

Realization of a Half Metal with a Record-High Curie Temperature in Perovskite Oxides

Zhehong Liu, Shuaikang Zhang, Xiao Wang, Xubin Ye, Shijun Qin, Xudong Shen, Dabiao Lu, Jianhong Dai, Yingying Cao, Kai Chen, Florin Radu, Wen-Bin Wu, Chien-Te Chen, Sonia Francoual, José R. L. Mardegan, Olaf Leupold, Liu Hao Tjeng, Zhiwei Hu, Yi-feng Yang,* and Youwen Long*

Half metals, in which one spin channel is conducting while the other is insulating with an energy gap, are theoretically considered to comprise 100% spin-polarized conducting electrons, and thus have promising applications in high-efficiency magnetic sensors, computer memory, magnetic recording, and so on. However, for practical applications, a high Curie temperature combined with a wide spin energy gap and large magnetization is required. Realizing such a high-performance combination is a key challenge. Herein, a novel A- and B-site ordered quadruple perovskite oxide LaCu₃Fe₂Re₂O₁₂ with the charge format of $Cu^{2+}/Fe^{3+}/Re^{4.5+}$ is reported. The strong $Cu^{2+}(\uparrow)Fe^{3+}(\uparrow)$ $Re^{4.5+}(\downarrow)$ spin interactions lead to a ferrimagnetic Curie temperature as high as 710 K, which is the reported record in perovskite-type half metals thus far. The saturated magnetic moment determined at 300 K is 7.0 $\mu_{\rm B}$ f.u.⁻¹ and further increases to 8.0 $\mu_{\rm B}$ f.u.⁻¹ at 2 K. First-principles calculations reveal a halfmetallic nature with a spin-down conducting band while a spin-up insulating band with a large energy gap up to 2.27 eV. The currently unprecedented realization of record Curie temperature coupling with the wide energy gap and large moment in LaCu₃Fe₂Re₂O₁₂ opens a way for potential applications in advanced spintronic devices at/above room temperature.

This implies that the charge carriers are completely (100%) spin-polarized at the Fermi level, making magnetic HMs highly promising for practical applications in advanced spintronic devices.^[1-6] However, the development of practicable spintronic devices for applications at temperatures close to room temperature (RT) requires the simultaneous consideration of certain synthetic performances of HM materials. First, the FM or FiM Curie temperature $(T_{\rm C})$ should be significantly higher than RT. Second, the energy gap (E_g) of the insulating spin channel should be wide enough to suppress the spin-flip transition caused by the thermal excitation of carriers to ensure 100% spin polarization in the working temperature region.^[7,8] Additionally, the electron spin polarization, which is proportional to magnetic moment must be high enough to inject a polarized spin effectively.[4,9-12] Perovskite oxide is one of the most important systems for half-metallic study. To date,

1. Introduction

Magnetic, including ferromagnetic (FM) and ferrimagnetic (FiM), half metals (HMs) are characterized by a metallic band structure for one spin channel (i.e., spin up) and an insulating band for the opposite spin channel (i.e., spin down).

Z. Liu, S. Zhang, X. Ye, S. Qin, X. Shen, D. Lu, J. Dai, Y. Cao, Y.-f. Yang, Y. Long
Beijing National Laboratory for Condensed Matter Physics
Institute of Physics
Chinese Academy of Sciences
Beijing 100190, China
E-mail: yifeng@iphy.ac.cn; ywlong@iphy.ac.cn
Z. Liu, S. Zhang, X. Ye, S. Qin, D. Lu, J. Dai, Y. Cao, Y.-f. Yang, Y. Long
School of Physical Sciences
University of Chinese Academy of Sciences
Beijing 100049, China
The ORCID identification number(s) for the author(s) of this article

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the highest $T_{\rm C}$ experimentally realized in perovskites is about 635 K.^[13] Although a wide variety of magnetic HMs has been reported in experiments, the development of a single-phase material that satisfies the three aforementioned requirements concurrently still remains a key challenge. For example, despite the high Curie temperatures observed in NiMnSb,^[3] Co₂FeSi,^[14]

