Strong enhancement of spin ordering by A-site magnetic ions in the ferrimagnet CaCu$_3$Fe$_2$Os$_2$O$_{12}$

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A$_2$O$_3$ perovskite is a kind of very important functional material with versatile physical properties. Although B-site chemical substitution with various magnetic ions has been widely investigated, the A-site doping with magnetic transition metal is little known. Here we report AA’$_1$B$_2$B’$_1$O$_{12}$-type A- and B-site ordered ferrimagnet CaCu$_3$Fe$_2$Os$_2$O$_{12}$ with magnetic transition metals occupying three different atomic sites (A’, B, and B’ sites). This compound is synthesized by a special high-pressure annealing process. It possesses a much higher Curie temperature $T_C$ of 580 K compared with that of the B-site-only ordered Ca$_2$FeOsO$_6$ ($T_C = 320$ K) without magnetic ion at the A site. First-principles numerical calculations reveal that this enhancement primarily originates from the additional spin interaction between the A’-site Cu$^{2+}$ and the B’-site Os$^{5+}$, generating a strong Cu$^{2+}$($↑$Fe$^{3+}$($↑$Os$^{5+}$($↑$) ferrimagnetic spin coupling. This work opens up an alternative way for enhancing the spin ordering temperature by introducing A-site magnetic ions.

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I. INTRODUCTION

In the past decades A$_2$O$_3$ perovskite oxides have received much attention due to the wide variety of physical properties and fascinating functionalities such as piezoelectricity, ferroelectricity, superconductivity, colossal magnetoresistance, and multiferroicity, etc. [1–5]. For the practical utilization of these performances, a high phase transition temperature near or even above room temperature (RT) is generally required. Since the crystal structure and the charge combination in a perovskite is highly flexible, B-site ordered double perovskite (DP) with magnetic ions is at present less studied. However, for a B-site ordered DP A$_2$B$_2$O$_6$, if three-quarters of the A sites are substituted by transition-metal A’, both an A- and B-site ordered quadruple perovskite (QP) with chemical formula of AA’$_1$B$_2$B’$_1$O$_{12}$ can form [13–19]. A unique feature for this specially ordered perovskite is that three different atomic sites (A’, B, and B’ sites) can all accommodate magnetic transition metals [see Fig. 1(a)]. As a consequence, multiple magnetic and electrical interactions can occur among A’, B, and/or B’ sites, giving rise to a series of intriguing physical phenomena such as inter-site charge transfer, charge disproportionation, spin-induced ferroelectricity, and FiM half-metallicity [20–24]. Besides, it is also highly expected that the strong coupling among these magnetic sublattices has important impacts on further enhancing the spin or charge ordering temperature.

In the ordered AA’$_1$B$_2$B’$_1$O$_{12}$ perovskite, the A-site substitution with smaller-size transition metal significantly decreases the average ionic radius for this atomic site. The B/B’O$_6$ octahedra thus become heavily tilting (typically, $\angle B/B’$O$_6$-B/B’ $\approx 140°$) and the A’-site transition metal forms square-planar coordinated A’O$_4$ units. As a result, high pressure is often needed to prepare the A- and B-site ordered perovskite. To date, although a large number of ABO$_3$ perovskites and B-site only ordered DPs have already been obtained, the family members of both A-site and B-site ordered QPs are very limited. In this paper, we report an A- and B-site...
ordered QP oxide, CaCu$_3$Fe$_2$Os$_2$O$_{12}$ (CCFOO). The advantage of both A- and B-site ordered CCFOO as compared with the B-site-only ordered Ca$_2$FeOsO$_6$ is clearly seen by the sharp enhancement of the FiM ordering temperature from 320 K in the latter to 580 K in the former due to the sharp enhancement of the FiM ordering temperature from 30 to 30 min, and then the temperature was slowly increased to 1073 K within 6 h. When this annealing process was finished, the heating power was shut down quickly, and then the pressure was gradually released. The residual KCl in the final product was washed out by de-ionized water.

