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First Principles Calculations for the New Ferrimagnet $Sr_8CaRe_3Cu_4O_{24}$

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By means of first principles calculations, we investigate the electronic and magnetic properties of the new perovskite material $Sr_8CaRe_3Cu_4O_{24}$, which shows an unusually high magnetic transition temperature (T_c=440K) comparing with other perovskite cuprates. Numerical results show that magnetic moments are almost located at Cu sites, and the moments of Cu1 and Cu2 align anti-parallel due to the superexchange interaction. The ground state is a ferrimagnetic insulator with a net magnetic moment of 1.00 μ_B/f.u., which is quantitatively consistent with the experimental one. These orbitals of Cu1 and Cu2, which carry magnetic moments, have large hybridization with the p_z orbital of O2, which is responsible for the strong exchange interaction and the high magnetic transition temperature. By mapping our numerical results to an effective Heisenberg Hamiltonian, we estimate the T_c using the mean-field theory. The calculated T_c is consistent with the experiment, which indicates that a simple Heisenberg model is suitable for this compound.

Key words: first principles calculations, ferrimagnet, effective Heisenberg model

Perovskite transition-metal oxides, which have a general formula ABO_3, have been investigated intensively. When the B-site is occupied by Mn, A-site is occupied by the trivalent rare-earth ions and divalent alkali-earth-metal ions, the perovskite oxides exhibit extraordinary magnetic, electronic, and structural properties[1]. It is believed that the double exchange mechanism in the presence of strong electron-phonon couplings arising from Jahn-Teller distortions is responsible for the observed properties in the manganite[2]. In addition to the doped rare-earth manganites mentioned above, the ordered double perovsite oxides without any manganese, A_2FeMO_6 (A=Ca, Sr, or Ba; M=Mo, Re or W), have also attracted much attention due to their peculiar physical properties[3]. It is shown that Sr_2FeMoO_6 and Sr_2FeReO_6 are half-metallic and their Curie temperature (T_c) are much higher than room temperature, which makes these materials candidates for realizing strong colossal magnetoresistance[3]. Kanamori and Terakura proposed that because the hybridization between d orbitals of the Fe and M atoms, a large spin magnetic moment appears at a non-magnetic $4d$ or $5d$ M ion, which is aligned antiferromagnetically with respect to the spin moment of Fe, and plays a significant role in the magnetic property of double perovsite oxides[4]. This mechanism has been confirmed by the electronic structure calculations[5].

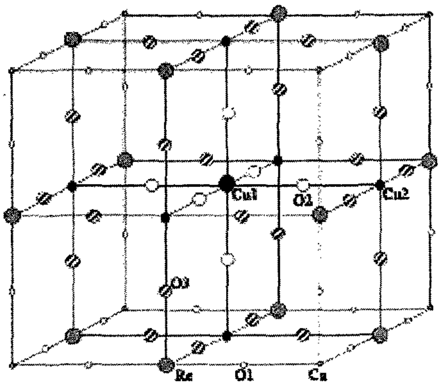

Fig.1 Crystal structure of $Sr_8CaRe_3Cu_4O_{24}$

In addition to these two types of material, other ordered perovskite transition-metal oxides have also been prepared and reported. Recently, a new perovskite material — $Sr_8CaRe_3Cu_4O_{24}$ was discovered[6]. $Sr_8CaRe_3Cu_4O_{24}$ forms the cubic perovskite ABO_3 structure, with a lattice constant of 7.971 angstrom. The A-sites are occupied by Sr exclusively, Ca, Re and Cu are located at the B-sites in an ordered way, and the unit cell contains eight perovskite-like blocks. According to the symmetry, the 24 O atoms in a unit cell can be sorted into three kinds, O1, O2 and O3. The four Cu atoms are sorted into two kinds, one Cu1, and three Cu2 as shown in Fig. 1. This material is an insulator, shows ferromagnetic (FM) behavior with T_c=440 K, and the spontaneous magnetization at T=0 is about 0.95 μ_B/f.u.(formula unit). This compound is peculiar since, first, the ferromagnetism in cuprates is very rare, and secondly, the T_c of known FM cuprate are usually quite low. For example, the T_c of $La_4Ba_2Cu_2O_{10}$, K_2CuF_4 and $SeCuO_3$ are 5, 6.5 and 26 K, respectively[6]. Therefore, it is interesting to see why a strong FM state is realized in this material. Meanwhile, experimental measurements only give the net magnetic moment, the detailed magnetic structure, such as whether Re has a magnetic moment or not and this material is FM or ferrimagnetism (FiM) is to be revealed theoretically.

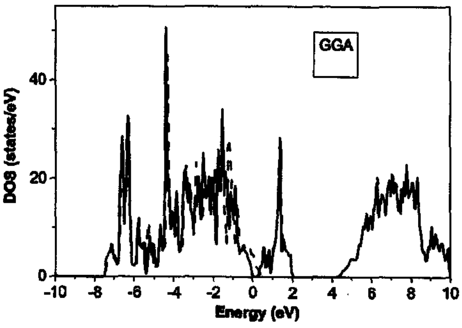

Fig2. Total DOS by GGA. The solid (dashed) line denotes the up (down) spin. Fermi level is set at the zero.

