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A better ferrimagnetic half-metal $LuCu_3Mn_4O_{12}$: Predicted from first-principles investigation

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ABSTRACT

Electronic structure calculations based on density functional theory (DFT) within the generalized gradient approximation (GGA) and GGA+*U* for manganite cuprate compound $LuCu_3Mn_4O_{12}$ have been performed, using the full-potential linearized augmented plane wave method. The calculated results indicate that $LuCu_3Mn_4O_{12}$ is ferrimagnetic and half-metallic in both GGA and GGA+*U* calculations. The minority-spin band gap is 0.7 eV within GGA, which is larger than that of $LaCu_3Mn_4O_{12}$ (0.3 eV), indicating its better half-metallicity. Further, the minority-spin gap enlarges from 0.7 to 2.8 eV with *U* taken into account, and simultaneously the Fermi level being shifted to the middle of the gap, making the half-metallic energy gap to be 1.21 eV. These results demonstrate that electronic correlation effect enhances the stability of half-metallic property. These facts make this system interesting candidates for applications in spintronic devices.

1. Introduction

In the past few years, considerable attention has been paid to the colossal magnetoresistance (CMR) effect in manganite perovskites from both experimental and theoretical point of view. The attractiveness of studying these systems comes from their new properties owing to various couplings of charge, spin and orbital degrees of freedom, and from possible applications as future new magnetoelectronic devices. Particularly, half-metallic (HM) materials, which are characterized by a metallic electronic structure for one spin channel, while an insulating property for the other spin channel are receiving more and more attention and are believed to be promising as ideal components of spintronic devices. Since there is only one electronic spin channel at the Fermi energy of HM materials, these materials may show a 100% spin polarization at the Fermi level without any external operation [1]. Therefore, to find new HM compounds with T_c values above room temperature is of both fundamental and technological importance.

Recently, it is reported that perovskite-type $CaCu_3Mn_4O_{12}$ without double exchange (DE) interaction exhibits large low-field response below T_c (T_c=355 K), with a value as large as 40% at 20 K [2]. Unlike common CMR materials which exhibit stable and high magnetoresistance (MR) only at high magnetic field up to several teslas, but in a narrow temperature range, $CaCu_3Mn_4O_{12}$ shows good MR response at room temperature and at low field. This is appealing since, for practical application, significant temperature stability is required. Thereafter, systematic theoretical calculations based on density functional theory (DFT) were performed on $CaCu_3Mn_4O_{12}$ to investigate its basic electronic and magnetic structures [3–5]. $CaCu_3Mn_4O_{12}$ crystallizes in a perovskite-like structure, space group $Im\bar{3}$ (No. 204), and has the peculiarity of containing Jahn–Teller Cu^{2+} at the A position of the ABO_3 perovskite. It is suggested to be a spin asymmetric ferrimagnetic (FiM) semiconductor with a small gap. An FiM interaction originates from the antiferromagnetic (AFM) coupling between Cu^{2+} and Mn^{4+} spins, giving a net spin moment of 9.0 μ_B per formula unit.

In $CaCu_3Mn_4O_{12}$, by substitution of Ca^{2+} by *R* (*R*=rare earths) an electron doping effect is induced that dramatically affects the magnetic and transport properties. This substitution would lead to the occurrence of a mixed $Mn^{4+}-Mn^{3+}$ valence at the B sublattice, thus giving to peculiar properties different from the prototype compound $CaCu_3Mn_4O_{12}$. Actually, $RCu_3Mn_4O_{12}$ compounds with all members of the rare earth series (R=$La^{3+}-Lu^{3+}$ and Y^{3+}) have been obtained experimentally [6–11]. It is reported that compounds of this family have the same space group as $CaCu_3Mn_4O_{12}$, and they are ferrimagnetic with Curie temperature over room temperature. Furthermore, theoretical investigations suggest a half-metallic behavior for *R*=La and Tb [5,12], which is of both fundamental and technological importance for spintronics.

