

Hydrogenated PdCoO₂: A layered Metallic Oxide with Robust Room-Temperature Ferromagnetism

Di Tian^{1,*}, Haotian Zheng^{2,*}, Zewei Huang^{1,*}, Sijie Wu¹, Pengcheng Li³, Cong Li¹, Jianbing Zhang¹, Xinyu Shu^{1,4}, Jinling Zhou¹, Yang Liu¹, Yanhong Gu¹, Meng Wang⁵, Di Yi^{3,6}, Tianxiang Nan⁷, Zhen Chen^{8,9}, Qing He¹⁰, Huaqiang Wu⁷, Shuyun Zhou^{1,11}, Weidong Luo^{1,2,†} and Pu Yu^{1,11,‡}

¹State Key Laboratory of Low Dimensional Quantum Physics and Department of Physics, Tsinghua University, Beijing 100084, China

²Key Laboratory of Artificial Structures and Quantum Control (Ministry of Education), School of Physics and Astronomy, Shanghai Jiao Tong University, Shanghai 200240, China

³School of Materials Science and Engineering, Tsinghua University, Beijing 100084, China

⁴School of Electronics and Information Engineering,

Hangzhou Dianzi University, Hangzhou, Zhejiang 310037, China

⁵School of Integrated Circuits and Electronics, MIIT Key Laboratory for Low-Dimensional Quantum Structure and Devices, Beijing Institute of Technology, Beijing 100081, China

⁶State Key Laboratory of New Ceramics and Fine Processing, Tsinghua University, Beijing 100084, China

⁷School of Integrated Circuits and Beijing National Research Center for Information Science and Technology, Tsinghua University, Beijing 100084, China

⁸Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing, China

⁹School of Physical Sciences, University of Chinese Academy of Sciences, Beijing 101408, China

¹⁰Department of Physics, Durham University, Durham DH13LE, United Kingdom

¹¹Frontier Science Center for Quantum Information, Beijing 100084, China



(Received 25 June 2025; accepted 16 October 2025; published 14 November 2025)

Layered oxide materials, with their two-dimensional crystalline architectures and tunable interlayer interaction, serve as a fertile field for harnessing emergent quantum phenomena. Among these materials, metallic delafossites (e.g., PdCoO₂) have emerged as a prominent system with extraordinary two-dimensional electronic properties, though their intrinsic lack of ferromagnetism has remained a fundamental constraint. Here, we report the creation of robust, bulk high-temperature ferromagnetism ($T_c > 420$ K) in inherently nonmagnetic PdCoO₂ through controlled hydrogenation while preserving the delafossite structure. This process induces layer-selective electron doping into CoO₂ layers, stabilizing Ising-type ferromagnetism with pronounced perpendicular magnetic anisotropy while preserving the material's exceptional metallicity. Remarkably, the system self-assembles into a superlattice of alternating metallic Pd and insulating ferromagnetic hydrogenated CoO₂ layers, enabling an unconventional anomalous Hall effect mediated by interlayer spin-charge coupling. These findings demonstrate that bulk ferromagnetism can be achieved in delafossite oxides while preserving their structural integrity, positioning hydrogenated delafossites as a versatile platform for exploring correlated quantum effects and designing multifunctional devices.

DOI: [10.1103/3mge-z9wv](https://doi.org/10.1103/3mge-z9wv)

Subject Areas: Condensed Matter Physics, Magnetism, Materials Science

I. INTRODUCTION

Layered oxide materials have emerged as a cornerstone of modern condensed matter physics and technology, where their two-dimensional (2D) architectures foster remarkable quantum phenomena. These systems have yielded breakthroughs such as the recent discovery of superconductivity in infinite-layer nickelates [1] and diverse emergent properties in Ruddlesden-Popper phases, from unconventional superconductivity [2–4] to hybrid improper ferroelectricity [5,6]. Beyond fundamental

*These authors contributed equally to this work.

†Contact author: wdluo@sjtu.edu.cn

‡Contact author: yupu@mail.tsinghua.edu.cn

Published by the American Physical Society under the terms of the [Creative Commons Attribution 4.0 International](https://creativecommons.org/licenses/by/4.0/) license. Further distribution of this work must maintain attribution to the author(s) and the published article's title, journal citation, and DOI.

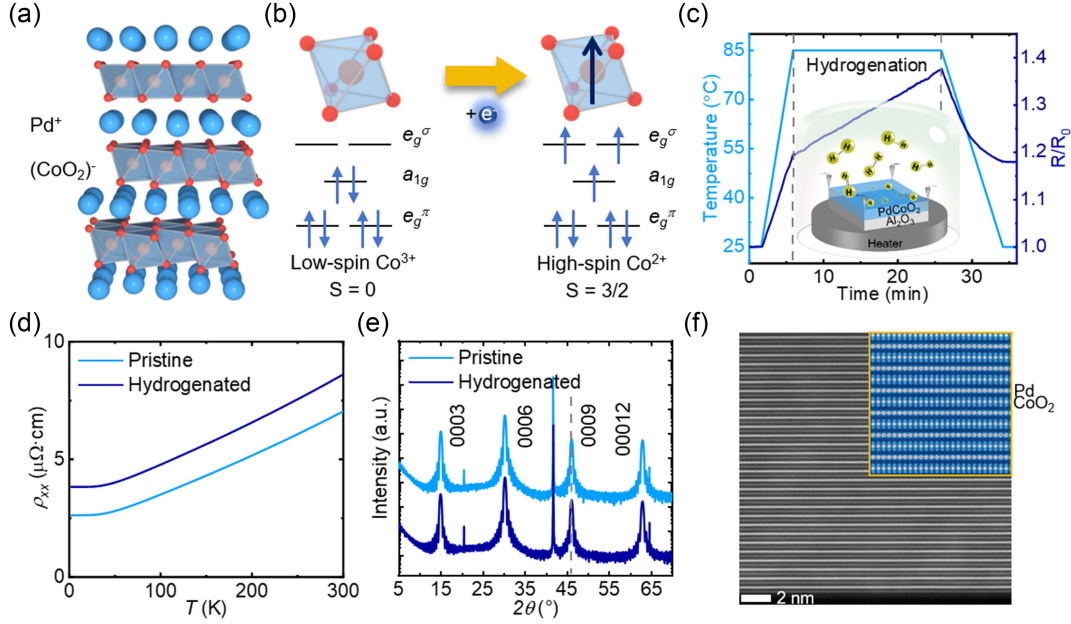


FIG. 1. Hydrogenation of PdCoO₂ thin films. (a) Layered crystalline structure of PdCoO₂, with triangular sheets of Pd separated by layers of CoO₂ octahedra. (b) Schematic illustration of the electronic structures of Co ions in low-spin Co³⁺ and high-spin Co²⁺ ions. (c) Time-dependent temperature and resistivity of PdCoO₂ during the hydrogenation process. The inset shows the experimental setup for hydrogenation. (d) Temperature-dependent longitudinal resistivity (ρ_{xx}) of pristine and hydrogenated PdCoO₂ thin films. (e) XRD $2\theta - \omega$ curves of pristine and hydrogenated PdCoO₂ thin films. (f) Cross-sectional HAADF-STEM images of the hydrogenated PdCoO₂ film. The zone axis is along the $[10\bar{1}0]$ direction of the sample. The inset shows a ptychographic HADDF-STEM image of hydrogenated PdCoO₂, clearly resolving the position of oxygen ions.

physics, layered oxides have become indispensable across numerous technological domains. Their unique architectures enable next-generation energy storage by creating ideal ion pathways while maintaining structural integrity [7] and drive innovations in memory technologies and advanced electronic devices [8,9].

