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A half-metallic A- and B-site-ordered quadruple perovskite oxide \( \text{CaCu}_3\text{Fe}_2\text{Re}_2\text{O}_{12} \) with large magnetization and a high transition temperature

Wei-tin Chen\(^1\),†, Masaichiro Mizumaki\(^2\), Hayato Seki\(^1\), Mark S. Senn\(^3\), Takashi Saito\(^1\), Daisuke Kan\(^1\), J. Paul Attfield\(^3\) & Yuichi Shimakawa\(^1,4\)

Strong correlation between spins and conduction electrons is key in spintronic materials and devices. A few ferro- or ferrimagnetic transition metal oxides such as \( \text{La}_{1-x}\text{Sr}_x\text{MnO}_3 \), \( \text{Fe}_3\text{O}_4 \), \( \text{CrO}_2 \) and \( \text{Sr}_2\text{FeMoO}_6 \) have spin-polarized conduction electrons at room temperature, but it is difficult to find other spin-polarized oxides with high Curie temperatures (well above room temperature) and large magnetizations for spintronics applications. Here we show that an A- and B-site-ordered quadruple perovskite oxide, \( \text{CaCu}_3\text{Fe}_2\text{Re}_2\text{O}_{12} \), has spin-polarized conduction electrons and is ferrimagnetic up to 560 K. The couplings between the three magnetic cations lead to the high Curie temperature, a large saturation magnetization of 8.7 \( \mu_B \) and a half-metallic electronic structure, in which only minority-spin bands cross the Fermi level, producing highly spin-polarized conduction electrons. Spin polarization is confirmed by an observed low-field magnetoresistance effect in a polycrystalline sample. Optimization of \( \text{CaCu}_3\text{Fe}_2\text{Re}_2\text{O}_{12} \) and related quadruple perovskite phases is expected to produce a new family of useful spintronic materials.
Materials with spin-polarized conduction electrons are of considerable interest in magnetic and electronic materials' research and for technological applications such as spin-polarized field emission and spin-polarized tunneling devices. The Heusler alloy NiMnSb was the first predicted half-metallic ferromagnet, and the oxides CrO$_2$ (refs 3,4) and Fe$_2$O$_4$ (refs 5,6) also have half-metallic electronic properties. For example, in CaCu$_3$B$_4$O$_{12}$ materials with addition to B-site ordered quadruple perovskite oxide with large ferromagnetization and a high magnetic ordering temperature. This leads to large tunneling magnetoresistance. The Heusler alloy NiMnSb was the first A-site-ordered perovskite structure. (A$A$B$B'_2$O$_6$), where the transition metal ions A and B are arranged alternately in a rock-salt manner, are useful materials for spintronics applications. An important example is Sr$_2$FeMoO$_6$, which is half-metallic and shows substantial TMR at room temperature. The B-site Fe$^{3+}$ and the B'-site Mo$^{5+}$ spins couple antiferromagnetically, leading to ferrimagnetism. Below the magnetic transition temperature ($T_m=410$ K) only the minority-spin bands, which mainly consist of Fe 3$d$ orbitals and Mo 4$d$ orbitals hybridized with O 2$p$ orbitals, cross the Fermi level, producing spin-polarized conduction electrons. A recent Monte Carlo study of Sr$_2$FeMoO$_6$ showed that the electron spin polarization is proportional to the core spin magnetization and depends on temperature and disorder. We have explored a strategy for enhancing spintronic properties relative to double perovskites by introducing further magnetic cations that can participate in a 1:3 order at the A sites, leading to the discovery of a new A- and B-site ordered quadruple perovskite oxide with large magnetization and a high magnetic ordering temperature.

The A- and B-site-ordered quadruple perovskite-structure oxide is derived from the A-site-ordered perovskite with general formula AA$'$B$'$B$_2$O$_6$, which consists of a framework with heavily in-phase tilted BO$_6$ octahedra and A'O$_4$ squares. Unlike the A site in the basic ABO$_3$ perovskites, which is usually occupied by alkali-metal, alkaline-earth or rare-earth cations, the A' site in AA$'$B$'$B$_2$O$_6$ can accommodate transition metal ions. The introduction of Fe and Re to the B lattice significantly near the magnetic transition temperature. Materials that have highly spin-polarized conduction electrons at room temperature and hence a magnetic transition temperature well above 300 K are therefore very desirable for further spintronic developments.