X. Wang, L. H. Tjeng, Z. Hu Max Planck Institute for Chemical Physics of Solids Nöthnitzer Straße 40, 01187 Dresden, Germany X. Shen, Y.-f. Yang, Y. Long Songshan Lake Materials Laboratory Dongguan, Guangdong 523808, China K. Chen, F. Radu Helmholtz-Zentrum Berlin fur Materialien und Energie Albert-Einstein-Str.15, 12489 Berlin, Germany W.-B. Wu, C.-T. Chen National Synchrotron Radiation Research Center Hsinchu 30076, Taiwan S. Francoual, J. R. L. Mardegan, O. Leupold Deutsches Elektronen-Synchrotron DESY Notkestraße 85, 22607 Hamburg, Germany





Figure 1. Comparison of the coupled performance $\alpha = T_C \times E_g \times M_N$ for state-of-the-art half-metallic oxides with $T_C \ge 300$ K. The dashed line serves as a guide for the eyes. The current LaCu₃Fe₂Re₂O₁₂ has a greatly enhanced α value. The reported data are taken from refs. [5,7,13–16,19–33].

 Mn_2FeReO_{6} ,^[15] and Fe_3O_4 ^[16] half metals, their spin-up (or spindown) energy gaps are usually rather small (0.4-0.9 eV). In contrast, several HMs such as LaCu₃Co₂Re₂O₁₂^[17] and BaNaO₄^[18] exhibit relatively large energy gaps (≥1.9 eV), while their corresponding Curie temperatures are considerably lower than RT. If one defines a coupled parameter $\alpha = T_{\rm C} \times E_{\rm g} \times M_{\rm N}$, where $M_{\rm N}$ represents the normalized saturated moment of each cation, then, characterizing the synthetic performance of HMs, we find that a high $T_{\rm C}$ is often incompatible with a large $E_{\rm g}$ and/or $M_{\rm N}$, as shown in Figure 1. Therefore, it is of utmost importance to identify a new HM that simultaneously possesses a high $T_{\rm C}$, wide E_{g} , and large magnetization for practical applications. In this study, using unique high-pressure and high-temperature synthesis techniques, an A- and B-site ordered quadruple perovskite oxide LaCu₃Fe₂Re₂O₁₂ (LCFRO) was prepared. This new compound shows unprecedented half-metal performance with a record-high $T_{\rm C}$ in perovskite oxides up to 710 K, a wide upspin $E_{\rm g}$ by \approx 2.27 eV, and a saturated moment as large as 8.0 $\mu_{\rm B}$ f.u.⁻¹.

2. Results and Discussion

Figure 2a illustrates the X-ray diffraction (XRD) pattern and the Rietveld refinement results for LCFRO at RT. All the diffraction peaks can be fitted based on an $AA'_{3}B_{2}B'_{2}O_{12}$ -type A-site and B-site ordered quadruple perovskite model with a cubic symmetry of *Pn*-3, yielding the lattice constant *a* = 7.4988(1) Å. The sharp diffraction peaks with the Miller indices *h* + *k* + *l* = odd, such as (111), (311), and (331) peaks, provide strong evidence of a rocksalt-type ordering between the B-site Fe and B'-site Re. Because of the distinct difference in X-ray scattering factors between Fe and Re, the degree of order between these two atoms can be examined by refining the occupancy parameter. In our refinement, the occupancy factors for both Fe and Re were nearly 100%, suggesting a negligible Fe–Re antisite disorder. In reality, if a small amount of antisite occupancy, such



Figure 2. Refined XRD pattern and crystal structure of A- and B-site ordered quadruple perovskite $LaCu_3Fe_2Re_2O_{12}$. a) Observed (black circles), calculated (red solid line), and difference profiles (blue solid line) are shown. The magenta ticks indicate Brag reflections. b) Schematic crystal structure with space group *Pn*-3. The atomic sites are La 2*a* (0.25, 0.25), Cu 6*d* (0.25, 0.75, 0.75), Fe 4*b* (0, 0, 0), Re 4*c* (0.5, 0.5), and O 24*g* (*x*, *y*, *z*). The CuO₄ square units and FeO₆ and ReO₆ octahedra are corner-sharing.