Among these versatile layered systems, metallic delafossites represent a unique class of quantum materials, combining extraordinary electronic states with natural heterostructure architecture [10–14]. Particularly, PdCoO₂ stands out with its extremely-high-conductivity rivaling noble metals [15,16]. Its crystal structure comprises alternating metallic triangular Pd lattices and insulating edge-sharing CoO₂ slabs [Fig. 1(a)]. This arrangement creates a quasi-2D Fermi surface dominated by the Pd-4d orbitals, resulting in ultrahigh carrier mobility resilient to defects [11,12,16–18]. These properties, coupled with its excellent chemical inertness, make PdCoO₂ promising for many applications [13,19–21], such as harsh-environment Schottky junctions, transparent conductors, and Terahertz radiation sources. Yet, its full potential remains untapped due to a critical absence of magnetism, as its low-spin Co³⁺ [$S = 0$, left panel of Fig. 1(b)] state intrinsically precludes the formation of magnetism. Indeed, no delafossite has exhibited robust room-temperature ferromagnetism until now [10]. Introducing magnetism on the Co sites would

provide a powerful probe to investigate the interlayer coupling between the strongly correlated CoO₂ layers and Pd-derived conduction band—a fundamental question in these layered oxide systems with distinct electronic dichotomy [10,22]. Moreover, such magnetic functionality would simultaneously unlock promising spintronic applications by combining PdCoO₂'s remarkable conductivity with magnetic ordering—an ideal combination for next-generation spin-dependent transport devices. Prior efforts to induce magnetism, through chemical doping or structural deformation, yielded either no magnetism [23] or a fragmented state with Curie temperature much lower than room temperature [24–26]. While progress in research has been achieved, yielding ferromagnetism with $T_c \sim 650$ K in an atomically mixed alloy of PdCo from the reduced PdCoO₂ system, the result was obtained at the sacrifice of the layered structure and exceptional conductivity of the delafossite PdCoO₂ compound [27]. These impasses define the essential scientific frontier for PdCoO₂ and other delafossites: Can a strategy be devised to activate robust high-temperature ferromagnetism while simultaneously preserving its hallmark conductivity inherent to the delafossite structure?

In this work, we demonstrate the successful realization of robust bulk ferromagnetism in PdCoO₂ within the preserved delafossite structure through thermal

annealing-driven hydrogenation, achieving a high Curie temperature of above 420 K, which overcomes the material's inherent nonmagnetic ground state. We reveal that the hydrogenation acts as a site-specific electron donor, triggering a spin-state transition from a low-spin Co³⁺ ($S = 0$) to a high-spin Co²⁺ ($S = 3/2$) state to generate the high-temperature ferromagnetism. Critically, this mechanism enables the coexistence of spatially confined itinerant electrons within the metallic Pd layers and 2D ferromagnetic ordering in the CoO₂ sublattices. Compared to the layered van der Waals magnetic materials—which typically suffer from low Curie temperatures, instability of air-sensitive compounds, and the lack of scalable synthesis methods [28,29]—our hydrogenated PdCoO₂ combines one of the highest reported Curie temperatures for 2D magnetic systems [28–32] with remarkable chemical stability and scalability. This dual electronic-magnetic architecture establishes a new paradigm for integrating high-temperature magnetism with prominent 2D electron transport.

II. HYDROGENATION OF PdCoO₂ THIN FILMS

The key to introducing magnetism into PdCoO₂ lies in successfully triggering a spin-state transition of cobalt ions from a low-spin Co³⁺ ($d^6, S = 0$) state to a high-spin Co²⁺ ($d^7, S = 3/2$) state. Hydrogenation [33–38] provides a promising pathway for this transition by providing electron doping in this system to transform Co³⁺ into Co²⁺. We note that in octahedral coordination, the low valence state (i.e., Co²⁺) suppresses the ligand-field splitting energy, leading to a more favored high-spin configuration [39] [right panel of Fig. 1(b)].

To experimentally realize this scenario, we first prepared epitaxial PdCoO₂ thin films (~18 nm) on (0001)-oriented sapphire substrates by oxide molecular-beam epitaxy (OMBE) (Sec. VII and Fig. S1 in the Supplemental Material [40]). Hydrogenation was then performed using a hydrogen spillover process [33–36], a technique widely employed for various oxide systems using heavy metals (e.g., Pd or Pt) as the catalyst. Notably, PdCoO₂ itself exhibits exceptional catalytic efficiency for hydrogen spillover [41], eliminating the need for external catalysts. The hydrogenation process was conducted by annealing the PdCoO₂ samples at a moderate temperature of 85 °C under a flow of industrial-grad hydrogen gas mixture (5% H₂/95% Ar) for 20 minutes, coupled with *in situ* resistance monitoring to track reaction kinetics [Sec. VII and Fig. 1(c)].

To probe the hydrogen incorporation of the hydrogenated films, we subsequently performed secondary ion mass spectrometry (SIMS) measurements. The SIMS results confirm significant hydrogen enrichment uniformly distributed within hydrogenated films compared to their pristine counterparts (Fig. S2 in Ref. [40]), consistent with the expected hydrogen uptake from our hydrogenation protocol. Notably, the resistivity of the films increases only

slightly after hydrogenation [Fig. 1(c)], suggesting that the materials retain the high conductivity of pristine PdCoO₂. This idea is further corroborated by temperature-dependent resistivity measurements [Fig. 1(d)], showing that the hydrogenated films maintain metallicity across the whole measurement temperature range. The room-temperature resistivity values remain safely below 10 $\mu\Omega \cdot \text{cm}$, demonstrating the preserved ultrahigh conductivity.

