Reports

Antiphase Domains and Reverse Thermoremanent Magnetism in Ilmenite-Hematite Minerals

Abstract. *Examination of synthetic ilmenite-hematite samples by transmission electron microscopy has for the first time revealed the presence of well-defined antiphase domains and antiphase domain boundaries in this mineral system. Samples quenched from 1300°C have a high density of domain boundaries, whereas samples quenched from 900°C have a much lower density. Only the high-temperature samples acquire reverse thermoremanent magnetism when cooled in an applied magnetic field. The presence of a high density of domain boundaries seems to be a necessary condition for the acquisition of reverse thermoremanent magnetism.*

The iron-titanium oxide minerals occur as accessory phases in most common rock types. Minerals of the ilmenite-hematite (Ilm-Hem) solid solution series ($FeTiO_3$-Fe_2O_3) are generally the second most abundant iron-titanium oxides present after minerals of the ulvospinel-magnetite series (Fe_2TiO_4-Fe_3O_4), and in some rocks Ilm-Hem minerals occur as the dominant or sole iron-titanium oxide minerals (*1*). The Ilm-Hem minerals are of great interest to mineralogists and petrologists because these minerals act as geothermometers and oxygen barometers when in equilibrium with an ulvospinel-magnetite phase (*2*). In addition, these minerals are of interest to those working in the fields of rock magnetism and paleomagnetism because samples having intermediate compositions in the range between $Ilm_{45}Hem_{55}$ and $Ilm_{75}Hem_{25}$ are ferrimagnetic and can have room-temperature saturation magnetizations as large as 30 A m^2/kg (30 emu/g) (*3, 4*). Both end members are antiferromagnetic below their respective Néel temperatures (T_N = 685°C for hematite; T_N = −217°C for ilmenite).

Minerals of the Ilm-Hem series are rhombohedral. Hematite belongs to the space group $R\bar{3}c$, and ilmenite belongs to the less symmetric space group $R\bar{3}$ because of its ordered distribution of Fe^{2+} and Ti^{4+} ions on alternate cation layers (*2*). The ferrimagnetic phases, having intermediate compositions between $Ilm_{45}Hem_{55}$ and $Ilm_{75}Hem_{25}$, have the hematite structure at high temperatures, presumably because cations are disordered over the layers, and have the ordered Ilm structure at low temperatures (*2, 5*). The transition temperature between the two structures has been estimated only for the composition range $Ilm_{65}Hem_{35}$ to $Ilm_{45}Hem_{55}$; it apparently decreases from approximately 1100°C for $Ilm_{65}Hem_{35}$ to 600°C for $Ilm_{45}Hem_{55}$ (*5*). Within this same intermediate range of compositions, the magnetic properties of the minerals are sensitive to the thermal history of the sample, and the strength of the magnetic moment of a given sample is generally acknowledged to increase as heat treatment is prolonged; some workers have suggested that this increase is due to an increase in the ordering of iron and titanium cations (*2, 5, 6*). Minerals having these compositions can acquire a reverse thermoremanent magnetization (reverse TRM). A reverse TRM results when a sample that is cooled from above its Curie temperature in an applied field acquires a remanent moment that is opposite in direction to that of the applied field. Reverse TRM has also been related to ordering in the Ilm-Hem system (*5–9*). On the basis of theoretical considerations, Néel (*10*) showed that reverse TRM most commonly results where two different magnetic phases are magnetically coupled (*8, 10*). The presence of a second, minor phase, termed the "X-phase" by Ishikawa and Syono (*8*), has been invoked to explain reverse TRM in Ilm-Hem phases (*6–8*). The X-phase, however, has never been observed directly, and investigators have noted that the analyzed Ilm-Hem grains are homogeneous down to the scale of the standard analytical techniques applied (x-ray diffraction, reflected light microscopy, and electron microprobe analysis). These observations make it clear that, if the reverse TRM in these minerals is due to a magnetic coupling between two phases, then the minor phase must be present on a very fine scale.