The sample quality and crystal structure were characterized by powder x-ray diffraction (XRD) using a Huber diffractometer (Cu $K\alpha_1$ radiation, 40 kV, 300 mA). Diffraction data were collected in the angle (220) range from 10° to 160° with steps of 0.01°. Crystallographic parameters were analyzed by Rietveld full-profile refinement using the GSAS program [25]. The valence states of Cu, Fe, and Os transition metals were identified by x-ray absorption spectra (XAS) performed at the National Synchrotron Radiation Research Center in Taiwan. The soft XAS at the Cu- and Fe-$L_{2,3}$ edges were measured with total electron yield at the beamline of BL08B. The hard XAS at the Os-$L_{2,3}$ edges were measured with transmission geometry at the BL07A beamline. X-ray magnetic circular dichroism (XMCD) measurements at the Cu- and Fe-$L_{2,3}$ edges were performed at the Deimos beamline of SOLEIL in Paris. The spectra were taken with circularly polarized x rays at 132 K and 2 T magnetic field considering that the sample was charging at low temperature and high magnetic field due to strong insulator and magnetoresistance effects.

Magnetic susceptibility and magnetization below 400 K were measured using a Quantum Design superconducting quantum interference device magnetometer. The data of high-temperature susceptibility in the 400–650 K range were collected using a MicroSense vibrating sample magnetometer. The zero-field-cooling (ZFC) and field-cooling (FC) modes were adopted for magnetic susceptibility measurements with a 0.1-T magnetic field. The resistivity was measured by adopting a four-probe method on a Quantum Design physical property measurement system. The photocurrent measurement was performed using a laser (PL2210A, PG403-SH, and PG703-DFG, EKSPLA), varying the wavelengths from 1.80 to 5.55 μm at room temperature. The photovoltaic signals were recorded by a Keithley 2400 electrometer.

First-principles numerical calculations were performed using the full-potential linearized augmented plane-wave method implemented in WIEN2K [26]. The lattice parameters and atom positions obtained in experiment were used for the numerical calculations. The structure optimization gives the lattice parameter $a = 7.523$ Å and the O atomic position to be 0.254, 0.426, and 0.555. The muffin-tin radii were 2.00 a.u. for Ca; 1.60 a.u. for O; and 1.90 for Cu, Fe, and Os. The maximum modulus for the reciprocal vectors was chosen such that $R_{MT}K_{max}$ = 7.0. A different value of $R_{MT}K_{max}$ = 8.0 was also tested and no significant changes were observed except slight variations in the energy convergence. We took the generalized-gradient approximation Perdew-Burke-Ernzerhof (GGA-PBE) exchange-correlation energy and used 1000 k-point meshes for the whole Brillouin zone, with an effective $U_{eff}$ = 5 eV for Cu, 4 eV for Fe, and 2 eV for Os in the GGA + U calculations. The nearest-neighbor effective exchange couplings between magnetic ions were calculated using the energy difference of four different magnetic structures: FiM1: Cu$^{2+}$(↑Cu$^{3+}$Os$^{5+}$); FiM2: Cu$^{2+}$(↑Fe$^{3+}$Os$^{5+}$); FiM3: Cu$^{2+}$(↓Fe$^{3+}$Os$^{5+}$); FiM4: Cu$^{2+}$(↑Fe$^{3+}$Os$^{5+}$).
FM: Cu\(^{2+}\)\((\uparrow)\)Fe\(^{3+}\)\((\uparrow)\)Os\(^{5+}\)\((\uparrow)\):

\[
E(\text{FiM1}) = E_0 + 12J_{\text{Cu-Fe}}S_{\text{Cu}}S_{\text{Fe}} - 12J_{\text{Fe-Os}}S_{\text{Fe}}S_{\text{Os}} - 12J_{\text{Cu-Os}}S_{\text{Cu}}S_{\text{Os}},
\]

