Electronic structures of siderite (FeCO₃) and rhodochrosite (MnCO₃): Oxygen *K*-edge spectroscopy and hybrid density functional theory

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ABSTRACT

Electronic transitions of siderite and rhodocrosite may have played a role in prebiotic synthesis by photochemical reactions in the Archean. In the work described here, I measured the electronic structures of siderite ($FeCO_3$) and rhodocrosite ($MnCO_3$) using O *K*-edge X-ray absorption and emission spectroscopy. At the same time, I present theoretical calculations of electronic structure using periodic density functional theory with several different exchange correlation functionals. To help verify the reliability of the basis sets and the exchange correlation functionals, I determined the optimized crystal structures of $FeCO_3$ and $MnCO_3$ in the antiferromagnetic (AF) rhombohedral unit cell. All three exchange-correlation functionals give static volumes and cell parameters that differ from experiment by <2%.

The O *K*-edge absorption spectra are assumed to measure the O(2p) density of states in the unoccupied orbitals that are primarily Fe(3d) and Mn(3d) in character. Emission spectra show the O(2p) density of states that comprise the occupied bonding orbitals. Using both spectra, I estimate the $O^{2-} \rightarrow Fe^{2+}$ band gap in $FeCO_3$ to be 4.4 ± 0.2 eV while the $O^{2-} \rightarrow Mn^{2+}$ in $MnCO_3$ is 5.8 ± 0.2 eV. Theoretical calculations of the density of states calculated using the PBE exchange correlation functional seriously underestimate the O(2p)-Mn,Fe(3d) band gaps while those calculated using the hybrid B3LYP exchange correlation functional (with 20% Hartree-Fock exchange) overestimate the band gaps. A modified B3LYP functional with 10% Hartree-Fock exchange, however, gives a band gap in close agreement with experiment for both phases. Simulated O *K*-edge spectra, obtained by Gaussian smearing of the projected O(2p) density of states, give a reasonable description of the O *K*-edge emission spectra but a poor description of the experimental O *K*-edge absorption spectra. However, the O *K*-edge absorption spectra are reasonably simulated by the total density of states. Excitations to the C-O antibonding states are predicted to lie near 4.6 eV in siderite.

Keywords: Siderite, rhodochrosite, oxygen *K*-edge spectroscopy, B3LYP, PBE, electronic structure, density functional theory, Archean, photochemistry