Transition metal oxides with an ordered double-perovskite structure AA$'$B$'$B$_2$O$_6$ where the transition metal ions B and B' are arranged alternately in a rock-salt manner, are useful materials for spintronics applications. An important example is Sr$_2$FeMoO$_6$, which is half-metallic and shows substantial TMR at room temperature. The B-site Fe$^{3+}$ and the B'-site Mo$^{5+}$ spins couple antiferromagnetically, leading to ferrimagnetism. Below the magnetic transition temperature ($T_m=410$ K) only the minority-spin bands, which mainly consist of Fe 3$d$ orbitals and Mo 4$d$ orbitals hybridized with O 2$p$ orbitals, cross the Fermi level ($E_F$), producing spin-polarized conduction electrons. A recent Monte Carlo study of Sr$_2$FeMoO$_6$ showed that the electron spin polarization is proportional to the core spin magnetization and depends on temperature and disorder. We have explored a strategy for enhancing spintronic properties relative to double perovskites by introducing further magnetic cations that can participate in a 1:3 order at the A sites, leading to the discovery of a new A- and B-site ordered quadruple perovskite oxide with large magnetization and a high magnetic ordering temperature.

The A- and B-site-ordered quadruple perovskite-structure oxide is derived from the A-site-ordered perovskite with general formula AA$'$B$'$B$_2$O$_6$, which consists of a framework with heavily in-phase tilted BO$_6$ octahedra and A'O$_4$ squares. Unlike the A site in the basic ABO$_3$ perovskites, which is usually occupied by alkali-metal, alkaline-earth or rare-earth cations, the A' site in AA$'$B$'$B$_2$O$_6$ can accommodate transition metal ions. The introduction of Fe and Re to the B lattice significantly near the magnetic transition temperature. Materials that have highly spin-polarized conduction electrons at room temperature and hence a magnetic transition temperature well above 300 K are therefore very desirable for further spintronic developments.

Figure 1 | Crystal structure of the A- and B-site-ordered quadruple perovskite CaCu$_3$Fe$_2$Re$_2$O$_{12}$. Ca and Cu ions are ordered in a 1:3 ratio at the A sites and Fe and Re ions are ordered in a rock-salt-type arrangement on the B sites of the ABO$_3$ perovskite structure, resulting in a framework of CuO$_4$ squares units and heavily tilted FeO$_6$ and ReO$_6$ octahedra.
disorder of 6.2(1)% was found. The SXRD structure refinement thus confirms that CaCu₃Fe₂Re₂O₁₂ has the quadruple perovskite structure with well-ordered A- and B-site cations. The fit is shown in Fig. 2 and the refined structure parameters and bond distances are listed in Tables 1 and 2.

Four of the 12 Cu–O distances are short, 2.006(5) Å, revealing the square-planar coordination of oxygen around the A’ site, and the resulting distortion leads to heavy tilting of the FeO₆ and ReO₆ octahedra. The cation valence states estimated from the observed cation–oxygen bond distances by a bond valence sum method are shown in Table 2. The bond valence sum values are very close to the formal values in the formula Ca²⁺Cu²⁺Fe³⁺²Re⁵⁺₂O₁₂. The charge difference between Fe³⁺ and Re⁵⁺ results in the high degree of rock-salt-type cation ordering at the B/B’ sites. The same formal charge distribution was observed in CaCu₃Fe₂Sb₂O₁₂ (ref. 35) and in the Ca₂Cu₂Fe₂Sb₂O₁₂ configuration (ref. 38).