\[
E(\text{FiM2}) = E_0 - 12J_{\text{Cu-Fe}}S_{\text{Cu}}S_{\text{Fe}} + 12J_{\text{Fe-Os}}S_{\text{Fe}}S_{\text{Os}} - 12J_{\text{Cu-Os}}S_{\text{Cu}}S_{\text{Os}},
\]

\[
E(\text{FiM3}) = E_0 - 12J_{\text{Cu-Fe}}S_{\text{Cu}}S_{\text{Fe}} - 12J_{\text{Fe-Os}}S_{\text{Fe}}S_{\text{Os}} + 12J_{\text{Cu-Os}}S_{\text{Cu}}S_{\text{Os}},
\]

\[
E(\text{FM}) = E_0 + 12J_{\text{Cu-Fe}}S_{\text{Cu}}S_{\text{Fe}} + 12J_{\text{Fe-Os}}S_{\text{Fe}}S_{\text{Os}} + 12J_{\text{Cu-Os}}S_{\text{Cu}}S_{\text{Os}}.
\]

### III. RESULTS AND DISCUSSION

Figure 1(b) shows the XRD pattern of CCFOO measured at room temperature. The presence of the sharp diffraction peaks with \(h + k + l = \text{odd such as (111) and (311)}\) peaks provides convincing evidence for the rocksalt-type ordered arrangement of Fe and Os cations [15]. The Rietveld analysis illustrates that the high-pressure product CCFOO crystallizes to an \(AA'B_2B'_{\text{Os}2}\)-type \(A\)-site and \(B\)-site ordered quadruple perovskite structure with space group \(Pn-3\) [see Fig. 1(a)]. In this structural symmetry, the \(A\)-site Cu and \(A'\)-site Cu atoms occupy the fixed atomic sites \(2a\) \((0.25, 0.25, 0.25)\) and \(6d\) \((0.25, 0.75, 0.75)\), and the \(B\)-site Fe and \(B'\)-site Os atoms are in an orderly distribution at the \(4b\) \((0, 0, 0)\) and \(4c\) \((0.5, 0.5, 0.5)\) sites, respectively. Detailed structure refinements for the occupancy factors of cations show a nearly ideal 1:3 ordering between \(A\)-site Ca and the \(A'\)-site Cu atoms (i.e., there is neither Ca-Cu antisite occupancy nor other elements occupying these two sites), while a small amount of Fe-Os antisite occupancy is found to occur by about 11%. The refined structural parameters are listed in Table I. Based on the related bond lengths, the bond valence sum (BVS) calculations respectively give the valence states of Cu, Fe, and Os to be 2.11, 2.87, and 5.23, indicating a \(\text{Cu}^{2+}_{\text{L}_{2-3}},\text{Fe}^{3+}_{\text{L}_{2-3}},\text{Os}^{5+}_{\text{L}_{2-3}}\)(\(\text{O}_{12}\)) charge combination, in agreement with the XAS measurements shown below.

The x-ray absorption spectrum at the 3d transition-metal \(L_{2,3}\) edges is highly sensitive to the valence state as well as the local environment of the transition metal. Figure 2(a) shows the Cu-\(L_{2,3}\) XAS of CCFOO together with \(\text{CuO}, \text{Cu}_2\text{O}, \text{NaCuO}_2\) as pure \(\text{Cu}^{2+}\), \(\text{Cu}^{3+}\), and \(\text{Cu}^{4+}\) references, respectively [27,28]. Obviously, the spectrum of \(\text{NaCuO}_2\) is shifted by 1.8 eV to higher energy relative to that of \(\text{CuO}\). The weak, but highest, energy of the \(\text{Cu}_2\text{O}\) spectrum is assigned to the \(s\)-related states since the \(3d\) states are fully occupied for the \(3d^{10}\) electronic configuration of \(\text{Cu}^{2+}\). One can see a sharp and symmetric peak at the Cu-\(L_{2,3}\) edges of CCFOO at an similar energy similar to that of \(\text{Cu}_2\text{O}\), but no \(\text{Cu}^{1+}\) and \(\text{Cu}^{2+}\)-related spectral feature demonstrating the same \(\text{Cu}^{2+}\) valence state [27-30]. Note that the CCFOO spectrum is shifted by about 0.45 eV to lower energy with respect to the \(\text{Cu}_2\text{O}\) spectrum, reflecting different Cu local environments. The unoccupied \(d(\pi^* - \pi)\) orbital is expected to have a lower energy in CCFOO than that in \(\text{Cu}_2\text{O}\) due to a longer Cu-O distance and a square-planar coordination in the former.

