by the movement of its left-hand boundary as the applied field is increased [Fig. 1(b)]. This left-hand boundary is a conventional free-standing 180° Bloch wall. In contrast, in regions where a 180° reversal in magnetization coincides exactly with the position of an APB (e.g., at regions labeled “2”), the reversal results from negative exchange coupling, and occurs without any out-of-plane rotation of the magnetic wall.

0031-9007/05/95(26)/268501(4)$23.00 268501-1 © 2005 The American Physical Society
magnetic moments. We refer to this type of boundary as a 180° “chemical” wall. A third type of magnetic wall appears as thick black bands, which are coincident with the positions of APBs (e.g., at regions labeled “3”). Such walls form when the negative exchange coupling between adjacent APDs is overcome at sufficiently large fields. We refer to these walls as 0° magnetic walls.

In the absence of demagnetizing fields outside the sample, the measured phase shift, $\phi$, varies with distance $x$ according to the equation:

$$\phi(x) = -\frac{e}{\hbar} \int B(x) t(x) dx,$$

where $B$ is the in-plane component of magnetic induction in the sample (in a direction perpendicular to $x$) and $t$ is the sample thickness. Equation (1) provides the basis for the experimental measurement of magnetic induction. The out-of-plane rotation of moments at a 180° Bloch wall is generally described by an expression of the form [10]

$$B(x) = B_0 \tanh \left( \frac{x}{w} \right),$$

where $B_0$ is the saturation induction and $2w$ is the wall width. Equation (2) provides an excellent fit to the phase profile of a 180° Bloch wall for $2w = 19$ nm [Fig. 2(a)]. In contrast, the phase profile on either side of a 180° chemical wall is nonlinear (see below), and the reversal in the slope of the phase at the center of the wall occurs much more abruptly [Fig. 2(b)]. A fit to the central portion of the wall yields $2w = 7$ nm [dashed line in Fig. 2(b)]. This value is close to the resolution limit of the measurements and provides an upper limit for the width of the chemical wall. For a 0° wall, the phase shift is described excellently by a profile of the form

$$B(x) = B_0 \tanh \left( \frac{x}{w} \right).$$

The $\tanh^2$ form results from the superposition of a 180° Bloch wall and a 180° chemical wall. An average of 13 measurements yielded $2w = (50 \pm 14)$ nm for 0° walls. Previous studies demonstrated that SR-TRM was observed only when APDs were below 80–100 nm in size. We suggest that this limit is imposed by the formation of 0° walls, which allow negative exchange coupling between adjacent domains to be overcome when the APDs are larger than approximately 50 nm in size.

A computational model of coupled cation and magnetic ordering was used to interpret the experimental measurements and, in particular, the nature of exchange coupling at APBs [11]. Spins are constrained to lie in the plane, so shape anisotropy and magnetostriction can be neglected. The starting point for the simulations was an $8 \times 8 \times 8$ supercell of fully cation-ordered ilm70, comprising 48 alternating Fe-rich and Ti-rich cation layers. APBs were introduced by interchanging Fe$^{2+}$ and Ti$^{4+}$ cations in half of the supercell. Monte Carlo simulations were performed at 850 and 1100 K (below the cation ordering transition temperature) to “anneal” the system, allowing it to relax to a state of metastable cation order. After annealing, the cation configuration was frozen in, and simulations of magnetic ordering were performed at lower temperatures.

The degree of cation order is defined as [12]

