Robust Half-Metallic Character and Large Oxygen Magnetism in a Perovskite Cuprate

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The new perovskite cuprate material $Sr_8CaRe_3Cu_4O_{24}$, which behaves ferrimagnetically and shows an unusually high Curie temperature ($T_C \sim 440$ K), is found from density-functional theory calculation to display several surprising properties after hole doping or chemical substitution: (1) Half metal (HM) is realized by replacing Re with W or Mo while T_C remains high; (2) hole-doped $Sr_8CaRe_3Cu_4O_{24}$ is also HM with high T_C . Moreover, we find that the O atoms will carry a large magnetic moment after hole doping, which is in sharp contrast to the generally accepted concept that magnetism in solids requires partially filled shells of d or f electrons in cations. The material $Sr_8CaRe_3Cu_4O_{24}$ is therefore expected to provide a very useful platform for material design and development.

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Spin-based electronics, or spintronics, is currently a rather hot topic, which offers opportunities for a new generation of multifunctional devices [1]. An ideal component for such devices is half-metallic ferromagnet, which is metallic for one spin channel and insulating for the other [2]. Intensive searches for half metal (HM) materials with high $T_{\rm C}$ have been made in recent years [3,4]. Up to the present, many works focus on the perovskite transition-metal oxides, in particular, the Mn-based and Fe-based compounds [5,6]. To find other new HM compounds with $T_{\rm C}$ above room temperature is of both fundamental and technological importance.

Since ferromagnetic (FM) cuprates are very rare, and usually show rather low $T_{\rm C}$, they have not been considered seriously as candidates of useful magnetic material. Recently a new perovskite cuprate material Sr₈CaRe₃Cu₄O₂₄ was synthesized [7]. This cuprate forms the cubic perovskite ABO_3 structure with space group Pm - 3m. The A sites are occupied by Sr exclusively, and Ca, Re, and Cu are located at the B sites in an ordered way. 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 [7]. This material has some unique physical properties: it is similar in structure to the cuprates showing high-temperature superconductivity upon carrier doping, while possessing a net magnetization, and its $T_{\rm C}$ is over room temperature (~440 K), much higher than other known cuprates. Unfortunately, this compound is an insulator, and cannot show any magnetoresistance. Therefore, we are interested in finding a way to make this compound electrically conductive, meanwhile keeping its high $T_{\rm C}$. There are two well-known methods to tailor the properties of perovskite materials: B-site substitution and carrier doping. The former modifies the band structure while the latter mainly shifts the Fermi level. As revealed in this Letter, this cuprate shows several peculiar properties after appropriate *B*-site substitution and carrier doping.

First let us consider the *B*-site element substitution. A valuable insight for possible material developing is available starting from the band structure of $Sr_8CaRe_3Cu_4O_{24}$ [8]. In Fig. 1 we show schematically the minority-spin e_g band of Cu1 and e_g -like band of Cu2, and the *p* band of



FIG. 1 (color online). (a) Schematic picture for the DOS of minority-spin e_g orbitals of Cu1 and Cu2, and the partial structure of (010) plane in Sr₈CaRe₃Cu₄O₂₄. (b) Schematic picture for the DOS of minority-spin e_g orbitals of Cu1 and Cu2, and the partial structure of (010) plane expected for Sr₈CaW₃Cu₄O₂₄ and Sr₈CaMo₃Cu₄O₂₄. (c) Schematic picture for the DOS of *p* orbital of O2 in Sr₈CaRe₃Cu₄O₂₄. (d) Schematic picture for the DOS of *p* orbital of O2 expected for hole-doped Sr₈CaRe₃Cu₄O₂₄. The dotted lines denote the Fermi level.