as 5%, is constrained for Fe and Re, the bond lengths of Fe–O and Re–O become unreasonable. Therefore, the occupancy factors of Fe and Re were fixed to unity to refine other parameters, and reasonable structural parameters (see Table S1, Supporting Information) and satisfied goodness-of-fit ($R_{wp} = 3.93\%$, $R_p = 2.56\%$) were obtained.

Figure 2b illustrates the schematic crystal structure of LCFRO, where La and Cu occupy at the A and A' sites at a 1:3 ratio in an orderly manner. Because the ionic radius of Cu is considerably lesser than that of La, the initially 12-fold coordinated A site is reduced to a fourfold coordination for the A'-site Cu, forming CuO₄ square-planar units. Moreover, the spatially isolated CuO₄ units are connected to the B/B'-site FeO₆/ReO₆ octahedra by sharing O atoms. According to the bond lengths of Cu-O and Fe-O, the bond valence sum (BVS) calculation indicates the formation of Cu^{2+} and Fe^{3+} charge states (see Table S1, Supporting Information). As the Re-O bond length refined for LCFRO (1.960 Å) is greater than that of $CaCu_3Fe_2Re^{5+}O_{12}$ (1.934 Å),^[29] the valance state of Re in LCFRO should be less than +5. On account of the charge balance requirement, an average Re4.5+ valence state is expected to occur in LCFRO, as confirmed by the X-ray absorption spectroscopy (XAS) described below.

XAS is a highly sensitive tool for identifying the valence state $^{[34]}$ and local environment of transition metals. $^{[35,36]}$







Figure 3. XAS and XMCD of LaCu₃Fe₂Re₂O₁₂. a–c) XAS near Cu- $L_{2,3}$ (a), Fe- $L_{2,3}$ (b), and Re- L_3 (c) edges. Some references with similar coordination are shown for comparison. d,e) XMCD for Cu- $L_{2,3}$ (d) and Fe- $L_{2,3}$ (e) edges measured at 50 K and 6 T. f) XMCD for Re- $L_{2,3}$ edges measured at 5 K and 5 T. The black and red lines indicate the photon spin aligning parallel (μ^+) and antiparallel (μ^-) to the applied magnetic field, respectively. The violet curve represents the difference spectra ($\mu^+-\mu^-$).

Figure 3a and Figure 3b depict the XAS spectra at the Cu- and Fe- $L_{2.3}$ edges of LCFRO together with CaCu₃Ti₄O₁₂ as a Cu²⁺ reference^[37] and CaCu₃Fe₂Os₂O₁₂ as an Fe³⁺ reference containing similar coordination environments, respectively.[38] These two spectra of LCFRO at Cu- and Fe-L2,3 edges exhibit similar shape and peak energy positions with Cu2+ and Fe3+ references, respectively, thus confirming the presence of Cu²⁺ and Fe³⁺ in LCFRO. Figure 3c depicts the Re-L₃ edge of LCFRO together with Sr₂FeReO₆ and Sr₂MgReO₆ as a Re⁵⁺ and a Re⁶⁺ reference, respectively.^[39] The energy position of the Re-L₃ edge for LCFRO is shifted toward a lower energy by ≈0.5 eV relative to the Re^{5+} reference, and 1.5 eV relative to Re^{6+} reference, which suggests the Re^{4.5+} valence state for LCFRO fulfilling the charge balance requirement. Combining the XAS spectra and BVS analysis, we thus conclude that the charge configuration of LCFRO is LaCu²⁺₃Fe³⁺₂Re^{4.5+}₂O₁₂.

