Itinerant ferromagnetism of the Pd-terminated polar surface of PdCoO$_2$

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The ability to modulate the collective properties of correlated electron systems at their interfaces and surfaces underpins the burgeoning field of “designer” quantum materials. Here, we show how an electronic reconstruction driven by surface polarity mediates a Stoner-like magnetic instability to itinerant ferromagnetism at the Pd-terminated surface of the non-magnetic delafossite oxide metal PdCoO$_2$. Combining angle-resolved photoemission spectroscopy and density-functional theory calculations, we show how this leads to a rich multi-band surface electronic structure. We find similar surface state dispersions in PdCrO$_2$, suggesting surface ferromagnetism persists in this sister compound despite its bulk antiferromagnetic order.

Delafossite oxide metals, surface ferromagnetism, electronic reconstruction.

Recent advances in the ability to fabricate transition-metal oxides with atomic-scale precision have opened new paradigms for controlling their quantum many-body states and phases (1–10). A prototypical example is the interface between the bulk insulating perovskite oxides SrTiO$_3$ and LaAlO$_3$, which supports a two-dimensional electron liquid (11) hosting a number of remarkable properties, from gate-tunable superconductivity (12) to magnetic order (13). The emergence of conductivity in this system is thought to be intricately linked to the polar nature of the interface between SrTiO$_3$ and LaAlO$_3$ (11, 14, 15). The carrier densities observed, however, are typically an order of magnitude smaller than would be expected from a pure electronic reconstruction driven by the so-called polar catastrophe (12, 15, 16), and the microscopic mechanism by which polarity may mediate a conducting interface has proved controversial (17–22). It is important, therefore, to investigate the influence of surface and interface polarity in other transition-metal-based oxides, both for developing improved understanding and for expanding the search of materials systems which may host novel surface or interface phases.

Here, we focus on the “ABO$_2$” delafossite oxides (23–28). Delafossites represent a particularly promising material class both because of their naturally layered structure and the potential to drastically alter their physical properties by changing the A- and B-site cations (29–31). Bulk MCoO$_2$ [M=Pt,Pd] are non-magnetic metals with simple single-band Fermi surfaces. They exhibit the highest conductivity of all known metallic oxides (26, 28, 32–34). They also host polar surfaces, opening the potential to stabilise local electronic environments and phases different to those of the bulk (35–37). We use angle-resolved photoemission spectroscopy (ARPES) to probe the Pd-terminated surface electronic structure of PdCoO$_2$. In agreement with our calculations from density-functional theory (DFT), these experiments demonstrate how the polarity induces a pronounced electron doping at the surface, which in turn mediates an intrinsic Stoner instability towards itinerant ferromagnetism. We find that a similar surface ferromagnetism persists in the sister compound PdCrO$_2$, which is antiferromagnetically ordered in the bulk. This points to an exciting opportunity to utilise polar surfaces and interfaces to induce new magnetic states in oxides as well as to generate naturally-occurring magnetic heterostructures.

Results

Surface termination-dependent measurements. PdCoO$_2$ is comprised of triangular-lattice metallic Pd planes separated by insulating CoO$_2$ layers. This crystal structure has natural cleavage planes above and below each Pd layer: inequivalent surface terminations would therefore be expected (Fig. 1(a)). Consistent with this, we find a strong variation in the relative intensity of Co 3p and Pd 4p core levels measured by X-ray photoelectron spectroscopy (XPS) at different patches of the cleaved sample surface (Fig. 1(b)). This is correlated with a marked difference in the electronic structure measured by ARPES (Fig. 1(c–e)). Across the sample, we find a steeply-dispersive state which we attribute as the Pd-derived bulk band (36). In Fig. 1(c), our measurements additionally show

Significance Statement

There has been widespread interest in using interfaces of transition-metal oxides as a platform to control not only their electronic structure, as in semiconductor heterostructures, but also to tune between different collective phases. A major goal is to realise states of the quantum many-body system that are not found in the bulk phase diagrams of the constituent materials. Here, we perform a combined experimental and theoretical study of the delafossite oxide metals PdCoO$_2$ and PdCrO$_2$, finding how electronic reconstructions at their polar surfaces drive instabilities to itinerant surface ferromagnetism. Neither compound supports ferromagnetism in bulk, with PdCrO$_2$ a bulk antiferromagnet, demonstrating how a delicate competition of magnetic correlations can be engineered by intrinsic self-doping at a polar surface or interface.