O2, noting that other bands have small contributions to states near the Fermi level and can be neglected for a qualitative argument. The minority-spin e_g bands of Cu1 and Cu2 are distributed on the two sides of the Fermi level, with a large interval between the two regions as shown in Fig. 1(a). Because of the Jahn-Teller distortion caused by Re [the (010) plane is shown in Fig. 1(a)], the degeneracy of the e_g band of Cu2 is lifted and the $d_{x^2-y^2}$ band becomes fully occupied. If one replaces Re by some other 5d or 4delements with smaller electronegativity, the Jahn-Teller distortion in the oxygen octahedron centered at Cu2 should decrease. The splitting of e_g band of Cu2 should decrease significantly, and as a result, it may cross the Fermi level as shown in Fig. 1(b). Tungsten (W) and molybdenum (Mo), the elements found in the column to the left of Re in the periodic table, can be good candidates for this purpose. Since replacing Re by other elements will not have much effect on the bands of Cu1, the spin-up channel remains insulating. As with $Sr_8CaRe_3Cu_4O_{24}$ [8], the spin-up e_{g} band of Cu1 and spin-down $d_{3r^2-r^2}$ band of Cu2 are partially occupied, which supports the strong $pd\sigma$ hybridization. Therefore, it is expected that replacing Re by W or Mo will result in a HM with high $T_{\rm C}$. The above idea is verified by accurate density-functional theory calculations as following.

Calculations have been performed with the WIEN2K package [9], which uses a full-potential, all-electron augmented plane-wave plus local orbital method. We adopt the standard generalized gradient approximation (GGA) [10], and use the LSDA + U (LSDA is local spin density approximation) method [11] to treat the electron-electron interaction effects with U = 10 eV and J = 1.20 eV for the d orbital of Cu [12]. All the results shown in the following are based on the fully optimized structure [13]. We have also confirmed that the main results are robust and do not change with the values of parameters.

For Sr₈CaW₃Cu₄O₂₄, we calculate both ferrimagnetic (FiM) and FM configurations for Cu1 and Cu2 moments. The spin-up e_g band of Cu1 and spin-down $d_{3z^2-r^2}$ band of Cu2 are partially occupied as shown in Fig. 2, while the majority-spin bands are fully occupied. Therefore, the magnetic properties of Sr₈CaW₃Cu₄O₂₄ are similar to those of Sr₈CaRe₃Cu₄O₂₄ [8]. The ground state is FiM; the magnetic moments are carried mainly by the Cu ions; the total moment per unit cell and the moments at Cu1 and Cu2 are 4.00, -0.89, and $1.02\mu_B$ respectively. Same as $Sr_8CaRe_3Cu_4O_{24}$ [8], in $Sr_8CaW_3Cu_4O_{24}$ the spin-up e_g orbital of Cu1 and spin-down $d_{3z^2-r^2}$ orbital of Cu2 strongly overlap with the spin-up and spin-down p_{τ} orbitals of O2, respectively, to form the strong $pd\sigma$ bond, which produces a strong superexchange interaction between the magnetic moments at Cu1 and Cu2. As a result, relative to the FM configuration, the FiM configuration gains energy by 0.046 Ry per formula unit. Comparing with the same energy difference of 0.036 Ry for $Sr_8CaRe_3Cu_4O_{24}$, we predict that the $T_{\rm C}$ of



FIG. 2 (color online). Total DOS (top) and partial DOS of the minority-spin (spin-up) d orbitals of Cu1 (middle) and the minority-spin (spin-down) d orbitals of Cu2 (bottom) of Sr₈CaW₃Cu₄O₂₄ with the Fermi level set at zero.

 $Sr_8CaW_3Cu_4O_{24}$ should be higher than 440 K. After replacing Re by W, the Jahn-Teller distortion in the oxygen octahedron centered at Cu2 becomes rather small [14], and as shown in Fig. 2 the splitting of e_g orbitals of Cu2 is reduced from that of $Sr_8CaRe_3Cu_4O_{24}$ (see Fig. 3 of Ref. [8]). Since the spin-down e_g -like bands of Cu2 cross the Fermi level, while the spin-up channel is still insulating as shown in Fig. 2, the new material $Sr_8CaW_3Cu_4O_{24}$ is a HM.

