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Magnetic mean-field modelling of solid solutions: theoretical foundations and application to the hematite–ilmenite system

K. Fabian,¹ V.P. Shcherbakov,^{2,3} S.A. McEnroe,⁴ P. Robinson¹ and B.P. Burton⁵

¹Geological Survey of Norway, N-7491 Trondheim, Norway. E-mail: Karl.Fabian@NGU.NO

² Geophysical Observatory 'Borok' of Russian Academy of Sciences, Borok, Yaroslvaskaya oblast, 152742, Russia

³Institute of Geology and Petroleum Technologies, Kazan (Volga region) Federal University, Russia

⁴Norwegian University of Science and Technology, N-7491 Trondheim, Norway

⁵NIST, 100 Bureau Drive, Gaithersburg, MD 20878, USA

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SUMMARY

A spatially averaged mean-field model for fully or partially ordered members of the ilmenite– hematite solid solution series is rigorously derived from the Heisenberg Hamiltonian by first assuming no temporal correlation of atomic spins, and then by spatially averaging over spins at equivalent atomic positions. The model is based on the geometry of exchange interactions between nearest and next-nearest neighbours and predicts magnetization curves in homogenous solid solutions with variable degree of order. While the general framework presented can also be applied to atomic scale models, and to other solid solution series, here the symmetries of the ilmenite–hematite lattice are exploited to show that four different sublattice magnetizations and six independent combinations of exchange constants determine the temperature variation of the magnetization curves. Comparing measured Curie temperatures T_C and $M_s(T)$ curves to model predictions results in accurate constraints for these combinations. It is also possible to calculate predictions for high-field magnetization slopes χ_{HF} , which not only improve accurate experimental determination of the Curie temperature but also provide a new magnetic method to estimate the order parameter for ilmenite–hematite solid solution samples.

Key words: Magnetic mineralogy and petrology; Rock and mineral magnetism.

1 INTRODUCTION

1.1 Hematite-ilmenite solid solutions

Solid solutions in the hematite-ilmenite system, (1 - x) Fe₂O₃ +x FeTiO₃, are naturally occurring minerals with complex magnetic properties. The expression of chemical order in the hematiteilmenite system in terms of magnetic properties has been studied by Brown et al. (1993) and Harrison (2006). Apparent singlephase samples of different composition and degrees of order exhibit self-reversal of thermoremanent magnetization (Nagata 1961; Hoffman 1992; Lagroix et al. 2004; Robinson et al. 2014) and can show exchange bias of their room-temperature hysteresis curve (Meiklejohn & Carter 1959; Harrison & Becker 2004; Harrison 2006; Fabian et al. 2011). Lamellar magnetism (Robinson et al. 2002, 2004) occurs when fine-scale exsolution and cation ordering is induced by slow cooling. Burton et al. (2008) summarized magnetic properties of synthetic, partially Fe-Ti ordered hematite–ilmenite solid solutions in the composition range x = 0.6– 1 and temperature range 0-500 K. This extended earlier published data based on a series of synthetic, partially Fe-Ti ordered samples prepared two decades earlier (Burton 1982). Also, Burton

(1982) and Burton (1991) qualitatively reconciled chemical orderdisorder and phase separation data with magnetic data in a consistent thermodynamic model.

1.2 Mean-field modelling

To understand better the variability of magnetic behaviour in the hematite-ilmenite system, we here describe a magnetic mean-field model reflecting the geometric arrangement of atoms in the unit cell and the distribution of Fe-Ti cations that depends on the chemical order. The fundamental model parameters are the exchange-coupling constants. Their geometry in ilmenite-hematite solid solutions was described by Ishikawa & Akimoto (1957) and Ishikawa et al. (1985) and many of their values for ilmenite and hematite were determined by inelastic neutron scattering of spin waves by Samuelson (1969) and Samuelson & Shirane (1970). Because these measurements only probe Fe³⁺-Fe³⁺ interactions and Fe²⁺-Fe²⁺ intralayer and next-nearest-neighbour interactions, Harrison (2006) estimated the remaining values by comparing measured $M_S(T)$ curves to modelling results from an atomic Monte-Carlo model. Alternative values were inferred from an atomic model based on density functional theory, where ground state energy differences modelled for

different spin states were projected onto the magnetic exchangecoupling constants of the Heisenberg Hamiltonian (Nabi *et al.* 2010), which depend on the Coulomb repulsion parameter U in the adopted generalized gradient approximation density functional theory (DFT) model.

In relation to the above methods, mean-field modelling assumes an intermediate role because it is based on finding a temporally and spatially averaged solution to the Heisenberg Hamiltonian. Meanfield theory dates back to the classical Curie-Weiss model of ferromagnetism and has been theoretically investigated thoroughly in several physical contexts distinguished by the spatial dimension D and the topology of the underlying lattice, and the dimension N of the spins, where N=1 allows unit spin values $\{-1, +1\}$, for N=2 the spins can rotate on a circle in the plane and for N=3 they are free to rotate on the unit sphere. Ising models with N=1 are mathematically best understood (Ising 1925) and a famous theory of Onsager provides an analytical solution for D = 2(Onsager 1944). The case N = 2 has been studied extensively in the theory of superconductors (XY-model) either for D=2 or D=3(e.g. Kosterlitz & Thouless 1973). The full Heisenberg model of a ferromagnet corresponds to N=3 and D=3. In the following, the mean-field equations for hematite-ilmenite solid solutions with variable composition and degree of order are derived in a way that can be generalized easily to other solid-solution systems. The derivation is based on the Heisenberg model with N = 3 and D = 3, and takes into account different spin values for Fe²⁺, Fe³⁺ and Ti⁴⁺ ions that can occupy the same sites.

When specializing to N = 1 and a small number of ion classes, the results vield efficient computation schemes for Curie temperatures and magnetization curves that can be applied to different natural solid-solution series. Besides the hematite-ilmenite system (Ishikawa & Akimoto 1957), also the important magnetiteulvöspinel series has been studied in detail by such mean-field models (Stephenson 1972). The general approach provides physical insight to the magnetic properties of solid solutions and can be applied to arbitrarily complex numerical calculations. In agreement with Landau theory, Fabian et al. (2013) found a peak for the high-field susceptibility near the Curie temperature in ferrimagnetic magnetite. This peak is absent in antiferromagnetic hematite. The mean-field calculations presented here verify the absence of a peak for antiferromagnetic, disordered solid solutions and predict a quantitative relation between peak area and average degree of order within a ferrimagnetic solid solution.