The ARPES measurements were performed by F.M., V.S., O.J.C., L.B., I.M., and P.D.C.K. and analysed by F.M. H.R. performed the density-functional theory calculations. S.K. and P.K. grew the samples.

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Fig. 1. Surface terminations of PdCoO$_2$. (a) Side view of the crystal structure of PdCoO$_2$, showing two possible surface terminations which can be expected. (b) XPS spectra ($h\nu = 120$ eV, after subtraction of a linear background and normalised by the area of the Co 3p peak) at different spatial locations of a cleaved crystal show varying relative ratios of Co and Pd core level peaks, consistent with a spatial dependence of the dominant surface termination. (c-e) Markedly different electronic structures are observed by ARPES ($h\nu = 90$ eV, $p$-polarisation, measured along $\Gamma - K$) at these locations, corresponding to predominantly (c) CoO$_2$, (e) Pd and (d) mixed surface terminations.

A pair of massive hole-like bands (Fig. 1(c), labeled ‘S-CoO$_2$’). These have been assigned previously as surface states from the CoO$_2$-termination (36, 37), consistent with our XPS measurements from the same sample region, which yield the greatest ratio of Co 3p : Pd 4p core-level spectral weight.

Measurements from a different patch of the same sample (Fig. 1(e)) reveal a completely different surface electronic structure, which we describe in detail below. Our XPS measurements exhibit a much larger spectral weight of the Pd than the Co-derived core-level peak for this sample region (Fig. 1(b)), and we thus attribute these as surface states originating from the Pd-terminated surface (‘S-Pd’). We note that for most regions where such states are visible, we observe a superposition of these spectral features with those of the CoO$_2$-terminated surface (e.g., Fig. 1(d)). This indicates a rather limited spatial extent of typical Pd-terminated regions, with a mixed surface termination within our probing light spot area ($\sim 50$ $\mu$m diameter). In the following we show our highest-quality ARPES data obtained from a sample which exhibits such a mixed surface terminations. Similar results were obtained from multiple samples.

Pd-terminated surface electronic structure. The measured Fermi surfaces and dispersions from such a mixed surface termination are shown in Fig. 2. The CoO$_2$-terminated surface states form hexagonal and nearly circular hole-like Fermi surfaces about the Brillouin zone centre, split-off by a surprisingly-large Rashba-like interaction arising due to a large energy scale of inversion symmetry breaking at this surface (37). We do not consider these further here.
Pd$^{1+}$ in the bulk. This, however, should manifest as a surface doping of $\approx 0.5$ electrons/unit cell, seemingly in contrast to the hole-doped copy of the bulk band observed experimentally here.

Moreover, rather than a simple rigid shift of the bulk Pd-derived valence band, our measured dispersions (Fig. 2(b,c)) reveal a much richer surface electronic structure. As well as the steep band discussed above, Fig. 2(b) shows a flat-topped band located $\sim 100$ meV below the Fermi level, and a pair of electron-like bands crossing $E_F$ near the Brillouin zone centre (all labeled ‘S-Pd’ in Fig. 2(b)). The outer of these electron pockets can also be seen in our Fermi surface measurements (Fig. 2(a)), while the innermost band is not clearly observed at the photon energy used. Additionally, multiple fully-occupied bands are found at the Brillouin zone face M-point (Fig. 2(c)).