$$Q = \frac{N_A^B - N_A^A}{N_A^B + N_A^A},$$

where $N_A^A$ and $N_A^B$ are the number of Ti cations on adjacent cation layers (labeled $A$ and $B$, respectively). Annealing at 850 K generated a mixture of ordered ($Q = 1$) and anti-
ordered \((Q = -1)\) APDs that were separated by cation-disordered APBs \([Q = 0, \text{Fig. 3(a)}]\). This state corresponds to high short-range cation order \((\langle Q \rangle = 0, \langle Q^2 \rangle > 0)\) [13]. The APBs are enriched in Fe relative to the APDs [a fundamental assumption in all models of SR-TRM, Fig. 3(b)], with the magnitude of this enrichment enhanced by the immiscibility of ilmenite and hematite at this temperature. Negative exchange coupling between adjacent cation layers leads to an alternating sequence of up and down spins throughout the supercell [Fig. 3(c)]. The center of the APB is antiferromagnetic, due to an equal concentration of Fe on adjacent layers. The ordered APD is ferrimagnetic, due to an unequal concentration of Fe on adjacent layers. The adjacent antiferromagnetic APD is also ferrimagnetic, but the net moment is antiparallel to that in the ordered APD. This reversal in the net moment results in the appearance of \(180^\circ\) chemical walls in Fig. 1. Unlike for a conventional \(180^\circ\) Bloch wall, no out-of-plane rotation of magnetic moments takes place. As the net magnetization at any point in the wall is proportional to \(Q\) [14],

the nonlinearity of the phase profile in Fig. 2(b) is a quantitative measure of the variation in \(Q\) across the APB, and suggests that \(Q\) continues to vary well away from the center of the wall.

Annealing at 1100 K results in partial disorder in the antiferromagnetic domain, as the system attempts to transform from short-range \((\langle Q \rangle = 0)\) to long-range \((\langle Q \rangle > 0)\) cation order, driven by the energy released by removing the APBs [Fig. 3(d)]. Although ilmenite and hematite are miscible at 1100 K, some compositional heterogeneity remains [Fig. 3(e)]. There is evidence of slight Fe enrichment at the APBs and, more significantly, partitioning of Fe be-
between the domains. The well-ordered domain contains >70% ilmenite, whereas the less well (anti)ordered domain contains <70% ilmenite. The spin profile [Fig. 3(f)] indicates a strong ferrimagnetic moment associated with the ordered domain and a weak ferrimagnetic moment with the antiderdered domain and boundary regions.

The Fe-enriched antiderdered regions fulfill all of the requirements of the x phase: they are the first to become magnetically ordered on cooling; they are very close to being antiferromagnetic, but carry a small net moment due to partial cation order; they are negatively exchanged coupled to the neighboring ordered APDs [Fig. 3(f)]; they are metastable, appearing only in systems that are partway through the transformation from short- to long-range order. These properties lead to a self-reversal in net magnetization on cooling (Fig. 4). Magnetic ordering in the Fe-enriched antiderdered domain sets in below 425 K, yielding a weak positive ferrimagnetic moment. Magnetic order spreads to the ordered domain on cooling below 350 K. Below 250 K, the moment of the antiderdered domain is outweighed by the oppositely oriented moment of the ordered domain, and the net magnetization reverses. In contrast, no net reversal is observed in the 850 K simulation, which contains equally well-ordered and antiderdered domains, despite the enhanced enrichment of Fe at the APB.

The experimental observations and computational simulations of exchange coupling at APBs provide an explanation for the origin of SR-TRM in natural dacitic pumices. In a separate study, microscopic studies of ilmenite-hematite grains from the Nevada del Ruiz and Pinatubo volcanoes revealed the presence of compositional and magnetic zoning, with the rims of the grains being slightly richer in Fe than the cores [15]. The rims are cation-disordered and antiferromagnetic, while the cores are cation-ordered and ferrimagnetic, leading to the suggestion that the rims act as the x phase. A transition from short- to long-range cation order will occur between the rim and the core. We suggest that this region of partial long-range order, and not the Fe-enriched rim, acts as the source of SR-TRM. This conclusion is supported by TEM observations of samples from Mount Pinatubo, which reveal the presence of ordered APDs with a size of 20–40 nm that are embedded in a relatively disordered matrix in the interior of the grains. This microstructure is consistent with the present predicted mixture of well-ordered and less well (anti)ordered domains in a transitional state between short- and long-range cation order [Fig. 3(d)] [16]. The ordered APDs are below the 50 nm limit required to prevent the formation of 0° walls, and will therefore be negatively exchange coupled to the surrounding matrix, resulting in SR-TRM according to the mechanism introduced here.

This research was supported by grants from the Research Council of Norway (Grant No. 163556 “The nature and origin of natural magnetic nanoscale materials” to S.M.) and by support from NERC (NE/B501339/1 “Mineral magnetism at the nanometre scale” to R.J.H.).

R.D.B. thanks the Royal Society for support.