Electronically driven spin-reorientation transition of the correlated polar metal Ca$_3$Ru$_2$O$_7$

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The interplay between spin–orbit coupling and structural inversion symmetry breaking in solids has generated much interest due to the nontrivial spin and magnetic textures which can result. Such studies are typically focused on systems where large atomic number elements lead to strong spin–orbit coupling, in turn rendering electronic correlations weak. In contrast, here we investigate the temperature-dependent electronic structure of Ca$_3$Ru$_2$O$_7$, a 4$d$ oxide metal for which both correlations and spin–orbit coupling are pronounced and in which octahedral tilts and rotations combine to mediate both global and local inversion symmetry-breaking polar distortions. Our angle-resolved photoemission measurements reveal the destruction of a large hole-like Fermi surface upon cooling through a coupled structural and spin-reorientation transition at 48 K, accompanied by a sudden onset of quasiparticle coherence. We demonstrate how these results from band hybridization mediated by a hidden Rashba-type spin–orbit coupling. This is enabled by the bulk structural distortions and unlocked when the spin reorient perpendicular to the local symmetry-breaking potential at the Ru sites. We argue that the electronic energy gain associated with the band hybridization is actually the key driver for the phase transition, reflecting a delicate interplay between spin–orbit coupling and strong electronic correlations and revealing a route to control magnetic ordering in solids.

Polar distortions in solids give rise to the well-known functionality of switchable macroscopic polarization in ferroelectrics (1, 2) and, when combined with strong spin–orbit coupling, can mediate giant spin polarizations of electronic states (3, 4). While typically found in insulators, ferroelectric-like distortions can remain robust against increasing itinerance, giving rise to so-called “polar metals” (5–10). Ca$_3$Ru$_2$O$_7$ is the bilayer member of the Ca$_{n+1}$Ru$_n$O$_{3n+1}$ Ruddlesden–Popper series. The small ionic size of Ca induces large coupled rotations and tilts of the RuO$_6$ octahedra that make up the perovskite-like building blocks of this structure, generating a noncentrosymmetric crystal structure (space group 36: Bb02, m; Fig. L4) (11, 12). A symmetry-allowed trilayer coupling between the two nonpolar octahedral tilt ($X$) and rotation ($X$) modes and a polar lattice mode ($\Gamma$) further mediates polar distortions, just as in Ca$_3$Ti$_2$O$_7$ and Ca$_3$Mn$_2$O$_7$, which are part of the well-known class of improper ferroelectrics (13–15). Unlike these sister compounds, however, Ca$_3$Ru$_2$O$_7$ is not an insulator. Its in-plane resistivity decreases upon cooling from room temperature, albeit with a linear temperature dependence indicative of a so-called “bad metal” state (16, 17).

At $T_N = 56$ K, the system undergoes a Néel ordering transition, where the spins align ferromagnetically within each bilayer, oriented along the $a$ axis, and are antiferromagnetically coupled between bilayers (18, 19). At a second phase transition at $T_S = 48$ K, the spins reorient to lie parallel to the in-plane $b$ axis (11, 18, 19). Simultaneously, an isostructural transition leads to a squashing of the unit cell along the $c$ direction (11). The resistivity exhibits a sudden jump on cooling through $T_S$, but, although its absolute value remains relatively high ($\rho_{ab}(5K) \approx 50 \mu\Omega cm$), the in-plane resistivity recovers a metallic temperature dependence to low temperature (16, 17). A rich noncollinear magnetic texture has been observed under the application of magnetic fields (20), pointing to an important role of spin–orbit coupling combined with the noncentrosymmetric crystal structure, while strong electronic correlations are expected to also play an important role in shaping the electronic and magnetic properties of this system (the single-layered sister compound Ca$_2$RuO$_4$ is a Mott insulator) (21).

Ca$_3$Ru$_2$O$_7$ thus stands as a particularly rich example of a correlated polar metal. Gaining a comprehensive understanding of its transport, magnetic, and electronic properties has, however, proved elusive to date. Here, we study its temperature-dependent electronic structure by angle-resolved photoemission spectroscopy (ARPES) (Materials and Methods). Our low-temperature measurements are shown in Fig. 1. Consistent with refs. 22 and 23, we find a significant spectral weight in the ruthenate | magnetism | correlated oxide | Rashba spin–orbit | angle-resolved photoemission

Significance

Methods to stabilize and control magnetic ordering in solids are strongly desired both for fundamental studies and to realize new spintronic technologies. The orientation of ordered magnetic moments is typically set by details of the crystalline environment in which they reside. Here, we report the discovery of a form of magnetic anisotropy which is instead driven by a striking reconfiguration of the underlying ferromagnetic system. We show for the oxide material Ca$_3$Ru$_2$O$_7$ how this arises from the interplay of spin–orbit coupling, local distortions of the crystal structure, and pronounced electronic correlations. Our findings suggest materials design approaches for manipulating magnetic textures and open pathways to creating large magnetoelastic-type couplings in solids.

