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

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(Dated: May 7, 2019)

The new perovskite cuprate material Sr\textsubscript{8}CaRe\textsubscript{3}Cu\textsubscript{4}O\textsubscript{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\textsubscript{8}CaRe\textsubscript{3}Cu\textsubscript{4}O\textsubscript{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 with the generally accepted concept that magnetism in solid requires partially filled shells of $d$ or $f$ electrons in cations. The material Sr\textsubscript{8}CaRe\textsubscript{3}Cu\textsubscript{4}O\textsubscript{24} is therefore expected to provide a very useful platform for material design and development.

Spin-based electronics, or spintronics, is currently a rather hot topic, which offers opportunities for new generation of multifunctional devices combining traditional charge-based microelectronics with spin-dependent effects\textsuperscript{1}. An ideal component for such devices is half-metallic ferromagnet, which is metallic for one spin channel and insulating for the other\textsuperscript{2}. The search for HM materials with high $T_c$ is intense in recent years\textsuperscript{3,4}. Up to present, many works focus on the perovskite transition-metal oxides, in particular the Mn-based and Fe-based compounds\textsuperscript{5,6}. To find other new HM compounds with $T_c$ above room temperature is of both fundamental and technological importance.

Since ferromagnetic (FM) cuprates are very rare, and usually show rather low $T_c$, they have not been considered seriously as candidates of useful magnetic material. Recently a new perovskite cuprate material Sr\textsubscript{8}CaRe\textsubscript{3}Cu\textsubscript{4}O\textsubscript{24} was synthesized\textsuperscript{7}. This cuprate forms the cubic perovskite $ABO_3$ structure with space group $Pm \sim 3m$. 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 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\textsuperscript{7}. This material has some unique physical properties: it is similar in structure to the cuprates showing high-temperature superconductivity upon carrier doping, while possesses a net magnetization; its $T_c$ is over room temperature ($\sim 440$K), much higher than other known cuprates. Unfortunately, this compound is an insulator, and cannot show any magnetoresistance. Therefore, it is interesting to find a way to make this compound electrically transportable meanwhile keeping its high $T_c$. 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\textsubscript{8}CaRe\textsubscript{3}Cu\textsubscript{4}O\textsubscript{24}.\textsuperscript{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 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). Due to 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 substitutes Re by some other 5$d$ or 4$d$ elements 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 the result, it may cross the Fermi level as shown in Fig.1 (b). Wusten (W) and molybdenum (Mo), the elements at the left column of Re in the Periodic Table, can be good candidates for this purpose. Since substituting Re with other elements will not affect much the bands of Cu1, the spin-up channel therefore remains insulating. Same as Sr\textsubscript{8}CaRe\textsubscript{3}Cu\textsubscript{4}O\textsubscript{24}, the spin-up $e_g$ band of Cu1 and spin-down $d_{x^2-y^2}$ band of Cu2 are partially occupied, which supports the strong $pd\sigma$ hybridization. Therefore, it is expected that substituting Re by W or Mo will result in a HM with high $T_c$. The above idea is verified by accurate density-functional theory calculations as following.

Calculations have been performed with the WIEN2K package\textsuperscript{9}, which uses a full-potential, all electron APW+lo method that allows one to carry out total energy calculations of high precision. We adopt the standard generalized gradient approximation (GGA)\textsuperscript{10}, use the LSDA+U method\textsuperscript{11} to treat the electron-electron interaction effects with $U = 10$ eV and $J = 1.20$ eV for the $d$ orbital of Cu\textsuperscript{12}. All the results shown in the following are based on the
fully optimized structure. 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 eₛ band of Cu₁ and spin-down dₓ²−y² 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 is similar to that 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 μB respectively. The orbital ordering in the d bands of Cu₁ and Cu₂ revealed in Ref. [8] still exists, which induces a large hybridization with the pₓ orbital of O₂, corresponding to the strong p贬值 bond, and produces a strong superexchange interaction between the magnetic moments at Cu₁ and Cu₂. As the result, relative to the FM configuration, the FiM configuration gains 0.046 Ry per formula unit. Comparing with the same energy difference of 0.036 Ry for Sr₈CaRe₃Cu₄O₂₄, we predict that the Tₙ of Sr₈CaW₃Cu₄O₂₄ should be higher than 440 K. After substituting Re by W, the Jahn-Teller distortion in the oxygen octahedron centered at Cu₂ becomes rather small [8], and as shown in Fig. 2 the splitting of eₛ orbitals of Cu₂ is reduced from that of Sr₈CaRe₃Cu₄O₂₄ (see Fig. 3 of Ref. [8]). Since the spin-down eₛ-like bands of Cu₂ cross the Fermi level, while the spin-up channel is still insulating as shown in Fig. 2, the new material Sr₈CaW₃Cu₄O₂₄ is a HM.

Since Mo and W lie at the same column of periodic table, the properties of Sr₈CaMo₃Cu₄O₂₄ are similar to that of Sr₈CaW₃Cu₄O₂₄. The energy difference between FiM and FM configuration is also large, so one can expect that Sr₈CaMo₃Cu₄O₂₄ still has high Tₙ. 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, Sr₈CaMo₃Cu₄O₂₄ is also a HM with high Tₙ.