Magnetic properties of CaCu₃Fe₂Re₂O₁₂. Magnetization measurements for CaCu₃Fe₂Re₂O₁₂ are shown in Fig. 3. A high-temperature Curie transition is observed at $T_C = 560$ K, below which a large magnetization develops with a saturation value of 8.7 µB per formula unit (f.u.) at 5 K. Spins from the Cu²⁺ (3d⁹, $S = 1/2$), Fe³⁺ (3d⁵, $S = 5/2$) and Re⁵⁺ (5d⁴, $S = 1$) ions all contribute to the net magnetization of CaCu₃Fe₂Re₂O₁₂. Ferromagnetic Cu²⁺ (↑)–Fe³⁺ (↑)–Re⁵⁺ (↑) alignment of the spins gives an ideal saturated magnetization of 17 µB f.u.¹⁻¹, neglecting orbital contributions, while the collinear ferrimagnetic combinations Cu²⁺ (↑)–Fe³⁺ (↑)–Re⁵⁺ (↑) and Cu²⁺ (↑)–Fe³⁺ (↑)–Fe³⁺ (↑)–Re⁵⁺ (↑) or Cu²⁺ (↑)–Fe³⁺ (↑)–Fe³⁺ (↑)–Re⁵⁺ (↑) are respectively predicted to give 11, 9 or 3 µB f.u.¹⁻¹. The observed saturated magnetization of 8.7 µB f.u.¹⁻¹ is thus close to the ferrimagnetic Cu²⁺ (↑)–Fe³⁺ (↑)–Re⁵⁺ (↑) value.

Ferromagnetic coupling between Cu²⁺ and Fe³⁺ moments was confirmed by magnetic circular dichroism (MCD) intensities from X-ray absorption spectroscopy (XAS) measurements at 15 K, as shown in Fig. 4. The observed XAS spectrum near the Cu edge is similar to that of square-planar Cu²⁺ in BiCu₃Mn₃O₁₂ (ref. 39), although satellite structures due to the charge-transfer screening process are seen in the present CaCu₃Fe₂Re₂O₁₂, and the Fe spectrum is similar to the typical Fe³⁺ O₆ signal in LaFeO₃ (ref. 40). The L₃-edge MCD intensities are negative for both Cu and Fe, and the L₂-edge intensities are positive for both metals—the coincident signs at each edge demonstrate that the spins of the A’-site Cu²⁺ and B-site Fe³⁺ ions couple ferromagnetically. The magnetic moments obtained from the MCD intensities by using magneto-optical sum rules are 0.86 µB (spin part, 0.82 µB) for Cu and 4.17 µB (spin part, 4.11 µB) for Fe, in reasonably good agreement with the expected moments for Cu²⁺ ($S = 1/2$) and Fe³⁺ ($S = 5/2$). Analysis of preliminary powder neutron diffraction also supports the spin ordering model, as shown in Supplementary Fig. 1 and Supplementary Table 1.

The ferrimagnetic spin structure of CaCu₃Fe₂Re₂O₁₂ differs markedly from those of related cation-ordered perovskites, most notably in having ferromagnetic coupling between A’-site Cu²⁺ and the dominant B-site Fe³⁺ spins, as illustrated in Fig. 5. The double-perovskite Ca₃Fe₅Sb₂O₁₁ with nonmagnetic Sb⁵⁺ ions at the B’ sites shows spin-glass behaviour at low temperatures due to geometric frustration of antiferromagnetic interactions within the tetrahedral B sublattice of Fe³⁺ moments (Fig. 5a). Introducing Cu²⁺ at the A’ site to give CaCu₂Fe₂Sb₂O₁₂ relaxes the spin frustration leading to ferrimagnetism below 170 K, but the Cu²⁺ spins couple antiferromagnetically with the B-site Fe³⁺ spins (Fig. 5b). This was confirmed by the MCD intensities of Cu²⁺ at the A’ site to give CaCu₂Fe₂Sb₂O₁₂ are negative/positive for Cu L₃/L₂-edges but negative/positive for Cu L₃/L₂-edges, in contrast to the spectra for CaCu₃Fe₂Re₂O₁₂ shown in Fig. 4. In charge-disproportionated CaCu₂Fe₂O₁₂ (CaCu²⁺Fe³⁺₂₋Fe³⁺₁O₁₂), the Cu²⁺ spins at the A’ site also couple antiferromagnetically.