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valence bands associated with the Ru $t_{2g}$ orbitals, but almost vanishing spectral weight at the Fermi level (Fig. 1B). Nonetheless, sharp features are still evident on low-energy scales ($\lesssim$50 meV; Fig. 1C), indicative of well-defined Fermi liquid-like quasiparticles, albeit with very low quasiparticle residue.

Our measured electronic structure exhibits a pronounced twofold symmetry throughout the Brillouin zone. At the $M_x$ point, an electron band intersects the Fermi level, giving rise to a small $M_z$-centered electron pocket (just visible in Fig. 1D). This derives from a band whose occupied bandwidth is only $\lesssim$15 meV, immediately below which another band disperses downward to higher binding energy (Fig. 1D). The electronic structure is markedly different along the $\Gamma$–$M_y$ direction. A dispersive state is evident, intersecting the Fermi level away from the Brillouin zone boundary (Fig. 1C). An extremely weak feature is also visible with approximately the same $k_F$ but opposite Fermi velocity (confirmed using measurements with different light polarization; Fig. 1C, Left Inset), indicating that this is the top of a $\Lambda$-shaped band which barely grazes the Fermi level.

Fermi surface measurements (Fig. 1D) show how this disperses along the perpendicular in-plane direction to form a very narrow boomerang-shaped hole-like Fermi surface, centered along the $\Gamma$–$M_x$ line but displaced away from the Brillouin zone boundary.

We thus assign the ground state of Ca$_3$Ru$_2$O$_7$ to be a low carrier-density compensated semimetal, in agreement with the small Fermi pockets found previously by Shubnikov–de Haas studies (17). An additional set of sharp and rather flat states is visible in Fig. 1C and D closer to the Brillouin zone center. These bands display a shallow local minimum at $\Gamma$, disperse upward toward their band maxima which are located $\approx$ 10 meV below the Fermi level (22), and then disperse back to higher binding energies, giving them a characteristic “M-shaped” appearance. They are also visible as increased spectral weight close to the Brillouin zone center in constant energy maps for energies below the Fermi level in Fig. 1D. Measurements using different light polarizations (SI Appendix, Fig. S1) indicate that there are at least three distinct states here, pointing to a rich multiband near-$E_F$ electronic structure. To further explore this, we show in Fig. 1E density-functional theory (DFT) calculations of the low-temperature electronic structure (Materials and Methods), renormalized in energy by a factor of $\approx$7.

The strong bandwidth renormalization needed to achieve a reasonable agreement with the measured low-energy electronic structure indicates that Ca$_3$Ru$_2$O$_7$ is a highly correlated metal, consistent with its low-quasiparticle residues. In such a complex multiband system as this, momentum- and orbital-dependent self-energies may generically be expected (22), and a simple bandwidth scaling cannot be expected to capture in detail the full influence of many-body interactions on the electronic structure. Indeed, the experimental Fermi velocities of the boomerang-shaped states crossing $E_F$ are renormalized only by a factor of $\approx$4 compared to corresponding features in the DFT, while the flat bands appear to require significantly higher renormalizations. The results shown here thus motivate future study of interaction effects in Ca$_3$Ru$_2$O$_7$ by state-of-the-art correlated electronic structure calculations, of the form that have recently proved extremely successful in describing the single-layer Sr-based sister compound (24, 25). Nonetheless, we note that a global bandwidth scaling of the calculated DFT still does a remarkably good job in reproducing the key experimental band structure features observed here, including the $M_z$-centered electron pocket, the
hole-like $\Lambda$-band offset from the $M_y$ point (located just below $E_F$ in the calculations), and the fully occupied M-shaped states just below the Fermi level.

The marked difference in the calculated electronic structure along the $\Gamma$–$M_x$ and $\Gamma$–$M_y$ directions demonstrates that the large anisotropy in the measured electronic structure along these directions can be fully explained on the basis of the orthorhombic crystal structure, without invoking an electronically driven nematicity as reported in a very recent study (23). Moreover, our calculations indicate that the flattened M-shaped dispersion at the Brillouin zone center, clearly evident in the experimental electronic structure in Fig. 1C, is the result of a band hybridization between the top of a hole-like band and the bottom of an electron-like band, with a gap opening at the Fermi level. We show below that this band hybridization is in fact key to understanding much of the important physics of $\text{Ca}_3\text{Ru}_2\text{O}_7$.

