

## Chemical and magnetic properties of rapidly cooled metastable ferri-ilmenite solid solutions: implications for magnetic self-reversal and exchange bias—I. Fe-Ti order transition in quenched synthetic ilmenite 61

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Accepted 2011 June 9. Received 2011 June 9; in original form 2010 November 12

### SUMMARY

Quenched ferri-ilmenite solid solutions X FeTiO<sub>3</sub> + (1 - X) Fe<sub>2</sub>O<sub>3</sub> with  $X \approx 0.60$  contain chemical and magnetic structures important for understanding the unusual magnetic properties in this series, including self-reversal in igneous rocks and exchange bias. Here we study a composition X = 0.61, annealed at 1055 °C, above the Fe-Ti ordering temperature, then quenched. Presence of two interface-coupled phases is established by pot-bellied character of the room-temperature magnetic hysteresis loop, and large negative magnetic exchange bias below 30 K. Transmission electron microscopy (TEM) dark-field imaging with the 003 reflection shows dominant Fe-Ti disordered antiferromagnetic and lesser ordered ferrimagnetic phases, the latter in lenses  $\leq 8$  nm thick. Parts of the ordered phase are in antiphase relationship, shown by high-resolution TEM imaging of Fe-rich and Ti-rich layers. TEM-EDX analyses indicate chemical phase separation during quench, with dominant compositions X = 0.56–0.63, extremes 0.50 and 0.70. Thermomagnetic experiments indicate compositions X = 0.56–0.61 are antiferromagnetic, X = 0.61–0.64 are ferrimagnetic.

A sample held  $\sim$ 5 min at 1063 K, increased in order, demonstrated by twofold increase in induced moment at 1 T. This then acquired self-reversed thermoremanent magnetization between 490 and 440 K. Progressive annealings of another sample at 773 K, 973 K, 1023 K and 1063 K, followed by cooling in a 1 T field, produced positive room-temperature magnetic exchange bias, only for 1023 K and 1063 K runs. These properties suggest growth of ordered regions from disordered regions, and expansion of some ordered domains against others across antiphase boundaries, thus creating self-organized structures essential for magnetic self-reversal and magnetic exchange bias.

**Key words:** Magnetic mineralogy and petrology; Rock and mineral magnetism; Microstructures; Phase transitions.

### **1 INTRODUCTION**

The haematite-ilmenite solid solution series X FeTiO<sub>3</sub> + (1 - X) Fe<sub>2</sub>O<sub>3</sub> with  $0 \le X \le 1$  is central for understanding the magnetic properties of oxidized natural environments including parts of the Earth's crust and some planetary bodies. Natural samples in the series are related to large remanent magnetic anomalies on the Earth and possibly on Mars (McEnroe *et al.* 2009). Natural rocks containing compositions with X = 0.53-0.71 were discovered to self-reverse spontaneously during cooling in a weak magnetic field, thus acquiring a remanence opposite to the Earth's magnetic field in

nature (Nagata *et al.* 1952; Uyeda 1958; Ishikawa & Syono 1963; Westcott-Lewis & Parry 1971; Nord & Lawson 1989; Hoffman 1992; Prevot *et al.* 2001; Ozima & Funaki 2001; Harrison *et al.* 2005). A haematite-ilmenite solid solution of similar composition provided the very first sample found to exhibit magnetic exchange bias at room temperature (Meiklejohn & Carter 1959). Today exchange bias is widely used in magnetic storage devices, often in combination with giant magnetoresistance (Nogués *et al.* 2005).

Our long-term research target has been to understand the magnetic properties of the whole haematite-ilmenite ( $Fe_2O_3$ -FeTiO\_3) solid solution series, and, most recently, the low-temperature properties in the composition range X = 0.6-1.0 between 0 and 500 K (Burton *et al.* 2008). Most of these samples were annealed below the Fe-Ti ordering transition, hence those with X < 0.87 obtain the properties of a ferrimagnet from adjacent-layer magnetic interactions at moderately low temperature (*T*). The ferri-ilmenite sample IIm61–1055 studied here is unusual in that it has been annealed at 1055 °C, above the Fe-Ti disorder–order transition, before quench.

Sample Ilm61-1055 resembles the quenched ferri-ilmenite samples from the Huruna dacite in Japan and synthetic analogues (Nagata et al. 1952; Uyeda 1957, 1958; Meiklejohn & Carter 1959; Ozima & Funaki 2001; Ozima et al. 2003). Also the Pinatubo ash from the Phillipines contains material of similar composition (Ozima et al. 1992; Hoffman & Fehr 1996; Prevot et al. 2001). Such samples played a vexing role in the history of geomagnetism, because they demonstrably acquire a thermoremanent magnetization inverse to the external field, strengthening the proposed opinion that all magnetically reversed lavas and sediments result from a rock-magnetic self-reversal process, while the geomagnetic field itself is constant in time. Only several years later, it was proved that such compositions are unusual, and that most lavas and sediments faithfully record a geomagnetic field which, over geological time, commonly reverses its polarity. As is now well known, the geographic record of such reversals, indelibly preserved in the remanent magnetism of seafloor basalts, provided the decisive key to our present ruling paradigm of global seafloor spreading and plate tectonics. However, magnetic self-reversal still is a possible complication in natural rocks, and has been proved to be a fairly common feature of glassy dacite volcanics worldwide (Nord & Lawson 1992; Ozima et al. 2003).

Here we start a series of three papers which try to develop a consistent interpretation of the physical and chemical processes which lead to self reversal and magnetic exchange bias in the haematite-ilmenite solid solution series. In this paper I, we primarily study two samples with  $X \approx 0.61$ . The paper proceeds in three sections: (1) Investigation of the general characteristics of the quenched sample Ilm61-1055; (2) Review of the most completely studied self-reversed natural samples and synthetic equivalents and (3) Detailed chemical characterization and magnetic experiments on our samples. Throughout the manuscript we use the words, phase and phases, to describe parts of synthetic mineral intergrowths. Although not 'physically separable' and 'homogeneous' in the Gibbsian sense, the different parts of these intergrowths do have distinctive internal structure and local composition variations that can be described as belonging to phase regions, and, some parts, in addition, are identical except they are in antiphase relationship.

Paper II gives detailed consideration to phase contact phenomena and chemical microstructures, and the possible phases at high temperature that provide the groundwork for magnetic phenomena at low temperature. Paper III contains models combining chemical and magnetic properties, which together can explain both selfreversal of thermoremanent magnetization, and magnetic exchange bias.

### 2 INITIAL INVESTIGATION OF ILMENITE 61 SAMPLE

### 2.1 Magnetic indications of a two-phase mixture

The first indication of unusual properties in sample Ilm61–1055 comes from its room-temperature (RT) hysteresis loop (Fig. 1B),



Figure 1. Room-temperature hysteresis loops of (A) an ordered sample X = 0.618 and (B) the quenched sample discussed here X = 0.61, showing significant differences. The sample in (A) shows a nearly saturated magnetization of 140 k A m<sup>-1</sup> at 1.3 T, whereas the quenched sample (B), with greater disorder, shows an apparently weaker magnetization of 50 k A m<sup>-1</sup>, but is far from saturated at 1.3 T, reflecting a significantly higher coercivity  $H_{\rm c}$ . The hysteresis shape indicates the presence of two phases with markedly different coercivity; (C) shows a hysteresis loop at 100 K for the quenched sample with a magnetization at least 190 k A  $\mathrm{m}^{-1}$  that is still not saturated at 7 T. The contrast in coercivity between (A) and (C) reflects the presence of fine quench microstructures in (C). Measured magnetic saturation values in weight-normalized units (Am<sup>2</sup> kg<sup>-1</sup>) after density ( $\rho$ ) correction based on a Vegards law [ $\rho = (1 - X) \rho_{\text{Hem}} + X \rho_{\text{Ilm}}$  in which  $\rho_{\text{Hem}} = 5300 \text{ kg m}^{-3}$ and  $\rho_{Ilm} = 4790 \text{ kg m}^{-3}$  (http://webmineral.com/data/)] result in volumenormalized values in A m<sup>-1</sup>. The correction for negative excess volumes of mixing is insignificant.

which indicates the presence of two phases; the first with high coercivity and apparently low magnetization, the second with high magnetization and lower coercivity. However, the measured magnetization of ~50 kA m<sup>-1</sup> is clearly not saturated at 1.3 T. When measured at 100 K (Fig. 1C), Ilm61–1055 shows a significantly increased magnetization of ~190 kA m<sup>-1</sup> in a field of 7 T, but still appears not to be saturated. A second sample of composition X =0.618 was annealed at 685 °C for ~39 months (Burton *et al.* 2008), whereby it likely attained an equilibrium degree of Fe-Ti ordering before quench. This sample has a RT magnetization of 140 kA m<sup>-1</sup> at 1.3 T (Fig. 1A).

Neutron diffraction experiments on a sample of X = 0.60 by Harrison & Redfern (2001), determined the average atomic occupancy of alternating Ti- and Fe-rich (A and B) ordered layers, and thus the order parameter

$$Q = (X_{\text{TiA}} - X_{\text{TiB}})/(X_{\text{TiA}} + X_{\text{TiB}}),$$

ranging from Q = 0 (completely disordered) to Q = 1 (completely ordered). Their experiment at 697 °C, closest to our 685 °C, yielded Q = 0.64. In Section 4.4, we will use the magnetic properties of our two samples to discuss how to estimate bulk values of Q in parallel with the neutron diffraction results of Harrison & Redfern (2001). Unfortunately, the Q estimates cannot be used directly to determine the proportions of disordered high-coercivity and ordered low-coercivity phases in the quenched sample, which apparently are responsible for its unusual magnetic properties.

Besides the two-component hysteresis loop at RT, field-cooled IIm61–1055 shows highly asymmetric hysteresis loops at low temperatures T < 30 K indicative of a strong magnetic exchange bias (Fig. 2). The sample was cooled in a 5 T field from RT to 5 K, producing a strong thermoremanent magnetization, before measuring the hysteresis loops during stepwise warming. To create magnetic exchange bias requires strong magnetic coupling across interfaces between two different magnetic phases. Therefore, its presence demonstrates that the sample contains at least two closely intergrown phases. The observed exchange bias of ~0.5 T is unusually strong and cannot be explained by a simple spin-glass behaviour in either phase.

Although the presence of two phases was indicated already by the RT hysteresis loop, it did not prove that the two phases are magnetically coupled, because the two parts of the loop could come from separate grains. Because the sample was not in a field-cooled state, the initial RT experiment could not detect magnetic exchange bias. Exchange bias has been reported in both natural and synthetic samples with different cooling history (Meiklejohn & Carter 1959; Ishikawa & Syono 1963; McEnroe *et al.* 2007a,b). However, already the first two sets of experiments together, indicated the need to investigate the origin of sample inhomogeneity by transmission electron microscopy (TEM).