**Itinerant surface ferromagnetism.** We demonstrate below that such a rich multi-band electronic structure of the Pd-terminated surface of PdCoO$_2$ is the result of an instability to itinerant surface ferromagnetism. Fig. 3 shows the dispersions of the bulk and Pd-terminated surface states extracted from the measurements shown in Fig. 2(b) as well as from equivalent measurements performed using a different photon energy and/or light polarisation. These different experimental conditions lead to varying transition matrix elements, selectively enhancing the visibility of different features, (see, for example, SI Appendix, Fig. S1), thus ensuring that we capture the dispersions of all bands accurately. If we assume that these surface states are spin-degenerate and extract their Luttinger count from our experimentally-measured Fermi surfaces, we find an electron count that is unphysically high. In contrast, if we treat them as spin-polarised, we find a surface carrier density that is $0.55 \pm 0.03$ electrons/unit cell higher than that of the bulk, which is close to the additional 0.5 electrons/unit cell that would be expected from the polar surface charge. We note that spin-polarised states are generically allowed at surfaces, where the breaking of inversion symmetry can lead to a momentum-dependent spin-splitting of the Rashba-type (38). If this was the origin of the surface state spin-polarisation here, however, then the spin-splitting should vanish at the zero-momentum $\Gamma$-point, where time-reversal symmetry enforces a Kramers degeneracy. In contrast, the clear splitting of spin-polarised bands that we observe at the $\Gamma$ point (Figs. 2(b) and 3) indicates that time-reversal symmetry is broken here (i.e., $E(k = 0, \uparrow) \neq E(k = 0, \downarrow)$). Moreover, a Rashba-like origin of the observed spin-polarised bands would be incompatible with the large ($\approx 430$ meV) energy splitting of the steep bands that we observe, which is more than three times the atomic spin-orbit coupling of Pd.$^*$ Together, these observations therefore rule out a Rashba origin of our observed spin-polarised surface states; instead, they provide conclusive empirical evidence that the Pd-terminated surface of PdCoO$_2$ is ferromagnetic.

Although the above conclusion is independent of theory, it

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$^*$We note that our non-magnetic calculations (Fig. 4(b), discussed below) show a Rashba-like spin splitting on the order of 50 meV, a realistic value given the atomic spin-orbit strength of $\approx 110$ meV. This is, however, significantly smaller than the exchange splitting observed experimentally as well as that found from our spin-polarised calculations. We thus conclude that Rashba-type interactions do not play a significant role here as compared to magnetic correlations. Whether they play a role in determining the detailed magnetic structure, for example in stabilising non-collinear magnetic states, is an interesting question for future study.

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Fig. 3. Itinerant surface ferromagnetism in PdCoO$_2$. Bulk and surface band dispersions exacted from ARPES measurements using different photon energies and light polarisations: linear horizontal (LH, p-polarisation), circular right (CR) and circular left (CL) polarisations.

Fig. 4. DFT supercell calculations and electron DOS. (a) Bulk $k_z$-projected electronic structure of PdCoO$_2$ (left) and corresponding electron DOS (right). (b) Non-magnetic supercell calculations (left), showing the formation of a flat surface state right at the Fermi level, leading to a large peak in the corresponding density of states (right). Additionally, a moderate Rashba-like spin-orbit splitting of the electron band near the $\Gamma$-point is observed. The calculations are projected onto the surface Pd layer (purple colouring) to highlight the surface states. (c) Spin-polarised supercell calculations (left) indicate how a Stoner-like transition spin-splits the states, giving rise to the $\alpha$-$\beta$ and $\gamma$-$\delta$ exchange-split pairs discussed in the main text. The spin majority and minority character as projected onto the surface Pd layer is shown by red and blue colouring, respectively.
is also reinforced by explicit calculations (Fig. 4, see Methods), which further demonstrate how the surface ferromagnetism arises as a result of an intrinsic Stoner-like instability driven by the polar surface charge. This mechanism is shown in Fig. 4. The band which forms the bulk Fermi surface, while steep at the Fermi level (34, 39), becomes much flatter above $E_F$ (evident, for example, along $\Gamma-K$ in the bulk $k_z$-projected calculations shown in Fig. 4(a)). Compensating the surface polarity should lead to electron doping of the surface layer, as discussed above. This will create a surface copy of the bulk band. Its flat band top, and the high density of states (DOS) associated with it, are pushed downwards towards the Fermi level, as evident in our non-magnetic supercell calculations shown in Fig. 4(b).