In this paper, by using first-principles calculations based on DFT, we will investigate the electronic and magnetic properties with the last member of the rare earth series Lu at the A site. Since Lu^{3+} is nonmagnetic, there only exist two magnetic sublattices in

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$LuCu_3Mn_4O_{12}$, as that in $LaCu_3Mn_4O_{12}$. Due to the smaller ion radii of Lu^{3+} than that of La^{3+}, it is expected that this could induce different magnetic and electronic properties. The calculated results show that, similar to $LaCu_3Mn_4O_{12}$, the investigated $LuCu_3Mn_4O_{12}$ is found to be an FiM half-metal with a net spin moment of 10 μ_B per formula. However the minority-spin gap is 0.7 eV at GGA calculation, which is much larger than that of an $LaCu_3Mn_4O_{12}$ [5]. This indicates the robustness of the half-metallicity in an $LuCu_3Mn_4O_{12}$. When the electronic correlation effect U is included, the insulating gap in the minority-spin channel increases to be as large as 2.8 eV, and simultaneously the Fermi level shifts to the middle of the energy gap, demonstrating that the electronic correlation effect U makes the half-metallicity more stable. In the present paper, we will discuss in detail the origin for this phenomenon.

2. Computational method

The geometry optimization was performed using the Vienna Ab-initio Simulation Package (VASP) code [13] employing the projected-augmented-wave (PAW) method [14,15]. The plane wave cut-off energy was chosen to be 500 eV. The k-points of $6\times6\times6$ are generated, using the Monkhorst–Pack scheme [16,17]. The exchange-correlation energy was treated in the generalized gradient approximation (GGA-PBE) [18]. The electronic and magnetic properties were performed using the full-potential linearized augmented plane wave (FPLAPW) plus local orbital method (LO) [19,20], as implemented in the WIEN2K code [21]. The spherical-harmonic expansion of the potential was performed up to $l_{max}=10$. The muffin-tin radii (R_{MT}) used are 2.45, 1.92, 1.88 and 1.67 bohr for Lu, Cu, Mn and O, respectively. The plane wave expansion cutoffs are 7.0 for expanding the wave function ($R_{mt}K_{max}$) and 14 for expanding the densities and potentials (G_{max}). For the exchange-correlation energy functional, the GGA-PBE was employed [18]. In the whole Brillouin zone, 1000 k-points were used. The Brillouin zone integration is carried out with a modified tetrahedron method [14]. The self-consistent calculations were considered to be converged when the energy convergence is less than 10^{-5} Ry. In addition, electron–electron Coulomb interactions for Cu and Mn are considered in a rotationally invariant way (GGA+U) [22]. In this paper, the effective parameter $U_{eff}=U-J$ was adopted, where U and J are Hubbard parameter and the exchange interaction, respectively. For simplicity, we use the U to denote the effective parameter U_{eff} in the following paper.