#### 2.2 TEM observations

A conventional TEM imaging, selected area electron diffraction (SAED), and energy-dispersive X-ray spectroscopy (EDXS) in scanning TEM mode were performed on a Philips CM20 FEG operating at 200 kV. Some grains of sample Ilm61–1055 were ground and dispersed in ethanol liquid. A drop of the liquid was placed on a Lacey carbon TEM grid. The first TEM observations in bright and dark field images without any reflections along the *c*-axis showed a homogenous phase with no indication of exsolution or any foreign material. Strong (006) reflections in electron diffraction suggested the presence of a predominant disordered phase consistent with the



**Figure 2.** Low-temperature magnetic hysteresis loops, after cooling in a 5 T field to 5 K, are notably shifted, indicating exchange bias due to magnetic exchange coupling across nanoscale interfaces.

annealing temperature of 1055 °C. However, there were also weak (003) reflections, only possible for the Fe-Ti ordered phase. An SAED image, taken through the (003) diffraction spot (Fig. 3c), shows predominantly dark regions reflecting disorder, with smaller illuminated regions where an Fe-Ti ordered phase runs completely through the sample thickness. The image is of a crushed grain where the thinnest edge is to the left, but the centre also appears very thin, probably as a result of conchoidal fracture during grain preparation, or bending of the foil. The largest 'see through' ordered regions are  $\sim$ 8 nm thick normal to (001), comprising five–six six-layer unit cells, and are elongated parallel to the (001) basal plane. This latter feature, also seen in electron micrographs by Lawson *et al.* (1981)



Figure 3. Dark field TEM images of Ilm61–1055 with the haematite-like disordered reflection (a) g = 006 and the ilmenite-like ordered reflection (b) g = 003. Selected area electron diffraction patterns are shown in (c) the <-110> zone axis and (d) the <100> zone axis. Image (a) taken through 006, shows no remarkable contrasts in illumination, but in (b) taken through 003 only the ordered regions are illuminated, representing a minority of the sample.

and Nord & Lawson (1989), and from the Mt Pinatubo dacite pumice (Prevot *et al.* 2001), can be explained easily, because there is almost no change in the *a* lattice parameter during the disorder–order phase transition, whereas *c* expands (Harrison *et al.* 2000; Harrison & Redfern 2001), inhibiting growth of the ordered phase in the *c* direction. The *c* expansion can also be seen from a tiny splitting of the (006) electron diffraction spots, which show a smaller  $2\theta$  angle (hence larger *c* lattice parameter) for the minority ordered phase, compared to the disordered phase.

### 2.3 Comparisons to earlier TEM studies

When Fe-Ti ordering occurs during cooling in a rhombohedral Fe-Ti oxide, the spontaneous local placement of alternate Ti layers occurs at random through the structure. Ordered domains with opposed placement grow outwards until they impinge on each other, producing narrow regions where the phases are chemically out-of-phase, described as 'antiphase domains (APDs)' or 'twins'. Such boundaries are energetically unfavourable and, if the sample is annealed just below the ordering temperature for some time, tend to be eliminated. However, if cooling is rapid, they are metastably frozen in,

as proved in cooling experiments by Nord & Lawson (1989, 1992) on a composition Ilm 70, documented by TEM imaging of the 003 reflection. In their sample, APDs develop when quenched above the ordering temperature. Interestingly, the higher the temperature of quenching is above the ordering temperature of  $\sim 1050$  °C, the fewer APDs are formed. Quenching just above the ordering temperature creates a greater number of APDs, making the intergrowth structure visibly finer. Nord & Lawson (1992) discuss four possible explanations for these different structures in samples quenched from the various initial temperatures. An important aspect relates to the difference in time which the samples spent close to the ordering temperature. Samples annealed initially below the ordering temperature are ordered and show no intergrowths, though the actual degree of order can vary. Samples quenched above the ordering temperature and containing intergrowths were annealed below the ordering temperature (800 °C as illustrated in their fig. 8 for 0.1, 1, 10 and 100 h), resulting in coarsening of the intergrowth with change in magnetic properties. A high density of such boundaries (shown by thin dark regions of disorder in their fig. 8) is only preserved with annealing times well less than 1 h just below the ordering transition. Ordering takes place more easily for Ti-rich than for Ti-poor IlmX

compositions, because a higher density of Ti atoms increases the gain in free energy by ordering. The finest intergrowths are achieved by quenching from a temperature just above the ordering transition in Ti-poor compositions (X < 0.6) where ordering is sluggish.

In terms of the pattern and size of intergrowths, our sample Ilm61-1055 (Fig. 3c) most closely resembles Nord & Lawson's (1989) sample of Ilm 60 quenched in 10 s from 1173 K (900 °C) (their fig. 4a), where they estimated the transition temperature at 1123 K (850 °C). Like our sample, the ordered regions are in the midst of a disordered matrix, are elongate parallel to (001) and are less than 10 nm thick. This demonstrates that the ordering we observe took place during quench. Fig. 3(c) also is similar to the image of a sample of Mt Pinatubo dacite pumice (Prevot et al. 2001, their fig. 2) with composition  $X \sim 0.55$ , presumably quenched more slowly under natural conditions, with elongate ordered regions  $\sim 10$  nm thick. A consistent observation of several authors is that rapidly chilled samples with dense intergrowths are less prone to show self-reversed thermoremanent magnetization than slightly more annealed samples with intermediate intergrowths. Long annealed samples with few intergrowths, for example, from slowly flowing lavas, are normal ferrimagnets with field-aligned thermoremanence. However, contrary to the general observation earlier, all Ilm 70 samples quenched above the ordering temperature by Nord & Lawson (1989) showed self-reversal.

### 2.4 High-resolution TEM imaging

To confirm the ordering relationships, high-resolution TEM imaging was used (Fig. 4). Here the resolution is so high that individual alternating Fe-rich and Ti-rich layers are visible as alternating light and dark stripes, respectively. Three of each exist per unit cell parallel to the basal plane causing the 003 reflections in the electron diffraction images. Fig. 4 is remarkable in that the light (Fe-rich) layers at the extreme left- and right-hand side of the image are lined up with each other, but are offset in the middle by one layer. Thus, the region in the centre is an APD separated from the surroundings by two antiphase domain boundaries (APB). Fig. 4 does not show clearly whether these boundaries contain a finite region of disordered structure, perhaps up to 2–3 nm thick, or whether the two ordered phases are in direct contact. Similar structures were observed by direct atomic imaging using high angle annular dark-field scanning TEM (Hojo *et al.* 2009).

# 3 OTHER NATURAL AND SYNTHETIC SAMPLES

# 3.1 Composition range involved in self-reversed thermoremanent magnetization

Surveying the available literature suggests that self-reversed thermoremanent magnetization has been observed in the composition range between ~IIm 75 and ~IIm 45. This is important because the presence of stable and metastable equilibria needed to produce selfreversing phases can help to constrain the applicable temperaturecomposition phase diagram. The first Fe<sub>2</sub>O<sub>3</sub>-FeTiO<sub>3</sub> phase diagrams that included features derived from both chemical and magnetic ordering were by Burton (1985), Burton & Davidson (1988) and Burton (1991). The most recent diagrams include one by Harrison (2006) and three alternate versions by Ghiorso & Evans (2008). In the interpretation of a Pinatubo sample by Prevot *et al.* (2001), this



Figure 4. HRTEM image of Ilm 61–1055 showing an antiphase domain (APD) within the ordered phase and the corresponding antiphase boundaries (APB).

© 2011 The Authors, *GJI*, **186**, 997–1014 Geophysical Journal International © 2011 RAS composition range has been extended as low as Ilm 35–30, though experimental work suggests that Fe-Ti ordering may be prohibitively slow for these compositions (Ishikawa 1958; Harrison & Redfern 2001).

#### 3.2 Agreed requirements for the self-reversal process

Most, but not all, models for the self-reversal process call upon at least two different coexisting phases, a disordered haematitelike phase with high coercivity, low magnetization and higher Néel temperature ( $T_N$ ), and an ordered lower coercivity, strongly ferrimagnetic (FM) phase, with lower Curie temperature  $T_C$ . In addition, the ordered phase occurs in phase-shifted A and B versions separated by APBs. A key assumption of several self-reversal models is that during ordering, the residual haematite-like (more disordered) phase is left with a higher Fe content, hence a higher  $T_N$ , whereas the more ordered FM phase is enriched in Ti and has a lower  $T_C < T_N$ . This assumption requires chemical phase separation related to ordering during quench, which has support in chemical details of the ordering process, and implied metastable equilibria in versions of the phase diagram of Ghiorso & Evans (2008).

When the alternately ordered A and B domains cool through their  $T_{\rm C}$  ( $\approx$ 300–50 °C for  $\sim$ Ilm 45 to Ilm 75), their Fe-rich layers, determining the FM direction, try to magnetize parallel to the external field. However, this violates the strong antiferromagnetic (AF) coupling across APB, whereby A- and B-ordered domains will be magnetically opposed to each other, in terms of their net moment orientations, though in-phase in terms of magnetic sublattice orientations. This strong AF coupling across the APB together with chemical phase separation is commonly considered to be the main cause of self-reversed thermoremanent magnetization, although the details of how this leads to self reversal are explained differently by a great diversity of models differing in composition and behaviour of the phases. While it is easy to describe these agreed upon requirements, it is more difficult to achieve them in terms of chemical evolution of microstructures, and the relations between microstructures and magnetic properties. These are considered in detail in Papers II and III.

#### 3.3 Disagreement on nature of magnetic coupling

Many self-reversal models are extremely sketchy as to the nature of magnetic coupling between the phases. Commonly, the minority disordered phase is denoted as an Fe-rich 'x-phase' that magnetizes at higher temperature with normal TRM, and the ordered phase as the Fe-poor majority phase that magnetizes with reversed TRM. In Paper III we describe a detailed ionic model of an interface where it turns out that the ordered A and B regions are certain to have opposite magnetic moments (see Nord & Lawson 1992, their fig. 12 for an explicit confirmation of this). Therefore, if the 'x-phase' were a disordered Fe-rich phase, the adjacent ordered phases could acquire a reversed remanence only in response to a normal (e.g. spin-canting) remanence of the disordered phase, which would be a magnetostatic response. Purely magnetostatic interaction, however, is contrary to the evidence of magnetic exchange bias, which is proof of magnetic exchange coupling at interfaces. Such strong exchange coupling was part of the early ideas concerning self-reversal developed by Uyeda (1957, 1958), Ishikawa (1958) and Ishikawa & Syono (1963), but was not employed in later models, including the petrologically sophisticated work of Nord & Lawson (1989,1992). However, for two of the Ilm 70 samples quenched above the Fe-Ti

ordering temperature by Nord & Lawson (1989,1992), a magnetic exchange bias (+2.7 mT and +12 mT) was measured by Lagroix *et al.* (2004), after 2.5T-field cooling from 400 K down to 150 K.