Figure 4a depicts the temperature dependence of magnetic susceptibility (χ) below 800 K. With decreasing temperature to $T_{\rm C} \approx 710$ K, the susceptibility experiences a sharp increase, indicating the occurrence of an FM or FiM phase transition. Here, the spin ordering temperature is determined by a tangent method as shown in Figure 4b. The inverse magnetic susceptibility between 725 and 800 K agrees well with the Curie–Weiss law (Figure 4c), resulting in a Weiss temperature of 698 K, in accordance with the value of $T_{\rm C}$. According to the fitted Curie constant (C = 5.26 emu K mol⁻¹ Oe⁻¹), the effective magnetic moment is calculated to be $\mu_{\rm eff}$ = 6.49 $\mu_{\rm B}$ f.u.⁻¹. Considering the spin moments of Cu2+ and Fe3+ as well as the spin-orbital coupling of Re4.5+, the effective moment of LCFRO is theoretically expected to be 9.07 $\mu_{\rm B}$ f.u.⁻¹. This considerable difference between the theoretical and experimental values suggests nonlocalized electronic behavior, i.e., there







Figure 4. Magnetic properties of $LaCu_3Fe_2Re_2O_{12}$. a) Temperature dependence of magnetic susceptibility measured at 0.1 T. b) The magnetic transition temperature determined by a tangent method to be 710 K. c) Temperature dependence of the inverse magnetic susceptibility, where the red line indicates the Curie–Weiss fitting at 725–800 K. d) Field dependence of magnetization (*M*) at some selected temperatures.

exist certain itinerant electrons in LCFRO. Field-dependent magnetization provides further evidence for the FM or FiM ordering in LCFRO. As depicted in Figure 4d, above T_{C} (e.g., at 800 K), linear magnetization behavior consistent with the paramagnetism is observed. However, below T_C, canonical magnetic hysteresis features are observed. The saturated moment observed at 300 K is 7.0 $\mu_{\rm B}$ f.u.⁻¹, which further increases to 8.0 $\mu_{\rm B}$ f.u.⁻¹ at 2 K. Moreover, the coercive force is extremely small (100 Oe) at 2 K and further decreases with increasing temperature. Because there exist three magnetic transition metals in LCFRO, four different collinear spin alignments, i.e., the $\begin{array}{lll} FM & Cu^{2+}(\uparrow)-Fe^{3+}(\uparrow)-Re^{4.5+}(\uparrow), & FiM & Cu^{2+}(\uparrow)-Fe^{3+}(\uparrow)-Re^{4.5+}(\downarrow), \\ Cu^{2+}(\uparrow)-Fe^{3+}(\downarrow)-Re^{4.5+}(\uparrow), & and & Cu^{2+}(\downarrow)-Fe^{3+}(\uparrow)-Re^{4.5+}(\uparrow) & can \end{array}$ possibly occur. If the spin only contribution is considered for Cu²⁺, Fe³⁺, and Re^{4.5+}, the corresponding saturated moments are 18.0, 8.0, 2.0, and 12.0 $\mu_{\rm B}$ f.u.⁻¹ for the four spin alignments, respectively. Based on the saturated moment measured at 2 K, the $Cu^{2+}(\uparrow)-Fe^{3+}(\uparrow)-Re^{4.5+}(\downarrow)$ FiM coupling is most likely to form in LCFRO.

The X-ray absorption magnetic circular dichroic (XMCD) can characterize the spin–spin coupling among the Cu, Fe, and Re ions and determine the spin and orbital moments of each element separately. Figure 3d–f depicts the XMCD spectra at the $L_{2,3}$ edges of Cu, Fe, and Re in LCFRO. Evidently, the L_3 (L_2) edges are all negative (positive) for Cu and Fe, but positive (negative) for Re, confirming the FM Cu²⁺(\uparrow)Fe³⁺(\uparrow) coupling as well as the AFM Cu²⁺(\uparrow)Fe³⁺(\uparrow)Re^{4.5+}(\downarrow) coupling, leading to the formation of the FiM Cu²⁺(\uparrow)Fe³⁺(\uparrow)Re^{4.5+}(\downarrow) spin alignment, as