The presumed high-low symmetry change in Ilm-Hem minerals of intermediate compositions has some of the structural properties that result in the formation of antiphase domains (APD's) and antiphase domain boundaries (APB's) (APD's are chemical domains and, as such, are distinct from magnetic domains). These structures have been observed in many alloys and ceramics, as well as in other mineral systems. As a sample goes through the order-disorder transition, ordering is initiated independently in different regions. When an ordered region has grown large enough to impinge on another ordered region, the two regions can interact in one of two different ways. If the cation layers of two regions are in phase (that is, if iron-rich layers of one region are adjacent to iron-rich layers of the other region), then the two regions will coalesce into one ordered domain (an APD). If the adjacent

Table 1. Thermal history of $Ilm_{70}Hem_{30}$ samples. Abbreviations: COF, controlled oxygen fugacity apparatus (quenched to room temperature in approximately 10 seconds); ST, evacuated, sealed silica tube technique (quenched to room temperature in approximately 1 minute); R, reverse; N, normal.

Sample No.	Synthesis				Anneal				TRM	
	Temperature (°C)	Technique	Time (hours)	Quench medium	Temperature (°C)	Technique	Time (hours)	Quench medium	Direction	Magnitude* (A m^2/kg)
13†	1300	COF	36	Mercury					R	1.936×10^{-1}
9‡	900	ST	336	Water					N	1.177×10^{-2}
13/9					900	ST	240	Water	N	1.134×10^{-2}
9/13					1300	ST	12	Water	R	1.153×10^{0}

*1 A m^2/kg = 1 emu/g. †Sample made from an appropriate mixture of Fe_2O_3 and TiO_2. ‡Sample made from an appropriate mixture of Fe_2O_3, TiO_2, and iron metal.

cation layers of the two ordered regions are out of phase with one another (antiphase), then a boundary (an APB) will be set up, and two APD's will exist. The APB's are generally considered to be disordered. Statistically, portions of the APB's, if randomly arranged in the structure, can be enriched in either iron or titanium. However, crystal chemical considerations make it seem more likely that the APB's will be iron-enriched, forming a hematite-like structure, rather than titanium-enriched. Titanium enrichment of the boundaries might require the less favorable juxtaposition of Ti^{4+} ions on adjacent layers, violating the avoidance principle. We hypothesized that iron-rich APB's could act as the X-phase during the formation of reverse TRM (*11*).

As part of a detailed study on the mechanism of acquisition of reverse TRM in this system, Lawson has synthesized minerals having a range of compositions between $\mathrm{Ilm}_{50}\mathrm{Hem}_{50}$ and $\mathrm{Ilm}_{100}\mathrm{Hem}_{0}$ by use of both standard controlled oxygen fugacity apparatus (*4*, *12*) and the evacuated, sealed silica tube technique (*6*, *7*, *13*). Samples in the controlled oxygen fugacity experiments were synthesized at 1300°C for at least 36 hours and quenched in mercury; those synthesized in silica tubes were held at 900°C for approximately 2 weeks and were quenched in water. Among the high-temperature samples, those having compositions between $\mathrm{Ilm}_{60}\mathrm{Hem}_{40}$ and $\mathrm{Ilm}_{75}\mathrm{Hem}_{25}$ acquire reverse TRM when cooled in an applied field of 13.9 A/m (0.175 Oe). Only the sample having the composition $\mathrm{Ilm}_{60}\mathrm{Hem}_{40}$ in the low-temperature series acquires a similar reverse TRM. Samples having all other compositions in both series acquire normal TRM's.

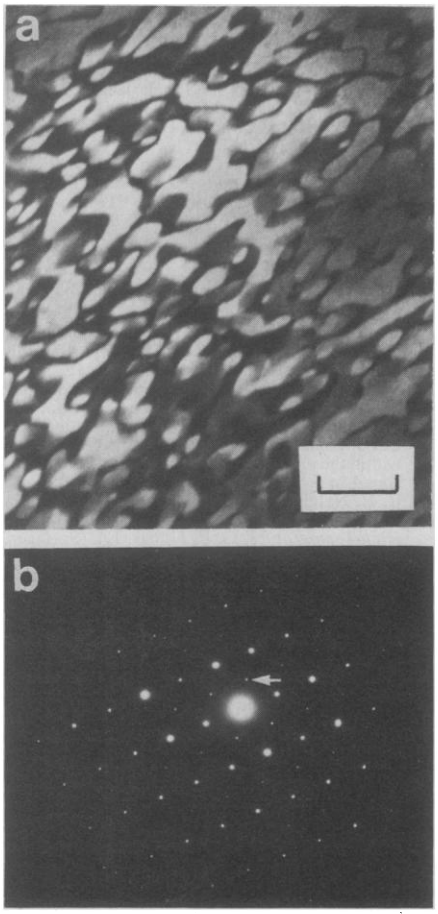

Fig. 1. (a) Dark-field transmission electron microscope image of antiphase domains and antiphase domain boundaries in the $\mathrm{Ilm}_{70}\mathrm{Hem}_{30}$ sample synthesized at 1300°C (sample 13). Scale bar is 100 nm. (b) Electron diffraction pattern of sample 13. The arrow indicates the (0003) superlattice reflection used to image (a).

