

Lamellar magnetism associated with nanoscale exsolution in the ilmenite-hematite solid solution



Richard J. Harrison¹, Rafal E. Dunin-Borkowski², Edward T. Simpson², Takeshi Kasama², Suzanne A. McEnroe³

1. Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge CB2 3EQ, rjh40@esc.cam.ac.uk
 2. Department of Materials Science and Metallurgy, University of Cambridge, Pembroke Street, Cambridge CB2 3QZ
 3. Geological Survey of Norway, N-7491, Trondheim, Norway



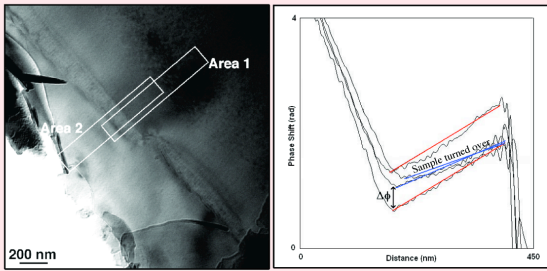
ABSTRACT

The ilmenite-hematite (FeTiO₃-Fe₂O₃) solid solution is one of the most important magnetic phases in nature. Unusual magnetic behaviour is often observed in intermediate compositions due to the interaction between cation ordering, magnetic ordering, and exsolution. This poster describes how this interaction leads to the phenomenon of lamellar magnetism in slowly-cooled metamorphic rocks. We also present the results of preliminary experiments to test the lamellar magnetism hypothesis directly using off-axis electron holography. The results are consistent with a significant enhancement of magnetization in regions that are exsolved on a very fine scale.

Metamorphic titanohematites from the Swedish Granulite Region carry an unusually strong and stable remanent magnetization, caused by the presence of exsolution microstructures at the nanometre scale. To provide insight into the effect of these precipitates on the bulk magnetic properties, we have performed a detailed series of Monte Carlo simulations, which model successfully the interaction between cation ordering, magnetic ordering, and exsolution in the ilmenite-hematite system. The simulations allow magnetic transitions in chemically heterogeneous systems to be studied. At low temperatures they predict an intergrowth of antiferromagnetic hematite and paramagnetic ilmenite. Despite the antiferromagnetic nature of the hematite component, the simulation cells as a whole are ferrimagnetic, with a small but significant net magnetization associated with the interface between exsolved phases. Competition between chemical and magnetic interactions leads to a characteristic cation distribution at the interface, which ensures a local imbalance between the numbers of up and down magnetic spins. The interface moment acts as a defect moment of the antiferromagnetic hematite, and has the magnitude, coercivity, and thermal stability required to explain the remanent properties of the metamorphic samples, thus establishing exsolved titanomagnetite as a potential carrier of strong remanence on Earth and other planets.

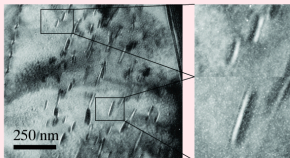
The magnetization of a hematite host containing fine scale ilmenite precipitates has been compared quantitatively with the magnetization of a region containing no exsolution lamellae using off-axis electron holography. The magnetization is determined from the holographic phase shift accumulated across each region. Analysis yields estimates of 3.8-4.7 mT for the exsolved region and 0.4-0.7 mT for the precipitate-free region, corresponding to an enhancement in magnetization by a factor of ~5. This is much lower than the theoretical maximum enhancement factor of ~22, indicating that there is a ~60:40 ratio of in-phase to out-of-phase lamellae. These results represent some of the smallest magnetic fields ever quantified using any technique at this spatial resolution, and further demonstrate why holography is at the forefront of attempts to understand mineral magnetism at the nanometre scale.

TRANSMISSION ELECTRON MICROSCOPY



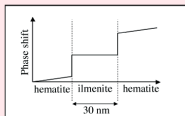
Electron holography has been used to compare the magnetic signal from regions containing abundant fine-scale exsolution lamellae with regions free from lamellae. The gradient of the holographic phase shift, $d\Phi/dx$, is proportional to the magnetic flux. To eliminate other contributions to the phase shift, a second hologram of the same area was recorded with the sample turned over. This has the effect of reversing the magnetic contribution to the phase, keeping other contributions the same. The difference in slope between the two measurements is then attributed to the magnetic contribution only.