#### 3.4 Magnetic core-shell model

Based on data on synthetic samples, Ishikawa & Syono (1963) proposed a magnetic core-shell model to explain the behaviour of samples, quenched above their Fe-Ti ordering temperatures, and then variously annealed below those temperatures to coarsen ordered regions at the expense of disordered regions, and then to reduce the extent of APB. In this model, cores of ordered phase are formed within a disordered matrix. Fe and Ti are redistributed along individual cation layers. In one set of alternate layers Ti moves out of the core and into a surrounding shell against the disordered matrix, while Fe moves into the core and out of the shell. In the other set of alternate layers, Fe moves out of the core into the shell and Ti moves into the core and out of the shell. The result would be that the core has one Fe-Ti ordering mode (A) and the shell against the disordered phase has the other mode (B). In this model, the B ordered shell represents the 'the x-phase' against the disordered phase. Due to its higher Fe-content the shell has weaker moment than the core, and also a higher  $T_{\rm C}$ , whereby it magnetizes earlier along the external field and by antiphase exchange coupling reverses the stronger moment of the inner A phase at its lower  $T_{\rm C}$ . As Fe-Ti ordering commences at different locations within the disordered host, it might produce cores with either A or B mode, each developing related shells with opposite mode. Once such a microstructure were established, it would be possible for all shells, regardless of mode, to adopt a normal magnetization, and all cores to then adopt a self-reversed magnetization. The problem lies not in the magnetic model, but in the chemical model by which shells could be established that are in exact antiphase relationship with cores. The proposed chemical model of Ishikawa & Syono (1963) is totally dependent on their concept of opposed diffusion along (001) layers.

There is an inherent problem with a model requiring diffusion mainly along (001) cation layers to create ordering. It is a fact that such diffusion requires far greater distance of transport than is required if Fe and Ti ions merely jump short distances between adjacent (001) layers so that alternate layers become enriched in Fe and Ti. We already considered diffusion along (001) layers as a possible mechanism for growth of exsolution lamellae, but quickly rejected it (Robinson *et al.* 2004). If such a diffusion were playing a leading role, then one would expect ilmenite lamellae in haematite and vice versa to be elongated normal to (001) layers, rather than parallel to (001).

#### 3.5 Possible roles of spin-canted magnetization

Hoffman (1992, see also Prevot *et al.* 2001, p. 77) attempted to get around problems by having the haematite-like disordered phase acquire a very weak spin-canted magnetization parallel to the field (with sublattice magnetizations 90° to the field). He then had the two adjacent ordered phases undergo 'symmetric rotations' so that their originally opposed magnetizations were both oppositely rotated until they reach a position directly opposed to the normal spin-canted moment of the disordered phase. In pure haematite, all positions are occupied by Fe<sup>3+</sup>, giving sublattice magnetizations of  $5\mu_{\rm B}$  (Bohr magneton), equivalent to the number of five unpaired d electrons in Fe<sup>3+</sup>. By contrast, the net spin-canted moment of pure haematite

is about 0.0114  $\mu_B$  per formula unit (pfu). For an equivalent disordered phase of composition IIm 60, with sublattice magnetizations  $3.2\mu_B$ , the spin-canted moment, if there is spin-canting with the same canting angle for this composition, would be about 0.0073  $\mu B$  pfu. This value is miniscule compared with the net FM moment of fully ordered IIm 60 which is  $2.4\mu_B$  pfu.

Somewhat similar alignments involving spin-canted moments were invoked in the very complex model proposed by Prevot et al. (2001), which, however, clearly has its seeds in the core-shell model of Ishikawa & Syono (1963). Their final crucial step (their fig. 7) seems to invoke opposite alignments of two FM phases with different degrees of ordering and different composition and Curie temperatures (380 °C for the shell, 270 °C for the core), where no reason for opposite alignment is discernible. However, Ishikawa & Syono (1963, their fig. 12) show that this opposite alignment is because of a postulated antiphase relationship across the phase boundary, which they proposed to be created by diffusion along (001) layers. If this origin of the antiphase relationship is accepted (although we consider it improbable), then the whole consideration of the spin-canted magnetization of the disordered phase becomes unnecessary to explain the self-reversal of an individual core-shell assemblage.

Despite the magnetic complexities, Prevot et al. (2001) present some interesting chemical suggestions based on their magnetic measurements. These are shown in their fig. 6, where an oval patch of ordered phase with postulated composition X = 0.54 resides in a disordered matrix of composition X = 0.53. However, at the border between these two phases there are Fe enriched reaction rims in which the ordered phase reaches composition X = 0.35 and the disordered composition reaches X = 0.30. Note that in this model both phases show major Fe enrichment, whereas, in a simple consideration of the phase diagrams, one might expect that local reaction would cause the disordered phase to become more Fe-rich, and the ordered phase more Ti-rich. This double Fe-enrichment, unexplained in their figure, provided us with ideas giving rise to plausible new metastable features of the phase diagram, as we explain in Paper II. There is an important warning in other experimental data (Ishikawa 1958; Ishikawa & Syono 1963; Harrison & Redfern 2001), however, suggesting that Fe-Ti ordering may be so sluggish for compositions more Fe-rich than X = 0.40, at T < 760 K, that it may not take place at all.

Most magnetic models at RT and above have the magnetic moments within the (001) basal plane of all phases. For uncertain reasons related to magnetic domain theory, Hoffmann & Fehr (1996) suggest the ordered FM phase in a Pinatubo sample has magnetic moments parallel to c. This was rejected by Ozima & Funaki (2001) and is in any case ruled out by the detailed neutron diffraction studies of Arai *et al.* (1985) on composition IIm 79 showing magnetic moments in the basal plane at all temperatures.

# 3.6 Newer model from Monte Carlo simulations and electron holography

Harrison *et al.* (2005) and Harrison (2006) constructed a model to explain magnetic self-reversal in annealed Ilm 70 intergrowths without spin canting. Their study combined Monte Carlo modelling with direct TEM observations of negative exchange coupling across antiphase boundaries of a synthetic sample using off-axis electron holography. The background for their model comes from the neutron diffraction experiments of Harrison & Redfern (2001), determining degrees of Fe-Ti ordering with temperature for compositions X = 0.60 and X = 0.65. The Monte Carlo model is based on empirical chemical and magnetic interaction parameters which are reasonably well known for this system. It explains chemical differences in ordered phases by changes taking place during coarsening, thereby producing self-reversal at lower temperature without any resort to magnetostatic coupling. The elusive 'x-phase' is explained, not as a disordered phase, but as a less strongly ordered Fe-enriched phase created near antiphase boundaries during the coarsening process. These authors explain the differences between '180° chemical domain walls', '180° magnetic domain walls' and '0° magnetic domain walls'. These concepts turn out to be very important and will be discussed and portrayed graphically in Paper III. The results of Harrison et al. (2005) and Harrison (2006) suggest that the negative magnetic coupling required for magnetic self-reversal can only be maintained when the antiphase domains are smaller than  $\sim$ 50 nm. However, the chemical separation to compositions Ilm 40 and Ilm 90 implied by the Monte Carlo model is probably too extreme to occur in nature, and could not explain RT self-reversal, because Ilm 90 is not FM at this or any other temperature (Burton et al. 2008). The overall explanation provided by these authors is convincing and is used extensively in Papers II and III.

### 4. ADDITIONAL MEASUREMENTS AND EXPERIMENTS ON ILMENITE 61 SAMPLE

### 4.1 Lattice parameter measurements

As noted in Section 2.2, for Ilm61–1055 the TEM data indicate (Fig. 3d) that the ordered phase has a larger c dimension than the disordered phase in agreement with neutron diffraction experiments (Harrison & Redfern 2001). However, a difference in c dimensions in our sample could be due either to the ordering itself, or to a Tienrichment of the ordered phase. We attempted to standardize TEM measurements of the c dimensions and compare results with composition reference curves for Fe-Ti disordered and ordered phases. Unfortunately, the inherent error in measuring lattice differences with TEM is too large. Also constructing reference curves for c lattice parameters versus composition at RT is difficult, because the ordered phases can have different degrees of order depending on thermal history.

However, high-resolution X-ray powder diffraction resulted in sharp diffraction peaks, and Rietveld refinement of the full diffraction pattern could successfully determine the lattice parameters based on the structural model of ordered ilmenite with X = 0.60. The resulting unit-cell parameters are a = 5.0681 Å (1), c = 13.9151Å (2), V = 309.53 (1) Å<sup>3</sup>. A calibration curve of cell volume versus X FeTiO<sub>3</sub>, provided by Richard Harrison, that we have used consistently (Burton *et al.* 2008), indicated a composition X = 0.61. We tested if line broadening could be detected that would indicate a spread of compositions. A plot of diffraction patterns of measured compositions Ilm 61.8 and 68.8, showed that the bases of the main peaks, though quite sharp (full width at half maximum of  $\sim 0.1$  –  $0.12^{\circ}$  in  $2\theta$ ), enclose each other and were too broad to estimate a composition range reliably. Peaks at high angles of  $2\theta$ , where peak separation is more detectable, were too weak to evaluate. In addition, the 003 diffraction peak indicative of Fe-Ti order in TEM diffraction is very weak in the X-ray powder diffraction pattern, and, also all other peaks hkl with k = 0 and l odd are practically negligible. The same procedures were used for our Ilm 61.8 sample annealed 39 months at 685 °C (see Fig. 1) with resulting unit-cell

parameters a = 5.0688 Å (1), c = 13.9160 Å (2), V = 309.64 (1) Å<sup>3</sup> and indicated composition X = 0.618.

### 4.2 TEM-EDX measurements of composition

To determine what composition changes had taken place during quench and the accompanying Fe-Ti ordering process, demonstrated by the TEM images and selected electron diffraction patterns, we performed energy dispersive X-ray (EDX) analyses in TEM at a very fine scale qualitatively coupled to the low-resolution TEM image of Fig. 3(c). This was possible because of the chemical simplicity of the sample, involving only Fe, Ti and O. The results indicate that some phase separation occurred even during rapid quench.

Altogether 150 EDX spots were analysed along three traverses (Tables 1A–1C), located near the western edge of the dark field TEM image in Fig. 3(c). In this region the electron beam 'saw through' the entire thickness of the sample, where Fe-Ti ordered regions (light) are surrounded by dark disordered regions (Fig. 3d).

Each traverse began at the left-hand edge and extended inwards for a distance of 103 nm with a step distance of 2.1 nm. This step distance compares to about 8 nm for the widest of the Fe-Ti ordered

Table 1A. TEM-EDX analyses of sample Ilm 61–1055 in traverse 13. X = 2Ti / (Ti + Fe).