We have examined synthetic samples having both normal and reverse TRM of composition $\mathrm{Ilm}_{70}\mathrm{Hem}_{30}$ by transmission electron microscopy in order to identify the X-phase responsible for the reverse TRM phenomenon. The thermal history of each sample is detailed in Table 1. The 1300°C $\mathrm{Ilm}_{70}\mathrm{Hem}_{30}$ sample (sample 13) has the strongest reverse TRM moment of any composition synthesized, and the 900°C $\mathrm{Ilm}_{70}\mathrm{Hem}_{30}$ sample (sample 9) has a normal TRM. To test the reproducibility of the sense of the TRM's (whether normal or reverse) and to check that synthesis technique is not a factor, a portion of the 1300°C $\mathrm{Ilm}_{70}\mathrm{Hem}_{30}$ sample (sample 13) was annealed at 900°C for 10 days (sample 13/9). Also, a portion of the 900°C $\mathrm{Ilm}_{70}\mathrm{Hem}_{30}$ sample (sample 9) was annealed at 1300°C for 12 hours (sample 9/13). Both annealing experiments were conducted using the silica tube technique. A normal TRM was acquired in sample 13/9, and a reverse TRM was acquired in sample 9/13.

The four samples of $\mathrm{Ilm}_{70}\mathrm{Hem}_{30}$ were mounted in epoxy resin and ground and polished mechanically to a thickness of approximately 10 μm before being placed in an argon ion milling apparatus for final thinning. The thin foils were examined in a transmission electron microscope (JEOL 200B) (*14*) operating at an accelerating voltage of 200 kV with a goniometric tilting stage.

The two samples characterized by reverse TRM were found to contain a well-defined APD microstructure, in which each domain is bounded by an APB. A typical example of the APD structure present in the sample synthesized at 1300°C is shown in Fig. 1a. The APD's are slightly elongated approximately parallel to the basal plane and are approximately 100 nm in the longest dimension. The APD structure was imaged in dark field by use of the ordered (0003) superlattice reflection (Fig. 1b). The microstructures associated with the low-temperature samples (samples 9 and 13/9) are very distinct from those associated with the high-temperature samples. Under the same operating conditions as were used to obtain dark-field images for the high-temperature samples, only rare APB's were seen. For the 1300°C $\mathrm{Ilm}_{70}\mathrm{Hem}_{30}$ sample that was subsequently annealed at 900°C, sample 13/9 (Fig. 2a), only two APD's are present within the field of view (which is approximately 2 μm wide), and they are separated by a long, straight APB. For this particular sample, each APD is larger than 2 μm in its long dimension. The electron diffraction pattern from which this sample was imaged (Fig. 2b) also shows sharp satellite reflections about (0003) (Fig. 2b, inset). The presence of these satellite reflections is probably due to the incipient formation of compositional fluctua-

