Lamellar Magnetism in the Rhombohedral Oxides: How does it work?

Peter Robinson[1], Suzanne A. McEnroe[2], Karl Fabian[1], Richard Harrison[3]

[1] Geological Survey of Norway, N-7491 Trondheim

[2] Norwegian University of Science and Technology, Trondheim

[3] Cambridge University, UK

Corresponding author: peter.robinson@ngu.no

Abstract: The ferrimagnetism of pure magnetite depends on opposite and unequal magnetic substructures in octahedral and tetrahedral sites. In practice, the magnetization is controlled by domain walls, which respond to the Earth field; thus induced magnetization dominates. Remanence is important only where grains are of single-domain or pseudo-single-domain size. Pure hematite is basically antiferromagnetic from equal and opposite magnetic moments in the (001) basal plane, with a weak remanence due to very slight 'canting' of opposite magnetic moments. Pure ilmenite, below its 57 K Néel *T* is a near perfect antiferromagnet with magnetic moments normal to (001). Metastable Fe-Ti ordered ferri-ilmenite solid solutions can be quite strong ferrimagnets due to opposite but unequal moments in alternate layers. If temperature falls rapidly during ordering, this can lead to antiphase domain structures and examples of self-reversed thermoremanent magnetization. As Ti content increases, Curie temperature falls, but intensity increases, until the amount of Fe^{3+} producing adjacent-layer magnetic interactions goes below a critical level near Ilm 85. Beyond this one can talk about the magnetic intensity of ferrimagnetic pure ordered ilmenite at 4μB pfu, but there are no Fe^{3+} ions interacting in adjacent layers to allow this. The metastable solid solutions break down by exsolution during slow cooling according to a complex phase diagram, with the end products antiferromagnetic hematite with 8-15% of ilmenite component in solid solution (titanohematite), and ilmenite with barely 1-5% of hematite component in solid solution (ferri-ilmenite). How then can hematite with ilmenite exsolution lamellae (ilmeno-hematite), or ilmenite with hematite lamellae (hemo-ilmenite) carry a strong and stable remanence, especially when one of the phases by itself is a very weak ferromagnet and the other is not magnetic at all above ~57K?

The answer is in the special chemical make-up of phase interfaces parallel to (001), caused by natural adjustments to charge imbalance between these phases. As first demonstrated in Monte Carlo simulations, later supported by Mössbauer studies, there is a strong aversion to placing Fe^{3+} hematite layers against Ti^{4+} ordered ilmenite layers, rather hybrid "contact layers" are created during exsolution, consisting mainly of a mix of Fe^{2+} and Fe^{3+} ions. These reduce, but do not eliminate interface charge imbalance. Moreover, since we are dealing with reducing imbalance rather than perfecting balance, there is peculiar charge ordering in the contact layers, by which Fe^{3+} ions are in octahedrons sharing faces with Ti octahedrons, and Fe^{2+} ions are in octahedrons sharing faces with Fe^{3+} octahedrons, quite contrary to the situation in ordered ferri-ilmenite solid solutions. This was discovered in the Monte Carlo simulations, and confirmed in bond-valence and density-functional-theory calculations.

The magnetic moment of contact layers derives directly from the fact that exsolution lamellae must always consist of an odd number of cation layers, bounded by two contact layers. Thus, the two contact layers are always magnetically coupled on one side either to adjacent Fe^{3+} layers inside a hematite lamella, or to adjacent Fe^{3+} layers in hematite surrounding an ilmenite lamella, and their magnetic moments are always in the same direction. In models involving an even number of cation layers, the magnetic moment of a lamella equals two times the magnetic moments of two hybrid contact layers in one direction, minus the magnetic moment of one unbalanced hematite layer, thus:

$2\,[(Fe^{2+}/2) + (Fe^{3+}/2)] - (Fe^{3+}) = 2 \times (4\mu B/2 + 5\mu B/2) - (5\mu B) = 2\,(4.5\mu B) - (5\mu B) = 4\mu B$

During exsolution there is a critical difference between grains with (001) parallel to the magnetizing field and those perpendicular to the field. When parallel, all lamellae will tend to gain magnetic moments parallel to the field; when perpendicular, the field will have no influence on the magnetic moment orientations, resulting in weak magnetizations. We call this '**the external force effect**', which has its greatest importance in samples with a strong lattice-preferred orientation of (001) planes, and none where the grains are randomly oriented. There is a second important geometrical effect depending on whether the lamellae are of ilmenite within a magnetized hematite host, or hematite within a non-magnetic ilmenite host. In the former, the magnetic field will influence the actual positions chosen by the lamellae within the host, so that contact-layer magnetic moments will be, as much as possible, in the field direction. In the latter case, the positioning of lamellae within the non-magnetic ilmenite host cannot be influenced by the field, but moments will be parallel to it.

These two characteristics have a strong influence on demagnetization behavior. In order to demagnetize or reorient the magnetization with ilmenite lamellae in a hematite host, magnetization directions of all surrounding hematite must be changed, giving higher stability and coercivity. Where magnetization is entirely in hematite lamellae, the host exerts no influence, so demagnetization and reorientation is easier, and stability and coercivity lower.

Important tests of lamellar magnetism have come from study of hysteresis loops at temperatures below ~57K, where the ilmenite is antiferromagnetic, with a magnetic moment perpendicular to (001), and there is coupling across phase interfaces. Initial theoretical studies suggested that upon cooling below T_N of ilmenite, the lamellar moments would be pulled out of parallel with (001), thus geometrically possible for them to interact with the ilmenite and create a substantial magnetic exchange bias under these conditions. Then came a surprising result. If a natural sample with an NRM is cooled below ilmenite T_N in the absence of a magnetic field, the NRM is capable of interaction with ilmenite to create exchange bias, indicating that the magnetic moment of the NRM cannot be exactly parallel to (001) even at room *T*, but must be at an angle sufficient allow antiferromagnetic coupling with ilmenite. With this observation in mind, neutron diffraction at room *T* showed, in one example of finely exsolved titanohematite, that the magnetic moment of the lamellar magnetism is tipped out of the basal plane by ca. 30^o, thus allowing the observed phenomenon in which the NRM can influence the direction of ilmenite magnetization as the sample is cooled in the absence of a field.

In recent efforts, it has been possible to determine the exact NRM orientation of sample chips, most with evidence of a lattice-preferred orientation, and place these in a known direction of an applied field. Here, results from experiments in a 5T field uniformly show a bimodal distribution of ilmenite magnetizations dictated by the scattered LPO, with relative intensities of positive and negative peaks easily predicted by NRM instrument placement. If placed positive, the negative bias peak dominates. If placed negative, the positive bias peak dominates. When then cooled in a 5T positive field, the lamellar moment becomes all positive, resulting in all negative ilmenite magnetization and a unimodal negative exchange bias. These results seem to be quite easily explained by distributions of lamellar NRMs at about 30^o to (001) planes, that cause ilmenite magnetizations normal to (001) on cooling. When cooled in a 5T field the lamellar NRMs are almost completely oriented parallel to the field. When ilmenite magnetization sets in, it orients by strong antiferromagnetic coupling across the phase interfaces and is thus entirely in a negative direction.

If these results, and current thinking, are correct, then the magnetism of hematite, including the lamellar magnetism is relatively easily oriented in a 5T field, whereas the anisotropy of thin ilmenite lamellae is so strong, that magnetic moments, once set during cooling, are relatively little reset by changing fields up to 5 T.

Keywords: ilmeno-hematite, hemo-ilmenite, magnetic exchange bias, exsolution, interface magnetic coupling.