We calculate the electronic structure and magnetic properties of this perovskite by using the WIEN2K package[7], which is an implementation of the density-functional APW+lo method. The upper limit of the angular momentum l_{max}=10 is adopted in the spherical-harmonic expansion of the Kohn-Sham functions insides the muffin-tin (MT) spheres, the MT sphere radii of 2.0, 2.0, 2.0, 1.9, and 1.5 a.u. are chosen for the Ca, Cu, Sr, Re, and O atoms, respectively, with RK_{max}=7.0, which results in about 5200 LAPWs and local orbitals per cell. We use 3000 k points in the Brillouin zone. As for the exchange-correlation potential, we adopt the standard generalized gradient approximation (GGA)[8], and use the LSDA+U method[9] to consider the electron-electron interaction, which is important for the electronic structure and magnetic properties of transition-metal compounds.

First, we calculate the electronic structure and magnetic properties within GGA, and show the density of states (DOS) in Fig.2. The calculated magnetic moment at Re is very small and can be neglected (about 0.001μ_B), which is different from the ordered double perovskites Sr_2FeReO_6 where Re has a large magnetic moment (about 0.80μ_B)[5]. The moments at Cu1 and Cu2 are anti-parallel, the values are -0.29 and 0.33μ_B, respectively. Since a formula unit has three Cu2 atoms and one Cu1 atom, GGA predicts that this compound is FiM. Due to hybridization with Cu atom, the O carries a small magnetic moment and has also contribution to the net magnetic moment. The calculated total magnetic moment is 0.99μ_B /f.u., which is in good agreement with the experimental one[6]. However, as shown in Fig. 2, the GGA calculation yields a metallic solution, which is inconsistent with experiment[6].

Table I. Calculated total energy, E_{tot} relative to the energy of FiM configuration in units of Ry, the total magnetic moments per unit cell μ_{tot}, the magnetic moment inside the muffin-tin sphere of Cu1, Cu2, and O2 in units of μ_B.

	E_{tot}	μ_{tot}	Cu1	Cu2	O2
FM	0.036	5.00	1.15	0.85	0.14
FiM	0	-1.00	1.09	-0.81	0.07

In spite of many successes in describing the ground-state properties of various materials, the LSDA and GGA usually yield poor results for the transition metal system due to neglect the localized d electron correlation. For example, La_2CuO_4, which was predicted by LSDA to be a nonmagnetic metal[10], whereas it is actually an antiferromagnetic (AFM) insulator. Therefore, we include the on-site electron-electron interaction and adopt the LSDA+U method[9] to make our further calculations. The *U* and *J* are taken as 10 and 1.2 eV for the *d* orbitals of Cu[11]. In order to investigate the ground state of the system and the magnetic interactions, we calculate both the AFM and FM configurations of Cu1 and Cu2 moments, and show the results in Table I. Similar to the result of GGA, the magnetic moment at Re atom is also very small. In both configurations, the magnetic moments are mainly located at Cu1 and Cu2 sites, and the magnitude almost independent of the configuration as shown in Table I. The total energy of AFM configuration is lower than that of FM, indicating that this compound is FiM. The calculated net magnetic moment is 1.00μ_B/f.u., which is quantitatively consistent with the experimental one[6].

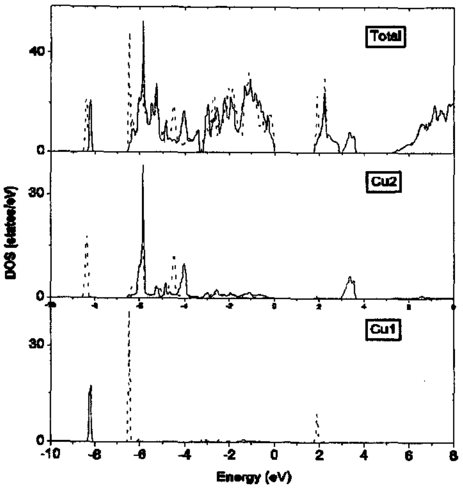

Fig.3 Total and projected DOS by LSDA+U. The solid (dashed) line denotes the up (down) spin. Fermi level is set at the zero.

The LSDA+U results of AFM configuration (ground state) are shown in Fig. 3-4 for total and projected DOS. The DOS near E_f comes mainly from the 3*d* state of Cu, 5*d* state of Re and 2*p* state of O and this material is an insulator with the energy gap of 1.68 eV, which is in agreement with experiment[6].