Since Mo and W lie at the same column of the periodic table, the properties of $Sr_8CaMo_3Cu_4O_{24}$ are similar to that of $Sr_8CaW_3Cu_4O_{24}$. The energy difference between FiM and FM configuration is also large, so one can expect



FIG. 3. Total DOS of $Sr_8CaMo_3Cu_4O_{24}$ with the Fermi level set at zero.

 $Sr_8CaMo_3Cu_4O_{24}$ to exhibit high T_C . As expected, the Jahn-Teller distortion in the oxygen octahedron centered at Cu2 is also rather small. As a result, the spin-down channel is metallic and the spin-up one is insulating as shown in Fig. 3. Therefore, $Sr_8CaMo_3Cu_4O_{24}$ is also a HM with high T_C .

Now let us turn to the effect of hole doping. It is interesting to note that, as shown schematically in Fig. 1(c), in Sr₈CaRe₃Cu₄O₂₄ the $p_x + p_y$ band of O2 is rather narrow and just below the Fermi level [15]. From the view of a rigid band model, doping hole shifts the Fermi level downward and causes it to cross the narrow $p_x + p_y$ band of O2. Therefore, we expect that this compound may display some peculiar properties related to O atoms after hole doping. In order to keep the band structure, hole doping is realized, for example, by A-site element substitution. Since the A-site substitution can be treated successfully by the virtual-crystal approximation (VCA) [16], we employ it in the present study to calculate the electronic and magnetic properties of $(Sr_{1-x}A_x)_8CaRe_3Cu_4O_{24}$ where A stands for a univalent cation, such as potassium (K). It is found that, different from replacing Re with W or Mo, doping holes has a very small effect on the geometric structure. Since the states just below the Fermi level are almost entirely due to the $p_x + p_y$ band of O2, the *d* bands of Cu1 and Cu2 are basically unaffected by the hole doping. Consequently, as with Sr₈CaRe₃Cu₄O₂₄, the ground state is FiM, and the energy difference between FM and FiM configurations is large, which implies a high $T_{\rm C}$ of $({\rm Sr}_{1-x}A_x)_8{\rm CaRe}_3{\rm Cu}_4{\rm O}_{24}$. The magnetic moments at Cu1 and Cu2 are almost independent of the hole doping as shown in Table I. However, in striking contrast to the parent compound, O2 carries a large magnetic moment after hole doping. At doping concentration of x = 0.2, the magnetic moment at O2 reaches $0.25\mu_B$, the largest value in the literature [17], and increases further with x as shown in Table I [18]. This phenomenon is very peculiar since it is generally believed that large magnetic moment is carried only by the transition-metal ions with unfilled d or f bands.

In addition to VCA calculations, we have also performed calculations by replacing one of the eight Sr ions

TABLE I. Calculated total magnetic moment per unit cell μ_{tot} , magnetic moments inside the muffin-tin spheres of Cu1, Cu2, and O2 in units of $\mu_{\rm B}$.

Doping	$\mu_{ m tot}$	Cu1	Cu2	02
0	-1.00	1.08	-0.81	0.07
0.05	-0.60	1.06	-0.81	0.12
0.1	-0.20	1.04	-0.80	0.16
0.15	0.20	1.05	-0.81	0.20
0.2	0.60	1.04	-0.80	0.25
0.25	1.00	1.04	-0.80	0.29
0.75	5.00	1.07	-0.79	0.59
1	7.00	1.08	-0.80	0.70

in the unit cell with one K ion. In this case, the six O2 atoms in the unit cell are sorted into two groups with three O atoms in each group. The magnetic moments are estimated as 0.24 and $0.13\mu_B$, for O2 atoms surrounding the K atom and the others, respectively. These results are consistent with those by VCA as summarized in Table I.

