Theoretical investigations of the canted antiferromagnetism in Co doped $BiFeO_3$

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$BiFeO_3$ is one of the most actively studied multiferroic materials that exhibits a robust ferroelectric order below ~ 1103 K and the formation of an antiferromagnetic (AFM) order below ~ 640 K [1]. Numerous researches have been conducted on this system in order to explore its potential in effecting electric field control of magnetic order for potential energy-efficient spintronic applications [2]. The magnetic order in $BiFeO_3$ is complex in nature. Close competition between various magnetic interactions, such as superexchange, Dzyaloshinskii-Moriya (DM) interaction and single ion anisotropy (SIA), lead to the formation of magnetic orders like the (1) G-type AFM order and (2) long period cycloidal order (~62nm). The formation of the latter order results in the cancelation of the weak canted magnetization (M) of the former order. The transition of the system from one magnetic order to the other is controlled by various stimuli, such as temperature, chemical doping, strain and pressure. By doping the system with Co ions, not only the stabilization of the canted G-type AFM order was observed, but also an enhancement of magnetization (M) and strong magnetoelectric coupling were reported [1,2]. In the present study, using first-principles calculations and by employing a constructed model spin Hamiltonian and Monte Carlo simulations, we have studied the stability of the canted G-type AFM as a function Co doping level.

Co^{3+} ion can exhibit various spin states, such as low (S=0), intermediate (S=1) and high (S=2) [3] (Here S represents the spin of Co^{3+} ions). This ambiguity pertaining to the electronic structure of doped Co^{3+} ions [4,5,6] further contributes to the complexities of the $BiFeO_3$ system. Our detailed investigations of various properties of the $BiFeO_3$ system as functions of Hubbard U parameter and the concentration of Co ions show that, (1) the spin state of Co^{3+} ions strongly depend on the U value (see Figure 1(a)), and (2) the calculated contractions of volume with increase of Co concentrations are in best agreement with the experimental observations corresponding to the mixed spin state of Co (see Figure 1(b)). Finite temperature Monte Carlo results considering a wide range of magnetic parameters, lead to identify the factors that enhance the stability of the canted G-type AFM phase. On one hand we observe that the strong tendency of the Co^{3+} high spin state to orient in the $\{111\}_{pc}$ plane, which is perpendicular to the direction of the spontaneous polarization, enhances the stability of the canted G-type AFM phase and on the other hand the formation of the intermediate spin state contributes to increase the magnitude of M (see Figure 1(c)). Our study indicates the existence of multiple spin states of Co in the system under investigation. These findings will expectedly stimulate further research in this direction. We have also endeavored to develop guidelines for designing of materials in order to enhance the multiferroic properties of $BiFeO_3$.

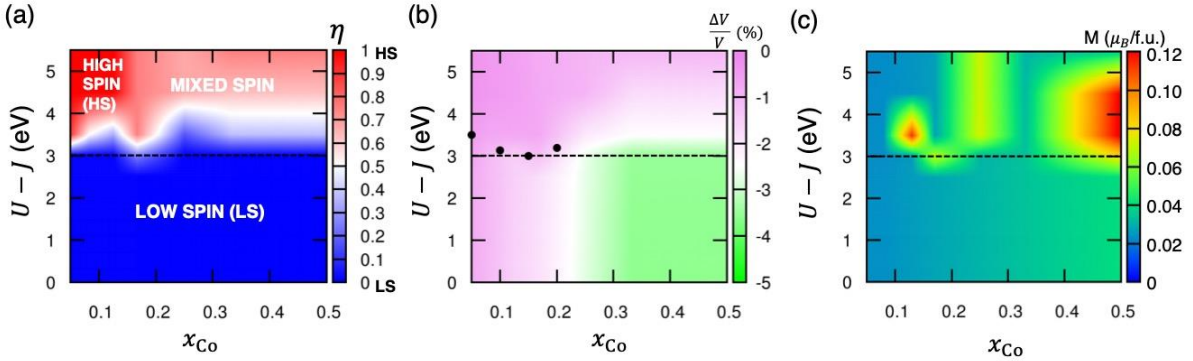

Figure 1 (a) Formation of Co^{3+} spin state as a function of (U - J) parameter and Co concentration (x_{Co}). η=1.0 and η= 0.0 denotes high spin (HS) and low spin (LS) state, respectively. (b) and (c), change of volume and calculated net magnetic moment as a function of U-J and x_{Co}, respectively. The black solid spheres represent the (U – J) values that correspond to the best agreement with the experimentally observed reduction of volume with the increase of Co concentration.

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