inferred from the magnetization results. By comparison, a similar FiM spin coupling is also observed in other isostructural perovskites, such as Na/CaCu₃Fe₂Os₂O₁₂, CaCu₃Fe₂Re₂O₁₂, and LaCu₃Co₂Re₂O₁₂.^[7,17,29,38] Furthermore, based on the sum rules of XMCD,^[40,41] we calculated the spin and orbital moments for Cu²⁺, Fe³⁺, and Re^{4.5+} (see Table S2, Supporting Information, for details). The calculated total moment is 0.63 $\mu_{\rm B}$ (spin part: 0.57 $\mu_{\rm B}$) per Cu²⁺, 3.98 $\mu_{\rm B}$ (spin part: 3.94 $\mu_{\rm B}$) per Fe³⁺, and -1.0 $\mu_{\rm B}$ (spin part: -1.36 $\mu_{\rm B}$) per Re^{4.5+}. Consequently, the total moment for each LCFRO formula is calculated to be 7.82 $\mu_{\rm B}$, which is close to the saturated moment measured at 2 K (8.0 $\mu_{\rm B}$ f.u.⁻¹). In addition, although the orbital contribution is negligible for the 3*d* Cu²⁺ and Fe³⁺, the 5*d* Re^{4.5+} exhibits a remarkable orbital moment (0.36 $\mu_{\rm B}$), suggesting a strong spin–orbit coupling effect.

Figure 5a depicts the temperature dependence of resistivity for LCFRO. At zero field, the magnitude of resistivity is 24 m Ω cm at 300 K and slightly increases to 89 m Ω cm at 2 K. When a magnetic field of 8 T is applied, the resistivity decreases significantly, leading to a negative magnetoresistance [MR = 100% × ($\rho(H) - \rho(0)$)/ $\rho(0)$] effect. Figure 5b presents the specific heat (C_p) data of LCFRO, which smoothly decrease with decreasing temperature. At lower temperatures, the specific heat can be well fitted using the function $C_p/T = \gamma + \beta T^2$, producing a considerable Sommerfeld coefficient $\gamma = 47.4(6)$ mJ mol⁻¹ K⁻². Such a notable γ value is indicative of itinerant electronic behavior. Thus, the intrinsic electric transport of LCFRO is expected to be metallic-like. The slight







Figure 5. Electrical transport and specific heat properties of LaCu₃Fe₂Re₂O₁₂. a) Temperature dependence of resistivity and magnetoresistance for LCFRO. b) Temperature dependence of specific heat between 2 and 100 K. The inset shows the fitting curve of specific heat below 8 K based on the function $C_p/T = \gamma + \beta T^2$ with $\gamma = 47.4(6)$ mJ mol⁻¹ K⁻² and $\beta = 1.23(2)$ mJ mol⁻¹ K⁻⁴. c) Field dependence of isothermal magnetoresistance between -8 and 8 T at selected temperatures. d) Comparison of isothermal low-field magnetoresistance and magnetization curves measured at 2 K for LCFRO.

resistivity upturn on cooling shown in Figure 5a most likely originates from the grain boundary effects due to the polycrystalline nature of the sample.^[7,17,29] In reality, the nonlocalized electronic behavior of LCFRO is consistent with the fitted Curie constant mentioned above. Figure 5c depicts the field dependence of MR measured at several fixed temperatures. A butterflyshaped feature can be observed (Figure 5c), suggesting the spin-dependent tunneling of spin-polarized conduction electrons through grain boundaries. As depicted in Figure 5d, at 2 K, the hysteresis field of MR (8000 Oe) is considerably larger than that of magnetization (100 Oe), indicating a spin-valve-type MR arising from the intergrain tunneling for the spin-polarized carriers. $^{[7,\widetilde{17},29]}$ Benefiting from the high degree of the B-site order (nearly 100%), LCFRO exhibits an enhanced low-field MR value (4.5% at 2 K and 1 T) compared to that of other isostructural compounds with some antisite occupation, such as NaCu₃Fe₂Os₂O₁₂ (0.1% at 2 K and 1 T) ^[7] and CaCu₃Fe₂Re₂O₁₂ (1.5% at 10 K and 1 T).^[29]

