



## **A new perspective on self-reversed thermo-remanent magnetization and room-temperature magnetic exchange bias in quenched and annealed ferri-ilmenite solid solutions**

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In the 1950's, rocks containing ferri-ilmenite solid solutions with compositions  $X \text{FeTiO}_3 = 0.53\text{-}0.71$  were discovered to self-reverse during cooling in a weak field. Such samples played a vexing early role in the history of geomagnetism, because they demonstrably acquire a thermoremanent magnetization (TRM) inverse to the external field, strengthening a common opinion, at that time, that reversed lavas result from a rock-magnetic self-reversal process, while the geomagnetic field polarity itself is constant in time.

Early self-reversal models postulated two distinct phases, a subsidiary phase with weak magnetization, and higher Fe content, Curie temperature, and coercivity, referred to as "the x phase", and a dominant phase with a strong magnetization, lower Fe content, Curie T temperature, and coercivity. The "x phase" magnetizes first at higher temperature parallel to the Earth field, and the dominant phase acquires a stronger magnetization at a lower temperature in an orientation opposite to the Earth field, either by direct antiferromagnetic coupling, or as a magnetostatic response to the previously acquired mineral magnetization.

Landmark work by Nord and Lawson, on quench and annealing experiments with TEM, showed that, during quench, the solid solution starts to order, but with alternate A and B positioning of Fe and Ti layers. With coarsening, the alternately and chaotically positioned domains merge along antiphase domain boundaries (APBs) that are inherently unstable. With further annealing, boundaries move and are eliminated due to coarsening of some domains and shrinking of others. They showed that quenched, or slightly annealed samples, show self-reversed TRM, but further annealing results in a coarse simple ferrimagnetic phase. They suggested that the "x phase" is represented by the disordered regions along the chemical antiphase boundaries.

Harrison visualized a solid solution sample, after quench and coarsening after annealing, which consisted of two kinds of regions, one dominated by A-ordering containing smaller regions of B-ordering and the other dominated by B-ordering with smaller regions of A-ordering. The key feature for self-reversal is that small and shrinking domains became progressively Fe-enriched compared to their larger neighbors, and the elusive "x-phase" is explained as a less strongly ordered Fe-enriched phase near APBs during coarsening. We pursued these studies further with TEM of the APB's and demonstrating chemical phase separation in a synthetic composition  $\text{FeTiO}_3 = 0.61$ . Subsequent annealing of this sample showed self-reversed TRM and room-temperature magnetic exchange bias. Analysis of charge balance across APB's showed the significant role of contact layers and disordered layers. Monte Carlo simulations demonstrated the necessity for Fe-enrichment in the diminishing phase. A theoretical approach to the ferri-ilmenite phase diagram showed potential for metastable chemical phase separation over a wide composition range, related to the order parameter Q, at temperatures well above phase separation over a limited composition range related to a chemical solvus. A key feature of the new perspective is the recognition of simple antiferromagnetic coupling across the APBs. Evidence suggests negative magnetic (antiferromagnetic) coupling required for magnetic self-reversal can only be maintained when the antiphase domains are smaller than  $\sim 50$  nm.