Eler	nent	Atom (per cent)	+/-	Х	Elei	ment	Atom (per cent)	+/-	Х	Eler	nent	Atom (per cent)	+/-	X
0	0	60.00	8.45	0.5095	17	0	60.00	8.35	0.5535	34	0	60.00	6.88	0.6255
	Ti	10.19	1.62			Ti	11.07	1.45			Ti	12.51	1.33	
	Fe	29.81	2.69			Fe	28.93	2.36			Fe	27.49	1.92	
1	0	60.00	8.11	0.6465	18	0	60.00	7.35	0.5865	35	0	60.00	8.18	0.6185
	Ti	12.93	1.32			Ti	11.73	1.00			Ti	12.37	1.48	
	Fe	27.07	2.71			Fe	28.27	2.00			Fe	27.63	1.51	
2	0	60.00	7.61	0.4170	19	0	60.00	7.76	0.5624	36	0	60.00	9.56	0.6710
	Ti	8.34	1.27			Ti	11.25	1.10			Ti	13.42	1.42	
	Fe	31.66	3.02			Fe	28.76	2.38			Fe	26.58	1.52	
3	0	60.00	8.70	0.6850	20	0	60.00	8.15	0.5745	37	0	60.00	8.35	0.6216
	Ti	13.70	1.83			Ti	11.49	1.10			Ti	12.41	1.37	
	Fe	26.30	2.07			Fe	28.51	2.12			Fe	27.59	1.91	
4	0	60.00	6.45	0.6415	21	0	60.00	6.19	0.6625	38	0	60.00	8.05	0.6080
	Ti	12.83	1.78			Ti	13.25	1.48			Ti	12.16	1.28	
	Fe	27.17	2.44			Fe	26.75	2.11			Fe	27.84	1.44	
5	0	60.00	9.68	0.6160	22	0	60.00	8.57	0.6005	39	0	60.00	6.87	0.5680
	Ti	12.32	1.78			Ti	12.01	1.48			Ti	11.36	1.10	
	Fe	27.68	1.99			Fe	27.99	2.14			Fe	28.64	2.19	
6	0	60.00	8.70	0.6080	23	0	60.00	7.20	0.5140	40	0	60.00	6.60	0.6055
	Ti	12.16	1.74			Ti	10.28	1.05			Ti	12.11	1.00	
	Fe	27.84	2.48			Fe	29.72	2.10			Fe	27.89	2.07	
7	0	60.00	9.37	0.5105	24	0	60.00	6.17	0.5926	41	0	60.00	6.23	0.5589
	Ti	10.21	1.23			Ti	11.85	1.07			Ti	11.18	1.23	
	Fe	29.79	2.60			Fe	28.14	2.15			Fe	28.83	2.03	
8	0	60.00	6.52	0.6092	25	0	60.00	7.59	0.5775	42	0	60.00	6.80	0.6295
	Ti	12.18	1.86			Ti	11.55	1.10			Ti	12.59	1.31	
	Fe	27.81	2.71			Fe	28.45	2.19			Fe	27.41	1.92	
9	0	60.00	8.00	0.6585	26	0	60.00	6.80	0.6750	43	0	60.00	7.50	0.5870
	Ti	13.17	1.22			Ti	13.50	1.42			Ti	11.74	1.33	
	Fe	26.83	1.96			Fe	26.50	1.54			Fe	28.26	1.92	
10	0	60.00	8.57	0.6480	27	0	60.00	7.59	0.5625	44	0	60.00	6.82	0.6030
	Ti	12.96	1.81			Ti	11.25	1.29			Ti	12.06	1.39	
	Fe	27.04	1.78			Fe	28.75	2.00			Fe	27.94	1.94	
11	0	60.00	5.84	0.5746	28	0	60.00	6.73	0.5300	45	0	60.00	7.20	0.5420
	Ti	11.49	1.70			Ti	10.60	1.04			Ti	10.84	1.25	
	Fe	28.50	2.48			Fe	29.40	2.22			Fe	29.16	1.95	
12	0	60.00	11.32	0.6675	29	0	60.00	13.47	0.5969	46	0	60.00	6.95	0.6140
	Ti	13.35	1.71			Ti	11.94	1.46			Ti	12.28	1.27	
	Fe	26.65	2.59			Fe	28.07	1.97			Fe	27.72	1.88	
13	0	60.00	9.30	0.5120	30	0	60.00	8.82	0.6225	47	0	60.00	7.67	0.5051
	Ti	10.24	1.23			Ti	12.45	1.10			Ti	10.10	1.07	
	Fe	29.76	2.00			Fe	27.55	2.12			Fe	29.89	1.63	
14	0	60.00	8.35	0.5821	31	0	60.00	9.71	0.6117	48	0	60.00	7.41	0.5500
	Ti	11.64	1.51			Ti	12.23	1.03			Ti	11.00	1.27	
	Fe	28.35	2.10			Fe	27.76	1.57			Fe	29.00	1.93	
15	0	60.00	6.35	0.6167	32	0	60.00	8.15	0.6335	49	0	60.00	7.23	0.6430
	Ti	12.33	1.16			Ti	12.71	1.35			Ti	12.86	1.38	
	Fe	27.66	2.33			Fe	27.29	1.51			Fe	27.14	1.92	
16	0	60.00	6.98	0.5790	33	0	60.00	7.76	0.6255					
	Ti	11.58	1.58			Ti	12.52	1.30						
	Fe	28.42	2.20			Fe	27.48	2.02						

Table 1B. TEM-EDX analyses of sample Ilm 61–1055 in traverse 16. X = 2Ti /(Ti+Fe).

Elen	nent	Atom (per cent)	+/-	Х	Eleı	nent	Atom (per cent)	+/-	Х	Eler	nent	Atom (per cent)	+/-	X
0	0	60.00	7.41	0.6555	17	0	60.00	6.14	0.6140	34	0	60.00	7.22	0.5930
	Ti	13.11	1.64			Ti	12.28	0.95			Ti	11.86	1.13	
	Fe	26.89	2.25			Fe	27.72	1.83			Fe	28.14	1.70	
1	0	60.00	7.67	0.6135	18	0	60.00	5.78	0.5760	35	0	60.00	6.67	0.5120
	Ti	12.27	1.12			Ti	11.52	0.89			Ti	10.24	1.10	
	Fe	27.73	2.48			Fe	28.48	1.82			Fe	29.76	1.66	
2	0	60.00	6.73	0.5575	19	0	60.00	5.45	0.6010	36	0	60.00	5.86	0.5995
	Ti	11.15	1.68			Ti	12.02	1.25			Ti	11.99	0.80	
	Fe	28.85	2.65			Fe	27.98	1.71			Fe	28.01	1.65	
3	0	60.00	7.17	0.6960	20	0	60.00	5.00	0.5990	37	0	60.00	5.49	0.6235
	Ti	13.92	1.29			Ti	11.98	0.90			Ti	12.47	1.11	
	Fe	26.08	2.32			Fe	28.02	1.67			Fe	27.53	1.60	
4	0	60.00	9.04	0.5520	21	0	60.00	5.83	0.6110	38	0	60.00	5.34	0.6425
	Ti	11.04	1.79			Ti	12.22	0.91			Ti	12.85	1.11	
	Fe	28.96	2.54			Fe	27.78	1.74			Fe	27.15	1.59	
5	0	60.00	7.86	0.5625	22	0	60.00	7.00	0.5475	39	0	60.00	7.09	0.5940
	Ti	11.25	1.18			Ti	10.95	0.84			Ti	11.88	1.14	
	Fe	28.75	2.30			Fe	29.05	1.76			Fe	28.12	1.59	
6	0	60.00	6.99	0.5394	23	0	60.00	5.79	0.5865	40	0	60.00	5.71	0.6247
	Ti	10.79	1.34			Ti	11.73	1.08			Ti	12.49	1.05	
	Fe	29.22	2.32			Fe	28.27	1.62			Fe	27.50	1.59	
7	0	60.00	6.86	0.6030	24	0	60.00	6.19	0.5725	41	0	60.00	7.50	0.5700
	Ti	12.06	1.17			Ti	11.45	0.82			Ti	11.40	1.10	
	Fe	27.94	1.76			Fe	28.55	1.67			Fe	28.60	1.68	
8	0	60.00	7.13	0.6140	25	0	60.00	5.28	0.6265	42	0	60.00	5.31	0.5945
	Ti	12.28	1.36			Ti	12.53	1.23			Ti	11.89	1.11	
•	Fe	27.72	2.16		•	Fe	27.47	1.59	0.0000		Fe	28.11	1.59	
9	U T	60.00	6.05	0.5970	26	0	60.00	6.22	0.6030	43	0	60.00	5.68	0.6253
	11	11.94	1.43			11	12.06	1.02			11	12.51	0.84	
10	Fe	28.06	2.08	0 (140	27	Fe	27.94	1.51	0 ( 120		Fe	27.50	1.60	0 (170
10	U T	60.00	6.26	0.6140	27	0	60.00	5.53	0.6420	44	0	60.00	5.69	0.6158
	11 E	12.28	1.13			11	12.84	1.13			11	12.32	1.25	
11	Fe	27.72	2.18	0 (025	20	Fe	27.16	1.60	0.5245	45	Fe	27.69	1.36	0.5064
11	U T.	60.00	6.32	0.6035	28	0	60.00	4.94	0.5345	45	0	60.00	8.84	0.5864
	11 E-	12.07	1.43			11 E-	10.69	0.79			11 E-	11./3	0.79	
10	re	27.93	2.06	0.5090	20	re	29.31	1.08	0 5770	10	re	28.28	1.08	0 (195
12	U Ti	00.00	0.72	0.5080	29	U Ti	60.00	0.24	0.5770	40	U Ti	60.00 12.27	7.09	0.0185
	II Ea	10.10	0.90			II Ea	28.46	0.85			II Ea	12.57	1.05	
12	ге	29.84	2.03	0 5 9 7 5	20	ге	28.40	1.08	0.6050	47	ге	27.03	6.22	0.6100
15	ті	11.75	1.05	0.5675	30	т	12.10	1.14	0.0050		т	12 20	1 11	0.0100
	TI Fe	28.25	2.03			Ee	27.90	1.14			Fe	27.80	1.11	
14	0	60.00	6.45	0.6600	31	0	60.00	5.20	0 5694	48	0	60.00	6.34	0.6120
14	т	13 20	1.40	0.0000	51	т	11 30	1.00	0.5074	40	т	12.24	1.01	0.0120
	Fe	26.80	1.40			Fe	28.62	1.09			Fe	27.76	1.01	
15	0	60.00	5 02	0.6310	37	0	60.00	6.24	0 5856	<u>40</u>	0	60.00	8 08	0.6165
15	Ti	12.62	0.92	0.0310	34	Ti	11 71	1 12	0.5650	77	Ті	12 33	1 10	0.0103
	Fe	27 38	1.89			Fe	28.28	1.12			Fe	27.67	1.10	
16	0	60.00	634	0 5745	33	0	60.00	6.00	0 5515		10	27.07	1.02	
10	Ti	11 49	1 20	0.5745	55	Ti	11.03	1 11	0.5515					
	Fe	28 51	1.20			Fe	28.97	1 59						
	10	20.31	1.07			10	20.77	1.57						

regions in Fig. 3(c). The minimum analytical spot size was 1.2 nm when in perfect focus, but locally slightly larger when in defocused locations, resulting in no overlap of the analysis spots. The spot size compares to a repeat distance of 1.39 nm for a six-atomic-layer unit cell along the *c*-axis.

The dark field TEM image (Fig. 3d), combined with the relative intensities of the  $00-\overline{6}$  ordered and disordered diffraction spots (Fig. 3d), suggest that the sample consists of a minority of the ordered phase and majority of the disordered phase. A quantitative traverse measuring pixel brightness across the bulk of the 006 peaks provided a list of intensities and distances. This yielded peak intensities of 197 and 219 for the ordered and disordered peaks, respectively, thus an ordered fraction 0.474. The same data can be used to measure the relative areas between the two Gaussian curves and yields the ordered fraction 0.458. Fig. 3(c), when viewed closely, shows a ragged and irregular distribution of light spots slightly elongated in a direction parallel to the (001) basal plane.

