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High pressure structural and electronic transitions in lithium ferrites

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Electronic, magnetic and structural transitions in strongly correlated transition-metal compounds have been among the main topics of condensed-matter research over recent decades, being especially relevant to understanding high-temperature superconductivity as well as heavy-fermion behavior. The definitive electronic phenomenon in such compounds is the breakdown of d- electron localization, causing a Mott (Mott-Hubbard) insulator-to-metal transition typically accompanied by a collapse of magnetic moments [1]. Such a transition does not necessarily imply a rearrangement of atoms, but in fact often exhibits an appreciable collapse in volume or even symmetry change [2]. The classic Mott transition observed in many systems involves a simultaneous insulator–metal transition, magnetic moment collapse and volume collapse.

Here, we have report structural, magnetic and electronic properties of the disordered α-LiFeO2 and ordered LiF5O8 compounds, which crystallize in the cubic (Fd3m and P4332 space group, respectively) structure, and ordered T- LiFeO2 (space group I41/amd), at pressures up to about 1 Mbar. The work is based on our experimental high-pressure studies employing: (i) diamond anvil cells, (ii) synchrotron powder and single crystal x-ray diffraction, (iii) 57Fe Mössbauer spectroscopy, (iv) electrical resistance, and (v) Raman spectroscopy. For the disordered LiFeO2 system, the crystal structure is stable at least up to 82 GPa, though a significant change in compressibility has been observed above 50 GPa. The changes in the structural properties are found to be on a par with a sluggish Fe3+ high- to low-spin (HS-LS) transition (S=5/2 → S=1/2) starting at 50 GPa and not completed even at ~100 GPa. The HS-LS transition is accompanied by an appreciable resistance decrease; however, the material remains a semiconductor up to 115 GPa and is not expected to be metallic even at about 200 GPa [3]. These features of the structural and electronic transition in α-LiFeO2 strongly contradict with the case of ordered T- LiFeO2, which undergoes a first-order isostructural transition above 50 GPa.

For the ordered spinel LiF5O8, an irreversible structural phase transition from the cubic phase to the orthorhombic (space group Cmcm) post-spinel structure has been observed above 40 GPa accompanied by about 4% volume reduction. Another noticeable change in the V(P) data, namely: a steeper decrease of unit-cell volume with pressure increase occurs above 60 GPa corroborating with a significant change of the electronic and magnetic properties resulting in the gradual formation of the nonmagnetic metallic high pressure state on the Fe3+ octahedral sites [4]. With this, 40% of Fe3+ occupying bicapped trigonal prism sites remain in the HS state. Thus, our studies demonstrate that in a material with a complex crystal structure, containing transition metal cation(s) in different environments, delocalization/metallization of the 3d electrons does not necessarily occur simultaneously and may propagate through different crystallographic sites at different degrees of compression. The effect of Fe3+ nearest and next nearest neighbors on the features of the electronic transition is discussed.

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