Figure 2(b) shows the Fe-\(L_{2,3}\) XAS of CCFOO together with \(\text{Fe}_{0.04}\text{Mg}_{0.96}\text{O}_3\) [31] and \(\text{Fe}_2\text{O}_3\) as high-spin Fe\(^{2+}\) and Fe\(^{3+}\) references with \(\text{FeO}_6\) octahedral coordination, respectively. The same energy position and very similar line shape of both CCFOO and \(\text{Fe}_2\text{O}_3\), but 1.9 eV lower than that of \(\text{Fe}^{2+}\) reference \(\text{Fe}_{0.04}\text{Mg}_{0.96}\text{O}_3\), demonstrate a high-spin \(\text{Fe}^{2+}\) state in CCFOO. We now turn to the Os-\(L_{2,3}\) XAS analysis. In Fig. 2(c) one can find that the white line in the Os-\(L_{2,3}\) XAS of CCFOO lies at the same energy position as that of \(\text{Sr}_2\text{FeOsO}_6\). This suggests that the Os\(^{5+}\) valence states in the present CCFOO [32]. Therefore, XAS measurements give unambiguous evidence for the presence of \(\text{Cu}^{2+}/\text{Fe}^{2+}/\text{Os}^{5+}\) valence states in the \(A\)- and \(B\)-site ordered CCFOO.

The magnetism of CCFOO was characterized by field-dependent magnetization measurements as shown in Fig. 3(a). The presence of canonical magnetic hysteresis loops at several selected temperatures reveals the ferromagnetic (FM) or FiM behavior. The saturated moment obtained at 2 K is about \(9.30 \mu_B/\text{f.u.}\). Even at 50 K, a considerable saturated moment can be observed (\(2.5 \mu_B/\text{f.u.}\)), indicating strong FM/FiM interactions. In addition, we find a moderate coercive force

<table>
<thead>
<tr>
<th>Parameter</th>
<th>CCFOO</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) (Å)</td>
<td>7.43264(3)</td>
</tr>
<tr>
<td>(r_0)</td>
<td>0.2580(3)</td>
</tr>
<tr>
<td>(r_1)</td>
<td>0.4304(5)</td>
</tr>
<tr>
<td>(r_2)</td>
<td>0.5574(4)</td>
</tr>
<tr>
<td>(G(2a)) for (\text{Ca})</td>
<td>1.098(9)</td>
</tr>
<tr>
<td>(G(6d)) for (\text{Cu})</td>
<td>1.035(3)</td>
</tr>
<tr>
<td>(G(4b)) for (\text{Fe}^1)</td>
<td>0.882(1)</td>
</tr>
<tr>
<td>(G(4b)) for (\text{Os}^1)</td>
<td>0.118(1)</td>
</tr>
<tr>
<td>(G(4c)) for (\text{Os}^2)</td>
<td>0.882(1)</td>
</tr>
<tr>
<td>(G(4c)) for (\text{Fe}^2)</td>
<td>0.118(1)</td>
</tr>
</tbody>
</table>

