Absence of charge localization in compressed magnetite from first principle computations

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Magnetite (Fe_3O_4) is a magnetic mineral, of interest as a carrier of paleomagnetic data and for use in magneto-optical devices. Magnetite occurs in the inverse spinel structure: in this structure *n* tetrahedral sites (*t*) are occupied by ions with a nominal 3+ charge, while the 2n octahedral (*o*) sites are equally occupied by 2+ and 3+ ions. Magnetite is an antiferrimagnet with the moments of the *o* Fe having the opposite direction from those on the *t* site. Under ambient condition the two *o* Fe are equivalent, implying that nominal charges on this site can be written as 2.5+. Charge localization on the *o* site has been invoked both under low temperature (T), in order to explain the Verwey transition where magnetite transforms from a metal to an insulator, as well as a high pressure (P). While structural distortions and charge localization under low T have been explored extensively, charge localization under P has not attracted a comparable amount of attention. Using in-situ Mössbauer spectroscopy evidence for a transition with increasing P from Fe^{3+}(*t*) and 2 $Fe^{2.5+}$(*o*) through an intermediate state of Fe^{3+}(*t*) and Fe^{2+},Fe^{3+}(*o*), the inverse spinel, to normal spinel with Fe^{2+}(*t*) and 2 Fe^{3+}(*o*) has been found. Here we test the hypothesis of charge ordering as a function of P by means of density functional methods. We apply all electron computations (LAPW) with the generalized gradient (GGA) as well as LDA+U approximations to the exchange and correlation potential to investigate the electronic and magnetic structure of the three Fe sites in the structure, breaking the equivalency of the *o* sites. We monitor the magnetic moments and the electronic density states associated with them and evaluate the charge density with Bader charges. While formal charges can not be inferred from this, the Bader analysis should be sensitive to finding charge differences between the various sites. We are, however, not able to find any discernable charge localization, electronic or magnetic differences for the two *o* sites for compression range explored (V/V_0>0.80).