2 DERIVING THE MEAN-FIELD MODEL FROM THE HEISENBERG HAMILTONIAN

The mean-field approximation is closely related to the classical Curie–Weiss theory of ferromagnetism that postulates a strong molecular field to explain the magnetization curve and Curie temperature of ferromagnetic substances. A quantum-mechanical foundation for molecular fields was discovered by Heisenberg (1928), who showed that in special geometric settings electron pairs with overlapping orbitals, due to their fermionic statistics, experience additional spin-dependent potentials that can be interpreted in terms of a very strong local field. Magnetic mean-field theory averages the Heisenberg Hamiltonian, by assuming statistically uncorrelated temporal spin fluctuations. Although mean-field theory has been exhaustively studied for many magnetic systems, especially spin glasses (Fischer & Hertz 1991), we include here a concise formu-

lation, partly to present a self-contained framework for our models and partly because our focus lies on some aspects of solid solutions, for which we could not find a corresponding treatment in the literature.

2.1 Mean-field approximation on the atomic scale

In analogy to the spin-glass Hamiltonian (Fischer & Hertz 1991) and the Heisenberg Hamiltonian of a diluted ferromagnet (Kaneyoshi *et al.* 1980), the exchange interaction between a system of N interacting quantum spins \vec{S}_i of the ilmenite–hematite solid solution with an external magnetic field \vec{h} can be described by the Hamiltonian

$$\mathfrak{H} = -\sum_{i\neq n} \mathbf{J}_{i,n} c_i c_n \, \vec{S}_i \vec{S}_n - g\mu_B \vec{h} \, \sum_i c_i \, \vec{S}_i. \tag{1}$$

The numbers $c_i \in \{0, 1\}$ represent a specific geometric configuration of the solid solution on the atomic scale, in that they are zero whenever a Ti atom replaces an Fe atom in the corresponding hematite site. The notation is sketched in Figs 1(a) and (b).

The constants $\mathbf{J}_{i,n}$ describe the exchange tensor, between atomic spins at sites *i* and *n*, while μ_B is the Bohr magneton and *g* is the gyromagnetic ratio ($g \approx 2$). By using a general exchange tensor, the effects of exchange anisotropy are formally represented, although this will be neglected for the numerical modelling. The magnetic quantum spins \vec{S}_i here represent single Fe²⁺ or Fe³⁺ ions. They will be spatially averaged only later to represent suitably chosen ion classes (e.g. sublattices of identical ions). The mean-field approximation replaces these spin vectors \vec{S}_i by normalized time averages

$$\vec{m}_i := \langle \vec{S}_i \rangle / S_i \tag{2}$$

and their corresponding temporal fluctuations

$$\vec{\delta}_i := \vec{S}_i - S_i \vec{m}_i. \tag{3}$$



Figure 1. Sketch of the mean-field approach. (a) For each pair of sites *i* or *n* in a large lattice there is an exchange tensor $J_{i,n}$ describing the exchange energy between spins S_i and S_n at these sites. (b) The information as to whether there are actually Fe atoms at these sites which could interact is encoded by the numbers $c_i \in \{0, 1\}$. (c) A spatial grouping of all sites into two classes. A mean-field model using these classes would average over the spins in each class and finally only need two average spins and three exchange couplings $J_{1, 1}, J_{2, 2}, J_{1, 2}$. (d) The same for nine classes and periodic boundaries. This is meant as an example that in numerical models the number of classes can be very large to represent complex geometric arrangements over many unit cells, for example, clustering of Fe atoms.

Substitution into eq. (1) leads to the still exact expression

$$\mathfrak{H} = \sum_{i \neq n} c_i c_n \left(-\mathbf{J}_{i,n} \vec{\delta}_i \vec{\delta}_n + \mathbf{J}_{i,n} S_i S_n \vec{m}_i \vec{m}_n - 2\mathbf{J}_{i,n} \vec{S}_i S_n \vec{m}_n \right) - g\mu_B \vec{h} \sum_i c_i \vec{S}_i.$$

$$(4)$$

At this point, the mean-field approximation is introduced, which consists in a time averaging of the spins, and in neglecting the time average of all pair correlations of the temporal fluctuations by setting

$$\left\langle \sum_{i \neq n} \mathbf{J}_{i,n} \vec{\delta}_i \vec{\delta}_n \right\rangle = 0.$$
⁽⁵⁾

This approximation is most reasonable when at elevated temperatures large numbers of independent spin waves are synchronously excited such that different regions of the system behave statistically independent. In this case, eq. (5) is justified by Bernoulli's theorem (weak law of large numbers). At low temperatures (near 0 K), discrepancies between mean-field predictions and Bloch's law (Bloch 1928) indicate that pair correlations are coherent and that their time average is not negligible. The partition function of the complete quantum-mechanical spin ensemble,

$$Z = \sum_{\text{all configurations}} \exp \frac{-\mathfrak{H}}{k T},$$
(6)

determines all thermodynamic quantities and in the mean-field approximation its temporal average is

$$\langle Z \rangle = \exp \left[\frac{-\sum_{i \neq n} c_i c_n S_i S_n \mathbf{J}_{i,n} \vec{m}_i \vec{m}_n}{k T} \right]$$

$$\times \prod_{p=1}^N \sum_{\sigma=-c_p S_p}^{c_p S_p} \exp \frac{\sigma c_p || 2 \sum_n S_n c_n \mathbf{J}_{p,n} \vec{m}_n + g \mu_B \vec{h} ||}{k T}.$$
(7)

The numerator of the last term can be interpreted as the projection of the quantum spin \vec{S}_p onto an effective field at the *p*th position given by

$$\vec{h}_{\text{eff},p} := \frac{2 c_p}{g \,\mu_B} \sum_n c_n \, S_n \mathbf{J}_{p,n} \vec{m}_n + c_p \, \vec{h}. \tag{8}$$

This definition shows that for $c_p = 0$ also the effective field is zero, and because also $c_p S_p = 0$, no spurious terms can occur in the last sum in eq. (7). The effective field (8) represents the quantummechanical version of the Curie–Weiss molecular field.