The magnetic signal from exsolved regions is found to be around 3-5 times higher than in regions that are free of fine-scale lamellae. This is good agreement with the enhancement of magnetization seen in natural samples.

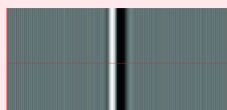


T. Kasama has produced a series of defocused images of ilmenite exsolution lamellae in hematite using the Lorentz mode of the TEM. The main feature of these images is the asymmetric contrast seen across the lamellae. A dark fringe is seen adjacent to a much lighter fringe. It is proposed this is an effect of the contact layer magnetization. Note that both white-black and black-white lamellae are observed in the experimental images, which may correspond to in-phase and out-of-phase lamellae, with opposed magnetizations.

Simulated Lorentz images were produced by E. Simpson, based on magnetic phase profiles consistent with the lamellar magnetism hypothesis. These were able to reproduce the asymmetric contrast across the lamellae.



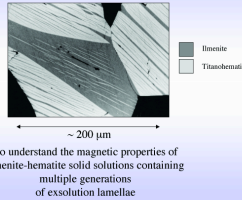
A simplified magnetic profile of an ilmenite lamella in hematite. The canted antiferromagnetic hematite, which has a small magnetic moment, surrounds the paramagnetic ilmenite. The large change in phase at the boundaries arises due to the hypothesized effect of the contact layers.



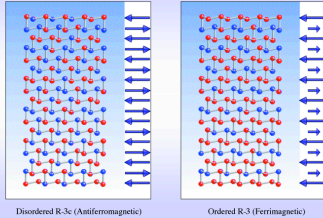
The simulated defocused image produced according to the assumed magnetic profile. The asymmetric contrast very closely resembles that seen in the defocused images.

INTRODUCTION

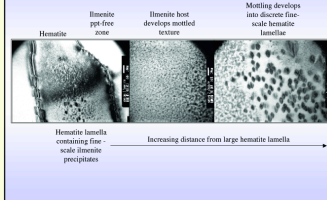
Nature of the problem



Crystal and Magnetic Structure of the Solid Solution



Transmission Electron Microscopy

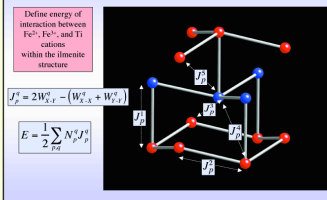


Intermediate members of the solid solution undergo a cation ordering phase transformation, involving partitioning of Fe and Ti cations onto alternating layers in the structure. Disordered distributions have a canted antiferromagnetic structure below the Curie temperature. Ordered distributions have a large ferrimagnetic moment. However, these are metastable with respect to an intergrowth of antiferromagnetic hematite and paramagnetic ilmenite, leading to fine-scale exsolution microstructures in slowly-cooled natural samples.

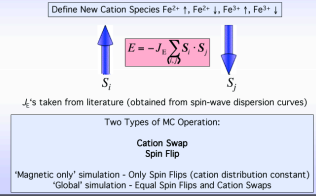
The saturation magnetization of exsolved samples is a factor of 2-5 greater than that expected for the weak canted antiferromagnetic moment of the hematite component.

ATOMISTIC MODEL OF CHEMICAL AND MAGNETIC ORDERING

Model for cation ordering

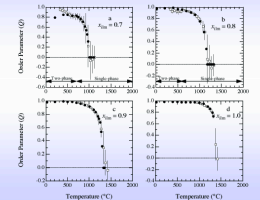


Including Magnetic Ordering in the Simulation

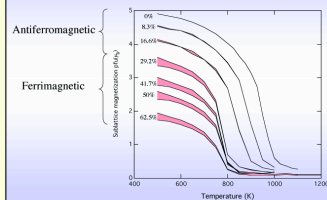


RESULTS OF MONTE CARLO SIMULATIONS

Monte Carlo Simulation of the R-3c to R-3c phase transition



'Global' Simulations (magnetic and cation ordering develop simultaneously)



Results of 'Global' Simulations

Hyperitectoid compositions lose their magnetization suddenly at 800K on entering the PM R-3c + PM R-3 field