EDX spectra were quantified according to the procedure of van Cappellen & Doukhan (1994). The method corrects for X-ray absorption on the basis of the principle of electroneutrality and requires the quantification of oxygen. The experimental k-factors of

Table 1C. TEM-EDX analyses of sample Ilm 61–1055 in traverse 19. X = 2Ti/(Ti+Fe).

Eleı	nent	Atom (per cent)	+/-	Х	Ele	ment	Atom (per cent)	+/-	Х	Eler	nent	Atom (per cent)	+/-	X
0	0	60.00	6.77	0.6470	17	0	60.00	5.53	0.5695	34	0	60.00	6.55	0.6338
	Ti	12.94	1.43			Ti	11.39	1.30			Ti	12.68	1.15	
	Fe	27.06	1.93			Fe	28.61	2.00			Fe	27.33	1.70	
1	0	60.00	7.37	0.4955	18	0	60.00	6.45	0.5924	35	0	60.00	7.09	0.6585
	Ti	9.91	0.95			Ti	11.85	0.93			Ti	13.17	1.16	
	Fe	30.09	2.12			Fe	28.16	1.78			Fe	26.83	1.26	
2	0	60.00	6.50	0.5725	19	0	60.00	5.38	0.6325	36	0	60.00	6.72	0.5760
	Ti	11.45	1.05			Ti	12.65	1.26			Ti	11.52	1.13	
	Fe	28.55	2.25			Fe	27.35	1.82			Fe	28.48	1.66	
3	0	60.00	6.13	0,6253	20	0	60.00	5.00	0.6408	37	0	60.00	5.34	0.6450
	Ti	12.51	1.40			Ti	12.82	1.23			Ti	12.90	1.04	
	Fe	27.50	1.95			Fe	27.19	1.77			Fe	27.10	1.58	
4	0	60.00	6.67	0.5755	21	0	60.00	7.65	0.6425	38	0	60.00	5.53	0.5820
	Ti	11.51	0.97			Ti	12.85	1.30			Ti	11.64	1.05	
	Fe	28.49	2.00			Fe	27.15	1.90			Fe	28.36	1.63	
5	0	60.00	7.09	0.5625	22	0	60.00	6.84	0.5910	39	0	60.00	6.39	0.5640
	Ti	11.94	1.37			Ti	11.82	1.22			Ti	11.28	1.00	
	Fe	28.05	1.98			Fe	28.18	1.84			Fe	28.72	1.65	
6	0	60.00	5.03	0.6110	23	0	60.00	6.78	0.6088	40	0	60.00	6.78	0.5745
	Ti	12.22	1.39			Ti	12.18	1.18			Ti	11.49	0.96	
_	Fe	27.78	2.12			Fe	27.83	1.72			Fe	28.51	1.57	
7	0	60.00	6.09	0.5785	24	0	60.00	9.40	0.6280	41	0	60.00	6.00	0.5636
	Ti	11.57	1.28			Ti	12.56	1.23			Ti	11.27	1.09	
	Fe	28.43	1.98			Fe	27.44	1.80			Fe	28.72	1.58	
8	0	60.00	5.06	0.5850	25	O T	60.00	5.82	0.5701	42	0	60.00	6.05	0.5335
	11	11.70	1.32			11	11.40	1.16			11	10.67	0.77	
~	Fe	28.30	1.97			Fe	28.59	1.84			Fe	29.33	1.59	
9	0	60.00	5.75	0.6668	26	O T	60.00	6.19	0.5675	43	0	60.00	6.19	0.5089
	11	13.34	1.02			11	11.35	1.22			11	10.18	1.01	
10	Fe	26.67	1.90	0 7010	~=	Fe	28.65	1.90	0.5055		Fe	29.83	1.61	0 570 5
10	0	60.00	6.04	0./010	27	U T	60.00	6.24	0.5255	44	0	60.00	/./4	0.5725
	11 E	14.02	1.40			11 E	10.51	0.85			11 E	11.45	0.81	
11	Fe	25.98	1.50	0 5955	20	re	29.49	1.79	0 ( ( 95	45	re	28.55	1.04	0 (595
11	0	60.00	5.60	0.5855	28	U T	60.00	5.69	0.6685	45	U T.	60.00	6.29	0.6585
	11 E-	11./1	1.41			11 E-	13.37	1.22			11 E-	13.17	1.12	
10	ге	28.29	2.01	0.5000	20	ге	20.03	1.70	0 (045	10	ге	20.85	1.05	0.5910
12	U Ti	11.70	3.04 1.27	0.3890	29	U Ti	12.00	0.29	0.0045	40	т	00.00	0.79	0.3810
	Fo	28.20	1.27			Fo	12.09	1.15			TI Ea	28.28	0.62	
13	0	28.20	5.27	0.6105	20	re O	60.00	6.20	0.6085	47	re O	20.30	6.45	0 6645
15	т	12 21	0.05	0.0105	50	Ti	12.17	1.21	0.0085		т	13 20	0.45	0.0045
	Ee	27.79	1.82			Fe	27.83	1.21			Fe	26.71	1.50	
14	0	60.00	5.40	0.6105	21	0	60.00	5 35	0 5614	18	0	20.71	5.58	0.6513
14	т	12 21	1 30	0.0105	51	Ti	11 23	1 13	0.5014	40	т	13.03	1.03	0.0515
	Fe	27 79	1.50			Fe	28 78	1.15			Fe	26.98	1.05	
15	0	60.00	8.86	0 5070	27	0	60.00	6.45	0.6600	<u>40</u>	0	60.00	6.86	0.6589
15	Ti	11.96	1 34	0.3717	54	Ti	13 20	1 13	0.0000	77	Ti	13.18	1 08	0.0500
	Fe	28.05	2.02			Fe	26.80	1.15			Fe	26.83	1.00	
16	0	60.00	6.18	0 6275	33	0	60.00	5.65	0 5811		10	20.05	1.21	
10	Ti	12.55	1.35	0.0275	55	Ti	11.62	0.82	0.0011					
	Fe	27.45	2.12			Fe	28.37	1.62						

titanium, iron and oxygen were calibrated using the bulk composition of the synthetic IIm 61–1055 sample and a natural garnet having a known chemical composition, by using the parameter-less correction method (van Cappellen 1990). Compositions and their errors in the traverses were then calculated as mole fraction FeTiO<sub>3</sub> (X IIm = 2Ti/[Ti + Fe]) directly from the ratio Ti/Fe (Table 2). These compositions are plotted versus distance in Fig. 5 for traverse 19. A cumulative curve of all composition measurements is shown

**Table 2.** Distribution of analytical error expressed as  $\pm X$  FeTiO<sub>3</sub>.

Error Class	Traverse 19 (per cent)	Traverse 16 (per cent)	Traverse 13 (per cent)	All 150 analyses (per cent)
< 0.0125	56	76	14	48.7
0.0125 to 0.015	44	14	58	38.7
0.015 to 0.018	0	10	28	12.7



Figure 5. Composition profile of the 50 TEM-EDX analyses for traverse 19, which is typical also of traverses 13 and 16, all taken at the left-hand feather edge of the sample in Fig. 3(c). Vertical extent of grey shading indicates +/- errors for each analysis point, which are all <0.015 for this traverse, and over half are <0.0125.



Figure 6. Cumulative curve showing all 150 TEM-EDX analyses for combined data of traverses 13, 16 and 19. Vertical extent of grey shading indicates +/- errors for each analysis point. 48 per cent of points show error <0.0125, 39 per cent from 0.0125 to 0.015, and 13 per cent from 0.015 to 0.018. See text for significance of dashed lines.

in Fig. 6. The corresponding frequency histogram is shown in Fig. 7 using a sliding window of width of 0.02 ( $\pm 0.01$ ).

In Fig. 6 marked changes in composition abundance are indicated by dashed lines. A small number of points (15.3 per cent) form a steep straight progression at low X < 0.56, with two minor shelves at 0.51 and 0.55. The bulk of analyses (66 per cent) lie between X = 0.56 and X = 0.64. Above lies another steep progression to X = 0.70 (18.7 per cent). The frequency histogram in Fig. 7 shows a strong central high with half maxima at X = 0.563 and X = 0.63, three slight internal peaks at X = 0.578, 0.608 and 0.616, a two shoulders between X = 0.51-0.56 and X = 0.63-0.68.

The ragged profile in Fig. 5 mirrors the ragged distribution of ordered patches in the dark field image of Fig. 3(c), suggesting that composition may be related to Fe-Ti order. Theoretically, the Fe-Ti ordered phases should be enriched in Ti and have larger X. However, we cannot verify this relation, because we cannot directly tie each chemical analysis spot to a lighter or darker area in Fig. 3(c).



Figure 7. Frequency distribution curve for all 150 TEM-EDX analyses from combined data of traverses 13, 16 and 19. Each point is located at a single analysis composition, and the associated number is a count of all analyses that fall within  $X = \pm 0.01$ . See text for significance of dashed lines and heavy lines.

Another feature of Fig. 5 is that commonly very low and very high analyses occur in the same vicinity. This would be expected if there were an initial chemical phase separation into Ti- and Fe-rich phases, and then, during the final stage of cooling, there had been further two-way diffusion across the phase boundaries, producing Ti-richer rims on the Ti-richer phase and Fe-richer rims on the Fericher phase. Because the analytical spots were smaller than the traverse interval distance, such mutual boundary diffusion cannot be proven with the present data.

# 4.3 Thermal magnetic experiments and chemical interpretation

Thermal magnetic experiments were carried out to learn more about phase compositions of the FM ordered phases, and the either AF or canted antiferromagnetic (CAF) disordered phases. Using a Vibrating Sample Magnetometer (VSM, Princeton Measurements Corp., Princeton, NJ), saturation magnetization  $M_s$  and saturation remanence  $M_{\rm rs}$  were determined as a function of temperature (Fig. 8). Both quantities are inferred from partial hysteresis loops, measured in steps of 20 mT from 0 T to 1 T during heating from RT  $\sim$  300 K up to 800 K in steps of 4 K (300-800 K) or 1 K (450-500 K). M<sub>s</sub> at each temperature was estimated from the zero-field value of the linear fit to the measurements between 0.8 T and 1 T. Although in case of non-saturated hysteresis loops, this method considerably underestimates the accurate value of  $M_s$  (Fabian 2006), it provides a more accurate determination of  $T_{\rm C}$  than the classical method using induced magnetization. The critical point of the  $M_s$ -curve shows that no magnetic ordering is present above 492  $\pm$ 5 K. By comparison to reference  $T_{\rm C}$  data (Burton et al. 2008), this excludes the presence of significant amounts of phases with lower ilmenite content than X = 0.56. The presence of phases richer in ilmenite, with lower ordering temperature, is not excluded by this observation. In fact, the structure of the  $M_{\rm rs}$  curve in Fig. 8 indicates the presence of phases of different magnetic structure and different composition. The onset of remanent magnetization occurs at  $480 \pm 5$  K, clearly below the  $M_s$  increase. A steep rise in remanence continues down to  $\sim$  455  $\pm$  5 K. The phases ordering at these two temperatures are



**Figure 8.** Thermomagnetic measurements of  $M_s$  and  $M_{rs}$  for Ilm61–1055 from two separate, partly overlapping, runs.  $M_s$  shows a transition temperature at about 490 K, whereas remanence sets in at about 480 K. Moreover,  $M_{rs}$  shows a prominent change of slope at about 450 K. Using observed values of  $T_C$  and theoretical values for  $T_N$  for the haematite-ilmenite solid solution, these temperatures can be related to different ilmenite contents varying between X = 0.56 and 0.64.

the compositions X = 0.61 and X = 0.64 based on the FM to PM transition given in Burton *et al.* (2008).

