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Spin-Canting Mediated Metallic State in Lightly Electron-Doped $CaMnO_3$

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1. Introduction

It is a new frontier in development of field effect transistor (FET) to utilize the metal-insulator transition of strongly correlated electron systems as a resistivity switch. This new kind of FET is sometimes called "Mott transistor", and is expected to overcome the limitation of existing semiconductor devices [1].

$CaMnO_3$ (CMO) is one of promising materials to realize the Mott transistor [2]. CMO is a G-type antiferromagnetic (G-AFM) insulator at low temperature. Small amounts of electron-doping to CMO cause the emergence of a weak ferromagnetic (FM) component in the background of the G-AFM order [3]. A recent experiment has revealed that this emergence of a weak FM component is accompanied with a drastic lowering of the electronic resistivity [4].

So far, the origin of the weak FM component has been studied, in terms of the double-exchange (DE) mechanism, and two scenarios have been proposed. One is the spin-canting in the G-AFM (canted G-AFM, cG-AFM in short) [5], and the other is the AFM-FM phase separation (PS) [6]. Although both scenarios are compatible with the experimental magnetic property, we cannot expect metallic behavior naively by the PS scenario with small metallic FM domains. On the other hand, in the spin-canting scenario, metallic behavior is naturally expected with the DE hopping of electrons in the entire system.

In this study, we give quantitative arguments of the FM component in cG-AFM as a function of electron-doping. In our previous study [7], the cG-AFM has been investigated only in the lightly doped region. Here, stability of the cG-AFM is again clarified by taking into account the highly doped region, together with the possibility of the AFM-FM PS.

2. Methodology

Stability of cG-AFM state is clarified by the detailed electronic structure calculations with the noncollinear version of local spin density approximation (LSDA). We use the projector augmented-wave method with plane-wave basis as implemented in the QMAS (Quantum MAterials Simulator) code [8]. The Perdew-Zunger version of the LSDA exchange-correlation potential was adopted. The plane-wave energy cutoff is set to 40 Ry. The $\boldsymbol{k}$-points sampling for the self-consistent-loop is set to 8×6×8 in the full Brillouin zone. The charge populations are estimated by Bader analysis. Details of our computational method are given in Ref. [7] and references therein.

For the sake of simplicity, the crystal structure is fixed to that of nondoped CMO [3]. The electron-doping is achieved by changing the electron filling with the compensating positive background to guarantee the charge neutrality of the system.

3. Results and Discussion

The experiment has suggested that magnetic moments of the G-AFM are aligned along the *b* axis in the nondoped case, and the FM component is induced along the *c* axis by the electron-doping [3]. Hence, the stability of the cG-AFM is examined by the rotation of Mn magnetic moments in the *bc* plane. As shown in Fig. 1(a), this rotation angle is given as θ.

In Fig. 1(b), the θ dependence of the total energy is given for several different N_e values with N_e denoting the number of doped electrons per formula unit. At N_e =0.00, G-AFM state is the most stable, and the FM state is higher than the G-AFM one by 99meV/f.u. When electrons are doped into the system, the energy minimum deviates from θ=0° and the cG-AFM state is stabilized. The stable θ becomes larger with increase of N_e. The FM state is also stabilized with increase of N_e, but is not a local minimum in the lightly electron-doped region ($N_e < 0.25$).

The θ's at the minimal energy for each N_e are evaluated by the polynomial fitting. The result is summarized with the corresponding Mn magnetic moment, M (μ_B/Mn), in Table I. The present results are compared with the experimental result for Ce-doped CMO [3], where the weak FM component is observed at $0.01 < N_e < 0.15$. The N_e de-

Table I. The N_e dependence of magnetic moment M (μ_B/Mn) and canting angle θ (degrees) is given. Experimental data are from Ref. [3].

N_e		0.00	0.05	0.10	0.15	0.20	0.25	0.50	1.00
θ	Exp.	0.00	12.1	27.1	31.2				
	Present	0.00	12.4	19.3	26.0	29.8	33.7	55.0	90.0
M	Exp.	2.44	2.25	2.48	2.05				
	Present	2.42	2.44	2.47	2.49	2.52	2.55	2.57	2.41