High-resolution x-ray diffraction (XRD) measurements confirm that hydrogenated PdCoO₂ retains phase purity and structural integrity, without observable peak shifts or broadening compared to the pristine material [Fig. 1(e)]. The negligible change in diffraction peaks rules out significant lattice expansion, indicating that hydrogen incorporation occurs without disrupting the host crystal framework. Cross-sectional scanning transmission electron microscopy (STEM) imaging along the $[10\bar{1}0]$ zone axis [Fig. 1(f)] further reveals a sharp film-substrate interface and well-ordered Pd and CoO₂ layers along the growth axis, corroborating the structural coherence posthydrogenation. Large-scale STEM images combined with energy-dispersive x-ray spectroscopy (EDS) mapping confirm homogeneous elemental distribution of Pd, Co, and O (Fig. S3), and exclude the formation of Co clustering or phase segregation. Collectively, these results demonstrate that the hydrogenation process preserves the exceptional conductivity and high-crystalline quality of PdCoO₂ samples while enabling selective magnetic modification with emergent ferromagnetism detailed in the subsequent section.

III. EMERGENT FERROMAGNETISM IN HYDROGENATED PdCoO₂

Our systematic investigation reveals a robust room-temperature ferromagnetic state in hydrogenated PdCoO₂. Figure 2(a) shows the typical magnetic hysteresis (M - H) loops of hydrogenated PdCoO₂ measured at 300 K with the magnetic field applied along both in-plane (IP) and out-of-plane (OOP, c -axis) directions. These results show a rectangular OOP loop with a saturated magnetization of around 0.3 μ_B/Co and an IP loop with nearly zero remanence, which unambiguously confirm perpendicular magnetic anisotropy (PMA)—a critical feature for spintronic applications—in the hydrogenated PdCoO₂. Temperature-dependent M - H measurements [Fig. S4(a) in Ref. [40]] show that the saturated magnetization of hydrogenated PdCoO₂ reaches 0.6 μ_B/Co at 3 K. Temperature-dependent magnetization (M - T) measurements [Fig. 2(b)] show robust magnetization persisting even above 400 K, surpassing the detection limit of the employed magnetometry. Fitting the high-temperature (350–400 K) data to the 2D Ising model ($M \propto (T_c - T)^\beta$, $\beta = 1/8$) [42] yields a Curie temperature (T_c) of 421.5 ± 0.1 K (where the error represents the 95% confidence interval from the fitting procedure), a

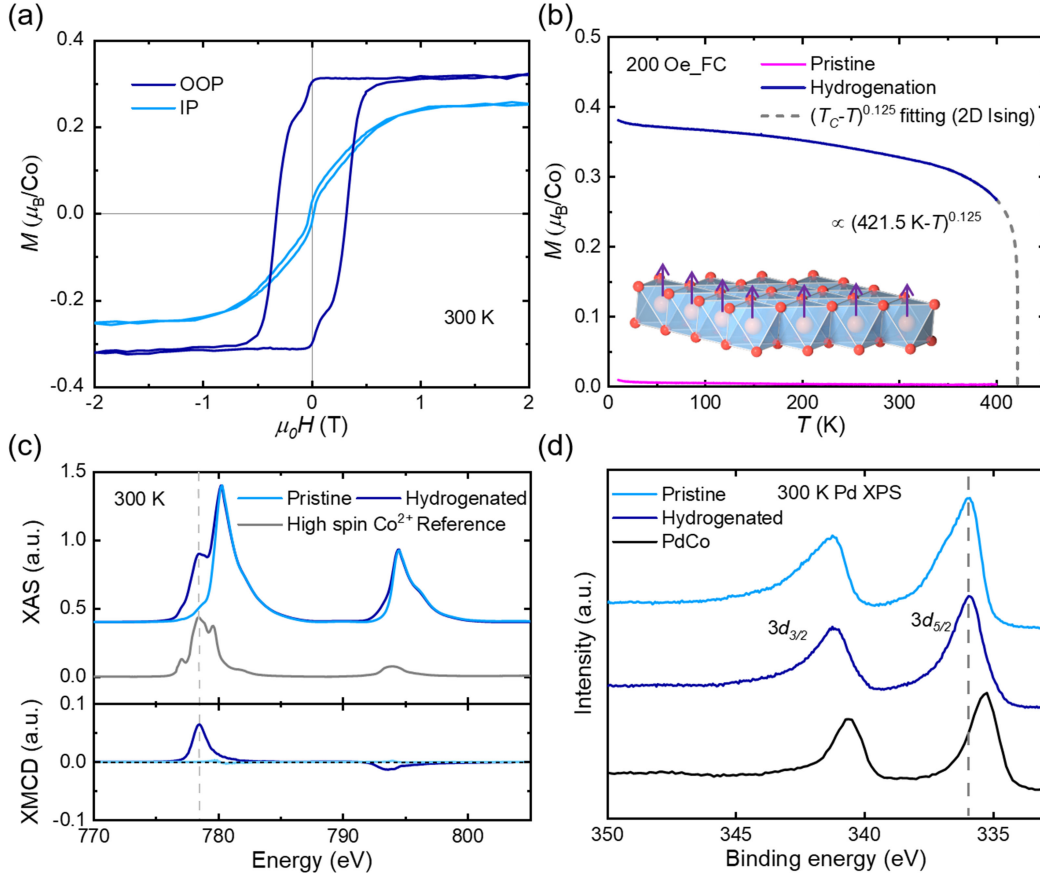


FIG. 2. Emergent room-temperature ferromagnetism in hydrogenated PdCoO₂ thin films. (a) Magnetic hysteresis loops of hydrogenated PdCoO₂ measured at 300 K along both out-of-plane (OOP) and in-plane (IP) directions. (b) Temperature-dependent OOP magnetizations of both pristine and hydrogenated PdCoO₂ samples. The measurements were carried out with a magnetic field of 200 Oe after a field cooling process (FC) at 6 T. The gray dotted line indicates the corresponding fitting curve using the equation $M \propto (T_c - T)^{0.125}$. The inset shows the schematic illustration of perpendicular magnetic anisotropy in hydrogenated PdCoO₂. (c) XAS (top panel) and XMCD (bottom panel) spectra measured at Co-L_{2,3} edges for both pristine and hydrogenated PdCoO₂ samples. The spectra were measured at 300 K. The XAS spectra of high-spin Co²⁺ are shown as a reference. The XMCD measurements were carried out with a magnetic field of 2 T. (d) XPS spectra of Pd 3d peaks for both pristine and hydrogenated PdCoO₂ samples measured at 300 K. The XPS data of PdCo alloy (black solid line) are shown as a reference.

prominent feature for this emergent ferromagnetism. The excellent agreement between the experimental data and the fitting of the 2D Ising model further confirms the 2D nature of the magnetism. Remarkably, the hydrogenation-induced magnetism in PdCoO₂ remains robust under ambient conditions and air exposure, highlighting its exceptional environmental resilience.