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**Table 1 | Refined structure parameters of CaCu₃Fe₂Re₂O₁₂ at room temperature.**

<table>
<thead>
<tr>
<th>Atom</th>
<th>Site</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>G</th>
<th>$U_{iso}$ (100 × Å²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>2a</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>1.0</td>
<td>1.2 (2)</td>
</tr>
<tr>
<td>Cu</td>
<td>6d</td>
<td>0.25</td>
<td>0.75</td>
<td>0.75</td>
<td>1.0</td>
<td>0.39 (2)</td>
</tr>
<tr>
<td>Fe</td>
<td>4b</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.938 (1)</td>
</tr>
<tr>
<td>Re</td>
<td>4b</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.062 (2)</td>
</tr>
<tr>
<td>Fe</td>
<td>4c</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.062 (1)</td>
<td></td>
</tr>
<tr>
<td>Re</td>
<td>4c</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.15 (1)</td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>24h</td>
<td>0.4496 (6)</td>
<td>0.7548 (5)</td>
<td>0.0691 (6)</td>
<td>1.0</td>
<td>0.37 (7)</td>
</tr>
</tbody>
</table>

Estimated s.d. of independent variables are shown in parentheses. Site occupation factors G; isotropic thermal parameters $U_{iso}$; space group: P3ı̅1 (no. 201); lattice parameter a = 7.44664(3) Å; residuals $R_w = 8.83$% and $R = 2.45$. 

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**Figure 2 | Fit to the SXRD pattern of CaCu₃Fe₂Re₂O₁₂ at room temperature.** Observed intensity points (crosses), the calculated profile (full curve) and the difference between the observed and calculated intensities (offset curve below) are shown. The ticks indicate the Bragg peak positions. The inset shows an expanded view of the low-angle (1 1 1) and (2 0 0) diffraction peaks from which additional Scherrer broadening of (1 1 1) due to limited-range coherence of Fe/Re cation order is seen.
**Table 2 | M–O distances and BVS calculated for CaCu$_3$Fe$_2$Re$_2$O$_{12}$ from the structure analysis results in Table 1.**

<table>
<thead>
<tr>
<th>Atom</th>
<th>M–O (Å)</th>
<th>BVS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>2.611 (5) × 12</td>
<td>2.10</td>
</tr>
<tr>
<td>Cu</td>
<td>2.006 (5) × 4</td>
<td>1.90</td>
</tr>
<tr>
<td>Fe</td>
<td>2.803 (5) × 4</td>
<td>3.12</td>
</tr>
<tr>
<td>Re</td>
<td>3.264 (5) × 4</td>
<td>4.91</td>
</tr>
</tbody>
</table>

BVS, bond valence sum; M, metal; O, oxygen.

Figure 3 | Magnetic properties of CaCu$_3$Fe$_2$Re$_2$O$_{12}$. (a) Temperature dependence of magnetic susceptibility measured under an external field of 10 kOe, with the magnetic transition observed at 560 K. (b) Magnetization-field measurements at 5 K, revealing a large saturated magnetization of 8.7 μB f.u.$^{-1}$. The low-field region is expanded in Fig. 7b.

Figure 4 | XAS and MCD intensities of CaCu$_3$Fe$_2$Re$_2$O$_{12}$. (a) XAS and MCD intensities near the Cu $L_2$ and $L_3$-edges. (b) XAS and MCD intensities near the Fe $L_3$ and $L_2$-edges. Data were obtained at 15 K. The red and blue curves, respectively, represent XAS spectra measured with photon spins parallel (↑) and antiparallel (↓) to the magnetization direction of the sample, in which a static magnetic field of 19 kOe was applied. The MCD intensity was calculated as the difference between the $I_+$ and $I_-$ absorption spectra. The coincident signs of the Cu and Fe MCD intensities at each $L$-edge show that their spins couple ferromagnetically.

Electronic structure and magnetotransport properties of CaCu$_3$Fe$_2$Re$_2$O$_{12}$. Spin-polarized electronic structure calculations converge to the observed ferrimagnetic CaCu$_3$$^+(\uparrow)$$^3^+(\downarrow)$$^3$Re$_5$$^+(\downarrow)$$^3$Re$_5$$^+(\downarrow)$ ground state irrespective of the initial spin structure, showing that this ground state is very stable. The total magnetic moment is 9.0 μB f.u.$^{-1}$ and the calculated magnetic moments inside the muffin-tin spheres for Cu, Fe and Re are respectively 0.39, 4.03 and −0.72 μB, which are slightly reduced from the ideal 2S values due to strong hybridization with O 2p orbitals. An important prediction from the calculations is that CaCu$_3$Fe$_2$Re$_2$O$_{12}$ is half-metallic with fully spin-polarized conduction electrons, as shown in Fig. 6. The electronic band structure has a large gap in the up(majority)-spin bands and only down(minority)-spin bands of mainly Re 5d hybridized with O 2p states cross the Fermi level ($E_F$). In contrast, Ca$_3$FeReO$_6$ is predicted to be an insulator with gaps at $E_F$ for both majority-spin and minority-spin bands and does not show metallic conductivity.