For interpreting the Néel temperature  $(T_N)$  of the Fe-Ti disordered phase, the curve of saturation magnetization,  $M_s$ , appears to



**Figure 9.** Hysteresis loops at 300 K for Ilm 61.8, annealed at 685 °C, and for Ilm61–1055 using a magnetic intensity scale in  $\mu_B$  projected from 0 to 300 K using a magnetic mean-field model. The magnetic moment per formula unit (pfu) at 0 K is directly proportional, for a given composition, to the Fe-Ti order parameter *Q*. For X = 0.60 and Q = 1, the magnetic intensity is 2.4  $\mu_B$ , which projects to 1.33  $\mu_B$  at 300 K (upper right-hand side). The nearly saturated magnetization of 0.85  $\mu_B$  at 300 K of the annealed 685 °C sample corresponds very closely to the projected value for Q = 0.64 determined at 697 °C in neutron diffraction experiments by Harrison & Redfern (2001). The loop for the quenched 1055 °C sample is far from saturated at 1.3 T, but data at 100 K (Fig. 1), where saturation is nearly achieved at 7 T, projected onto the same intensity scale, gives 0.7  $\mu_B$  that is equivalent at 0 K to a *Q* value of 0.54.

be the pertinent one. Here the calibration curve is somewhat less reliable, but is usually taken as a nearly straight line between endmember haematite and end-member ilmenite, and thus at slightly lower temperature than the  $T_{\rm C}$  curve for the ordered phase in this range. In the curve of  $M_{\rm s}$  versus temperature (Fig. 8), the first visible onset of a possible field-induced spin-canted magnetization occurs at ~492 K, and there is no obvious low-temperature limit to this process. This temperature corresponds approximately to a composition X = 0.56.

When viewed in conjunction with Figs 6 and 7, the composition X = 0.61 falls above the middle of abundant compositions, but actually close to the absolute peak of the frequency curve of Fig. 7. The composition X = 0.64 falls above the half-maximum in Fig. 7. The composition X = 0.56 falls almost exactly at the low edge (half maximum) of the abundant compositions in Fig. 7.

These results indicate that compositions with a well developed FM structure are unlikely to extend in any abundance below X = 0.61, and the bulk of the ferrimagnetism is achieved with magnetization of compositions between X = 0.61 and 0.64, probably with minor additions from more Ti-rich compositions. The results also indicate that the abundant compositions X = 0.56–0.61 are predominantly AF, and this conclusion likely extends to compositions below X = 0.56. What is not yet safe to conclude is whether the AF structures also include some of the compositions above X = 0.61.

If we take X = 0.605 crudely as the boundary between disordered AF and ordered FM, then we can use the analyses in Figs 6 and 7 to estimate percentages of each: the AF part of central peak X = 0.563-0.60 contains 53 of 150 analyses or 35.3 per cent; the low Ti fringe X = 0.42-0.563 contains 28 of 150 or 18.7 per cent, making a total 54 per cent AF material. The FM part of central peak X = 0.605-0.628 has 38 analyses (25.3 per cent), the high-Ti fringe X = 0.628-0.70 has 31 (20.7 per cent) with a total of 46 per cent FM material. This estimate is similar to the two ratios of 0.474 and 0.458 from the estimated relative intensities of the 006 TEM diffraction spots for the ordered and disordered phases.

# 4.4 Saturation magnetization of quenched and ordered samples

The neutron diffraction experiments on X = 0.60 and 0.65 of Harrison & Redfern (2001) show that at elevated temperature these solid solutions are only partially ordered. Above 600 °C, their Q values decrease with temperature, and apparently represent the equilibrium degree of order. Our sample Ilm61.8, annealed for 39 months at 685 °C, was quenched from close to the 697 °C of one of the neutron measurements of Harrison & Redfern (2001) which gave partial order of Q = 0.64 for X = 0.60.

The theoretical FM moment per formula unit of a ferri-ilmenite with mean composition X and order parameter Q at 0 K is

$$\mu(X,Q) = 4XQ\mu_{\rm B}.$$

The corresponding saturation magnetization at 0 K is

$$M_{\rm s}(X,Q) = \mu(X,Q)Z/V(X,Q) = 4\mu_{\rm B}XQZ/V(X,Q),$$

where V(X,Q) is the volume of the unit cell and Z = 6 the number of formula units per unit cell. To compare this 0 K value to our hysteresis curves at positive temperature, we use a theoretical  $M_s(T)$ -curve for Q = 1 and X = 0.6 from a mean field model, which predicts the correct Curie temperature for this composition. Thereby, a saturated magnetic moment measured at any positive temperature can be extrapolated to the corresponding  $M_{\rm S,0}^{\rm meas}$  at 0 K. The ratio  $M_{\rm S,0}^{\rm meas}/$  $M_{\rm s}(X=0.6, Q=1)$  then gives an estimate for the bulk Q value of the sample. These relationships are shown in Fig. 9, where the vertical scale is in Bohr magnetons. All values are extrapolated from 0 K to the 300 K conditions of hysteresis experiments. The nearly saturated magnetization of the annealed sample in Fig. 9 at 0.85  $\mu_{\rm B}$  agrees well with the extrapolated saturated magnetization based on the above Harrison & Redfern (2001) value of Q = 0.64. A similar loop on the Ilm61-1055 quenched sample does not saturate within 1.3 T. However, a nearly saturated 7 T hysteresis loop at 100 K of Ilm61–1055 yields a magnetic Q value ( $Q_m$ ) of 0.54,

which in Fig. 9 determines the extrapolated  $M_s$  at 300 K, which is almost three times larger than the induced magnetization in 1.3 T.

The magnetically inferred  $Q_m$  does not represent the Q of the ordered part of Ilm61–1055, but a mean order of the entire sample. The fact that all Q values of 0.400, 0.387 and 0.447 obtained by Harrison & Redfern (2001) on their quenched X = 0.60 sample at temperatures 203°C, 298°C and 399°C, respectively, are lower, could result from different thermal histories during quench compared to our sample.

Although the saturation magnetization is the same in all samples with the same X and Q values, the fields required to reach saturation may depend considerably on sample texture. There also could be a constant slope at high fields due to field-induced spin-canting. However, estimating this effect from high-field loops in the basal plane of a pure haematite crystal (Fabian *et al.* 2011) gives a slope of 0.0071  $\mu_{\rm B}$  / T per haematite formula unit at 300 K. To estimate canting for X = 0.60, high-field slope measurements of Ilm61.8 at different temperatures between 100 K and 290 K were extrapolated to 0 K by dividing them by an almost linear variation of  $M_{\rm s}(T)$  in this temperature range. This yields an almost constant slope of 0.007  $\pm$  0.003  $\mu_{\rm B}$  / T at 0 K, while a paramagnet would show a higher slope at low temperatures. In any case, this effect is of negligible size and field-induced spin-canting, though present, is of little significance for explaining insufficient saturation in Ilm61–1055.

The predominant influence is the abundance of magnetically coupled boundaries between ordered and disordered phases as well as chemical APB developed in the quench microstructure. The strong AF coupling across these boundaries prevents adjacent A- and B-ordered domains from acquiring parallel magnetizations except in very high fields. The annealed sample with calculated  $Q_m \approx 0.64$  and large ordered domains nearly saturates at 1.3 T at 300 K, while the quenched sample with a calculated  $Q_m$  of 0.54, and small ordered domains is far from saturation even at 7 T at 100 K. Here the remaining high-field slope at 7 T still by far exceeds the slope estimated for field-induced spin-canting.

# 4.5 Mean Q values versus volume fractions of ordered and disordered phases

Only bulk Q values are measured by neutron diffraction, or determined from saturation magnetization  $(Q_m)$ , while the TEM images of Ilm61–1055 show mainly an Fe-Ti disordered matrix, with subordinate Fe-Ti ordered regions. To clarify the relation between structure and Q we denote the volume fraction of ordered phase as Y, thus 1 - Y is the volume fraction of disordered phase. It is then possible to distinguish the value  $Q_o$  of the ordered phase from the value  $Q_d$  for the disordered phase. In the simplest case  $Q_o = 1$  and  $Q_d = 0$ , but in quenched samples equilibrium disorder can exist in the ordered phase making  $Q_o < 1$ , and if the quench is not perfect, incipient order might be found in the matrix, leading to  $Q_d > 0$ . Unfortunately, both quantities are not directly measurable, but because the bulk value is  $Q = Q_o Y + Q_d (1 - Y)$ , one has the

relation

 $Y = (Q - Q_{\rm d})/(Q_{\rm o} - Q_{\rm d}).$ 

For Ilm61–1055 the relative TEM spot intensities suggest Y = 0.474 and Y = 0.458, while combined results of TEM-EDX analyses and thermal magnetic experiments suggest Y = 0.46.

The first three examples in Table 3 rely on Q values given by, or estimated from Harrison & Redfern (2001). The third example allows a small degree of order in the disordered phase. The last two examples use  $Q_m = 0.54$  based on the magnetic saturation experiment in Fig. 9. To obtain Y = 0.46-0.47 from  $Q_m = 0.54$  and  $Q_d = 0$ , would require  $Q_o > 1$ , which is obviously impossible, so a small degree of order must be introduced into the disordered matrix. Possibly  $Q_d$  also contains an effect of contact layers along phase boundaries.

#### 4.6 Low-temperature magnetic phenomena in Ilm 61-1055

The RT hysteresis loop of Ilm 61–1055 in Fig. 1 is symmetric because it originated from zero-field cooling, but also later cooling in 1 T, or 1 mT fields from 400 °C (above  $T_{\rm C}$ ) produced no magnetic exchange bias, and also no magnetic self-reversal in the untreated sample. The loop is a superposition of a very highly coercive fraction attributed to the disordered phase, and an almost reversible high-field fraction attributed to the induced rotation of the ordered FM phase.

On the other hand, the sample does exhibit striking negative magnetic exchange bias after field cooling (in 5 T) from RT down to 5 K and subsequent warming up to 20 K (Fig. 2). At 30 K and above, the hysteresis curves are again symmetric. A temperature of 25 K has been reported as the onset of spin-glass behaviour in the ordered Ilm 61.8 sample by Burton *et al.* (2008). This has been ascribed (Robinson *et al.* 2010) to local pockets of Ti-rich composition acquiring a very hard double-layer magnetization component parallel to the *c*-axis at very low temperature, which is incompatible with the adjacent-layer magnetization of the enclosing ferrimagnetically ordered ilmenite, thus creating significant magnetic frustration.

In a classical spin-glass interpretation, such hard frustrated moments could acquire a TRM by cooling in a strong positive field, which adds to the ferrimagnetically ordered phase and delays movement to a negative magnetization when a negative field is applied, thus creating an apparent negative exchange bias similar to that observed in Fig. 2. However, this mechanism leads to an overall upward shift of the loop, which is not observed. Based on our previous independent observations of the ordered phase, we considered that spin-glass based exchange bias is at best a minor effect in the disordered phase.