Table I. Refined structure parameters of CCFOO and the BVS values for \(\text{Cu}, \text{Fe}, \text{and Os}\) at room temperature. Space group: \(Pn-3\); atomic sites: \(\text{Ca} 2a\) \((0.25, 0.25, 0.25); \text{Cu} 6d\) \((0.25, 0.75, 0.75)\); \(\text{Fe} 4b\) \((0, 0, 0)\); \(\text{Os} 4c\) \((0.5, 0.5, 0.5)\); \(\text{O} 24g\) \((x, y, z)\). The BVS values \(\langle V_i \rangle\) were calculated using the formula \(\langle V_i \rangle = \sum_{j=1}^{8} S_{ij} \langle S_j \rangle = \exp[(r_0 - r_1)/0.37]\). The value of \(r_0 = 1.679\) for \(\text{Cu}, 1.759\) for \(\text{Fe}\), and 1.868 for \(\text{Os}\). For the \(B\)-site \(\text{Fe}\) and \(B'\)-site Os, six coordinated oxygen atoms were used. For the \(A'\)-site \(\text{Cu}\), twelve coordinated oxygen atoms were used. \(G\): site occupancy.
FIG. 2. (a) XAS of Cu-\(L_2,3\) edges, (b) Fe-\(L_2,3\) edges, and (c) Os-\(L_3\) edges. The XAS of related references are also shown for comparison. (\(\sim 0.27\) T at 2 K), which is slightly suppressed with increasing temperature. The temperature dependence of magnetic susceptibility was measured as shown in Fig. 3(b). With decreasing temperature, the susceptibility experiences a sharp...

FIG. 3. (a) Field-dependent magnetization measured at different temperatures. (b) Temperature-dependent magnetic susceptibility measured at 0.1 T with ZFC and FC modes. (c,d) XMCD for Fe- and Cu-\(L_2,3\) edges. The photon spin is aligned parallel (\(\mu^{+}\) black line) and antiparallel (\(\mu^{-}\) red line) to the applied magnetic field, respectively. The difference spectra are shown in blue. Increase at the onset of about 580 K, revealing strong FM or FiM coupling as demonstrated by the magnetization results mentioned above. The present CCFOO possesses a high \(T_C\) in the \(A\)-site ordered and \(B\)-site ordered or disordered QPs; compare [13–22,33–38].

In CCFOO, all the transition-metal ions Cu\(^{2+}\) (\(S_{Cu} = 1/2\)), Fe\(^{3+}\) (\(S_{Fe} = 5/2\)), and Os\(^{5+}\) (\(S_{Os} = 3/2\)) can possibly take part in the spin interactions. Both the collinear Cu\(^{2+}\)(↑)Fe\(^{3+}\)(↑)Os\(^{5+}\)(↑) FM state and the FiM Cu\(^{2+}\)(↑)Fe\(^{3+}\)(↑)Os\(^{5+}\)(↓) state produce unreasonably large saturated moments (19.0 and 13.0 \(\mu_B\)/f.u., respectively) with regard to the experimental observation in the assumption of local-electron model without considering the spin-orbital coupling (SOC) of Os\(^{5+}\). Actually, the SOC effect of Os\(^{5+}\) is not significant due to the \(d^7\)-electron configuration as confirmed by theoretical calculations [7,9,11,12,32]. In addition, the FiM coupling of Cu\(^{2+}\)(↑)Fe\(^{3+}\)(↑)Os\(^{5+}\)(↓) gives a too small spin moment (1.0 \(\mu_B\)/f.u.). In comparison, only the Cu\(^{2+}\)(↑)Fe\(^{3+}\)(↑)Os\(^{5+}\)(↓) FiM state yields a spin moment (7.0 \(\mu_B\)/f.u.) that is comparable with the experimental value obtained at 2 K (5.0 \(\mu_B\)/f.u.). The small amount of Fe-Os anticorupancy as well as the strong hybridization between the Os-5\(d\) and O-2\(p\) orbitals (shown later) should be responsible for the reduced spin moment observed in experiment. Furthermore, the Cu\(^{2+}\)(↑)Fe\(^{3+}\)(↑) FM alignment can be confirmed by XMCD measurement at the Cu- and Fe-\(L_2,3\) edges. As seen in Figs. 3(c) and 3(d), the same sign of XMCD spectra at the Fe- and Cu-\(L_2,3\) edges reveals the FM coupling between the \(A'\)-site Cu\(^{2+}\) and the \(B\)-site Fe\(^{3+}\) ions, in coherence with the proposed Cu\(^{2+}\)(↑)Fe\(^{3+}\)(↑)Os\(^{5+}\)(↓) ferrimagnetic spin alignment.