To elucidate the origin of this emergent ferromagnetism, we performed x-ray absorption spectrum (XAS) and x-ray magnetic circular dichroism (XMCD) measurements at Co L-edges [Figs. 2(c) and S4(b)]. For pristine PdCoO₂, the XAS spectra exhibit a characteristic line shape consistent with a low-spin Co³⁺ state with no observable XMCD signal, in agreement with previous reports [43]. Upon hydrogenation, however, the XAS spectra display a distinct pre-edge shoulder with multiplet splitting. Differential spectra between pristine and hydrogenated samples align

closely with reference spectra [44] taken from a high-spin Co²⁺ state, which suggests the partial conversion of a low-spin Co³⁺ state to a high-spin Co²⁺ state in PdCoO₂ via hydrogenation-induced electron doping. Notably, the dip feature in M - H hysteresis [Fig. 2(a)] observed near zero field likely reflects the interplay between hydrogenation-induced local valence heterogeneity and the intrinsic frustration of the triangular Co lattice—analogueous to the frustrated antiferromagnetic order PdCrO₂ [45].

The XMCD signal in ferromagnetic hydrogenated samples emerges at energies corresponding to the Co²⁺ spectral weight [gray dashed line, Figs. 2(c) and S4(b)], directly linking the macroscopic magnetic moment to the high-spin Co²⁺ state. Based on the XMCD sum rule [46], the magnetizations of the hydrogenated samples are calculated to be around 0.4 μ_B/Co and 0.6 μ_B/Co at 300 K and 3 K, respectively, quantitatively matching the macroscopic results

[Fig. S4(a)]. Furthermore, the complementary x-ray photoelectron spectroscopy (XPS) measurements [Fig. 2(d)] show negligible change in Pd-3d binding energies, confirming that Pd remains in its nominal Pd¹⁺ oxidation state [47]. These results establish that hydrogenation selectively dopes electrons mainly into CoO₂ layers, driving a spin-state transition from a low-spin Co³⁺ state to a high-spin Co²⁺ state to form high-temperature ferromagnetism.

IV. THEORETICAL INSIGHTS INTO THE EMERGENT MAGNETISM

To unravel the atomic-scale mechanism of the hydrogenation-induced ferromagnetism, we performed density-functional theory calculations with Coulomb corrections (DFT + *U*) (Sec. VII). For pristine PdCoO₂, our calculations reproduce the quasi-2D Fermi surface with the conduction bands predominantly composed of Pd-4d states (Fig. S5), consistent with previous studies [18]. Considering the experimentally obtained saturated magnetization (around 0.6 μ_B /Co at 3 K) and the magnetic moment of the high-spin Co²⁺ ($S = 3/2$) state, we estimate the hydrogen concentration to be around 20% per Co in the studied sample, which is in qualitative agreement with the value (around 25%) estimated from the quantitative

analysis of XAS spectra (Fig. S6). Therefore, to model the hydrogenated structure, we construct a supercell containing two hydrogen atoms for every nine formula units (i.e., H₂ – Pd₉Co₉O₁₈) to account for the estimated hydrogen concentration. Our calculations reveal that the hydrogen ions (protons) preferentially bond to oxygen anions within CoO₆ octahedra [left panel of Fig. 3(a)]. These findings are consistent with our earlier studies on proton intercalation [37]. In the case of PdCoO₂, we note that its natural layered structure composed of alternating CoO₂ and Pd layers creates strong anisotropy in electronic transport so that the interlayer electron transfer is significantly hindered. Consequently, when the O-H bonds are formed within the CoO₂ layer as revealed by our theoretical calculations [Fig. 3(a)], the electron donated by hydrogen is readily accepted by the adjacent Co sites through charge transfer [right panel of Fig. 3(a)]. We note that cobalt's facile redox chemistry makes it an ideal electron acceptor to realize Co³⁺ to Co²⁺ reduction. Furthermore, the orbital-resolved spin-polarized density-of-states calculations for Co²⁺ reveal a complete occupation of all five 3d orbitals in the majority-spin channel, whereas only the e_g^π bands are occupied in the minority-spin channel [Fig. 3(b)]. This occupancy is starkly different from that of the pristine sample and strongly confirms the formation of a high-spin

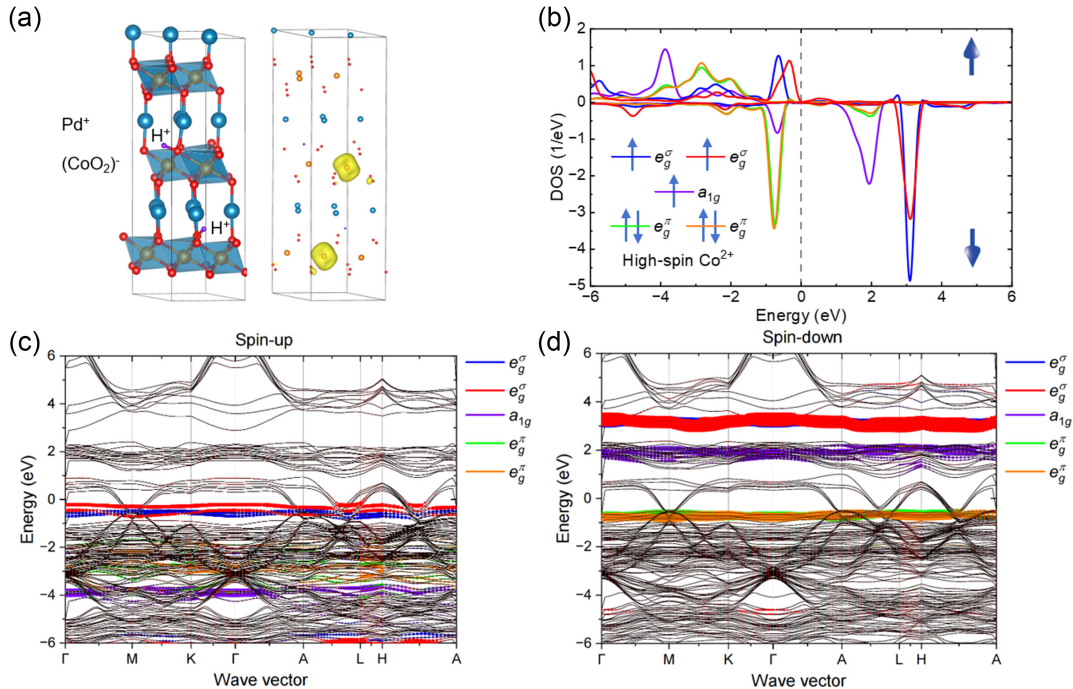


FIG. 3. First-principles calculations of hydrogenated PdCoO₂. (a) Calculated crystal structure of hydrogenated PdCoO₂. The structure considered contains two hydrogen atoms for nine chemical units (i.e., H₂Pd₉Co₉O₁₈ as shown in left panel), and the corresponding distributions of the spin density are presented in real space by the yellow clouds (right panel). (b) Atomically resolved spin-polarized density of states projected onto 3d orbitals of Co²⁺ ions. The inset illustrates the corresponding electronic configuration with the high-spin state. (c),(d) Spin-polarized electronic band structures of H₂Pd₉Co₉O₁₈ for spin-up (c) and spin-down (d) channels. The band dispersion was projected onto 3d states of Co²⁺ as indicated by the colored lines.