In order to clarify the origin of large magnetic moment at O2, we show the density of states (DOS) of $(Sr_{0.8}A_{0.2})_8CaRe_3Cu_4O_{24}$ in Fig. 4. (The DOS of other doping x is similar to that of x = 0.2.) The p_z state of O2, which strongly overlaps with the d states of Cu1 and Cu2, forms a wide band. As a result, the exchange splitting of the p_z state of O2 is very small, and makes only a small contribution to the magnetic moment. So we can conclude that the magnetic moment at O is not induced by the magnetic ions Cu, completely different from other known materials with magnetic moment at O atoms. It is intriguing to note that the spin-up $p_x + p_y$ band of O2 appears in the energy window centered at ~ -1.2 eV and is fully occupied, while the spin-down states are obviously higher in energy than the spin-up one and cross the Fermi level. This clearly indicates that the exchange splitting of $p_x + p_y$ state of O2 is rather large, and the magnetic moment at O2 is carried mainly by the $p_x + p_y$ state. The mechanism of this exchange splitting can be attributed to the Stoner instability as shown schematically in Fig. 1(d), namely, when the Fermi level crosses the narrow $p_x + p_y$ band of O2 upon hole doping, the holes fully polarize in order to reduce the total energy. Furthermore, the fully polarized holes lead this compound to a HM as can be seen from Fig. 4.

Having clarified where the magnetic moment of O comes from, we try to understand the reason why it is rare in oxides and thus needs fine tuning by material design. As discussed above, there are two essential factors for this phenomenon: the p band of O should be narrow and located nearby the Fermi level. It is well-known that for perovskite ABO_3 compound, the occupied d state shifts to



FIG. 4 (color online). DOS of $(Sr_{0.8}A_{0.2})_8CaRe_3Cu_4O_{24}$ with the Fermi level set at zero.

lower energy and the weight of the O 2p states increases at the top of valence band as the atomic number of the transition-metal B increases from 22 (Ti) to 29 (Cu) [19]. This is the reason O has the main contribution to the top of valence band of Sr₈CaRe₃Cu₄O₂₄. In contrast, in manganites and many other oxides the state just below the Fermi level comes from the *d* band of Mn mixing with the *p* band of O. Since Sr₈CaRe₃Cu₄O₂₄ has the cubic symmetry, the angle of Cu1-O2-Cu2 is 180°, the e_g orbital of Cu1 and the e_g -like orbital of Cu2 cannot hybridize with $p_x + p_y$ orbital of O2 due to symmetry. On the other hand, the t_{2g} orbitals of Cu1 and Cu2 are fully occupied, and located in low energy regions due to the large Coulomb interaction, therefore the hybridization between these orbitals with the $p_x + p_y$ orbitals of O2 is rather small. Consequently, the $p_x + p_y$ band of O2 is very narrow, and the DOS is rather high. In contrast, in most perovskite ABO₃ materials, the BO_6 octahedron tilts with the angle of *B*-O-*B* smaller than 180°. Consequently the e_g orbital of B can overlap with the $p_x + p_y$ orbitals of O, which makes the band of the latter wide, having typically a band width of 5-7 eV. As this value is larger than the intra-atomic exchange strength, the O is nonmagnetic in most oxides. Since the radii of univalent cation A, such as K, are slightly larger than that of Sr ions, hole doping into Sr₈CaRe₃Cu₄O₂₄ through substituting Sr by K will slightly enlarge the tolerance factor. Therefore, the CuO₆ octahedron is not expected to tilt upon such hole doping treatment.

Large magnetic moments at O2 upon hole doping are also observed when the LSDA scheme is adopted, which tends to underestimate the magnetic moment. Therefore, the present result is robust with respect to U, and is likely to be observed experimentally. Our theoretical prediction may fail in several exceptional cases, where the system happens to be close to a quantum critical point, or an instability to the triplet superconductivity. In any case, interesting physical properties are expected, and deserve careful experimental investigations.

In summary, using a density-functional calculation we investigate the effect of element substitution and hole doping on the material $Sr_8CaRe_3Cu_4O_{24}$. Our study reveals that a HM with high T_C can be realized by replacing Re with W or Mo, and that hole doping to the material will also result in a HM with high T_C and unusually large magnetic moments at O atoms due to the Stoner instability. The material $Sr_8CaRe_3Cu_4O_{24}$ is therefore expected to provide a very useful platform for material design and development, and potential products of the research in this direction can be very useful for spintronics applications.

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