The resistivity of CCFOO was measured on a polycrystalline pellet pressed under 6 GPa. As shown in the inset of Fig. 4, the magnitude of resistivity gradually increases with decreasing temperature and reaches \(10^4\) \(\Omega\) cm at low temperatures, suggesting the semiconducting or insulating...
behavior. The resistivity data cannot be fitted well with either the thermal active model or the Mott variable-range hopping mechanism. We therefore resorted to optical measurements to characterize the electrical feature. Figure 4 represents the values of photocurrent excited by optical radiation with various wavelengths at RT. When the optical wavelength decreases to about 1.35 μm, the signal of the photocurrent starts to sharply increase, revealing that the narrowest energy band gap in the polycrystalline CCOO is roughly equal to 0.92 eV at RT. Note that in the present A- and B-site ordered CCOO, the electrical transport is dominated by the corner-sharing Fe/OsO₆ octahedra. The observed Fe-Os antisite occupancy can thus possibly reduce the resistivity moderately.

The electronic structures of CCOO were further investigated by the first-principles calculations. To determine the magnetic ground state, generalized-gradient approximation (GGA) and GGA + U spin-polarized calculations were performed for different magnetic structures. The GGA calculations always converge to the FiM Cu₂⁺(↑)Fe³⁺(↑)Os⁵⁺(↓) ground state regardless of the initial configuration. The GGA + U calculations using $U_{\text{eff}} = 5$ eV for Cu, 4 eV for Fe, and 2 eV for Os, following the common choices in the literature [9,11,14,39,40], also yield the same magnetic ground state, in agreement with experimental analysis. Other values of $U_{\text{eff}}$ in a wide range around the above choices have also been tested and no qualitative change was found in the magnetic ground state. A total magnetic moment of 7.01 $\mu_B$/f.u. is obtained by calculations, and the atomic contributions of Cu, Fe, and Os inside the muffin-tin spheres are 0.627, 4.043, and $-1.421$ $\mu_B$, respectively. The values of the ionic magnetic moments are slightly reduced from their ideal values because of the strong hybridization with O-2p orbitals. Calculations with spin-orbit interactions yield only slight changes in the atomic spins to 0.603, 4.013, and $-1.315$ $\mu_B$ for Cu, Fe, and Os, respectively, with a total moment of 7.19 $\mu_B$/f.u.

Figure 5 shows the calculated electronic band structures and partial densities of states with the above choices of $U_{\text{eff}}$. The insulating nature of CCOO is revealed: The majority spin has an energy gap of about 1.8 eV, whereas the minority spin has an energy gap of about 1.0 eV at the ground state, agreeing with the photocurrent measurement as shown in Fig. 4. The wide energy gap could provide protection to the high-temperature FiM ordering. Consistent with previous experimental analysis [9,41], in the present CCOO, Cu₂⁺ has one localized hole on its $b_{1g}$ orbital, Fe³⁺ is fully polarized with a half-filled 3d-shell, and Os⁵⁺ has half-filled $t_{2g}$ orbitals. The strong on-site Coulomb repulsion and Hund couplings should be responsible for the obtained energy gap. Note that the electronic states near the Fermi level are dominated by the Os-5d orbitals which hybridize strongly with the O-2p orbitals. It is therefore expected that appropriate element doping only on Os may tune the spin and electronic properties of the present high-$T_C$ FiM insulator CCOO. Actually, when the Os is replaced by Re, half-metallic behavior is observed in CaCu₃Fe₂Os₂O₁₂ [14].