3. Results and discussion

3.1. Crystal structure

The investigated $LuCu_3Mn_4O_{12}$ has body-centered cubic phase with space group $Im\bar{3}$ (No. 204). We carried out geometry optimizations for the $LuCu_3Mn_4O_{12}$ with and without spin polarization based on the experimentally determined crystal structure [11]. The optimized results show that the total energy of non-spin-polarization is 6.41 eV higher than that of spin-polarization, suggesting that the ground state of $LuCu_3Mn_4O_{12}$ is spin polarized. Optimized lattice parameters, some selected interatomic distances and angels of $LuCu_3Mn_4O_{12}$ along with the corresponding experimental values (in the parentheses) are listed in Table 1. For comparison, we also listed those of the $LaCu_3Mn_4O_{12}$ in Table 1. It is found that our optimized crystal structure and parameters are in good agreement with the experimentally determined values [11]. In some details, we noticed that the optimized lattice parameter (a) of the $LuCu_3Mn_4O_{12}$ is 7.2870 Å (corresponding experimental value of 7.2409 Å), which is smaller than that of the $LaCu_3Mn_4O_{12}$. This is reasonable since that ionic radii of an Lu (0.98 Å) is smaller than that of an La (1.18 Å). It is seen that the Mn–O bond distances are 1.929 Å (compared with the experimental values of 1.915 Å), the O–Mn–O angles are 87.213° and 92.787°, corresponding to the experimental values of 87.49° and 92.51°, respectively. This results in the Mn–O–Mn angle to be 141.631° (experimental value of 141.483°). Thus, the Mn-3d orbitals cannot be represented by the standard t_{2g}/e_g representations as in an ideal octahedron. The $\bar{3}$ symmetry at Mn sites splits the five 3d orbitals to $3z^2-r^2$, $\{x^2-y^2, xy\}$, $\{xz, yz\}$. Distortion is also observed for the CuO_4 unit. The Cu–O bond distances are 1.963 Å in the $LuCu_3Mn_4O_{12}$, which is comparable with that of 1.956 Å in $LaCu_3Mn_4O_{12}$ [5]. The O–Cu–O angles are 81.790° and 98.210° in the distorted square plane, instead of 90° as in an ideal square plane, which is much more distorted than that in the $LaCu_3Mn_4O_{12}$ [5]. This distortion causes the symmetry of CuO_4 to be lowered from the ideal square plane with D_{4h} symmetry to a planar rectangular shape with the pseudo-D_{4h} symmetry. The Cu^{2+} ion at the 6b site has an mmm symmetry, whereas the Lu site is in an $m\bar{3}$ position. The crystal structure of an $LuCu_3Mn_4O_{12}$ is shown in Fig. 1.

Table 1
Optimized lattice constants and selected bond lengths and angles of spin-polarized $LuCu_3Mn_4O_{12}$ with the experimental data in the parentheses. The data for $LaCu_3Mn_4O_{12}$ is also listed for comparison.

	$LuCu_3Mn_4O_{12}$	$LaCu_3Mn_4O_{12}$[a]
a/Å	7.2870 (7.2409)[b]	7.327
O 24g (0 y z)		
y	0.2963 (0.29727)	0.3037
z	0.1764 (0.17655)	0.1811
Mn–O/Å	1.929 (1.9149)	1.941
Cu–O/Å	1.963 (1.9439)	1.956
Lu–O/Å	2.513 (2.500)	2.591
Mn–O–Mn/°	141.631 (141.483)	141.453
Mn–O–Cu/°	108.325 (108.470)	109.006
O–Cu–O/°	81.790 (82.10)	85.383
	98.210 (97.90)	94.617
O–Mn–O/°	87.213 (87.49)	89.918
	92.787 (92.51)	90.082

[a] Ref. [5].
[b] Ref. [11].

3.2. Magnetic properties

To investigate the magnetic structure of an $LuCu_3Mn_4O_{12}$, we analyzed the energy of this system by varying the magnetic moment of the cell. We used the fixed spin moment (FSM) method within the GGA approximation for the exchange-correlation, which allows calculating the total energy as a function of the fixed total magnetic moment in the unit cell [23]. The results are shown in Fig. 2, where the minimum of the FSM curve is located at around 10 μ_B per unit cell. At this situation, the calculated magnetic moments are for Mn, 2.50 μ_B and for Cu, -0.26 μ_B. The rest of the magnetic moment resides inside the O spheres and the interstitial region. It is clear that in $LuCu_3Mn_4O_{12}$, Cu–Mn is an AFM coupled, and Cu–Cu and Mn–Mn are ferromagnetic (FM) coupled, which is consistent with the experimentally determined magnetic property [11]. This magnetic configuration is similarly found in $CaCu_3Mn_4O_{12}$ and $LaCu_3Mn_4O_{12}$ [3–5]. Further, we performed total energy calculations with an antialignment of Cu and Mn spins within GGA. The results give the total magnetic moment of the cell 10 μ_B,