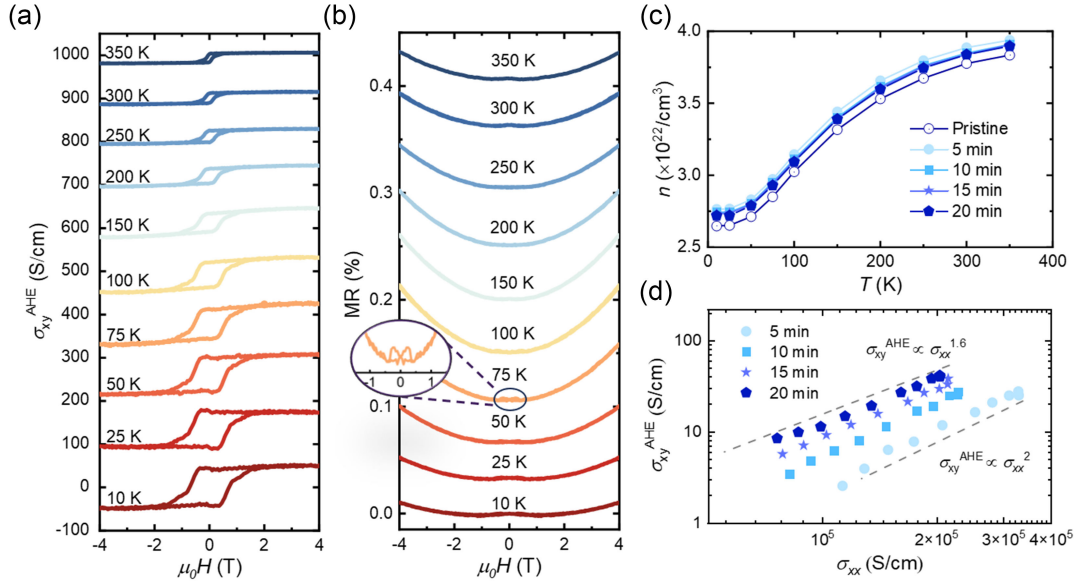


FIG. 4. Magneto-transport measurements of hydrogenated PdCoO₂. (a) Anomalous Hall hysteresis loops measured at different temperatures. (b) Magnetoresistance curves as a function of magnetic field for a hydrogenated PdCoO₂ sample measured at various temperatures. The magnetic field was applied along the OOP direction. The inset displays the enlarged MR curve measured at 75 K near zero field. (c) Temperature dependence of carrier density extracted from Hall signals of PdCoO₂ under different hydrogenation durations. (d) Logarithmic plot of σ_{xy}^{AHE} versus σ_{xx} for PdCoO₂ under different hydrogenation durations. The gray dashed lines indicate the scaling of $\sigma_{xy}^{\text{AHE}} \propto \sigma_{xx}^{1.6}$ and $\sigma_{xy}^{\text{AHE}} \propto \sigma_{xx}^2$.

Co²⁺ state, which is consistent with our XAS and XMCD measurements.

Strikingly, the hydrogenated system retains metallicity with the Fermi level dominated by the Pd-4*d* states, while the band dispersion of the high-spin Co²⁺ is spin polarized but located below the Fermi level [Figs. 3(c) and 3(d)]. This intriguing electronic band structure is further corroborated by the Fermi surface of the hydrogenated system (Fig. S7 in Ref. [40]), which nicely preserves the pristine 2D metallic character. These results establish hydrogenated PdCoO₂ as a self-assembled superlattice, where 2D metallic Pd layers coexist with insulating and ferromagnetic CoO₂ layers. To confirm the robustness of our calculations, we examine multiple hydrogen configurations, including H₂ – Pd₉Co₉O₁₈ with distinct hydrogen-site arrangements and H – Pd₉Co₉O₁₈ (one hydrogen atom for every nine formula units), both of which exhibit consistent results. This spatially partitioned architecture, with simultaneous high conductivity and robust magnetism, provides a unique platform to explore the correlated electron physics in engineered heterostructures.

V. EXOTIC ANOMALOUS HALL EFFECT IN HYDROGENATED PdCoO₂

To investigate the interplay between ferromagnetism in the CoO₂ layers and itinerant electrons in the Pd layers, we carried out anomalous Hall conductivity (AHC) and magnetoresistance (MR) measurements with hydrogenated

PdCoO₂ samples. The AHC data exhibit squarelike hysteresis loops among the measurement temperature range [Fig. 4(a)], suggesting that the conducting electrons become spin polarized as a result of scattering by the magnetic Co²⁺ ions. Concurrently, the MR curves show a positive-field dependence [Fig. 4(b)] akin to that of pristine PdCoO₂ [Fig. S8(a) in Ref. [40]], in which, however, the AHE is absent [Fig. S8(b)]. At fields above the coercive field, the MR curves follow the empirical parabolic relationship of MR, characteristic of metallic systems. Near the coercive magnetic field, hysteretic anomalies can be clearly resolved [inset of Fig. 4(b)], which is attributed to the scattering between the conducting electrons in Pd layers and the magnetization in CoO₂ layers.