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 pₓ+pᵧ band of O₂ is rather narrow and just below the Fermi level [8]. From the view of a rigid band model, doping hole shifts the Fermi level downward and causes it to cross the narrow pₓ+pᵧ 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) [17], we employ it in the present study to calculate the electronic and magnetic properties of (Sr₀₈₋ₓAₓ)₈CaRe₃Cu₄O₂₄ with A stands for a univalent cation. It is found that, different from replacing Re with W or Mo, doping hole has small effect on the geometric structure. Since the states just below the Fermi level are almost entirely due to the pₓ+pᵧ band of O₂, the d bands of Cu₁ and Cu₂ are basically unaffected by the hole doping. Consequently, same as Sr₈CaRe₃Cu₄O₂₄, the ground state is FiM, and the energy difference between FM and FiM configuration is still large, which implies a high Tₙ of (Sr₀₈₋ₓAₓ)₈CaRe₃Cu₄O₂₄. 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 x = 0.2, the magnetic moment at O₂ reaches 0.25 μB, the largest value in literatures [12], and increases further with x as shown in Table I. 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 order to clarify the origin of large magnetic moment at O₂, we show the density of states (DOS) of (Sr₀₈₋ₓAₓ)₈CaRe₃Cu₄O₂₄ in Fig. 4. (The DOS of other doping x is similar to that of x = 0.2.) The pₓ 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 pₓ state of O₂ is very small, which has only 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 pₓ+pᵧ band of O₂ appears in the energy window centered at ~ -1.2 eV and are 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 pₓ+pᵧ state of O₂ is rather large, and the magnetic moment at O₂ is carried mainly by the pₓ+pᵧ 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 pₓ+pᵧ 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 ABO₃ compound, the occupied d state shifts to 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) [17]. This is the reason why 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 eₛ 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 at low energy region 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 $ABO_3$ materials, the $BO_6$ octahedron tilts with the angle of $B$-O-$B$ smaller than $180^\circ$, consequently the $e_g$ orbital of $B$ can overlap with the $p_x+p_y$ orbitals of O, and makes the band of the latter wide, typically of band width of 5-7eV. As it is larger than the intra-atomic exchange strength, the O is non-magnetic in most oxides. Since the radii of univalent cation A, such as potassium (K), is slightly larger than that of Sr ion, hole doping into Sr$_8$CaRe$_3$Cu$_4$O$_{24}$ through substituting Sr by K will slightly enlarge the tolerance factor. Therefore, the Cu$O_6$ 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 substitution and hole doping on the material Sr$_8$CaRe$_3$Cu$_4$O$_{24}$. 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$_8$CaRe$_3$Cu$_4$O$_{24}$ 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.

We are grateful to Dr. E. Takayama-Muromachi, and Dr. M. Isobe for discussions. Calculations have been performed on Numerical Materials Simulator (HITACHI SR11000) at the Computational Materials Science Center, National Institute for Materials Science. This work was partially supported by Japan Society for the Promotion of Science (Grant-in-Aid for Scientific Research (C) No. 15540355).
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TABLE I: Calculated total magnetic moment per unit cell $\mu_{\text{tot}}$, magnetic moments inside the muffin-tin spheres of Cu1, Cu2 and O2 in units of $\mu_B$.

| Doping | \(\mu_{\text{tot}}\) | Cu1 | Cu2 | O2 |
|--------|-----------------|-----|-----|-----|
| 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|

**Figure Captions**

Fig. 1: (a) Schematic picture for the density of states (DOS) of minority spin $e_g$ orbitals of Cu1 and Cu2, and the partial structure of (010) plane in Sr$_8$CaRe$_3$Cu$_4$O$_{24}$. (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 Sr$_8$CaW$_3$Cu$_4$O$_{24}$ and Sr$_8$CaMo$_3$Cu$_4$O$_{24}$. (c) Schematic picture for the DOS of $p$ orbital of O2 in Sr$_8$CaRe$_3$Cu$_4$O$_{24}$. (d) Schematic picture for the DOS of $p$ orbital of O2 expected for hole-doped Sr$_8$CaRe$_3$Cu$_4$O$_{24}$. The dotted lines denote the Fermi level.

Fig. 2: 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 Sr$_8$CaW$_3$Cu$_4$O$_{24}$ with the Fermi level set at zero.

Fig. 3: Total DOS of Sr$_8$CaMo$_3$Cu$_4$O$_{24}$ with the Fermi level set at zero.

Fig. 4: DOS of (Sr$_{0.8}$A$_{0.2}$)$_8$CaRe$_3$Cu$_4$O$_{24}$ with the Fermi level set at zero.
(a) $d_{x^2-y^2}$ of Cu2

(b) $d_{3z^2-r^2}$ of Cu2

(c) $p_x + p_y$ band of O2

(d) $p_z$ band of O2
The image shows a plot representing the density of states (DOS) as a function of energy (in eV). The plot includes several lines indicating different contributions:

- **Total DOS**: Black line
- **$p_x + p_y$ of O2**: Red line
- **$p_z$ of O2**: Green line

The x-axis represents energy in electron volts (eV), ranging from -10 to 8 eV, while the y-axis represents the DOS, ranging from -20 to 20. The plot provides insights into the electronic structure of the system by visualizing the distribution of energy levels.