From the partition function $\langle Z \rangle$, the free energy $F = -k T \log \langle Z \rangle$ is calculated as

$$F = \sum_{i \neq n} c_i c_n S_i S_n \mathbf{J}_{i,n} \vec{m}_n \vec{m}_n$$
$$-k T \sum_{p=1}^N c_p \log \left[\sum_{\sigma=-S_p}^{S_p} \exp \frac{\sigma g \mu_B || \vec{h}_{\text{eff},p} ||}{k T} \right].$$
(9)

The sum inside the natural logarithm is a geometric series such that eq. (9) simplifies to

$$F = \sum_{i \neq n} c_i c_n S_i S_n \mathbf{J}_{i,n} \vec{m}_n \vec{m}_n - k T \sum_{p=1}^N c_p \log \frac{\sinh\left((2 S_p + 1)g\mu_B ||\vec{h}_{\text{eff},p}||/(2 k T)\right)}{\sinh\left(g\mu_B ||\vec{h}_{\text{eff},p}||/(2 k T)\right)}.$$
(10)

Magnetic mean-field modelling 1031

2.2 Spatial averaging of the mean-field approximation

Apart from the mean-field approximation (5), the last expression for F still exactly describes the magnetic interaction of a large number N of atoms in the solid solution, typically in the order of the Avogadro number. To obtain a tractable computational method, it must be further simplified by spatial averaging, whereby the Natoms are gathered into a small number L of classes of symmetrically equivalent atoms as shown in Figs 1(c) and (d). It is assumed that the atoms in *i*th class have small equivalent neighbourhoods B(i), where exchange interaction occurs. The first term of F is then averaged to

$$F_1 = N/L \sum_{i=1}^{L} \sum_{j \in B(i)} p_i \, p_j \, S_i S_j \, J_{i,j} \, m_i \, m_j, \qquad (11)$$

where now i, j = 1...L run over the small number of classes, while $p_i, p_j \in [0, 1]$ are the probabilities of $c_i = 1$ or $c_j = 1$ for the members of classes i and j, respectively. This formulation implicitly introduces the additional assumption that these probabilities describe independent events, that is, that the conditional probabilities $\mathbb{P}(c_i = 1|c_j = 1)$ and $\mathbb{P}(c_i = 1|c_j = 0)$ are the same. Otherwise, the coefficient in eq. (11) would be $\mathbb{P}(c_i = c_j = 1)$, which then might be different from $p_i p_j$. Only for mathematical simplicity, the exchange tensors have been replaced by scalar exchange constants $J_{i,j}$ between the members of classes i and j, describing isotropic exchange interaction, and m_i now denotes a scalar magnetization of atoms in class i along a single direction. Performing the following calculations for the more general tensorial and vectorial quantities is not fundamentally different.

Spatial averaging over the second term in eq. (10), that is, replacing c_i by p_i , requires further approximation. This is best understood by separately studying the mathematical function

$$\phi_a(\xi) := \log\left(\frac{\sinh(2\,a+1)\,\xi}{\sinh\xi}\right),\tag{12}$$

that appears in eq. (10) and is plotted in Fig. 2 for relevant values of *a*. Note that neither ϕ_a nor ξ have physical units. The derivative

$$\phi'_{a}(\xi) := (2a+1)\coth(2a+1)\xi - \coth\xi$$
(13)

is essentially the Brillouin function $B_J(\xi) = 1/(2J)\phi'_J(\xi/(2J))$. When $\xi > 1$, such that $e^{-\xi}$ and $e^{-(2a+1)\xi}$ are negligible $\phi_a(\xi) \approx 2 a \xi$ is almost a linear function. In the case of $\mu_B h_{\text{eff},p} \gg kT$, which is below T_C , the second term of F is therefore well approximated by

$$F_2 \approx -g \,\mu_B \sum_{p=1}^N c_p \, S_p |h_{\text{eff},p}|, \qquad (14)$$

and because $h_{\text{eff}, p}$ depends linearly on c_i and m_i , this can be averaged over the members of the *L* classes to define an average effective field for class *j* by

$$h_{\text{eff},j} := \frac{2}{g \,\mu_B} \sum_{i=1}^L p_i \, S_i J_{j,i} m_i + h.$$
(15)

With this definition the asymptotic value of F_2 is

$$F_2 \approx -N/L \, g \, \mu_B \, \sum_{j=1}^L p_j \, S_j |h_{\mathrm{eff},j}|.$$
 (16)

In the vicinity of $\xi = 0$ the function $\phi_a(\xi) \approx \log (2 a + 1)$ is almost constant, and depends on ξ only in second order. Also in this case the spatial averaging can be directly performed, and it is therefore not critical to use the approximation (15) also near $\xi = 0$ where it is less accurate. Doing so in eq. (10) yields an approximate mean-field



Figure 2. $\phi_a(\xi)$ for a = 1, ..., 5 together with asymptotic behaviour for $\xi \gg 1$ and near $\xi = 0$. Replacing eq. (8) by its asymptotic value, eq. (15) leads to significant deviations only for $0.1 \le \xi \le 1$, where local variations of the effective field may become important. In the mean-field approach where $\xi = g\mu_B ||\vec{h}_{\text{eff},p}||/(2 k T)$, such values of ξ occur near the Curie temperature where the effective-field energy is close to the thermal activation energy.

average free energy

$$\bar{F} := \frac{L}{N}F = \sum_{i=1}^{L} \sum_{n \in B(i)} p_i p_n S_i S_n J_{i,n} m_i m_n - k T \sum_{j=1}^{L} p_j \phi_{S_j} \left(\frac{g\mu_B |h_{\text{eff},j}|}{2 \, k \, T} \right),$$
(17)

where $h_{\text{eff},j}$ is given by eq. (15). If a minimum of \overline{F} lies within the hypercube $[-1, 1]^L$ it is a solution of the set of L equations $\frac{\partial \overline{F}}{\partial m_i} = 0$, which for general values of $J_{i,n}$ requires the validity of the system of scalar equations

$$m_i = B_{S_i} \left(\frac{g \,\mu_B}{k \, T} h_{\text{eff},i} \right),\tag{18}$$

where i = 1...L, and B_S denotes the spin S Brillouin function. This nonlinear system of L equations for the L unknown magnetizations can be solved to obtain possible mean-field magnetization states of the system. Because solutions of eq. (18) may also correspond to maxima or saddle points of \overline{F} , a numerical method must exclude these possibilities.

3 MEAN-FIELD MODELLING OF HEMATITE-ILMENITE SOLID SOLUTIONS

3.1 Exchange constants

The geometry of local exchange coupling in ilmenite–hematite solid solutions as shown in Fig. 3 has been described by Ishikawa & Akimoto (1957).

Exchange constants of hematite were determined by inelastic neutron scattering of spin waves by Samuelson & Shirane (1970). They relate exclusively to Fe³⁺-Fe³⁺ interactions. Neutron measurements for ilmenite have been used to infer the intralayer and next-nearest-neighbour Fe^{2+} - Fe^{2+} interactions (Samuelson 1969). Next-neighbour interlayer interactions do not occur in perfectly ordered ilmenite because every second layer contains only Ti4+ ions. There are no direct measurements that constrain the value of $Fe^{2+}-Fe^{3+}$ interactions. By inverse fitting of measured T_C values to Monte Carlo models, Harrison (2006) estimated values for Fe^{2+} -Fe³⁺ next-neighbour interactions and Fe²⁺-Fe²⁺ next-neighbour interlayer interactions. Density functional theory (DFT) calculations by Nabi et al. (2010) for ilmenite, hematite and ilmenite-hematite interfaces provided theoretical estimates for all exchange constants. These DFT calculations used the generalized gradient approximation that depends on a Coulomb repulsion parameter U, and two solutions for U = 6 eV and U = 8 eV are provided by Nabi *et al.* (2010). A brief overview of the different terminologies for the exchange constants in the literature is listed in Table 1. In the following we use the terminology from Fig. 3 that corresponds to that of Nabi *et al.* (2010).