To further elucidate this interfacial coupling phenomena, we systematically varied the hydrogenation duration and traced the evolution of AHC response. Because of the systematic change of hydrogen incorporation, it is possible to uncover a systematic evolution of both the magnetization and the AHC (Fig. S9 in Ref. [40]). Despite increasing hydrogen incorporation with the annealing duration, carrier density remains nearly constant among these samples [Figs. 4(c) and S9(c)], consistent with the theoretical prediction of an intact Pd-derived Fermi surface (Fig. S7). Figure 4(d) displays the remanent anomalous Hall conductivity σ_{xy}^{AHE} versus longitudinal conductivity σ_{xx} on a double-logarithmic scale in a series of hydrogenated PdCoO₂ states. Remarkably, σ_{xy}^{AHE} scales with σ_{xx} as a power-law dependence [48], $\sigma_{xy}^{\text{AHE}} \sim \sigma_{xx}^{\alpha}$, where α decreases

from above 2.0 to 1.6 with prolonged hydrogenation [Figs. 4(d) and S9(d)]. This scaling starkly contrasts with conventional high-conductivity systems (e.g., $\sigma_{xx} \sim 10^6$ S/cm), where intrinsic Berry-curvature mechanisms ($\alpha \sim 0$) typically dominate the AHC [48]. Instead, it aligns with behaviors observed in ferromagnetic metals with localized magnetic scattering [49,50]. We attribute this anomalous exponential scaling to the unique electronic dichotomy of hydrogenated PdCoO₂, where the 2D metallic transport in Pd layers coexists with the insulating, ferromagnetic CoO₂ layers. In this system, interfacial magnetic proximity effects override conventional Berry-curvature mechanisms to dominate the AHC, which establishes hydrogenated PdCoO₂ as a novel platform for realizing unconventional AHC mechanisms in hybrid metallic and ferromagnetic-insulating architecture.

Finally, we demonstrate that the ferromagnetic state in PdCoO₂ is fully reversible. Thermal annealing at elevated temperatures (e.g., 700 °C) removes hydrogen, restoring the pristine nonmagnetic state of PdCoO₂ (Fig. S10 in Ref. [40]). This reversibility, combined with tunable magnetic properties (Fig. S9 in Ref. [40]), enables precise control of magnetism without compromising structural integrity or metallicity, positioning PdCoO₂ as a promising platform for reconfigurable spintronic devices.

VI. CONCLUSIONS

To summarize, in this work, we report the emergence of robust, bulk, room-temperature ferromagnetism in the inherently nonmagnetic layered oxide PdCoO₂ through hydrogenation-induced electron doping while preserving the delafossite crystal structure. By integrating 2D metallic charge transport and spin-polarized channels within a single material, this work unlocks opportunities to explore interfacial spin-orbit phenomena, engineer magnetic proximity effects, and design heterostructures with emergent quantum phases. Our strategy of layer-selective electronic state engineering via hydrogenation is readily generalizable to other delafossites and related layered oxides, offering a versatile route to tailor correlated electronic states and functionalities for next-generation quantum materials and device applications.

VII. METHODS

Sample growth and hydrogenation. Thin films of PdCoO₂ were synthesized in an oxide molecular-beam epitaxy (MBE) system (DCA, R450) on (0001)-oriented Al₂O₃ substrates. The substrates were annealed in air at 1050 °C for 5 hours to obtain a step-and-terrace morphology prior to the growth. During deposition, the substrates were heated at 420 °C under a chamber background pressure of 4×10^{-6} Torr of distilled ozone (about 80% ozone and 20% oxygen). The fluxes of palladium and cobalt evaporated from the effusion cells were calibrated

using a quartz crystal microbalance. The palladium and cobalt shutters were precisely regulated to enable the sequential deposition of alternating monolayer doses of palladium and cobalt, following the atomic layer sequence of PdCoO₂ along the *c* axis. We note that this setup is capable of growing high-quality oxide thin films with a wafer size up to 2 inches. After the deposition, the substrates were cooled down to room temperature while keeping the same chamber pressure with ozone concentration. The film was then removed from the chamber and annealed in oxygen at 700 °C for 10 hours in a tube furnace to further improve the crystalline quality. The hydrogenation process was performed by annealing PdCoO₂ thin films at 85 °C under a flow of hydrogen gas mixture (5% H₂/95% Ar), with *in situ* resistance monitoring to track reaction kinetics. For most experiments, the annealing duration was fixed at 20 minutes; however, to systematically modulate the magnetization and the corresponding anomalous Hall effect, the duration was varied between 5, 10, 15, and 20 minutes.

Crystalline structure, magnetism, and magnetotransport measurements. X-ray diffraction (XRD) measurements were performed with a high-resolution diffractometer (Smartlab, Rigaku) using monochromatic Cu K α 1 radiation ($\lambda = 1.5406$ Å) at room temperature. The magnetization was measured in an MPMS (Quantum Design) SQUID magnetometer using the vibrating sample magnetometer mode as a function of both magnetic field and temperature, in which the maximum magnetic field is 7 T and the maximum temperature is 400 K. The diamagnetic signal from the substrate was subtracted from the raw data. Hall bar devices (150 $\mu\text{m} \times 50 \mu\text{m}$) were fabricated through standard lithography-etching method from the thin-film samples. The transport measurements were performed in a PPMS setup (Quantum Design DynaCool system, 9 T) with an in-plane dc current.

Secondary ion mass spectrometry measurements. SIMS measurements were carried out using a TOF-SIMS 5-100 instrument (IONTOF GmbH) to probe the hydrogen concentration of the PdCoO₂ hydrogenated samples. The sputtering area was 250 $\mu\text{m} \times 250 \mu\text{m}$, and the detecting area was set as 100 $\mu\text{m} \times 100 \mu\text{m}$ to minimize the influence of the edge region. The interface position between the thin film and the substrate was indexed by the simultaneously measured depth profile of the aluminum (Al) signal from the Al₂O₃ substrate. All samples were measured under the same conditions.

STEM measurements and electron ptychography. High-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) experiments were conducted using an aberration-corrected electron microscope (Thermo Fisher Scientific, Titan Themis) with a probe-forming aperture semiangle of 25 mrad at 300 keV, with the beam current set to 50 pA. The STEM lamellas were extracted from the thin film using a Ga⁺ ion beam via the standard

lift-out method in a focused ion beam (FIB) system (Thermo Fisher Scientific, Helios 5 CX). Prior to the FIB milling, a protective layer of Pt was deposited on the film surface via electron beam-induced deposition to prevent ion beam damage. The lamella was then transferred and mounted onto a copper grid, followed by thinning to electron transparency. During thinning, the accelerating voltage of the Ga^+ ion beam was gradually reduced from 30 to 5 kV. Finally, a low-energy ion milling step at 2 kV and 5.0 pA was applied to minimize the amorphous damage layer. Energy-filtered four-dimensional scanning transmission microscopy (4D-STEM) datasets were acquired using an aberration-corrected microscope (JEOL, JEM-ARM300F2) equipped with a Gatan K3 camera and the STEMx modular system. The electron probe had a convergence semiangle of 24.3 mrad and focused approximately 20 nm above the sample. The scan step size was 0.52 Å, and the beam current was approximately 10 pA. The algorithms and parameters for multislice electron ptychography can be found in previous publications [51,52].