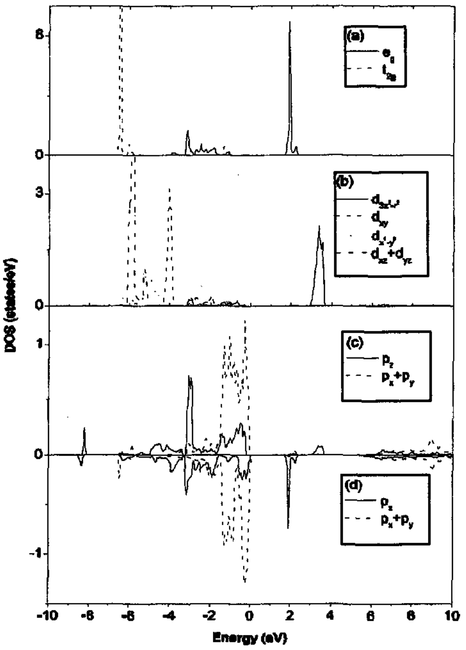

Fig.4 Projected DOS by LSDA+U. Fermi level is set at the zero. (a) For minority spin *d* orbitals of Cu1. (b) For minority spin *d* orbitals of Cu2. (c) For spin-up *p* orbitals of O2. (d) For spin-down *p* orbitals of O2.

The spin-up orbitals of Cu1 and spin-down orbitals of Cu2 are fully-filled as shown in Fig. 3, thus both of them are not active. It is interesting to note that Re-O3 bond is shorter than that of Cu2-O3. Therefore, there is a Jahn-Teller distortion in the oxygen octahedron centered at Cu2 consisting of four O3 and two O2 atoms with the bond length of Cu2-O2 smaller than that of Cu2-O3. Consequently, the e_g orbital of Cu2 splits into d_{3z2-r2} and d_{x2-y2}. The former which points to O2 has a higher energy than the latter. Thus as shown in Fig. 4b, all 3*d* orbitals of Cu2 except for minority spin (spin-up) d_{3z2-r2} orbital are fully occupied. Consequently, the magnetic moment of Cu2 is carried entirely by the d_{3z2-r2} orbital. In contrast, three crystallographic directions of Cu1 are completely equivalent, and the oxygen octahedron centered at Cu1 site is free of any distortion. Therefore, different from Cu2, the e_g and t_{2g} orbitals of Cu1 are still fully degenerate, and all *d* orbitals except for the e_g orbital of minority spin (spin-down) are fully occupied as shown in

Fig. 4(a). Thus the magnetic moment of Cu1 is carried completely by the e_g orbital. On the other hand, the O2, neighboring with the magnetic ions Cu1 and Cu2, carries a small but nonvanishing moment. The spin-down p_z orbital of O2, which points to the Cu1, strongly overlaps with the spin-down e_g orbital of Cu1, and forms a rather strong $pd\sigma$ hybridization and a relatively dispersive band. While the spin-up p_z orbital of O2 also forms a rather strong $pd\sigma$ band with the spin-up d_{3z2-r2} orbital of Cu2. Noting that the e_g orbital of Cu1 and d_{3z2-r2} orbital of Cu2 carry moments, there is a strong exchange interaction between the magnetic moments at Cu1 and Cu2, which results in the high transition temperature.

As shown in Table I, the magnetic moments are almost localized at Cu sites. When one flips the magnetic moment direction of Cu1 in AFM configuration, i.e. changing to FM configuration, the change of the magnitude of magnetic moments in Cu1 and Cu2 is very small, and the total energy will increase 0.036 Ry. Based on these observations, we introduce an effective Heisenberg Hamiltonian

$$H=\Sigma_{<ij>}J_{eff}S_iS_j$$

to the magnetic property of this material. Where J_{eff} is the effective exchange interaction, the S_i and S_j denote the magnetic moments at Cu1 and Cu2 sites, respectively, and the sum $<ij>$ is taken over the nearest neighbor Cu sites. Normalizing the spin vectors to unity, we estimate the effective exchange coupling J_{eff}= 0.036Ry/12= 0.04eV, from the energy difference between the FM and AFM configurations. With this exchange coupling J_{eff}, we obtain the T_c is 530 K, by the mean-field theory, which is slightly higher than the experimental one 440 K[6]. Noted that the mean-field theory usually overestimates the T_c by about 20-30%, our result agrees with the experiment.

In summary, using the first principles calculations, we have investigated the electronic and magnetic properties of $Sr_8CaRe_3Cu_4O_{24}$. Our results show that the magnetic moments are mainly located at Cu sites, the ground state is a FiM insulator with a net magnetic moment of 1.00 μ_B/f.u., which is quantitatively consistent with the experimental one. These orbitals in Cu1 and Cu2, which carry magnetic moments, have large hybridization with the p_z orbital of O2, which is responsible for the strong exchange interaction and the high magnetic transition temperature. By mapping our results to an effective Heisengberg Hamiltonian, we estimate the T_c using the mean-field theory. The obtained result is consistent with the experiment, indicates a simple nearest neighbor model is suitable for this material.

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