Resistivity and magnetoresistance measurements on a ceramic pellet of CaCu$_3$Fe$_2$Re$_2$O$_{12}$ are shown in Fig. 7. The resistivity is near 10 mΩ cm at room temperature and the observed slight increase on cooling (inset of Fig. 7a) would correspond to an unrealistically small gap energy of <1 meV if CaCu$_3$Fe$_2$Re$_2$O$_{12}$ was semiconducting. This suggests that grain boundary resistances mask the underlying metallic conductivity. The observed conducting behaviour of CaCu$_3$Fe$_2$Re$_2$O$_{12}$ is different from the insulating behaviour of CaCu$_3$Fe$_2$Sb$_2$O$_{12}$ (ref. 35) and the semiconductivity of charge-disproportionated CaCu$_3$Fe$_2$O$_{12}$ (ref. 38). Spin-polarized conduction is revealed by the decrease in low-temperature resistivity of the sample under magnetic fields with a sharp low-field magnetoresistance contribution at magnetic fields <3 kOe. This is indicative of spin-dependent tunnelling of spin-polarized conduction electrons through grain or domain boundaries. Close inspection shows that the hysteresis in low-field magnetoresistance slightly differs from that in the magnetization, as the peak-to-peak magnetoresistance separation does not coincide with the coercive field value (Fig. 7b). The behaviour is similar to that observed in half-metallic Sr$_2$FeMoO$_6$ and suggests a spin-valve-type magnetoresistance sensitivity to the intergrain tunnelling of spin-polarized conduction carriers. Although the observed magnetoresistance ratio of our ceramic CaCu$_3$Fe$_2$Re$_2$O$_{12}$ sample is small, most likely due to the slight Fe/Re antisite disorder and the effect of small (∼140 nm) B-cation-ordered domains as discussed for Sr$_2$FeMoO$_6$ (ref. 26), the low-field magnetoresistance indicates that conduction electrons are spin-polarized in the quadruple perovskite CaCu$_3$Fe$_2$Re$_2$O$_{12}$.
Discussion

The new quadruple perovskite CaCu₃Fe₂Re₂O₁₂ synthesized by high-pressure and -temperature synthesis is cation ordered at both A and B sites, and has a cubic structure with formal charge distribution Ca²⁺ Cu²⁺Fe³⁺²Re⁵⁺²O₁₂. Strong antiferromagnetic coupling of Re⁵⁺ spins to those of Cu²⁺ and Fe³⁺ results in ferrimagnetic CaCu²⁺(↑)Fe³⁺(↑)²Re⁵⁺(↓)₂O₁₂ order with a high transition temperature (560 K) and a large magnetization.
(8.7 μB f.u.−1). XAS-MCD and neutron diffraction measurements confirm the ferrimagnetic spin structure. Electronic structure calculations predict that the ferrimagnetic ground state is half-metallic with only minority-spin bands crossing the Fermi level, producing highly spin-polarized conduction electrons. Resistivity measurements confirm spin-polarized conduction and a low-field spin-valve-type magnetoresistance is evident, although further optimization to suppress Fe/Re disorder fully is needed. The combination of a high magnetic ordering temperature and large magnetization, in comparison to double-perovskite analogues, and spin-polarized conductivity demonstrates that the introduction of further magnetic cations that can participate in a 1:3 order at the A sites is a good strategy for discovery of a new family of spintronic quadruple perovskite oxide materials.

Methods
Sample preparation. A polycrystalline sample of CaCu3Fe2Re2O12 was prepared by a solid-state reaction at a high temperature and high pressure. Stoichiometric amounts of CaF2, CuO, Fe2O3, and ReO3 were well mixed and the mixture was sealed in a DTA-type cubic anvil high-pressure apparatus and treated at 10 GPa and 1400 K for an hour.

