**Magnetic States and Intervalence Charge Transfer of Ti and Fe Defects in *α*-Al2O3: The Origin of the Blue in Sapphire**

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Aiming to identify the spin configuration and its alignment of Ti and Fe of ground-state configuration in blue sapphire, we investigate various spin configurations of Ti and Fe in Al2O3 in search of the spin configuration which give the lowest energy. To examine the electronic, energetic, and structural properties, we perform first-principles density-functional-theory calculations within the PBEsol generalised gradient functional with adding Hubbard U potential. From the total energy results, we show that the high-spin state of TiIV-FeII with an anti-ferromangetic alignment between Ti and Fe is the ground state for both edge- and face-sharing orientations. Among several meta-stable states, the high-spin state of TiIII-FeIII with an anti-ferromagnetic alignment is connected to the TiIV-FeII ground state. An optical transition from the highest occupied Fe defect level to the lowest unoccupied Ti leads to an excited state of the high-spin TiIII-FeIII configuration together with a donation of electron from FeII to TiIV. It explains that the TiIV-FeII is the ground state and the intervalence charge transfer of TiIV-FeII to TiIII-FeIII would be responsible for the color of blue in sapphire. We find that both edge- and face-sharing alignments can be found in nature since their ground state energies are different by only 0.02 eV. However, only the edge-sharing alignment would be expected to be the origin of the blue in sapphire. The corresponding optical excitation energies of this transfer of edge- and face-sharing alignments are 1.99 and 1.36 eV, respectively.