From a spin-polarised calculation (Fig. 4(c)) we find that the density of states at $E_F$ is sufficiently high to trigger a Stoner transition. The band at the Fermi level therefore exchange splits into a pair of spin-polarised bands (labelled $\alpha$ and $\beta$), which can be identified as the experimentally-observed flat ($\alpha$ in Fig. 3) and steep ($\beta$) states. Consistent with previous DFT calculations (35), we also find how additional near-$E_F$ surface states inherit a similar exchange splitting, forming the majority-spin and minority-spin $\gamma$ and $\delta$ bands observed at the Brillouin zone centre in our ARPES measurements (Fig. 3).

We note that the surface magnetism observed here is thus qualitatively different to the recent observations of ferromagnetism arising due to uncompensated moments at the surface of, for example, antiferromagnetic (AF) EuRh$_2$Si$_2$ (40). Instead, it reflects an intrinsic instability of the underlying electronic structure which can be triggered by a pronounced self-doping of the system in response to its polar surface charge. From our extracted Luttinger areas, we estimate a total magnetisation, $M = (N^+ - N^-)\mu_B = (0.59 \pm 0.03)\mu_B$/unit cell.

As the wavefunctions of the surface states are mostly localised on the surface Pd layer (see SI Appendix, Fig. S2), this layer also hosts the largest moment (found to be 0.46 $\mu_B$ in our calculations, see Methods). Nonetheless, finite orbital mixing with the subsurface CoO$_2$ block means that the near-surface Co also inherits a finite, but much smaller, moment, found to be 0.12 $\mu_B$ in our calculations.

### Ferromagnetic surface of PdCrO$_2$

Finally, we show our measurements of the Pd-terminated surface of the sister compound, PdCrO$_2$ (Fig. 5). As in PdCoO$_2$, the bulk band, which is also responsible for the high bulk conductivity of PdCrO$_2$ (41), is evident as a steeply-dispersing state with the largest moment (found to be 0.46 $\mu_B$ in our calculations). Consistent with previous DFT calculations (35), we also find how additional near-$E_F$ surface states inherit a similar exchange splitting, forming the $\gamma$ and $\delta$ bands observed at the Brillouin zone centre. This electronic structure is consistent with previous measurements of the chromate (42). Moreover, there is an almost one-to-one correspondence with the surface states that we observe for the Pd-terminated surface of PdCoO$_2$, allowing us to again assign the $\alpha$ and $\beta$ bands as an exchange-split pair in PdCrO$_2$, and the $\gamma$-band as a spin-majority band, with its spin-minority partner being unoccupied. Excitingly, while the CoO$_2$ layer in PdCoO$_2$ is band insulating and non-magnetic, the CrO$_2$ layer in bulk PdCrO$_2$ is Mott insulating, and hosts local-moment $\uparrow$ $\downarrow$ order on the Cr sites (41). Combined with the analysis of PdCoO$_2$ presented above, however, our measurements indicate that PdCrO$_2$ nonetheless also supports ferromagnetism at its Pd-terminated surface.

### Discussion

Together, our findings demonstrate how electronic reconstructions at polar surfaces can be exploited to trigger incipient instabilities of the underlying quantum many-body system, here driving a Stoner transition at the Pd-terminated surfaces of PdCoO$_2$ and PdCrO$_2$. This suggests strategies for creating two-dimensional ferromagnets, a topic which has been attracting considerable recent attention in the field of van der Waals materials (43, 44). The co-existence of ferromagnetism with the inherent breaking of inversion symmetry at the surface further opens possibilities to realise significant Dzyaloshinskii-Moriya interactions, providing routes to stabilise modulated magnetic states (45).