Crystal structure analysis. A SXRD experiment was carried out for phase identification and crystal structure analysis. The room-temperature SXRD pattern obtained with a wavelength of 0.48836 Å was recorded on the image plate of a large Debye–Scherrer camera installed at beamline BL20B2 in SPring-8. The powder sample was placed in a 0.1 mm glass capillary tube to minimize absorption and rotated during the measurement. The obtained data were analysed with the Rietveld method by using the TOPAS software package.

Magnetic and transport property measurements. Magnetic properties were measured with a commercial magnetometer (Quantum-Design Magnetic Properties Measurement System). Temperature dependence of the magnetic susceptibility was measured at 5–700 K in an external magnetic field of 10 kOe. Field dependence of the magnetization was measured at several temperatures under fields ranging from −50 to 50 kOe. X-ray MCD spectra were obtained by a total electron yield method from X-ray absorption experiments conducted at beamline BL25SU in SPring-8. The powder sample was pasted uniformly on a sample holder by using carbon tape. The spectra at 15 K were obtained using parallel (I+) and antiparallel (I−) photon spins along the magnetization direction of the sample, to which a static magnetic field of 19 kOe was applied. The MCD intensity was defined as the difference between the absorption spectra (I− − I+) in the sample. Transport properties of the sample were measured in a conventional four-probe configuration. The temperature dependence of the resistivity and magnetoresistance were measured under magnetic fields ranging from −50 to 50 kOe.

Electronic structure calculation. The electronic structure of CaCu3Fe2Re2O12 was calculated by full-potential linearized augmented plane-wave first-principles calculations with the WIEN2k code. The lattice constant and atomic position parameters obtained from the structural refinement were used for the calculation. The full-potential linearized augmented plane-wave radii for Ca, Cu, Fe, Re, and O were respectively 2.0, 1.9, 1.9, 1.9 and 1.60 a.u. An effective sphere radius was used for the calculation.

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12. Zener, C. Interaction between the d-shells in the transition metals. II. Magnetic and transport property measurements. Temperature dependence of the magnetic susceptibility was measured at 5–700 K in an external magnetic field of 10 kOe. Field dependence of the magnetization was measured at several temperatures under fields ranging from −50 to 50 kOe. X-ray MCD spectra were obtained by a total electron yield method from X-ray absorption experiments conducted at beamline BL25SU in SPring-8. The powder sample was pasted uniformly on a sample holder by using carbon tape. The spectra at 15 K were obtained using parallel (I+) and antiparallel (I−) photon spins along the magnetization direction of the sample, to which a static magnetic field of 19 kOe was applied. The MCD intensity was defined as the difference between the absorption spectra (I− − I+) in the sample. Transport properties of the sample were measured in a conventional four-probe configuration. The temperature dependence of the resistivity and magnetoresistance were measured under magnetic fields ranging from −50 to 50 kOe.

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Neutron powder diffraction for magnetic structure analysis. Neutron powder diffraction from a ~0.8 g polycrystalline CaCu3Fe2Re2O12 powder sample in a 5-mm-diameter vanadium was carried out using the D20 diffractometer at the Institut Laue-Langevin (ILL), Grenoble, France. The diffraction patterns were collected with a neutron wavelength of 2.4194 Å. The crystal and magnetic structures of data collected at 5 K were fitted by the Rietveld method using the General Structure Analysis System software package and the obtained results are shown in Supplementary Fig. S1 and Supplementary Table S1. Fe/Re inversion was not refined as these two elements have very similar nuclear scattering factors; b(Fe) = 9.5 fm and b(Re) = 9.2 fm.

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Author contributions

W.-t.C. and Y.S. conceived and designed the study. W.-t.C., J.P.A. and Y.S. wrote the manuscript. All of the authors contributed to the interpretation and discussion of the experimental results. M.M. performed the XAS-MCD experiments. Y.S. calculated the electronic structure. T.S. and D.K. prepared the sample and measured the structural and physical properties. M.M. performed the XAS-MCD experiments. Y.S. calculated the electronic structure. All of the authors contributed to the interpretation and discussion of the experimental results. W.-t.C., J.P.A. and Y.S. wrote the manuscript.

Additional information

Supplementary Information accompanies this paper at http://www.nature.com/naturecommunications

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