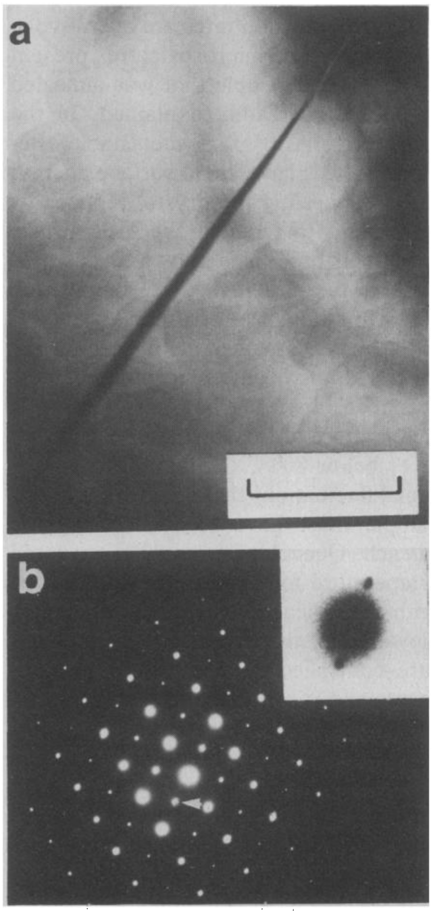

Fig. 2. (a) Dark-field transmission electron microscope image of large antiphase domains in the $\mathrm{Ilm}_{70}\mathrm{Hem}_{30}$ sample synthesized at 1300°C and subsequently annealed at 900°C (sample 13/9). Note the large size of the two domains, which are separated by a single boundary. The scalloped texture is a surface phenomenon created during ion milling. Scale bar is 1 μm. (b) Electron diffraction pattern of sample 13/9. The arrow indicates the (0003) reflection. Inset shows the satellite reflections surrounding the (0003) reflection.

tions which can form by spinodal decomposition within the Ilm-Hem solvus (*15*). From the separation of the satellites shown in Fig. 2b, the wavelength of these modulations is calculated to be approximately 3.5 nm.

Although the temperature of the order-disorder transition for Ilm$_{70}$Hem$_{30}$ has not been determined, from an extrapolation of Ishikawa's data (*5*) we can reasonably assume that it is between 1100° and 1200°C. The domain structure that is present in the 1300°C Ilm$_{70}$Hem$_{30}$ sample must have formed during the quench from the synthesis temperature. All samples synthesized at 1300°C were quenched to room temperature in approximately 10 seconds. Clearly then, for the domain structure to form during quenching, diffusion of iron and titanium, at least between layers separated by several angstroms, must be very rapid. The sample synthesized at 900°C and then annealed at 1300°C also formed fine APD's upon quench.

If rapid diffusion rates are operative in this system, the microstructures present in the 1300°C sample that was annealed at 900°C are readily explained. In the long term, APB's are metastable. Because APB's have some surface energy, during annealing the crystal reduces its free energy by reducing the APB surface area. This process is known as coarsening. For samples having the composition Ilm$_{70}$Hem$_{30}$, a heat treatment at 900°C for 10 days is sufficient to coarsen the APD's dramatically. Because the most recent estimates place the consolute temperature of the solvus in this system at or below 800°C (*2*, *16*), the compositional fluctuations that are present in this sample must have formed during the quench. Quenching from 900°C to room temperature for experiments conducted with the silica tube technique is much slower than that for the high temperature–controlled oxygen fugacity experiments and is generally on the order of 1 minute. We reasonably assume that, during quenching, once the sample is within the spinode, there is sufficient time for diffusion to take place over the distances necessary to form the observed 3.5-nm compositional fluctuations.

No discrete precipitates that could represent an X-phase were discovered in the Ilm$_{70}$Hem$_{30}$ samples during examination with the transmission electron microscope. However, the observed magnetic properties can be explained on the basis of the presence of the aforementioned APD and APB microstructures. In order to illustrate the mechanism for the onset of reverse TRM, we consider a generalized scenario incorporating features of earlier models with our observations. In this scenario, an ordered sample containing a small amount of X-phase (APB's) is cooled in an applied field from above its Curie temperature to room temperature. The cation ordering of the major phase (APD's) and the formation of the X-phase (APB's) take place at a much higher temperature than that at which the magnetic ordering takes place. During cooling, the X-phase (APB's) will become magnetic before the ordered regions (APD's) because the APB's (i) probably lie between cation layers composed mainly of ferric and ferrous iron, (ii) have the structure like that of the high-temperature disordered phase, (iii) are iron-enriched relative to the bulk of the material (APD's), and thus (iv) will have a higher Curie temperature than that of the ordered regions. Magnetically, the X-phase acts like a normal ferrimagnet in that the direction of its magnetic moment is parallel to the applied field. After further cooling, the Curie temperature of the ordered regions (APD's) is reached. At this temperature, because of a presumed antiferromagnetic coupling between the X-phase (APB's) and the ordered regions (APD's), the direction of the magnetic moment of the ordered regions becomes the reverse of that of the X-phase and thus the reverse of the applied field. The precise nature of this presumed coupling is as yet unexplained, but such coupling appears to be required for any model of reverse TRM. Although the X-phase (APB's) has a higher iron concentration than the ordered regions (APD's), the ordered regions are much more important volumetrically and consequently contain much more total iron. As a result, at room temperature the reverse TRM of the ordered regions dominates the sample.