3.2 Space-averaged mean-field model

To obtain a general model of a space-averaged hematite–ilmenite solid solution, we represent each type of Fe-ion in the magnetic unit cell by an average moment. The magnetic unit cell, based on that of Fe–Ti ordered ilmenite, contains 12 puckered layers in the *c*-direction. Each layer may contain up to four Fe³⁺ or Fe²⁺ ions, as many as two in up and two in down positions. In the most general case, this gives rise to 48 different average magnetic moments $m(L, t, \pi)$, where L = 1, 2, ..., 12 is the layer, t = 2, 3 is the ion type Fe^{t+} and $\pi = \pm 1$ denotes the up-down position. In a partially ordered Ilmx solid solution ($x \in [0, 1]$), with $Q \in [-1, +1]$ representing the degree of chemical order, the probability $\mathbb{P}(L, t)$ to find an Fe^{t+} ion at an Fe/Ti site in layer *L* is

$$\mathbb{P}(L,3) = 1 - x; \ \mathbb{P}(L,2) = \frac{x}{2} \begin{cases} 1 - Q & \text{for } L \equiv 0 \mod 2\\ 1 + Q & \text{for } L \equiv 1 \mod 2. \end{cases}$$
(19)

This assumes that in the positive ordered state Q = 1, all Ti ions have moved to the even layers ($L \equiv 0 \mod 2$), while for the antiordered state Q = -1, the Ti ions have moved to the odd layers. To calculate the average effective field acting on an ion of type t in layer L and position π , one has to add all contributions from all possible neighbouring ions weighed by their respective probability

$$h_{\rm eff}(L, t, \pi) = \sum_{t', L', \pi'} S(t') \mathbb{P}(L', t') m(L', t', \pi') \nu(\Delta L, \pi, \pi') \times J_{tt'}(\Delta L, \pi, \pi').$$
(20)

Here ΔL represents the periodic difference

$$\Delta L = \operatorname{absmin}\left\{L' - L + 12\mathbb{Z}\right\}$$
(21)

and $\nu(\Delta L, \pi, \pi')$ denotes the multiplicity of the geometric situation, that is, the number of equivalent neighbours, and $J_{tt'}(\Delta L, \pi, \pi')$ is the exchange constant for the geometric link.

For $S \subset \mathbb{Z}$, absmin $S := \max\{m : |m| = \min |S|\}$.

Note that symmetry requires

$$J_{tt'}(-\Delta L, -\pi, -\pi') = J_{tt'}(\Delta L, \pi, \pi'),$$

$$v(-\Delta L, -\pi, -\pi') = v(\Delta L, \pi, \pi').$$



Figure 3. Geometric configuration of local neighbours involved in exchange interactions. Letters indicate those sites where exchange interactions with the highlighted central position (circle) are taken into account, provided they are occupied by an Fe instead of a Ti atom. Sites with equal letters have the same interaction constants. The signs indicate whether an atomic position is upward (+) or downward (-) puckered. (a) Exchange coefficients J_1 and J_6 describe exchange coupling to the two unique neighbours directly above and below the central atom. (b) J_2 belongs to the only intralayer interaction. (c) J_3 is the strongest, and J_4 and J_5 are equal slightly less strong nearest-neighbour interlayer interactions. (d) J_7 and J_8 are weak next-nearest-neighbour interactions, as J_6 in (a). If the central atom is upward puckered, all interactions are mirror symmetric with respect to the central *c*-plane.

Table 1. Different nomenclatures for exchange constants in ilmenite–hematite solid solutions. The first three columns refer to the nomenclatures of Nabi *et al.* (2010); Ishikawa & Akimoto (1957); Ishikawa *et al.* (1985); Harrison (2006), ν is the geometric multiplicity of the interaction as shown in Fig. 3. The type of interaction is either intralayer (intra), nearest-neighbour interlayer (nn) or next-nearest-neighbour (nnn).

Nabi <i>et al</i> .	Ishikawa et al.	Harrison	ν	type
$\overline{J_1}$	J_{3}^{0}	J^1	1	nn
J_2	J_1^1	J^2	3	intra
J_3	J_2^0	J^3	3	nn
J_4	J_1^0	J^4	3	nn
J_5	J_{1}^{0}	J^4	3	nn
J_6	J_3^1	J^5	1	nnn
J_7	J_4^1		6	nnn
J_8	J_5^1		3	nnn
	J_2^1		3	intra
	J_{6}^{1}		3	intra

Based on the crystal structures of ilmenite and hematite, meanfield models for ordered and disordered solid solutions were set up according to eq. (18). To permit a maximal degree of freedom for possible symmetry breaking, both models consider four atomic layers in the *c*-planes, each containing Fe^{2+} , Fe^{3+} , and Ti^{4+} ions in either an upper or lower position. For the ordered case, where every odd layer contains only Fe^{2+} , Fe^{3+} , while every even layer contains only Fe^{3+} , Ti^{4+} , this results in a maximal number of 12 different classes of Fe atoms. In the disordered case, up to 16 classes need to be considered. However, in none of the numerically calculated cases intralayer or mirror symmetry were broken, such that only the four different ion classes, corresponding to Fe^{2+} , Fe^{3+} in even and odd layers, are of practical importance.

4 HEMATITE-ILMENITE SOLID SOLUTIONS

While the intention of this article is to provide a simple and intelligible unified method to develop mean-field models for solid-solution series of rock-magnetic importance on arbitrary levels of sophistication, it also provides some new insight into the specific system of ilmenite–hematite solid solutions. There is a huge body of literature on mean-field and micromagnetic properties of hematite, which has been extensively reviewed and extended by Morrish (1994). The theoretical approach presented here largely reproduces this work in a more general setting that encompasses hematite–ilmenite solid solutions of any degree of order.

4.1 Independent exchange parameters

The geometry of the exchange interactions as shown in Fig. 3, together with the averaging assumptions of the mean-field model, implies that only some specific combinations of exchange coefficients determine the mean-field behaviour of hematite–ilmenite solid solutions. In the case of hematite, where only $Fe^{3+}-Fe^{3+}$ interactions occur, this has been discussed by Morrish (1994), and his arguments remain essentially valid for the solid solutions, although three types of $Fe^{k+}-Fe^{l+}$ interactions with $(k, l) \in \{(2, 2), (2, 3), (3, 3)\}$ need to be considered. Analysis of the full equations reveals that the effective field at each site only depends on the following six

Table 2. Expressions in mean-field energy.