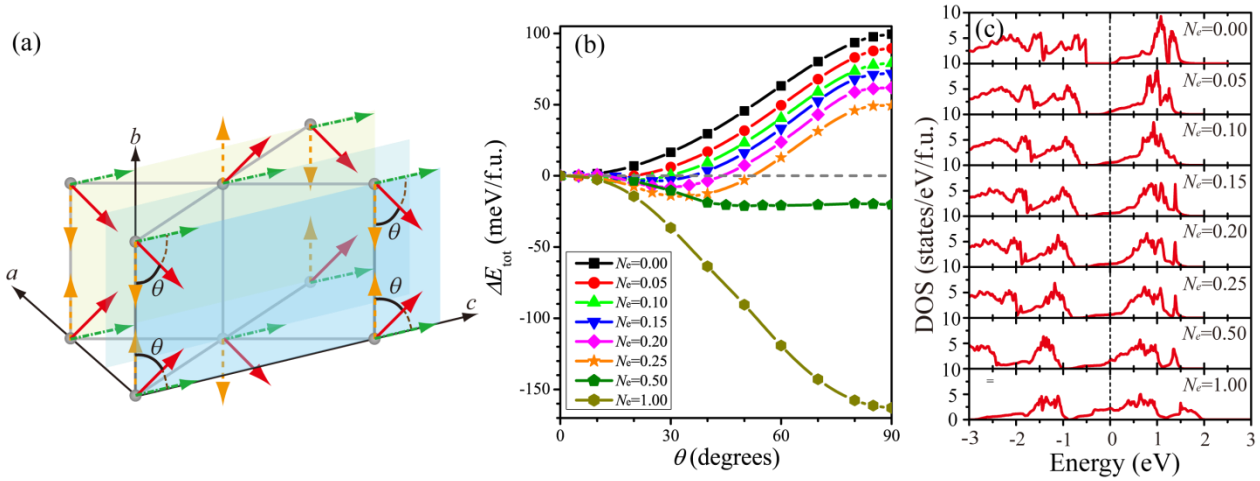

Fig. 1. (a) A schematic view of the cG-AFM is given. The dashed arrows represent the G-AFM configuration. The solid arrows represent the cG-AFM configuration with the canting angle θ within bc plane. The dashed and dot arrows represent the FM configuration. (b) The canting angle (θ) dependence of the total energy is given. The total energy is measured with reference to that at θ=0◦ at each N_e. The θ=0◦ and θ=90◦ indicate G-AFM and FM, respectively. (c) The DOS's for each N_e are given at the global minimum in Fig.1(b). The energy zero corresponds to the Fermi energy, except for N_e=0.00. At N_e=0.00, the energy zero is set to the conduction band bottom.

pendence of θ is in good agreement with the experimental one. The value of M is also consistent with the experiment.

The θ dependence in Fig. 1(b) is explained qualitatively by the DE model. From the result at N_e=0.00, the G-AFM is stabilized by the superexchange interaction, which is proportional to $-M_{\mathrm{i}}M_{\mathrm{j}}\cos 2\theta$. With increase of N_e, the DE electron hopping, which is in the form of $-t\sin\theta$, works effectively. Shifts of stable canting angle would suggest N_e dependence of the hopping magnitude t. The result at N_e=1.0 apparently suggests an importance of intersite Hund's exchange interaction in the form of $-M_{\mathrm{i}}M_{\mathrm{j}}\sin^2\theta$, in the highly doped region.

The DOS's for each N_e are shown in Fig. 1(c). At N_e =0.00, the system is an insulator with the band gap of 0.50 eV. The DOS's for the cG-AFM state show the broadening of the band width with increase of N_e. This is due to an increase of electron hopping among neighboring Mn's, and the system shows stronger metallic character, as observed in the experiment [4].

The reasonable agreement between our calculation and the experiment [3] suggests that the FM component in Ce-doped CMO is explained by the spin-canting from the G-AFM, despite that the randomness in the potential and ionic size difference by the substitution of Ce^{4+} for Ca^{2+} are neglected in the present calculations. This fact implies that electronic mechanism is dominant for the emergence of the weak FM component in Ce-doped CMO.

The system does not show the tendency toward the AFM-FM PS in the lightly electron-doped region, since the FM state is stabilized only in the highly doped region, which is far from the doped region for the experimental weak FM phase. On the other hand, the AFM-FM PS has been reported in La-doped CMO [9]. In this case, doped electrons are strongly localized to a certain site through the electron-lattice coupling, and an FM domain or polaron is stabilized [10]. Oxygen vacancy, which is inevitable in realistic situations, is another source for the emergence of the weak FM component. Since the AFM-FM PS is unfavorable for the metallic nature as mentioned before, the doping element dependence, including oxygen vacancy, is quite important on the evaluation of functionality as a resistivity switch. This point should be clarified carefully, by taking into account the substitution effect for Ca^{2+} or the presence of oxygen vacancy.

4. Conclusion

We studied the origin of the weak FM component accompanied with the metallic character in lightly electron-doped CMO. The present results have shown that the cG-AFM state is stabilized by the electron-doping through the DE mechanism. The magnetic and electronic phase change in lightly Ce-doped CMO is reasonably interpreted by the spin-canting. However, a possibility of the AFM-FM PS still remains, and the doping element dependence remains to be clarified.

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References

[1] C.H. Ahn *et al.*, Nature **424** (2003) 6952.
[2] P.-H. Xiang *et al.*, Adv. Mater. **23** (2011) 5822.
[3] E.N. Caspi *et al.*, Phys. Rev. B 69 (2004) 104402.
[4] P.-H. Xiang *et al.*, Appl. Phys. Lett. 94 (2009) 062109.
[5] P.-G. De Gennes, Phys. Rev. 118 (1960) 141.
[6] E. Dagotto, T. Hotta and A. Moreo, Phys. Rep. **344** (2001) 1.
[7] H. Ohnishi *et al.*, Phys. Rev. B **85** (2012) 165128.
[8] http://qmas.jp/
[9] C.D. Ling *et al.*, Phys. Rev. B **68** (2003) 134439.
[10] H. Meskine, *et al.*, Phys. Rev. Lett. **92** (2004) 056401.