Instead, we favour an interpretation similar to lamellar exchange bias (McEnroe *et al.* 2007) in which the magnetic domains expected in these intergrowths in a 5 T field would be strongly pinned below 25 K so that the rotation of the moments of the FM regions require formation of new domain walls, making the inversely magnetized

**Table 3.** Q values and volume fractions (Y) of ordered and (1–Y) disordered phases. Q values estimated from Harrison & Redfern 2001, Ilm 60, Table 3 or Fig. 7(a), unless otherwise indicated.

	$Q$ or $Q_{\rm m}$	Table 3	$Q_0$	Fig.7(a)	$Q_{\rm d}$	Note	$Y_{\text{calc}}$	TEM Est Y
1	0.45	399°C	0.70	Relaxed	0		0.643	0.474, 0.458
2	0.39	298 °C	0.85	More relaxed	0		0.459	0.474, 0.458
3	0.39	298 °C	0.70	Relaxed	0.10	Small order	0.483	0.474, 0.458
4	0.54	This paper	0.85	More relaxed	0.28	More order	0.456	0.474, 0.458
5	0.54	This paper	0.90	More relaxed	0.22	More order	0.471	0.474, 0.458

state energetically unfavourable (Shcherbakov *et al.* 2009). This behaviour is an obvious subject for future investigation.

# 4.7 Self-reversal and exchange bias induced by annealing ilmenite 61 sample

A piece of Ilm61–1055 was heated and annealed at 1063 K (790 °C) for  $\sim$ 5 min. This temperature is just below the disorder–order transition and growth or coarsening of the ordered A and B regions should take place. This short annealing led to a twofold increase of the induced moment in 1 T, which we interpret as a result of increased ordering of the initially quenched sample (see later). The sample was then used to identify and quantify the occurrence of self-reversed thermoremanent magnetization and the temperature range over which it is acquired.

10 full-temperature sweeps from 723 K ( $450 \,^{\circ}$ C) down to RT were made, each represented by a single point in Fig. 10. In all experimental runs, we found no indication for chemical changes below 723 K, however they cannot be fully ruled out on the basis of the neutron diffractions experiments (Harrison & Redfern 2001) which show a slight increase in ordering with slow cooling down to 673 K ( $400 \,^{\circ}$ C).

The initial external field for each full-temperature sweep was -1 mT at 723 K. During the run, the field was then switched to +1 mT at different switching temperatures ( $T_S$ ) for the remaining cooling sweep. At RT the field was switched off, and then remanence m was measured. By this procedure the sample crosses the magnetic self-reversal temperature ( $T_{SR}$ ), either in a positive ( $T_S > T_{SR}$ ), or a negative ( $T_S < T_{SR}$ ) external field. If self-reversal occurs over a wide temperature range, different degrees of partial self-reversal would be recorded.

In Fig. 10, the final remanence *m* is plotted as a function of the switching temperature  $T_{\rm S}$ , and clearly marks the temperature  $T_{\rm SR}$ , and the temperature range where self-reversal takes place.

Therefore, the remanent moment  $m = -210 \text{ nAm}^2$  for  $T_S = 673 \text{ K}$ (400 °C) represents a self-reversed magnetization acquired during cooling from 673 K to RT in a positive field of 1mT, while the remanent moment  $m = +232 \text{ nAm}^2$  for  $T_s = 373 \text{ K} (100 \,^\circ\text{C})$  represents a self-reversed magnetization acquired during cooling from 723 K to 373 K in a negative field of -1 mT, possibly slightly enhanced by a remanence acquired below 373 K in +1 mT. Even though the concept of this plot is somewhat complex, its interpretation is simple. It shows that the acquisition of self-reversed remanence occurs only in a narrow temperature interval between 493 K and 443 K (220°C and 170°C), whereby at  $T_{\rm S} \sim 463$  K (190 °C) the self-reversed moment cancels the directly acquired thermoremanent moment. This very narrow temperature interval, where self-reversal occurs and is completely fixed, indicates a direct link between two antiferromagnetically coupled phases, one with weak Fe-Ti ordering, weak FM moment and higher  $T_N$ , and one phase with strong Fe-Ti ordering, strong FM moment and lower  $T_{\rm C}$ , as originally postulated by Uyeda (1958). This result also favours an exchange-coupling mechanism over a more gradual process like magnetostatic interaction.

RT hysteresis loops of the annealed Ilm 61-1055 sample are shown in Fig. 11. Each loop was measured after heating the sample to the indicated temperature for approximately 5 min inside the He flow of the VSM furnace. A field of +1 T was applied during heating and cooling. The figure shows the results of successive experiments on the same sample after heating to 500°C (773 K), 700°C (973 K), 750°C (1023 K) and 790 °C (1063 K). Available evidence from the results of Harrison & Redfern (2001) indicates that there would be minimal change in quench intergrowth structure at 500°C. At the higher temperatures, considerable expansion and coarsening of Fe-Ti ordered regions with reduction in area of APB is expected. This is particularly true at 790 °C (1063 K), which is not far below the Fe-Ti order-disorder transition at 830 °C (1103 K). In the range of experiments there is a progressive opening of the loop, particularly evident between the 700°C and 750°C annealed samples. Also the induced magnetic moment at 1 T more than doubles, with the largest



**Figure 10.** Self-reversal within a sample of IIm 61–1055, which was reheated to 1063 K (790 °C) for approximately 5 min. Each data point represents the room-temperature remanence after cooling the sample in a field of -1 mT from 723 K (450 °C) down to the switching temperature  $T_S$ , where the field was switched to +1 mT during the remaining cooling to RT. Note that negative remanence at  $T_S = 673$  K (400 °C) results from cooling in +1 mT between 673 K and RT, while positive remanence at  $T_S = 423$  K (150 °C) results from the established self-reversal between 493 K and 448 K (220 °C and 175 °C) in a -1 mT field and not from cooling in +1 mT between 423 K and RT.

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Figure 11. Room-temperature hysteresis loops of Ilm61–1055 after short progressive annealing at 500 °C, 700 °C, 750 °C and 790 °C. Vertical scale of magnetic moment in  $\mu$ Am<sup>2</sup> and horizontal scale in Tesla.

increase between 750°C and 790°C. This probably originates from an increase of Y or  $Q_0$ , or from both. Despite this, there is no significant decrease in coercivity, as can be seen by comparing the 790 °C annealed loop in Fig. 11 with the loop for Ilm61.8 in Fig. 1(A). An explanation for this is that chemical antiphase domain walls with AF interactions are still present in sufficient abundance to hinder magnetic saturation.

Fig. 12 shows details of the RT hysteresis loops after heating to 750°C (1023 K) and 790 °C (1063 K). The loops were measured between -1 T and 1 T, but only the interval from -300 mT to 300 mT is displayed together with the hysteresis differences in the lower panels. Hysteresis difference only shows true exchange bias, and is not influenced by an upward shift of the loops. The 750°C loop shows intercepts ( $H_c$ ) on the zero axis at +40.2 and -31.0 mT giving a shift of +8.8 mT in  $H_c$ . The 790 °C loop shows symmetrical intercepts, but the hysteresis difference plot shows a larger asymmetry, illustrating the difference between these two contrasting ways to report magnetic exchange bias. The apparent positive shift is in agreement with the loop shown by Meiklejohn & Carter (1959), where the shift by  $H_c$  difference is ~40 mT.

A consistent explanation of the above observations will be developed in the forthcoming companion papers. There we will provide theoretical evidence that both the magnetic self-reversal and the positive hysteresis shift occur in samples where a majority of larger Ti-enriched A- and B-ordered regions are mixed with a minority of smaller Fe-enriched A- and B-ordered regions, and where these regions are separated by chemical antiphase boundaries, across which there is AF interaction.

### **5** CONCLUSIONS

We studied a quenched IIm 61 composition experimentally, to understand the origin of the unusual magnetic properties of intermediate members of the haematite-ilmenite solid solution series, and as a basis for developing a comprehensive model in two forthcoming papers. The main conclusions of the experiments presented here are as follows:

1. Even though sample Ilm61–1055 appears homogenous in Xray diffraction, it has a complex hysteresis loop at RT and negative magnetic exchange bias at and below 20 K, implying interface exchange coupling between different phases.

2. Dark-field TEM images taken through the 003 reflection show a dominant disordered matrix phase with patches of Fe-Ti ordered phases. These patches are elongate parallel to (001) and have a maximum thickness of  $\sim$ 8 nm.

3. High-resolution TEM provided direct imaging of Fe- and Tirich layers in ordered regions that are in antiphase relationship.

4. Closely spaced traverses of TEM-EDX analyses across ordered patches in the disordered matrix, show a distribution of compositions. The dominant observed range is X = 0.56-0.63, with a fringe extending down to X = 0.51 and up to X = 0.70.

5. Thermomagnetic measurements of  $M_{\rm rs}(T)$  and  $M_s(T)$  suggest that the most abundant FM phases have compositions X = 0.64-0.61 and the dominant AF phases have X = 0.61-0.56.

6. Two methods of estimating relative intensities of the 006 TEM diffraction peaks of ordered and disordered phases suggest volume fractions (Y) of the ordered phase of 0.474 and 0.458. Combined results of TEM-EDX analyses and thermal magnetic experiments suggest a similar ratio 0.46.

7. To make magnetic estimates of the mean degree of ordering, we develop a method to extrapolate  $M_s$  measurements at positive temperature to T = 0 K. For sample IIm 61.8, annealed for 39 months at 685 °C, we obtain  $M_s(0 \text{ K}) = 150 \text{ k} \text{ A m}^{-1}$  consistent with an equilibrium value of Q = 0.64 from neutron experiments at 697 °C on a similar sample (Harrison & Redfern 2001). For the quenched IIm 61–1055 sample we estimate a magnetic value of  $Q_m > 0.54$ . However, we cannot differentiate between a lower value  $Q_o$  for the ordered regions and a higher value of  $Q_d$  for the disordered regions.

8. The original Ilm61–1055 sample shows no exchange bias at RT, and no evidence for self-reversed thermoremanent magnetization. Short annealing at 1063 K led to more ordering, increasing the 1T-induced moment by a factor of two at RT. The annealed sample then acquires self-reversed thermoremanence, which was studied with respect to the details of its acquisition process. This showed that normal thermoremanent magnetization of a minority Fe-enriched phase sets in at ~490 K, self-reversed thermoremanent magnetization begins to dominate at ~460 K and self-reversed thermoremanent magnetization begins to dominate at ~460 K.



**Figure 12.** Details of the room-temperature hysteresis loops after heating to 750 °C (1023 K) and 790 °C (1063 K). Vertical scale of magnetic moment in  $\mu$ Am<sup>2</sup>. The loops were measured between -1 T and 1 T, but only the interval from -300 mT to 300 mT is shown. The lower panels shows the hysteresis differences with a positive asymmetry in both loops.

9. Samples, progressively annealed briefly at 773, 973, 1023 and 1063 K followed by cooling in a field of 1T from  $T_{\rm C}$  to RT, showed positively shifted hysteresis loops for the 1023 and 1063 runs but not for the lower annealing temperatures.