To obtain a deeper insight into the stability and electronic properties of LCFRO, first-principles calculations were carried out using the WIEN2K.^[42] First, based on the Covex Hull analysis, one found that the formation energy of LCFRO is significantly lower than that of the sum of the starting materials (see Table S3, Supporting Information, for details), suggesting the high thermodynamic stability of LCFRO we prepared. Then, spin-polarized density functional theory (DFT+U) calculations were conducted for the four different magnetic configurations mentioned above. The magnetic configuration always converges to the FiM $Cu^{2+}(\uparrow)-Fe^{3+}(\uparrow)-Re^{4.5+}(\downarrow)$ state irrespective of the

initial spin structure, agreeing well with the magnetization and XMCD results. Moreover, the magnetic moments are found to be 0.55, 4.03, and $-1.09 \ \mu_{\rm B}$ f.u.⁻¹ inside the muffin-tin spheres for Cu, Fe, and Re, respectively, with a total moment of 8.00 $\mu_{\rm B}$ f.u.⁻¹ as determined in experiments. Figure 6 shows the calculated electronic structures near the Fermi level for up and down spins of LCFRO. A half-metallic nature with fully spin-polarized conduction bands can be clearly observed. Specifically, the down (minority)-spin bands mainly composed of the hybridized Re 5*d* and O 2*p* states cross the Fermi energy and contribute to electrical conduction. By contrast, the up (majority)-spin bands create a wide energy gap by ≈2.27 eV. Such a wide gap is sufficient to suppress the spin-flip transition that may be caused by thermal excitation of the carriers, thus ensuring that the halfmetallic performance is maintained at RT. To further confirm the half metallicity of LCFRO, different electron-electron correlation energies, i.e., $U_{\rm eff}$ values, were used for DFT+U calculations. Variations in U_{eff} did not result in any qualitative change in the electronic structure and only had a limited effect on the up-spin energy gap (from 2.1 to 2.4 eV in the $U_{\rm eff}$ range of 4.0– 5.0 eV for Cu, 2.0-3.0 eV for Re, and 4.0 eV for Fe). In addition, when the spin-orbital coupling effects as well as moderate compression and tensile strains are also considered during the calculations, the half-metallic property of LCFRO is robust, and only the up-spin energy gap changes somewhat (see Figures S1 and S2, Supporting Information).

To understand the high $T_{\rm C}$ of LCFRO, the magnetic exchange interactions were calculated based on the Heisenberg spin model:^[43] $H = \sum_{(ij)} J_{ij} S_i \times S_j$, where J_{ij} denotes





Figure 6. Electronic structure of $LaCu_3Fe_2Re_2O_{12}$. Calculated density of states (DOS) and spin-polarized band structures. The results were obtained by GGA+*U* with U = 5 eV for Cu, 4 eV for Fe and 2 eV for Re. The total DOS (light gray) and partial DOS of La (orange curves), Cu (green curves), Fe (red curves), Re (blue curves), and O (cyan curves) are all shown for comparison.

the exchange interaction between the magnetic ions, and S_i and S_j represent the spin vectors of Cu, Fe, and Re at the i and j sites, respectively. For simplification, we only consider three nearest-neighbor interactions, namely, J_{Cu-Fe} , J_{Cu-Re} , and J_{Fe-Re} . Theoretical calculations indicate that all three interactions are antiferromagnetic, but the specific AFM exchange intensities of $J_{Fe-Re}S_{Fe}(\uparrow)S_{Re}(\downarrow)$ (47.34 meV) and $J_{Cu-Fe}S_{Cu}(\uparrow)S_{Re}(\downarrow)$ (46.52 meV) are considerably stronger than that of $J_{Cu-Fe}S_{Cu}(\uparrow)S_{Fe}(\downarrow)$ (8.23 meV). Consequently, the weaker Cu–Fe AFM interaction is overcome and the compound displays a long-range Cu²⁺(\uparrow)–Fe³⁺(\uparrow)–Re^{4.5+}(\downarrow) FiM ordering with a T_C as high as 710 K. Theoretically, according to the mean-field approximation, T_C can be estimated to be \approx 670 K for LCFRO,^[44]

