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Fe^{2+}/Fe^{3+} charge ordering in contact layers of lamellar magnetism: Bond valence arguments

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ABSTRACT

Fe^{2+}/Fe^{3+} charge ordering in the contact layers of lamellar magnetism in the hematite-ilmenite series is not a postulate of the lamellar magnetism hypothesis. Such ordering is possible, however, and a model was suggested earlier in which contact layer Fe^{2+} octahedra share faces with ilmenite layer Ti^{4+} octahedra, and contact layer Fe^{3+} octahedra share faces with hematite layer Fe^{3+} octahedra, thus copying the shared-face configurations of ilmenite and hematite, respectively. This model and related charge-balance matters could be explored using bond-valence theory, a simplified picture of complex bonding which takes into account the relationship between bond strength and bond distance, but ignores magnetism. This has now been done, and shows that local oxygen charge satisfaction is strongly favored by a different charge-ordering scheme, in which contact layer Fe^{3+} octahedra share faces with ilmenite layer Ti^{4+} octahedra, and contact layer Fe^{2+} octahedra share faces with hematite layer Fe^{3+} octahedra. A new, more sophisticated, Monte Carlo simulation of the interface, including electrostatic and magnetic interaction parameters of cations, reported in detail elsewhere, independently shows the same charge-ordering scheme. For the cation ordered metastable ilmenite 50 composition, bond-valence theory indicates that, unlike the contact layers, the favored charge ordering scheme in Fe layers would have the same shared-face configurations as ilmenite and hematite.

Keywords: Crystal chemistry, bond valence, hematite, ilmenite, magnetic properties, lamellar magnetism, order-disorder, Fe charge ordering