XAS and XMCD measurements. Soft XAS and XMCD at Co L edges were carried out at beamlines I06-1 and I10-1 of Diamond Light Source and beamlines 4.0.2 and 6.3.1 of Advanced Light Source, with a total electron yield mode at normal incidence measurement geometry. The XAS spectra were normalized to the photon flux measured with the photocurrent from a clean gold mesh. For the XMCD measurements, the x-ray incidence was fixed to normal with a magnetic field (2 T) applied along the x-ray beam, and a 100% circular polarized x-ray was employed.

First-principles calculations. Density-functional theory [53,54] calculations were carried out with the Vienna *Ab initio* Simulation Package (VASP). All calculations were performed with the generalized-gradient approximation (GGA) of the Perdew-Burke-Ernzerhof formula [55]. The plane-wave kinetic-energy cutoff is 500 eV, and a $9 \times 9 \times 2$ Γ -centered Monkhorst-Pack k-mesh [56] is adopted for the calculations. For structural optimization, the atomic positions are relaxed until the force on each atom is less than 0.005 eV/Å. The electronic band structure of the hydrogenated material is calculated using a $\sqrt{3} \times \sqrt{3} \times 3$ supercell. To better describe the local magnetic moments carried by the Co 3d electrons, spin-polarized GGA + *U* calculations are performed using the Dudarev formulation [57] with *U* = 3 eV on the Co 3d orbitals.

ACKNOWLEDGMENTS

This study was financially supported by the National Key R&D program of China (Grant No. 2023YFA1406400), the National Natural Science Foundation of China (NSFC Grants No. 52025024, No. 52388201, No. 12421004, and No. 52273227), and the National Key R&D program of China (Grants No. 2022YFA1402400, and No. 2021YFA1400100).

This study used resources of the Center for High Performance Computing at Shanghai Jiao Tong University.

DATA AVAILABILITY

The data that support the findings of this article are not publicly available. The data are available from the authors upon reasonable request.

-
- [1] D. Li *et al.*, *Superconductivity in an infinite-layer nickelate*, *Nature (London)* **572**, 624 (2019).
 - [2] Y. Maeno *et al.*, *Superconductivity in a layered perovskite without copper*, *Nature (London)* **372**, 532 (1994).
 - [3] H. Sun *et al.*, *Signatures of superconductivity near 80 K in a nickelate under high pressure*, *Nature (London)* **621**, 493 (2023).
 - [4] E. K. Ko *et al.*, *Signatures of ambient pressure superconductivity in thin film $\text{La}_3\text{Ni}_2\text{O}_7$* , *Nature (London)* **638**, 935 (2025).
 - [5] Y. S. Oh, X. Luo, F. T. Huang, Y. Wang, and S. W. Cheong, *Experimental demonstration of hybrid improper ferroelectricity and the presence of abundant charged walls in $(\text{Ca}, \text{Sr})_3\text{Ti}_2\text{O}_7$ crystals*, *Nat. Mater.* **14**, 407 (2015).
 - [6] M. J. Pitcher *et al.*, *Tilt engineering of spontaneous polarization and magnetization above 300 K in a bulk layered perovskite*, *Science* **347**, 420 (2015).
 - [7] Y. Lyu *et al.*, *An overview on the advances of LiCoO_2 cathodes for lithium-ion batteries*, *Adv. Energy Mater.* **11**, 2000982 (2020).
 - [8] C. A. P. de Araujo, J. D. Cuchiaro, L. D. McMillan, M. C. Scott, and J. F. Scott, *Fatigue-free ferroelectric capacitors with platinum electrodes*, *Nature (London)* **374**, 627 (1995).
 - [9] B. H. Park *et al.*, *Lanthanum-substituted bismuth titanate for use in non-volatile memories*, *Nature (London)* **401**, 682 (1999).
 - [10] A. P. Mackenzie, *The properties of ultrapure delafossite metals*, *Rep. Prog. Phys.* **80**, 032501 (2017).
 - [11] P. J. W. Moll, P. Kushwaha, N. Nandi, B. Schmidt, and A. P. Mackenzie, *Evidence for hydrodynamic electron flow in PdCoO_2* , *Science* **351**, 1061 (2016).
 - [12] V. Sunko *et al.*, *Rashba-like spin splitting via kinetic-energy-coupled inversion-symmetry breaking*, *Nature (London)* **549**, 492 (2017).
 - [13] T. Harada, *Thin-film growth and application prospects of metallic delafossites*, *Mater. Today Adv.* **11**, 100146 (2021).
 - [14] M. D. Bachmann *et al.*, *Directional ballistic transport in the two-dimensional metal PdCoO_2* , *Nat. Phys.* **18**, 819 (2022).
 - [15] C. W. Hicks, A. S. Gibbs, A. P. Mackenzie, H. Takatsu, Y. Maeno, and E. A. Yelland, *Quantum oscillations and high carrier mobility in the delafossite PdCoO_2* , *Phys. Rev. Lett.* **109**, 116401 (2012).
 - [16] Y. Zhang *et al.*, *Crystal-chemical origins of the ultrahigh conductivity of metallic delafossites*, *Nat. Commun.* **15**, 1399 (2024).
 - [17] M. Tanaka *et al.*, *Origin of the metallic conductivity in PdCoO_2 with delafossite structure*, *Physica (Amsterdam)* **245B**, 157 (1998).