To understand the high Curie temperature compared to that of Ca₃FeOsO₆, the magnetic exchange interactions of CCOO were calculated using the spin model [42,43] $H = \sum_{i,j} J_{ij} S_i \times S_j$, where $S_i$ and $S_j$ are the spin vectors of Cu, Fe, or Os ions at the sites $i$ and $j$, respectively, and $J_{ij}$ is the exchange interaction between the nearest-neighbor spin pair. Since previous calculations for Ca/Sr₂FeOsO₆ and La/BiCu₂Fe₂OsO₁₂ have shown that the exchange interactions $J_{\text{Fe-Fe}}, J_{\text{Os-Os}}, J_{\text{Cu-Cu}}$ between the neighboring atoms of the same type are relatively small and can be safely neglected [7,10,11,40,44], we consider here only three nearest-neighbor interactions, $J_{\text{Fe-Os}}$, $J_{\text{Cu-Fe}}$, and $J_{\text{Cu-Os}}$ as shown in Fig. 6(b), and derive them by calculating the energy differences of the four magnetic configurations, i.e., FiM1, FiM2, FiM3, and FM1 mentioned before. These calculations yield $E(\text{FiM2} - \text{FiM1}) = 0.567$ eV/f.u., $E(\text{FiM3} - \text{FiM1}) = 0.692$ eV/f.u., and $E(\text{FM1} - \text{FiM1}) = 1.7$ eV/f.u. Obviously, the FiM1 spin structure with Cu²⁺(↑)Fe³⁺(↑)Os⁵⁺(↓) coupling has the lowest energy. The derived AFM exchange interactions are $J_{\text{Cu-Fe}} S_{\text{Cu}} S_{\text{Fe}} = 9.19$ meV, $J_{\text{Fe-Os}} S_{\text{Fe}} S_{\text{Os}} = 32.8$ meV, and $J_{\text{Cu-Os}} S_{\text{Cu}} S_{\text{Os}} = 38.0$ meV, revealing a strong spin coupling between the A'-site Cu ions and the B'-site Os ions.

Previous studies for Ca₃FeOsO₆ [9,11] have yielded a similar exchange interaction between the B'-site Fe and Os ions.
with $J_{\text{Fe-Os}}S_{\text{Fe}}S_{\text{Os}} = 31$ meV [see Fig. 6(a)], indicating that the variations in bond length ($d_{\text{Fe-Os}} = 3.713$ Å for CFCOO and 3.855 Å for Ca$_2$FeOsO$_6$) and bond angle ($\angle \text{Fe-Os} = 139.9^\circ$ for CFCOO and 152.4$^\circ$ for Ca$_2$FeOsO$_6$ in average) cannot be primarily responsible for the sharp enhancement of the Curie temperature from 320 K in Ca$_2$FeOsO$_6$ to 580 K in CFCOO. The enhancement thus should be associated with the introduction of the A'-site Cu$^{3+}$ magnetic ions. As shown in Fig. 6(b), all the exchange interactions in CFCOO are mediated through the O ions and their values are proportional to the hybridization integral of the magnetic ions with the O 2$p$ orbitals and inversely proportional to the Coulomb energy (plus the charge transfer energy). Because the Os 5$d$ orbitals are more extended and locate near the Fermi energy and have a smaller on-site Coulomb interaction as well as a stronger hybridization with the O 2$p$ orbitals, the spin couplings to the Os spins, i.e., the $J_{\text{Fe-Os}}S_{\text{Fe}}S_{\text{Os}}$ and $J_{\text{Cu-Os}}S_{\text{Cu}}S_{\text{Os}}$, are relatively stronger as derived in our numerical calculations. In contrast, the coupling between Cu and Fe ($J_{\text{Cu-Fe}}S_{\text{Cu}}S_{\text{Fe}}$) is much smaller considering that the Cu 3$d$-hole orbital is more localized with a large Coulomb interaction and the half-filled Fe 3$d$ orbitals are pushed further away to higher energies and hybridize less with the O 2$p$ orbitals. Therefore, introducing the A'-site Cu$^{3+}$ ions provides an additional Cu($\uparrow$)Os($\downarrow$) AFM coupling as strong as that of the B-site Fe($\uparrow$)Os($\downarrow$). Note that this also introduces slight magnetic frustrations because of the Cu($\uparrow$)Fe($\downarrow$) AFM interaction. However, it is much stronger Cu$^{2+}$($\uparrow$)Os$^{5+}$($\downarrow$) and Fe$^{3+}$($\uparrow$)Os$^{5+}$($\downarrow$) AFM exchange energies that dominate the weaker Cu$^{2+}$($\uparrow$)Fe$^{3+}$($\downarrow$) interaction and lead to the Cu$^{2+}$($\uparrow$)Fe$^{3+}$($\downarrow$)Os$^{5+}$($\downarrow$) long-range ferrimagnetic spin order. Thereby, the present A- and B-site ordered perovskite CFCOO has a much higher $T_C$ (580 K) relative to that of the A-site nonmagnetic Ca$_2$FeOsO$_6$ ($T_C = 320$ K). In theory, the Curie temperature can be estimated within the mean-field approximation by solving the equation [42,43]