By comparison, the current LCFRO exhibits the highest $T_{\rm C}$ among perovskite-related HMs. For example, the $T_{\rm C}$ of the simple ABO3 perovskite $La_{0.7}Sr_{0.3}MnO_3$ is ≈ 350 K, while the $T_{\rm C}$ of the well-known double perovskite Sr₂FeMoO₆ (\approx 400 K) is still considerably lesser than that of LCFRO. The HM of the quadruple perovskite CaCu₃Fe₂Re₂O₁₂ has a higher $T_{\rm C} \approx 560$ K. However, when the A-site Ca is substituted by La and additional electrons are introduced into the B'-site Re (Re⁵⁺ \rightarrow $Re^{4.5+}$), a sharp increase in T_C up to 710 K is observed in the current LCFRO. Because the Fermi levels are dominated by Re in these two isostructural compounds, increasing the density of electrons in Re is an effective approach to enhance the spin interactions of $J_{Fe-Re}S_{Fe}S_{Re}$ and $J_{Cu-Re}S_{Cu}S_{Re}$, and consequently, the FiM ordering temperature $T_{\rm C}$.^[29,45] Even in all the half-metal oxides, the $T_{\rm C}$ of LCFRO is only lower than that of Fe₃O₄ (\approx 850 K),^[19] but the small E_g of Fe₃O₄ (\approx 0.5 eV) limits its potential application at RT.^[16] In addition to the superior $T_{\rm C}$, the current LCFRO also possesses a large saturated moment and a wide up-spin energy gap. As a result, if we compare the coupled parameter α (= $T_C \times E_g \times M_N$) for the reported half-metallic oxides in experiments with $T_C \ge 300$ K, the current LCFRO outperforms the rest, yielding a record-high coupled performance, as represented in Figure 1.

3. Conclusion

An A- and B-site ordered quadruple perovskite oxide LaCu₃Fe₂Re₂O₁₂ with space group *Pn*-3 was synthesized using high-pressure and high-temperature methods. The compound exhibited the highest $T_C \approx 710$ K and a large saturated moment of 8.0 μ_B f.u.⁻¹ among all the half-metallic perovskite oxides. Benefitting from the high degree of order between the B-site Fe and B'-site Re, the low-field MR was enhanced significantly compared to those of other isostructural materials. DFT calculations revealed the half-metallic nature of LCFRO, where the down-spin channel exhibited a conducting nature, while the up-spin channel resulted in a wide energy gap of ~2.27 eV. The rare combination of high T_C , wide spin gap, and large saturated moment makes the current LCFRO an unprecedented HM with promising applications in advanced spintronic devices at or even well above RT.

4. Experimental Section

Sample Preparation: Polycrystalline LaCu_3Fe_2Re_2O_{12} was prepared using stoichiometric mixtures of La_2O_3, CuO, Fe_2O_3, Re, and Re_2O_7





powders with high purity (\geq 99.9%). After being ground thoroughly, the mixtures were pressed into a gold/platinum capsule and treated at 9 GPa on a cubic anvil-type high-pressure apparatus, then heated at 1273 K for 1 h. After the heating treatment, the samples were quenched to room temperature and the pressure was released slowly.