$C_{2,1} = B^{2,3} 5(1-x)$ $C_{2,2} = B^{3,3} 5(1-x)$ $C_{2,3} = B^{3,3} 5(1-x)$	$A_{2,3} = A^{2,3} 5(1-x)$	$C_{24} = A^{3,3} 5(1-x)$
	-,- 、 、 ,	2, .
$C_{3,1} = A^{2,2} 2 (1-Q)x$ $C_{3,2} = A^{2,3} 2 (1-Q)x$ $C_{3,2} = A^{2,3} 2 (1-Q)x$	$a_{3,3} = B^{2,2} 2 (1 - Q)x$	$C_{3,4} = B^{2,3} 2 (1 - Q)x$
$C_{4,1} = A^{2,3} 5(1-x)$ $C_{4,2} = A^{3,3} 5(1-x)$ $C_{4,2} = A^{3,3} 5(1-x)$	$A_{4,3} = B^{2,3} 5(1-x)$	$C_{4,4} = B^{3,3} 5 (1-x)$

Table 3. Literature values for exchange constants for hematite–ilmenite solid solutions and an example for an alternative fit to experimental values of T_C .

A ^{2, 2}	A ^{2, 3}	A ^{3, 3}	$B^{2, 2}$	B ^{2, 3}	B ^{3, 3}	Reference
-102.75	-236.175	-455.4	24.66	9.635	-7.4	Harrison (2006); Samuelson & Shirane (1970)
0.	-247.7	-402.7	4.	-41.3	-33.1	Nabi <i>et al.</i> (2010), $U = 8 \text{ eV}$
0.	-290.3	-533.1	12.	-45.3	-57.6	Nabi <i>et al.</i> (2010), $U = 6 \text{ eV}$
-87.7	-253.7	-386.9	27.4	1.1	28.3	Alternative fit



Figure 4. Experimentally determined Curie temperatures on a series of synthetic hematite–ilmenite solid solution samples from Burton (1982). Data for samples with $x \ge 0.6$ are taken from Burton *et al.* (2008). (a) Curie temperatures as determined from the indicated $M_s(T)$ curves. The dashed line represents previous calculations by Ishikawa & Akimoto (1957). (b) Top: the $M_s(T)$ measurement (black) for Ilm23 shows primarily the Curie temperature of magnetice, which is magnetically predominant, though volumetrically negligible. Only the derivative (grey) clearly indicates the lower ordering temperature of Ilm23. Bottom: a clear peak in high-field susceptibility occurs at the magnetice Curie temperature. No discernable peak occurs at the lower ordering temperature of Ilm23.

combinations of the 24 exchange constants:

$$A^{k,l} = J_1^{k,l} + 3J_3^{k,l} + 3J_4^{k,l} + 3J_5^{k,l}$$
(22)

$$B^{k,l} = 3J_2^{k,l} + J_6^{k,l} + 6J_7^{k,l} + 3J_8^{k,l}.$$
(23)

Here J_1, \ldots, J_8 are the exchange constants in the nomenclature of Nabi *et al.* (2010), and the superscripts denote to which $Fe^{k+}-Fe^{l+}$ interaction the combination applies. When, in addition, variable composition x and degrees of order Q are taken into account it turns out that still only a small number of combinations occur in the mean-field energy. These combinations are listed in Table 2.

The dependence of $C_{p,q}$ as defined in Table 2 on order Q and composition x make it possible to determine individual factors $A^{k,l}$ and $B^{k,l}$ by varying these parameters. Different literature values for the exchange constants result also in different values for the $A^{k,l}$ and $B^{k,l}$ as seen in Table 3, such that deviations between these predictions should lead to measurable effects.

4.2 Constraints from experimental Curie temperatures

Experimental Curie temperatures as shown in Fig. 4 and reported by Burton *et al.* (2008) can be fit by adjusting $A^{k, l}$ and $B^{k, l}$. Although there are uncertainties related to the measurement of T_C (Fabian *et al.* 2013), the values for the hematite–ilmenite series are relatively well established. Fig. 4 shows that for x < 0.4 the determination of T_C is complicated by the fact that the solid solutions are predominantly disordered with Q almost zero in this region such that already tiny amounts of magnetite create a considerable signal, overprinting the signal from the almost antiferromagnetic solid solution.

Using least-squares minimization it is possible to create alternative fits to those of Harrison (2006) and Nabi *et al.* (2010) because the predicted Curie temperatures depend not very sensitively on the values for $A^{k,l}$ and $B^{k,l}$. To create such fits, it is necessary to calculate T_C in dependence of $A^{k,l}$ and $B^{k,l}$ for any x and Q. Because at the Curie temperature the character of the solution $m_i = 0$ for i = 1, ..., L to the set of equations (18) changes from a minimum above T_C to a maximum below T_C , this allows for a simple method



Figure 5. Difference $\Delta T_C(x) = T_C(Q=0) - T_C(Q=1)$ between the Curie temperatures $T_C(Q=0)$ of the disordered and $T_C(Q=1)$ the ordered solid solution as a function of composition *x*. The two lines represent different modelling results that both fit the experimental data. The solid line is based on the exchange constants from Harrison (2006), and the dashed line is based on the exchange constants for the alternative fit listed in the last line of Table 3. This result indicates that based on current data it is not possible to decide whether ordered or disordered phases have higher T_C .

to determine the Curie temperature by linearizing eq. (18) around this zero solution. Directly at T_C the linear system obtained has at least two solutions corresponding to the emergent positive and negative branches of spontaneous magnetization. For a linear system, this means that the solution becomes singular at T_C , and the determinant of the linear system is zero. In the case of hematite–ilmenite solid solutions, this leads to the condition that at T_C the following determinant vanishes:

$$\begin{vmatrix} 4 T - 2 C_{1,1} & 5 C_{1,2} & 2 C_{1,3} & 5 C_{1,4} \\ C_{2,1} & 75 T - 35 C_{2,2} & -14 C_{2,3} & -35 C_{2,4} \\ 2 C_{3,1} & -5 C_{3,2} & 4 T - C_{3,3} & -5 C_{3,3} \\ 14 C_{4,1} & -35 C_{4,2} & -14 C_{4,3} & 75 T - 35 C_{4,4} \end{vmatrix} = 0,$$
(24)

where $C_{i,j}$, as defined in Table 2, depend on x and Q. The resulting fourth-order equation in T can be solved for any composition x, order parameter Q, and for any values for the exchange constants $A^{k,l}$ and $B^{k,l}$. The largest real solution then corresponds to the predicted value of T_C . This equation generalizes a similar equation of Ishikawa & Akimoto (1957).