$$\langle S_i^z \rangle = \frac{S_i(S_i + 1)}{3k_B T} \sum_j J_{ij} \langle S_j^z \rangle.$$  

The $T_C$ is given by the largest eigenvalue of the matrix $\Theta_{ij} = S_i(S_i + 1)J_{ij}/3k_B$. Here $k_B$ is the Boltzmann constant. We obtain the $T_C = 1800$ K for CFCOO, which is also much higher than that estimated for Ca$_2$FeOsO$_6$ ($\sim 600$ K) [11].

Here we point out that recent experimental studies reveal intriguing spintronic properties such as spin Seebeck, spin wave, spin transfer, and spin pumping in FM/FiM insulators as those observed in FM metals [45–49]. Moreover, since there is no moving charge in magnetic insulators, the dissipative losses associated with the magnetization dynamics are often exceptionally low. It means that a FM/FiM insulator with a high spin ordering temperature (>RT) and a wide energy band gap is favorable for possible applications in spintronics. Although a few spinel oxides and B-site ordered DPs possess relatively high FiM transition temperatures, the related band gaps are usually too small (<0.5 eV) [41,50–52]. Fortunately, the present CFCOO simultaneously possesses a high $T_C$ (~580 K) and a considerable energy band gap (~1.0 eV), providing a promising candidate for multifunctional spintronic devices with potential applications well above RT.

### IV. CONCLUSIONS

In summary, a ferrimagnet CaCu$_3$Fe$_2$Os$_2$O$_{12}$ with a high spin ordering temperature of 580 K was prepared under high-pressure and high-temperature conditions. This compound crystallizes to both A-site and B-site ordered quadruple perovskite structure with space group $Pn$-3. The charge states are confirmed to be Cu$^{2+}$/Fe$^{3+}$/Os$^{5+}$, which are in an orderly distribution at fixed atomic sites. The introduction of A'-site Cu$^{2+}$ leads to strong Cu$^{2+}$($\uparrow$)Fe$^{3+}$($\downarrow$)Os$^{5+}$($\downarrow$) FiM coupling, which is responsible for the high spin ordering temperature. The fully filled Os-$t_{2g}^{3+}$ orbitals dominate the electronic properties near the Fermi level and open the band gap, providing an opportunity for manipulating the magnetic and electrical properties by doping the Os site alone. Although the B-site chemical doping in a perovskite has already been widely studied for many years to increase the spin or charge ordering temperatures, there is little study on A-site substitution with magnetic transition metals. The present work provides a rare example on sharply enhancing the $T_C$ by introducing additional magnetic ions at the A site.
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