Moreover, creating interfaces between disparate magnetic systems offers powerful opportunities for tailoring magnetic interactions (46). This is of both fundamental interest and potential technological applicability, for example enabling the electrical switching of magnetisation in ferromagnetic/antiferromagnetic bilayers (47). Our study indicates how such magnetic heterostructures can naturally be realised at the Pd-terminated surface of PdCrO$_2$. Targeted engineering of magnetic competition could be further aided by the flexibility of the delafossite oxide series. For example, electron doping on the Pd site of PdCrO$_2$ could be used to drive a Stoner transition of the bulk Pd layers, forming an intrinsic superlattice of...
two-dimensional itinerant ferromagnets and triangular-lattice
local-moment antiferromagnets. Polar interfaces of delafossites with other materials provide further routes to create and
manipulate rich electronic and magnetic phase diagrams in
these systems. More generally, our study further highlights the
powerful role that polar interfaces can be expected to
play not only in controlling electronic structures, but also
for determining the collective phases that can be stabilised,
opening routes for the targeted creation and manipulation of
multifunctional designer oxide heterostructures.

Note: After preparing our paper for publication, we be-
came aware of an independent study by spin-polarised scanning
tunnelling microscopy, which observed real-space signatures
of Stoner ferromagnetism at the Pd-terminated surface of
PdCoO₂, in agreement with the conclusions of our study drawn
from a momentum-space perspective (48).

Materials and Methods

Angle-Resolved-Photoemission. Single-crystals of PdCoO₂ and
PdCrO₂ were grown by a flux method in sealed quartz tubes
(26, 49). These were cleaved in situ at the measurement tem-
perature of T = 10 K. ARPES measurements were performed at
the I05 beamline of Diamond Light Source, UK, using a Scienta
B1000 electrostatic analyzer and variable light polarisations with photon
energies between 60 and 120 eV (50).

Density-functional theory. DFT calculations were performed using
the full-potential FPLO code (51–53), utilising the Perdew-Burke-
Ernzerhof (54) formalism and including spin-orbit coupling. The
surface electronic structure was calculated employing a symmetric
slab containing 9 Pd layers, with a vacuum gap of 15 Å. For the
inner layers of the slab, the bulk experimental crystal structure (34)
was used, while the surface atomic positions were relaxed. We note
that, for the unrelaxed surface, we do not stabilise a magnetic state.

By fully relaxing the topmost Pd layer to minimise forces on the
surface Pd atoms, we obtain a sizable increase of the Pd-O distance,
and find a stable ferromagnetic state with a magnetic moment of
0.55 μB/unit cell. The moment is predominantly carried by the
surface Pd (0.40 μB) with minor contributions from the subsurface
Co (0.10 μB) and O (0.04 μB) just below the surface. As shown in
SI Appendix Fig. S3, the peak at the Fermi level deriving from the
Pd-related surface state becomes considerably narrower for the
relaxed surface with the increased Pd-O distance compared to the
unrelaxed one. This leads to a strong increase (by about 50%) of the
DOS(EF) and the respective Pd 4d DOS, strongly favouring a magnetic
splitting of these states in a Stoner picture. The stability of the
ferromagnetic surface state slightly increases if not only the
surface Pd, but also the CoO₂ layer nearest the surface is relaxed,
increasing the magnetic moment to 0.62 μB/unit cell (Pd: 0.46 μB,
Co: 0.12 μB, O: 0.05 μB). These structural relaxations are used for
the calculations presented in the main text. For the DOS shown in
Fig. 4, a boxcar smoothing of 25 meV has been used to remove
unphysical spikes appearing in the calculated DOS for the supercell.

Experimentally, we find that the surface states at Ω are all
located below EF (Fig. 2g(i)), unlike for our supercell calculations.
In general, we note that the exact ordering of bulk and different
surface features in our calculations is sensitive to application of
a Hubbard U term on the Co sites, as well as an intrinsic off-
stoichiometry of the slab due to the polar nature of the structure.
Taking into account the strong Coulomb repulsion at the Co-site
in a mean field way, applying DFT+U (U = 4 eV (37)), the total
moment remains almost unchanged, but the contribution of Pd
increases sizably (Pd: 0.54 μB, Co: 0.05 μB, O: 0.04 μB). As a
consequence, this leads to a larger splitting in energy of the Pd
dominated surface states, as shown in SI Appendix Fig. S4, but
does not qualitatively influence any of the conclusions presented here.

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