The last line in Table 3 reports one alternative fit for $A^{k,l}$ and $B^{k,l}$ obtained in this way, but many other fits are equally good, depending heavily on the weighing and error estimates for the experimental data points. The main reason for choosing the shown solution is that it illustrates the open problem whether disordered or ordered solid solutions in the ferrimagnetic region 0.4 < x < 0.87 have higher T_C . Fig. 5 shows that while the exchange constants of Harrison (2006) result in higher T_C for disordered solid solutions, the alternative fit gives higher T_C for the ordered case when x < 0.83 and lower T_C when x > 0.83. The question therefore cannot be resolved based on our current experimental data.

4.3 $M_s(T)$ curve shape

Another important application of mean-field modelling is the prediction of $M_s(T)$ curves for any choice of parameters $A^{k,l}$, $B^{k,l}$, xand Q as shown in Fig. 6, which for convenience is based on the exchange couplings from Harrison (2006). Figs 6(a) and (b) show the sublattice magnetizations for x = 0.6 in the disordered and perfectly ordered states. It is based on 16 (a) and 12 (b) classes of iron atoms in the hematite lattice and demonstrates that for the chosen exchange constants no symmetry breaking occurs such that only 4 or 3 different magnetization branches occur as used in the simplified model for the Curie temperature determination. In Fig. 6(a) the total magnetization of the antiparallel sublattices is zero, making the completely disordered state a perfect antiferromagnet. In the ordered configuration in Fig. 6(b), only the Fe³⁺ ions in neighbouring Fe and Ti layers cancel each other, while Fe²⁺ ions occur only in Fe layers. Because neighbouring layers are antiparallel due to negative exchange coupling, all Fe²⁺ ions are aligned in the same direction and produce a net ferrimagnetic moment. Also, the shape of the overall magnetization curve thus reflects the Fe²⁺ sublattice only, and not the significantly different curve shape for the Fe³⁺ sublattice magnetization.

A 3-D view of the variation of this curve shape with composition x is shown for Q = 1 in Fig. 6(c). It includes the variations of T_c and $M_s(0)$ as marginal projections. 2-D plots are provided in Figs 6(d)–(f).

In a similar way, the change of the $M_s(T)$ curve can be studied for a constant composition x as a function of order Q. Fig. 6(g) provides a 3-D view of this variation for x = 0.6. Here T_C is almost constant and $M_s(0)$ varies linearly. Yet the variation at other temperatures is not completely linear, as can be seen best by comparing the normalized curves for Q = 1 and Q = 0.1 in Fig. 6(h).

All these calculations are numerically fast and accurate for bulk materials whenever the fundamental assumptions of the mean-field approach are met.

4.4 High-field susceptibility and magnetic order

Experimental evidence as presented in Fig. 7 shows that ferrimagnetically ordered solid solutions exhibit a peak in high-field susceptibility. Here a field H_0 is considered high if it is considerably larger than the remanent coercivity H_{cr} , and the high-field susceptibility for $H_0 \ll H_{cr}$ is

$$\chi_{\rm HF}(H_0, T) := \frac{\partial M}{\partial H}(T, H_0), \tag{25}$$

slightly above T_C . The measurement procedure for these curves is described in Fabian et al. (2013), where this peak is related to the para-effect that increases the in-field saturation magnetization (Holstein & Primakoff 1940) and provides an independent experimental method to constrain T_C in ferrimagnets. The para-effect is due to an improved average statistical alignment of the thermally activated ion spins in applied fields of an achievable magnitude (1-10 T), which near T_C can significantly increase the effective field and therefore also increase the apparent M_s . Fig. 7(a) shows that in Ilm43 this peak is absent, or at least almost completely suppressed. According to experimental data of Ishikawa & Akimoto (1957), ilmenite-hematite solid solutions are disordered between x = 0 and x = 0.4. Fig. 7(a) thus provides evidence that in general there is no peak of $\chi_{\rm HF}$ in disordered solid solutions. For hematite, Fabian *et al.* (2013) argued that antiferromagnetic coupling prevents improved mean statistical alignment of both sublattices parallel to the field to lower the combined magnetic field and exchange energy. As long as field-induced spin canting due to H_0 is small, the susceptibility perpendicular to the sublattice magnetization,

$$\chi_{\perp} := \frac{\partial m_{\perp}(T, H)}{\partial H}(T, H_0) \approx \frac{M_s}{h_{\text{eff}}}(T), \qquad (26)$$

is the main contribution to the antiferromagnetic susceptibility below T_C . It is only negligibly influenced by the para-effect and shows no peak near T_C .

The peak in the parallel susceptibility χ_{\parallel} , as visible in Figs 7(b) and (c), can be calculated from our mean-field model and confirms the suggestion and measurements of Fabian *et al.* (2013) that in



Figure 6. Modelling results for magnetization curves of hematite–ilmenite solid solutions in dependence of composition *x* and order parameter *Q* based on the exchange constants from Harrison (2006). (a) Sublattice magnetization μ in units of μ_B per formula unit of Ilm60. In the disordered state Fe²⁺ and Fe³⁺ ions cancel each other in neighbouring layers. (b) In perfectly ordered Ilm60, only the Fe³⁺ residing in Ti layers cancel their moments with Fe³⁺ in Fe layers. Because Fe²⁺ ions reside only in Fe layers, their moments all point in the same direction. (c) $M_s(T)$ curves for perfectly ordered (*Q*=1) hematite–ilmenite solid solutions in a 3-D view show variation of T_C and $M_s(0)$. (d) T_C for ordered and disordered solid solutions differ by less than 5 K in the region x < 0.87 where ferrimagnetism occurs. (e) $M_s(T)$ curves, in units of μ_B per formula unit, for hematite–ilmenite solid solutions with *Q*=1 versus (f) with *Q*=0.5. (g) $M_s(T)$ curves for Ilm60 as a function of *Q* in a 3-D view show linear variation $M_s(0)$ and almost constant of T_C . The slight variation in curve shape is best seen in the normalized curves in (h).

magnetically disordered (Q = 0) systems, this peak disappears. Because the peak occurs near T_C , its quantitative calculation by meanfield methods will be affected by the approximation in eq. (14), illustrated in Fig. 2, and therefore may be less accurate, though essentially correct.

