Pressure Stimulated Charge-Crossover in Transition-Metal Oxides and Hydroxides

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Mössbauer spectroscopy, x-ray diffraction (XRD), and electrical resistance (R(P,T)) studies were applied to investigate the high properties of the Mott insulator antiferromagnetic layered $Fe(OH)_2$ and $CuFeO_2$. In $Fe(OH)_2$ an unforeseen process by which a gradual Fe^{2+} oxidation takes place, starting at ~8 GPa reaching 70% Fe^{3+}-abundance at 40 GPa. Based on XRD and R(P,T) data it is unequivocally concluded that this non-reversible process, $Fe^{2+} \rightarrow Fe^{3+} + e^{-}$, results in Fe^{2+} converting into Fe^{3+} with no structural transition. The "ousted" electrons form a deep band within the $Fe(OH)_2$ high-pressure electronic-manifold becoming weakly-localized at P > 50 GPa. This process is attributed to an effective ionization potential created by the pressure-induced orientation deformed $(OH)^{-1}$ dipoles and the unusual small binding energy of the valence electron in $Fe^{2+}(OH)_2$.

Magnetic properties of the 2D spin-frustrated $CuFeO_2$ delafossite have been studied up to 100 GPa. The partially disordered spin arrangement at ambient pressure in the 11 – 16 K range, transforms with pressure to a long-range ordered "5-sublattice" phase with a distinct T_N, a similar role played by external magnetic field in neutron studies. This phase gradually substitutes for the "4-sublattice" magnetic ground state present at ambient pressure, reaching 100% at 19 GPa. The twofold increase of T_N at 19 GPa is explained in terms of the unusual increase of the intra-planar direct exchange $J_{||}$ caused by the anomalous anisotropic compression of $CuFeO_2$ in which *c/a* increases with pressure. With further pressure increase at ~ 30 GPa, about half of the Fe^{3+} and Cu^{1+} ions undergo a *reduction-oxidation*1 transition: $\left(Fe^{3+}, Cu^{1+}\right) \xrightarrow{P} \left(Fe^{2+}, Cu^{2+}\right)$ explained by pressure-induced *band overlap*. New magnetic sublattices are formed composed of Fe^{2+}(S=2) and Cu^{2+}(S=1/2) enhancing dramatically the T_N. At 50 GPa both Fe ions undergo a spin transition and finally at 80 GPa a *Mott* transition into a metallic state takes place.