10. The experimental results and TEM observations and measurements indicate a chemical evolution of local compositions and the disorder–order structure during quench from high temperature and subsequent annealing. The resulting textures strongly influence the magnetic behaviour after cooling to RT and below. A Monte Carlo model of Harrison *et al.* (2005) and Harrison (2006) describes such an evolution by coarsening during annealing, starting from an initial state similar to the structure observed in Ilm61–1055. A detailed comprehensive model for chemical evolution and for natural self-reversed thermoremanent magnetization and magnetic exchange bias, based on the results presented here, will be developed in the companion Papers II and III.

### ACKNOWLEDGMENTS

This research was supported by grant 189721 from the Research Council of Norway (Nanomat Program) in the EU Matera Program, and visiting fellowships to the Institute of Rock Magnetism, which is supported by an NSF Instruments and Facilities Grant. Major manuscript preparation took place while PR and SAM were resident at BGI, Bayreuth, where SAM held an EU Marie Curie Fellowship. The manuscript was greatly improved by comments and suggestions from Mark Dekkers, France Lagroix and Natalie Huls of NIST. To each of these persons and institutions we extend our grateful acknowledgment.

#### REFERENCES

- Arai, M., Ishikawa, Y. & Takei, H., 1985. A new oxide spin glass system of (1-x) FeTiO<sub>3</sub> – x Fe<sub>2</sub>O<sub>3</sub>. IV. Neutron scattering studies on a re-entrant spin glass of 79FeTiO3–21Fe2O3 single crystal, *J. Phys. Soc. Japan*, **54**, 2279–2286.
- Burton, B.P., 1985. Theoretical analysis of chemical and magnetic ordering in the system Fe<sub>2</sub>O<sub>3</sub>-FeTiO<sub>3</sub>, *Am. Mineral.*, **72**, 329–336.
- Burton, B.P., 1991. The interplay of chemical and magnetic ordering, in *Reviews in Mineralogy*, Vol. 25, pp. 301–321, ed. Lindsley, D. H., Min. Soc. America.
- Burton, B.P. & Davidson, P.M., 1988. Multicritical phase relations in minerals, in *Structural and Magnetic Phase Transitions in Minerals*, pp. 60–90, eds Ghose, S., Coey, J. M. D. & Salje, E. Springer-Verlag New York, NY.
- Burton, B.P., Robinson, P., McEnroe, S.A., Fabian, K. & Boffa Ballaran T., 2008. A low-temperature phase diagram for ilmenite-rich compositions in the system Fe<sub>2</sub>O<sub>3</sub>-FeTiO<sub>3</sub>, *Am. Mineral.*, **93**, 1260–1272.
- van Cappellen, E., 1990. The parameter less correction methods in X-ray microanalysis, *Microsc. Microanal. Microstruct.*, **1**, 1–22.
- van Cappellen, E. & Doukhan, J.C., 1994. Quantitative X-ray analysis of ionic compounds, *Ultramicroscopy*, 53, 343–349.
- Fabian, K., 2006. Approach to saturation analysis of hysteresis measurements in rock magnetism and evidence for stress dominated magnetic

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anisotropy in young mid-ocean ridge basalt, *Phys. Earth planet. Inter.*, **154**, 299–307.

- Fabian K., Robinson, P., McEnroe S.A., Heidelbach, F. & Hirt, A., 2011. Experimental study of the magnetic signature of basal-plane anisotropy in hematite, in *The Earth's Magnetic Interior*, IAGA Special Sopron Book Series Vol. 1, pp. 311–320, eds Petrovský, E. *et al.*, Springer, Dordrecht, doi:10.1007/978-94-007-0323-0\_22.
- Ghiorso, M.S. & Evans B.W., 2008. Thermodynamics of rhombohedral oxide solid solutions and a revision of the Fe-Ti two-oxide geothermometer and oxygenbarometer. *Am. J. Sci.*, **308**, 957–1039.
- Harrison, R.J., 2006. Microstructure and magnetism in the ilmenite-hematite solid solution: a Monte Carlo simulation study, *Am. Mineral.*, 91, 1006–1023.
- Harrison, R.J. & Redfern, S.A.T., 2001. Short- and long-range ordering in the ilmenite-hematite solid solution. *Phys. Chem. Minerals*, 28, 399– 412.
- Harrison, R.J., Redfern, S.A.T. & Smith, R. I., 2000. In situ study of the R3- to R3-c phase transition in the ilmenite-hematite solid solution. *Am. Mineral.*, 85, 1694–1705.
- Harrison, R.J., Kasama, T., White, T.A., Simpson, E.T. & Dunin-Borkowski, R.E., 2005. Origin of self-reversed thermoremanent magnetization, *Phys. Rev. Lett.*, **95**, 268501, doi:10.1103/PhysRevLett.95.268501.
- Hoffman, K.A., 1992. Self-reversal of thermoremanent magnetization in the ilmenite-hematite system: order-disorder, symmetry and spin alignment. *J. geophys. Res.*, 97, 10 883–10 895.
- Hoffman, V. & Fehr, K.Th., 1996. Micromagnetic, rockmagnetic and mineralogical studies on dacitic pumice from the Pinatubo eruption (1991, Philipines) showing self-reversed TRM. *Geophys. Res. Lett.*, 23, 2835–2838.
- Hojo H., Fujita, K., Mizoguchi, T., Hirao, K., Tanaka, I., Tanaka, K. & Ikuhara, Y., 2009. Magnetic properties of ilmenite-hematite solid-solution thin films: direct observation of antiphase boundaries and their correlation with magnetism. *Phys. Rev. B*, **80**, 075414–1 to 075414–5.
- Ishikawa, Y., 1958, An order-disorder phenomenon in the FeTiO<sub>3</sub>-Fe<sub>2</sub>O<sub>3</sub> solid solution series. J. Phys. Soc. Japan, 13, 838–837.
- Ishikawa, Y. & Syono, Y., 1963. Order-disorder transformation and reverse thermo-remanent magnetism in the FeTiO<sub>3</sub>-Fe<sub>2</sub>O<sub>3</sub> series. *J. Phys. Chem. Solids*, 24, 517–528.
- Lagroix, F., Banerjee, S.K. & Moskowitz, B.M., 2004. Revisiting the mechanism of reversed thermoremanent magnetization (rTRM) based on observations from synthetic ferrian ilmenite (y = 0.7), *J. geophys. Res.*, **109**, B12108, doi:10.1029/2004JB003076
- Lawson, C.A., Nord, G.L., Jr., Dowty, E. & Hargraves, R.B., 1981. Antiphase domains and reverse thermoremanent magnetism in ilmenite-hematite minerals, *Science*, 213, 1372–1374.
- McEnroe, S.A., Carter-Stiglitz, B., Harrison, R.J., Robinson, P., Fabian, K. & McCammon, C.C., 2007a. Magnetic exchange bias of more than 1 Tesla in a natural mineral intergrowth. *Nature Nanotechnol.*, 2, 631–634, doi:10.1038/nnano.2007.292.
- McEnroe, S.A., Robinson, P., Langenhorst, F., Frandsen, C., Terry, M.P. & Boffa Ballaran, T., 2007b. Magnetization of exsolution intergrowths of hematite and ilmenite: Mineral chemistry, phase relations, and mag-

netic properties of hemo-ilmenite ores with micron-to nanometer-scale lamellae from Allard Lake, Quebec. J. geophys. Res., **112**, B10103, doi:10.1029/2007JB004973.

- McEnroe, S.A., Fabian, K., Robinson, P., Gaina, C. & Brown, L.L., 2009. Crustal magnetism, lamellar magnetism and rocks that remember, *Elements*, 5, 241–246.
- Meiklejohn, W.H. & Carter, R.E., 1959. Exchange anisotropy in rock magnetism, J. appl. Phys., 30, 2020.
- Nagata, T., Uyeda, S. & Akimoto, S., 1952. Self-reversal of thermoremanent magnetism in igneous rocks, J. Geomag. Electr., 4, 22–38
- Nogués, J., Sort, J., Langlais, V., Skumryev, V., Suriñach, S., Muñoz, J.S. & Baró, M.D., 2005. Exchange bias in nanostructures, *Phys. Rep.*, 422, 65–117.
- Nord, G.L., Jr. & Lawson, C.A., 1989. Order-disorder transition-induced twin domains and magnetic properties in ilmenite-hematite, *Am. Mineral.*, 74, 160–176.
- Nord, G.L., Jr. & Lawson, C.A., 1992. Magnetic properties of ilmenite70 hematite30: effect of transformation-induced twin boundaries, *J. geophys. Res.*, 97, 10 897–10 910.
- Ozima, M. & Funaki, M., 2001. Magnetic properties of hemoilmenite single crystals in Haruna dacite pumice revealed by the Bitter technique, with special reference to self-reversal of thermoremanent magnetization, *Earth Planets Space*, **53**, 111–119.
- Ozima, M., Funaki, M., Hamada, N., Aramki, S. & Fujii, T., 1992. Selfreversal of thermo-remanent magnetization in puroclastics from the 1991 Eruption of Mt. Pinatubo, Philippines, *J. Geomag. Geoelectr.*, **44**, 979–984.
- Ozima, M., Oshima, O. & Funaki, M., 2003. Magnetic properties of pyroclastic rocks from the later stage of the eruptive activity of Haruna Volcano in relation to the self-reversal of thermo-remanent magnetization, *Earth Planets Space*, 55, 183–188.
- Prevot, M., Hoffman, K. A., Goguitchaichvili, A., Doukhan, J-C., Shcherbakov, V. & Bina, M., 2001. The mechanism of self-reversal of thermoremanence in natural hemoilmenite crystals: new experimental data and model, *Phys. Earth planet. Inter.*, **126**, 75–92.
- Robinson, P., Harrison, R.J., McEnroe, S.A. & Hargraves, R.B., 2004. Nature and origin of lamellar magnetism in the hematite-ilmenite series, *Am. Mineral.*, 89, 725–747.
- Robinson, P., Fabian, K. & McEnroe, S.A., 2010. The geometry of ionic arrangements and magnetic interactions in ordered ferri-ilmenite solid solutions and its effect on low-temperature magnetic behavior, *Geochem. Geophys. Geosyst.*, **11**, 005Z17, doi:10.1029/2009GC002858.
- Shcherbakov, V.P., Fabian, K. & McEnroe, S.A., 2009. A mechanism of exchange bias for nanoparticles embedded in an antiferromagnetic matrix, *Phys. Rev. B*, 80, 174419, doi:10.1103/PhysRevB.80.174419.
- Uyeda, S., 1957. Thermo-remanent magnetism and coercive force of the ilmenite-hematite series, J. Geomag. Geoelectr., 9, 61–78.
- Uyeda, S., 1958. Thermo-remanent magnetization as a medium of paleomagnetism, with special reference to reverse thermo-remanent magnetism, *Jap. J. Geophys.*, 2, 1–123.
- Westcott-Lewis, M.F. & Parry, L.G., 1971. Thermoremanence in synthetic rhombohedral iron-titanium oxides, *Austr. J. Phys.*, 24, 735–742.