To illustrate this quantitatively, Fig. 8 reports a set of mean-field calculations for differently ordered ilmenite–hematite solid solutions of composition Ilm40, at the lower boundary of compositions where chemical order can occur (Harrison 2006; Ghiorso & Evans

2008; Robinson *et al.* 2012). The mean-field calculation assumes that the field is aligned with the sublattice magnetizations and therefore concerns the high-field susceptibility $\chi_{\text{HF},\parallel}$. To quantify the peak size in an applicable way, the peak area *a* is calculated as the integral

$$a = \int_{T_{\min}}^{T_{\max}} \chi_{\rm HF}(H_0, Q, T) - \chi_{\rm HF}(H_0, 0, T).$$
(27)



Figure 7. $M_S(T)$ curves and high-field magnetic susceptibility $\chi_{HF}(T)$ according to Fabian *et al.* (2013) for Ilm43 (sample Ilm40-160278) (a), Ilm72 (sample Ilm70-191073) (b) and Ilm81 (sample Ilm80-030676) (c) (Burton 1982). In (a), the absence of a recognizable peak near $T_C \approx 320 \pm 5$ C shows that the Ilm43 solid solution is predominantly disordered and antiferromagnetic, while the presence of a magnetite component is clearly indicated by a peak in $\chi_{HF}(T)$ near $T_C \approx 520 \pm 5$ C. For the partially chemically ordered solid solutions Ilm72 (b) and Ilm81 (c), each $\chi_{HF}(T)$ curve has a broad peak near the respective Curie temperatures resulting from the ferrimagnetic para-effect slightly above T_C . Note the different *T* scales in (b) and (c).



Figure 8. Left: Modelled magnetic high-field susceptibility $\chi_{\text{HF},\parallel}$ for different ordering states of Ilm40, using exchange constants of Harrison (2006) and applied fields between 1.2 and 1.5 T. A completely disordered solid solution shows no peak near its Néel temperature ($T_N \approx 596$ K), while at Q = 0.2 the modelled peak at an identical T_C is clearly visible. Right: a bilogarithmic plot of peak area *a* as a function of *Q* indicates almost quadratic increase of *a* with Q ($T_{\min} = 520$ K, $T_{\max} = 610$ K).

This reflects the integral of the deviation from the disordered highfield susceptibility $\chi_{\rm HF}(H_0, 0, T)$ for Q = 0 over a temperature interval around T_C . Fig. 8(b) indicates that peak area growth is almost quadratical with Q. A fit to the numerical computation yields a $\propto Q^{1.89}$. Experimentally, peak area is a more robust quantity than peak maximum height because slight variations, for example, in composition strongly affect height but not area. A quantitative comparison of this theoretical relation to experimental data requires an independent and reliable method to determine the bulk degree of order Q in hematite-ilmenite solid solutions. In addition, due to the predicted nonlinear variation of a with order Q, even the smallscale structure of the solid solution will be important. An equal mixture of two homogenous compounds with Q = 0.2 and Q = 0.8should have a different peak area a (~0.3518) than the homogenous average-order solid solution with Q = 0.5 ($a \sim 0.2698$). A quantitative experimental study of a in relation to Q and its nanostructure in hematite-ilmenite solid solutions is an important aim for future research.

5 DISCUSSION AND CONCLUSIONS

We derive a rigorous mean-field model to calculate magnetization curves and Curie temperatures for solid solutions of natural minerals as a function of their degree of chemical order. The model is based on ionic configurations and requires the corresponding exchange constants as input. Due to the inherent constraints of the mean-field approach, quantum effects at low temperatures and correlations of thermal fluctuations near T_C are neglected. This is related to the well-known limitation of mean-field models to correctly represent spin-glasses (Fischer & Hertz 1991), and means that modelling results for ilmenite content $0.87 \le x < 1$ must be regarded with care, because due to the loss of Fe percolation in the ordered state hematite–ilmenite solid solutions in this composition range show locally variable clustering and spin-glass behaviour (Ishikawa *et al.* 1985; Burton *et al.* 2008; Harrison 2009). The additional simplification achieved by averaging over unit cells, leading to not more than 48 classes of ions, is sufficient to predict Curie temperatures for a bulk system with long-range order, below the percolation threshold of about Ilm87. For systems between Ilm87 and Ilm100 it is assumed and experimentally verified that spin-glass behaviour occurs due to the formation of interacting clusters of Fe-ions, separated by weak, partly ferromagnetic and partly antiferromagnetic links, which necessarily are in a state of frustrated equilibrium (Ishikawa et al. 1985; Burton et al. 2008; Harrison 2009). Such clusters cannot be modelled with a 16-class mean-field model, but the presented methods can be applied to studying numerical periodic-boundary mean-field models that contain large number of classes representing complex Fe-ion networks. Such models should be better apt to grasp the complexity of the spin-glass phase, but it is unclear whether this is sufficient to understand the experimental results (Ishikawa et al. 1985; Burton et al. 2008). At the very end of the solution series, for Ilm100, mean-field modelling works again, because the geometric situation is both, simple and spatially homogenous, and the model predicts the correct antiferromagnetic Néel temperature.

The here developed mean-field method is readily extendable to 3-D models and to inhomogenous systems like lamellar intergrowths. It can be used for rapid and robust prediction of $M_s(T)$ curves and thus can be applied to parameter studies. Inverse fitting of exchange constants can be achieved by minimizing the misfit between measured and predicted T_C values from a linearized T_C calculation. By applying the described method to the hematiteilmenite solid solution system, we find that the range of values for the exchange constants, consistent with available measurement data, is still too large to decide whether the ordered or the disordered solid solution of a given composition has higher T_C . We also derive numerically an approximately quadratic relation between the area of the peak in high-field susceptibility and the chemical order parameter. This supports a previous observation that antiferromagnetic, disordered, hematite-ilmenite solid solutions show no peak in high-field susceptibility, while it clearly occurs in ordered ferrimagnetic materials. Experimental verification of a quantitative relation

between peak area and ordering state Q would provide a powerful and simple technique to determine average bulk order Q in hematite–ilmenite solid solutions. However, future calibration measurements will require hematite–ilmenite solid solution samples of identical composition but with different Q values determined by independent means, for example, neutron powder diffraction (Harrison & Redfern 2001).