- [18] V. Eyert, R. Frésard, and A. Maignan, *On the metallic conductivity of the delafossites PdCoO₂ and PtCoO₂*, *Chem. Mater.* **20**, 2370 (2008).
- [19] T. Harada, S. Ito, and A. Tsukazaki, *Electric dipole effect in PdCoO₂/β-Ga₂O₃ Schottky diodes for high-temperature operation*, *Sci. Adv.* **5**, eaax5733 (2019).
- [20] T. Harada, K. Fujiwara, and A. Tsukazaki, *Highly conductive PdCoO₂ ultrathin films for transparent electrodes*, *APL Mater.* **6**, 046107 (2018).
- [21] P. Yordanov *et al.*, *Generation of terahertz radiation via the transverse thermoelectric effect*, *Adv. Mater.* **35**, 2305622 (2023).
- [22] J. F. Mendez-Valderrama *et al.*, *T-linear resistivity from magneto-elastic scattering: Application to PdCrO₂*, *Proc. Natl. Acad. Sci. U.S.A.* **120**, e2305609120 (2023).
- [23] Q. Song *et al.*, *Growth of PdCoO₂ films with controlled termination by molecular-beam epitaxy and determination of their electronic structure by angle-resolved photoemission spectroscopy*, *APL Mater.* **10**, 091113 (2022).
- [24] F. Mazzola *et al.*, *Itinerant ferromagnetism of the Pd-terminated polar surface of PdCoO₂*, *Proc. Natl. Acad. Sci. U.S.A.* **115**, 12956 (2018).
- [25] T. Harada *et al.*, *Anomalous Hall effect at the spontaneously electron-doped polar surface of PdCoO₂ ultrathin films*, *Phys. Rev. Res.* **2**, 0132282 (2020).
- [26] M. Brahlek *et al.*, *Emergent magnetism with continuous control in the ultrahigh-conductivity layered oxide PdCoO₂*, *Nano Lett.* **23**, 7279 (2023).
- [27] G. Rimal *et al.*, *Effective reduction of PdCoO₂ thin films via hydrogenation and sign tunable anomalous Hall effect*, *Phys. Rev. Mater.* **5**, L052001 (2021).
- [28] C. Gong and X. Zhang, *Two-dimensional magnetic crystals and emergent heterostructure devices*, *Science* **363**, eaav4450 (2019).
- [29] Q. H. Wang *et al.*, *The magnetic genome of two-dimensional van der Waals materials*, *ACS Nano* **16**, 6960 (2022).
- [30] K. S. Burch, D. Mandrus, and J. G. Park, *Magnetism in two-dimensional van der Waals materials*, *Nature (London)* **563**, 47 (2018).
- [31] M. Gibertini, M. Koperski, A. F. Morpurgo, and K. S. Novoselov, *Magnetic 2D materials and heterostructures*, *Nat. Nanotechnol.* **14**, 408 (2019).
- [32] B. Huang *et al.*, *Emergent phenomena and proximity effects in two-dimensional magnets and heterostructures*, *Nat. Mater.* **19**, 1276 (2020).
- [33] Y. Zhou *et al.*, *Strongly correlated perovskite fuel cells*, *Nature (London)* **534**, 231 (2016).
- [34] H. Yoon *et al.*, *Reversible phase modulation and hydrogen storage in multivalent VO₂ epitaxial thin films*, *Nat. Mater.* **15**, 1113 (2016).
- [35] N. Lu *et al.*, *Enhanced low-temperature proton conductivity in hydrogen-intercalated brownmillerite oxide*, *Nat. Energy* **7**, 1208 (2022).
- [36] H. Han *et al.*, *Reversal of anomalous Hall effect and octahedral tilting in SrRuO₃ thin films via hydrogen spillover*, *Adv. Mater.* **35**, 2370020 (2023).
- [37] N. Lu *et al.*, *Electric-field control of tri-state phase transformation with a selective dual-ion switch*, *Nature (London)* **546**, 124 (2017).
- [38] C. Leighton, *Electrolyte-based ionic control of functional Oxides*, *Nat. Mater.* **18**, 13 (2019).
- [39] F. Lloret, M. Julve, J. Cano, R. Ruiz-García, and E. Pardo, *Magnetic properties of six-coordinated high-spin cobalt(II) complexes: Theoretical background and its application*, *Inorg. Chim. Acta* **361**, 3432 (2008).
- [40] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/3mgc-z9wv> for Figs. S1–S10, which provide details of the sample preparation, experimental measurements, and theoretical calculations.
- [41] G. Li *et al.*, *In situ modification of a delafossite-type PdCoO₂ bulk single crystal for reversible hydrogen sorption and fast hydrogen evolution*, *ACS Energy Lett.* **4**, 2185 (2019).
- [42] E. Ising, *Beitrag zur theorie des ferromagnetismus*, *Z. Phys.* **31**, 253 (1925).
- [43] H.-J. Noh *et al.*, *Orbital character of the conduction band of delafossite PdCoO₂ studied by polarization-dependent soft x-ray absorption spectroscopy*, *Phys. Rev. B* **80**, 073104 (2009).
- [44] M. Wang *et al.*, *Manipulate the electronic and magnetic states in NiCo₂O₄ films through electric-field-induced protonation at elevated temperature*, *Adv. Mater.* **31**, 1900458 (2019).
- [45] M. Mekata, T. Sugino, A. Oohara, Y. Oohara, and H. Yoshizawa, *Magnetic structure of antiferromagnetic PdCrO₂ Possible degenerate helices on a rhombohedral lattice*, *Physica (Amsterdam)* **213–214B**, 221 (1995).
- [46] C. T. Chen, Y. U. Idzerda, H. J. Lin, N. V. Smith, G. Meigs, E. Chaban, G. H. Ho, E. Pellegrin, and F. Sette, *Experimental confirmation of the x-ray magnetic circular dichroism sum rules for iron and cobalt*, *Phys. Rev. Lett.* **75**, 152 (1995).
- [47] H. J. Noh, J. Jeong, J. Jeong, E. J. Cho, S. B. Kim, K. Kim, B. I. Min, and H. D. Kim, *Anisotropic electric conductivity of delafossite PdCoO₂ studied by angle-resolved photoemission spectroscopy*, *Phys. Rev. Lett.* **102**, 256404 (2009).
- [48] N. Nagaosa, J. Sinova, S. Onoda, A. H. MacDonald, and N. P. Ong, *Anomalous Hall effect*, *Rev. Mod. Phys.* **82**, 1539 (2010).
- [49] H. Toyosaki *et al.*, *Anomalous Hall effect governed by electron doping in a room-temperature transparent ferromagnetic semiconductor*, *Nat. Mater.* **3**, 221 (2004).
- [50] T. Miyasato, N. Abe, T. Fujii, A. Asamitsu, S. Onoda, Y. Onose, N. Nagaosa, and Y. Tokura, *Crossover behavior of the anomalous Hall effect and anomalous Nernst effect in itinerant ferromagnets*, *Phys. Rev. Lett.* **99**, 086602 (2007).
- [51] Z. Chen *et al.*, *Electron ptychography achieves atomic-resolution limits set by lattice vibrations*, *Science* **372**, 826 (2021).
- [52] Z. Dong *et al.*, *Visualization of oxygen vacancies and self-doped ligand holes in La₃Ni₂O_{7-δ}*, *Nature (London)* **630**, 847 (2024).
- [53] P. Hohenberg and W. Kohn, *Inhomogeneous electron gas*, *Phys. Rev.* **136**, B864 (1964).

- [54] W. Kohn and L. J. Sham, *Self-consistent equations including exchange and correlation effects*, *Phys. Rev.* **140**, A1133 (1965).
- [55] J. P. Perdew, K. Burke, and M. Ernzerhof, *Generalized gradient approximation made simple*, *Phys. Rev. Lett.* **77**, 3865 (1996).
- [56] H. J. Monkhorst and J. D. Pack, *Special points for Brillouin-zone integrations*, *Phys. Rev. B* **13**, 5188 (1976).
- [57] S. L. Dudarev, G. A. Botton, S. Y. Savrasov, C. J. Humphreys, and A. P. Sutton, *Electron-energy-loss spectra and the structural stability of nickel oxide: An LSDA+U study*, *Phys. Rev. B* **57**, 1505 (1998).