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Thermodynamic stability and electronic response to phonon mode in silver diflouride polymorphs

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Two polymorphic forms have been reported for solid AgF_2 at ambient pressure: a layered $Ag^{II}F_2$ (α) and a charge density wave $Ag^{I}Ag^{III}F_4$ one (β). The α phase is better known of the two. It has recently received attention due to numerous structural and electronic similarities with oxocuprate precursors of high-temperature superconductors [1]. The key common feature of AgF_2 and undoped oxocuprates is the presence of antiferromagnetic sheets of $A^{II}B_2$ stoichiometry(AgF_2 resp. CuO_2). Correspondingly, structural, electronic and magnetic properties of α form at ambient and high pressures have been thoroughly examined in number of experimental and theoretical studies [1–4]. β form has been observed before only once as a red-brown amorphous product of reaction of $AgBF_4$ with $KAgF_4$ in anhydrous HF [5]. It is known to undergo rapid exothermic conversion to the alpha form when temperature is raised from -80°C to ca. 0°C: $Ag^{I}Ag^{III}F_4 \rightarrow 2Ag^{II}F_2$ [5] and its has been confirmed in an early theoretical study, which assumed that β form adopts that of $KAgF_4$ type structure. In the present work, we have thoroughly scrutinized the relative thermodynamic stability and lattice dynamics of the two phases, $Ag^{II}F_2$ and Ag^{I} $Ag^{III}F_4$, in a comparative theoretical and experimental study employing Raman spectroscopy and Density Functional Theory (DFT). We provide theoretical evidence for dynamical stability of both polymorphs, calculate thermodynamic potentials, perform normal mode analysis and discuss relative thermodynamic stability of the two phases.

The individual $Ag^{II}F_2$ α-phase layers are isoelectronic with $[CuO_2]$ sheets in oxocuprates [1]. Both systems are AFM semiconductors with charge-transfer band gap. In $Ag^{II}F_2$ (α) we have identified Ag–F bond stretching modes of B_{2g} symmetry with unusually strong response to on-site Coulombic correlation. The response of electronic structure to the B_{2g} mode is characterized by modulation of intervalence charge transfer (ICT), which is accompanied by bandgap closure and subsequent reopening as the system progresses from antiferromagnetic $Ag^{II}Ag^{II}F_4$ to diamagnetic mixed-valence $Ag^{I}Ag^{III}F_4$ state. AgF_2 in this respect is analogous to oxocuprates family.

Refs
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