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REFERENCES

- Bloch, F., 1928. Zur Theorie des Ferromagnetismus, Z. Physik, 61, 206.
- Brown, N.E., Navrotsky, A., Nord, G.L.J. & Banerjee, S.K., 1993. Hematiteilmenite (Fe₂O₃-FeTiO₃) solid solutions: determinations of Fe–Ti order from magnetic properties, *Am. Mineral.*, **78**, 941–951.
- Burton, B.P., 1982. Thermodynamic analysis of the systems CaCO₃-MgCO₃, α -Fe₂O₃ and Fe₂O₃-FeTiO₃, *PhD thesis*, State University of New York at Stony Brook, Stony Brook, NY, USA.
- Burton, B.P., 1991. The interplay of chemical and magnetic ordering, *Reviews in Mineralogy and Geochemistry*, 25, 303–322.
- 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 Fe₂O₃-FeTiO₃, *Am. Mineral.*, **93**, 1260–1272.
- Fabian, K., Robinson, P., McEnroe, S.A., Heidelbach, F. & Hirt, A.M., 2011. Experimental study of the magnetic signature of basal-plane anisotropy in hematite, in *The Earth's Magnetic Interior*, Vol. 1 of IAGA Special Sopron Book Series, pp. 311–320, eds. Petrovsk, E., Ivers, D., Harinarayana, T. & Herrero-Bervera, E., Springer-Verlag.
- Fabian, K., Shcherbakov, V.P. & McEnroe, S.A., 2013. Measuring the Curie temperature, *Geochem. Geophys. Geosyst.*, 14(4), 947–961.
- Fischer, K.H. & Hertz, J.A., 1991. Spin Glasses, Cambridge Univ. Press.
- Ghiorso, M. & Evans, B., 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., 2009. Magnetic ordering in the ilmenite-hematite solid solution: a computational study of the low-temperature spin glass region, *Geochem. Geophys. Geosyst.*, **10**, 1–17.
- Harrison, R.J. & Becker, U., 2004. Magnetic and chemical ordering in the ilmenite-hematite solid solution: from lamellar magnetism to self reversals, *Geochim. Cosmochim. Acta*, 68, A80.

- Harrison, R.J. & Redfern, S.A.T., 2001. Short- and long-range ordering in the ilmenite-hematite solid solution, *Phys. Chem. Miner.*, **28**, 399–412.
- Heisenberg, W., 1928. Zur Theorie des Ferromagnetismus, Z. Physik, 49, 619-636.
- 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.
- Holstein, T. & Primakoff, H., 1940. Field dependence of the intrinsic domain magnetization of a ferromagnet, *Phys. Rev.*, 58, 1098–1113.
- Ishikawa, Y. & Akimoto, S., 1957. Magnetic properties of the FeTiO₃— Fe₂O₃ solid solution series, *J. Phys. Soc. Japan*, **12**, 1083–1098.
- Ishikawa, Y., Saito, N., Arai, M., Watanabe, Y. & Takei, H., 1985. A new oxide spin glass system of (1 x) FeTiO₃-x Fe₂O₃. i. magnetic properties, *J. Phys. Chem. Solids*, **54**, 312–325.
- Ising, E., 1925. Beitrag zur Theorie des Ferromagnetismus, Z. Phys., 31, 253–258.
- Kaneyoshi, T., Fittipaldi, I.P. & Beyer, H., 1980. A theory of a diluted ferromagnet, *Phys. Status Solidi b*, **102**, 393–401.
- Kosterlitz, J.M. & Thouless, D.J., 1973. Ordering, metastability and phase transitions in two-dimensional systems, *J. Phys. C: Solid State Phys.*, 6, 1181–1203.
- Lagroix, F., Banerjee, S.K. & Moskowitz, B.M., 2004. Revisiting the mechanism of reversed thermoremanent magnetization based on observations from synthetic ferrian ilmenite (y = 0.7), *J. geophys. Res.*, **109**, B12108, doi:10.1029/2004JB003076.
- Meiklejohn, W.H. & Carter, R.E., 1959. Exchange anisotropy in rock magnetism, J. Appl. Phys., 30, 2020, doi:10.1063/1.1735116.
- Morrish, A.H., 1994. Canted Antiferromagnetism: Hematite, World Scientific.
- Nabi, H.S., Harrison, R.J. & Pentcheva, R., 2010. Magnetic coupling parameters at an oxide-oxide interface from first principles: Fe₂O₃-FeTiO₃, *Phys. Rev. B*, **81**, 214432, doi:10.1103/PhysRevB.81.214432.
- Nagata, T., 1961. Rock Magnetism, revised edition, Maruzen.
- Onsager, L., 1944. Crystal statistics. I. A two-dimensional model with an order-disorder transition, *Phys. Rev.*, 65, 117–149.
- Robinson, P., Harrison, R.J., McEnroe, S.A. & Hargraves, R.B., 2002. Lamellar magnetism in the haematite-ilmenite series as an explanation for strong remanent magnetization, *Nature*, 418, 517–520.
- 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., Harrison, R.J., Miyajima, N., McEnroe, S.A. & Fabian, K., 2012. Chemical and magnetic properties of rapidly cooled metastable ferri-ilmenite solid solutions: implications for magnetic self-reversal and exchange bias, II. Chemical changes during quench and annealing, *Geophys. J. Int.*, **188**, 447–472.
- Robinson, P., McEnroe, S.A., Fabian, K., Harrison, R.J., Thomas, C. & Mukai, H., 2014. Chemical and magnetic properties of rapidly cooled metastable ferri-ilmenite solid solutions: implications for magnetic selfreversal and exchange bias, IV. The fine structure of self-reversed thermoremanent magnetization, *Geophys. J. Int.*, **196**, 1375–1396.
- Samuelson, E., 1969. Spin waves in antiferromagnets with corundum structure, *Physica*, 43, 353–374.
- Samuelson, E. & Shirane, G., 1970. Inelastic neutron scattering investigation of spin waves and magnetic interactions in α -Fe₂O₃, *Phys. Status Solidi b*, **42**, 241–256.
- Stephenson, A., 1972. Spontaneous magnetization curves and Curie points of spinels containing two types of magnetic ion, *Phil. Mag.*, 25, 1213– 1232.

Sample Label	a (Å)	<i>c</i> (Å)	$V(Å^3)$	Est. Comp. x (per cent)
Ilm 10 904C 6-19-77 powder	5.0409(1)	13.7775(2)	303.19(1)	13.0
Ilm 20 (Nov.16,1973) powder	5.0460(1)	13.8037(2)	304.38(1)	22.7
*Ilm 40 887C	5.0557(1)	13.8528(2)	306.64(1)	40.5
Ilm 40 16021978 powder	5.0571(1)	13.8569(2)	306.90(1)	42.5
Ilm 54.6 600C 28h	5.0657(1)	13.8978(2)	308.86(1)	56.6

 Table A1. Inferred chemical compositions of some synthetic ilmenite solid solutions of Burton (1982).

APPENDIX

Table A1 lists lattice parameters from high-resolution X-ray diffraction of some ilmenite solid solutions of Burton (1982) used in this study and inferences concerning their compositions. Diffraction and parameter refinements were performed by Tiziana Boffa Ballaran at Bayerisches Geoinstitut, Bayreuth. From the resulting unit cell volumes, average compositions x (mol.%FeTiO₃) were inferred using a standard working curve. Many of the results used here were published in Burton *et al.* (2008), but several samples lie outside the composition range x > 0.60 covered there. Table A1 lists the parameters and composition inferences for the additional samples used in this paper, also, for comparison, one other Ilm40 sample (*) not used here. The composition inferences are used for Figs 4 and 7.