Crystal Structure Analysis: XRD measurements were conducted on a Huber diffractometer with the wavelength $\lambda = 1.5406$ Å. The XRD data were analyzed by using the Rietveld refinement program GSAS.^[46]

Spectral Characterization: The Cu- $L_{2,3}$ and Fe- $L_{2,3}$ XAS were measured at beamline TLS11A of the synchrotron NSRRC in Taiwan. The Re- L_3 XAS was measured at beamline P09 at PETRA III at DESY in Hamburg. The Cu- $L_{2,3}$ and Fe- $L_{2,3}$ XMCD were measured at the VEKMAG end station^[47] of the HZB/BESSY II/Germany synchrotron radiation facility, and the Re- $L_{2,3}$ XMCD was measured at P09.

Magnetic, Transport, and Heat Properties Measurements: The magnetic susceptibility and isothermal magnetization were measured on a commercial superconducting quantum interference device magnetometer (Quantum Design, MPMS-7 T). Both zero-field-cooling (ZFC) and field-cooling (FC) mode with a field 0.1 T were used to collect the magnetic susceptibility at temperature range of 2–800 K. The field dependence of isothermal magnetization was measured at some selected temperatures 2, 150, 300, 400, 600, and 800 K between –7 and 7 T. The electrical transport properties were measured using a standard four-probe method on a physical property measurement system (Quantum Design, PPMS-9 T) from 2 to 300 K. The specific heat (C_p) was measured by a pulse relaxation method on the PPMS with temperatures varying from 2 to 100 K at 0 T.

Electronic Structure Calculation: The first-principles calculations were carried out using the full-potential linearized plane wave method as implemented in WIEN2K.^[42] The space group, lattice parameters and atomic positions used in calculations were provided by structural refinement. The muffin-tin radius of La, Cu, Fe, Re, and O atoms were chosen as 2.50, 1.97, 2.02, 1.95, and 1.73 a.u., respectively. The maximum modulus of the reciprocal vectors K_{max} was chosen such that $R_{\rm MT}K_{\rm max} = 8.0$. The generalized-gradient approximation Perdew–Burke–Ernzerhof (GGA-PBE) exchange correlation energy was taken, and 1000 k-point grids for the Brillouin zone were used.^[48] In the GGA + U calculation, the effective $U_{\rm eff}$ was set to 5 eV for Cu, 4 eV for Fe, and 2 eV for Re. Four different collinear magnetic structures [FM: Cu²⁺(\uparrow)Fe³⁺(\uparrow)Re^{4.5+}(\downarrow); FiM3: Cu²⁺(\downarrow)Fe³⁺(\downarrow)Re^{4.5+}(\downarrow);

$$E_{FM} = E_0 + 12 J_{Cu-Fe} S_{Cu} S_{Fe} + 12 J_{Fe-Re} S_{Fe} S_{Re} + 12 J_{Cu-Re} S_{Cu} S_{Re}$$
(1)

$$E_{FiM1} = E_0 + 12 J_{Cu-Fe} S_{Cu} S_{Fe} - 12 J_{Fe-Re} S_{Fe} S_{Re} - 12 J_{Cu-Re} S_{Cu} S_{Re}$$
(2)

$$E_{FiM2} = E_0 - 12 J_{Cu-Fe} S_{Cu} S_{Fe} - 12 J_{Fe-Re} S_{Fe} S_{Re} + 12 J_{Cu-Re} S_{Cu} S_{Re}$$
(3)

$$E_{FiM3} = E_0 - 12 J_{Cu-Fe} S_{Cu} S_{Fe} + 12 J_{Fe-Re} S_{Fe} S_{Re} - 12 J_{Cu-Re} S_{Cu} S_{Re}$$
(4)

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

The project was conceived by Z.L. and Y.L. Samples were prepared by Z.L., who performed the structural, magnetic, transport, and heat measurements with help from X.Y., S.Q., X.S., D.L., and J.D. The XAS and XMCD measurements were conducted by X.W., C.C., K.C., F.R., W.W., Z.H., S.F.O.L., and J.R.L.M. The theoretical calculations were carried out by S.Z., Y.C., and Y.Y. All the authors discussed the results. The paper was written by Z.L., Y.L., S.Z., L.H., and Y.Y. with feedback from all authors. The project was supervised by Y.L. and Y.Y.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

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