Samples synthesized or annealed at 900°C, which is below the order-disorder transition for Ilm$_{70}$Hem$_{30}$, have much larger domains or no domains at all and consequently have a much smaller volume of APB's than samples synthesized or annealed at 1300°C. Presumably some critical volume of APB's is necessary for the acquisition of reverse TRM. In samples containing less than the critical volume, the APB's are unable to effectively couple magnetically with the main body of the domains, and a normal TRM results.

Our hypothesis whereby APB's act as the X-phase during the acquisition of reverse TRM is consistent with all experimental data from mineralogic, petrologic, and magnetic studies and, at present, it is the only one that is consistent. Three of the four major restrictions on the character of the X-phase, (i) iron enrichment, (ii) disordered iron-titanium distribution, and (iii) metastability during long-term annealing, are satisfied when APB's are equated with the X-phase. The fourth restriction, that the X-phase and ordered regions be coupled antiferromagnetically, cannot be substantiated or contradicted on the basis of our observations or any present models of APD and APB formation. However, antiferromagnetic coupling appears to be a necessary condition for the acquisition of reverse TRM (*17*).

CHARLES A. LAWSON
Department of Geological and
Geophysical Sciences,
Princeton University,
Princeton, New Jersey 08544
GORDON L. NORD, JR.
U.S. Geological Survey,
Reston, Virginia 22092
ERIC DOWTY, ROBERT B. HARGRAVES
Department of Geological and
Geophysical Sciences,
Princeton University

References and Notes

1. D. Rumble, Ed., *Oxide Minerals* (Short Course Notes, Mineralogical Society of America, Washington, D.C., 1976).
2. D. H. Lindsley, in *ibid.*, p. L1.
3. R. B. Hargraves and S. K. Banerjee, *Annu. Rev. Earth Planet. Sci.* **1**, 269 (1973).
4. M. F. Westcott-Lewis and L. G. Parry, *Aust. J. Phys.* **24**, 719 (1971).
5. Y. Ishikawa, *J. Phys. Soc. Jpn.* **13**, 828 (1958).
6. K. A. Hoffman, *Geophys. J.* **41**, 65 (1975).
7. S. Uyeda, *Jpn. J. Geophys.* **2**, 1 (1958).
8. Y. Ishikawa and Y. Syono, *J. Phys. Chem. Solids* **24**, 517 (1963).
9. M. F. Westcott-Lewis and L. G. Parry, *Aust. J. Phys.* **24**, 735 (1971).
10. L. Néel, *Adv. Phys.* **4**, 191 (1955). Theoretically, it is possible for a homogeneous, single-phase sample to acquire a reverse TRM. However, there are no experimental data supporting this interpretation for the Ilm-Hem minerals.
11. Ishikawa (*5*) suggested that the X-phase "may be a ferrimagnetic thin layer on the surface of the ordered domain, whose composition and Curie point are slightly different from those within the domain." This thin layer would correspond to an APB.
12. R. H. Nafziger, G. C. Ulmer, E. Woermann, in *Research Techniques for High Pressure and High Temperature*, G. C. Ulmer, Ed. (Springer, Berlin, 1971), p. 9.
13. C. A. Lawson, *Carnegie Inst. Washington Yearb.* **77**, 917 (1978).
14. Use of trade names in this report is for descriptive purposes only and does not constitute endorsement by the U.S. Geological Survey.
15. J. W. Cahn [*Trans. AIME* **242**, 166 (1968)] gives a general discussion on the theory of spinodal decomposition and on how microstructures formed by this mechanism can be recognized.
16. D. H. Lindsley, *Geol. Soc. Am. Bull.* **84**, 657 (1973). The suggestion of Hoffman (*6*) that the consolute temperature of the solvus is at least 1200°C is not supported by the results of any experimental petrologic studies.
17. We have recently observed the presence of APD's and APB's in Ilm-Hem grains having a composition of approximately Ilm$_{57}$Hem$_{43}$ contained in the White River ash from the Yukon Territory.
18. We thank H. Evans, F. Senftle, P. Smith, W. Maze, and S. Bergman for critically reading the manuscript. Support for the synthesis experiments was provided by D. Lindsley at the State University of New York at Stony Brook and by H. Yoder at the Geophysical Laboratory of Carnegie Institution of Washington. Magnetic experiments were supported by NSF grant EAR 80-08207.

2 April 1981; revised 16 June 1981