Fig. 2A shows the temperature-dependent evolution of the electronic structure through the two phase transitions. For temperatures below the structural and spin-reorientation transition, $T_S$, the spectral linewidths gradually broaden with increasing sample temperature (Fig. 2B), as can generically be expected from electron–electron and electron–phonon interactions. While $\text{Ca}_3\text{Ru}_2\text{O}_7$ is sometimes considered to be in an insulating state above $T \approx 30$ K, our spectroscopic measurements clearly demonstrate that well-defined quasiparticle-like states persist up to $T_S$. In contrast, we find a sudden and dramatic loss of quasiparticle coherence when warming through $T_S$, with extremely broad linewidths above the transition indicative of a high scattering rate. The electronic structure is also markedly altered across the transition. While the transition at $T_S$ is known to be first order (16, 26, 27), the corresponding thermal hysteresis is small (26), and we do not observe it (or signatures of coexisting domains) within the temperature resolution of our experiments ($\approx 2$ K). While weak and broad remnants of the original Fermi crossings still persist above $T_S$ (evident as shoulders at $k_y \approx \pm 0.55 \ \AA^{-1}$ in Fig. 2B), the state around the Brillouin zone center now no longer appears to bend back to form an M-shaped dispersion. Rather, it crosses directly through $E_F$, forming a large hole-like Fermi surface centered at $\Gamma$ (Fig. 2C), consistent with a known transition in the Hall coefficient from large and negative values at low temperatures to small and positive values above $T_S$ (28, 29). We note in passing that this high-temperature Fermi surface is twofold rather than fourfold symmetric, again reflecting the large orthorhombicity of the lattice. The evident loss of quasiparticle coherence, despite the pronounced increase in carrier density, upon warming through $T_S$ is interesting and requires further detailed study. Qualitatively it may be related to the multiband nature of $\text{Ca}_3\text{Ru}_2\text{O}_7$.

The creation of new Fermi pockets, and the additional density of states associated with these, will open new channels for inter- and intraband scattering. Moreover, there are a large number of bands with turning points expected in the vicinity of the Fermi level; recent work has emphasized the potential for strong scattering for all states in the Brillouin zone to be associated with the presence of hot spots localized in $k$ space (30). We note, however, that this is a complex system with both a structural and a magnetic transition occurring here, and we do not exclude that additional contributions from electron–lattice and electron–magnon coupling could contribute to the changes observed experimentally.

We focus below on the origin of the unusual moment orientation-dependent Fermi surface transition at $T_S$. Our measurements indicate that once the large, zone-centered Fermi surface is established upon warming through $T_S$, the electronic structure evolves only gradually, with no further qualitative changes as the temperature is increased to above the 56-K Néel transition (Fig. 2A and B). Such an insensitivity to the antiferromagnetic ordering at $T_N$ might naively suggest that it is the structural, rather than spin-reorientation, aspect of the phase transition at $T_S$ which underpins the dramatic changes in electronic structure observed there. We show below, however, that this is in fact not the case.

Fig. 3 shows the electronic structure calculated by DFT for the experimental crystal structures above and below the structural transition at $T_S$ and for the spin oriented along different in-plane crystallographic directions. For the spin moment oriented along the $a$ axis and for the 50-K crystal structure (Fig. 3A, found for $T_S < T < T_N$), the hybridization of the electron- and hole-like bands at the Brillouin zone center is evidently suppressed. This gives rise to the large Fermi surfaces observed experimentally around the Brillouin zone center. A similar lack of band hybridization of the near-$E_F$ states is found when considering the equivalent spin configuration but for the low-temperature crystal structure (Fig. 3B), pointing to an insensitivity of the low-energy electronic structure to the structural component of the transition at $T_S$. In contrast, when the moment is rotated to lie along
Fig. 3. Asymmetric spin-orbit-driven band hybridization. (A) Calculated electronic structure from density-functional theory for the experimental crystal structure at \( T = 50 \) K (\( T > T_s \)) and with the spin moments aligned along the in-plane \( a \) axis, as observed experimentally for \( T_s < T \leq T_e \). (B and C) Equivalent calculations for (B) the low-temperature crystal structure (for \( T = 8 \) K) with spin moments still oriented along the \( a \) axis and (C) the low-temperature crystal structure with spin moments along the \( b \) axis, as observed experimentally for \( T < T_s \). The schematics in A–C show representative views of the Ru sites in a RuO\(_2\) bilayer, showing the tilt and resulting local polarization (purple arrows) and the spin moment orientation (green arrows). C, Inset shows the corresponding electronic structure calculated without including spin-orbit coupling, indicating that the hybridization gap which opens at the Fermi level is between spin-majority-like (red) and minority-like (blue) Ru \( t_{2g} \) states and opens via spin-orbit coupling. (D) The magnitude of the hybridization gap grows smoothly as the moment is rotated away from the \( a \) axis within both \( ab \) and \( ac \) (green points) planes.

The relevant hybridized states at the Fermi level here derive from spin-minority–like and spin-majority–like Ru \( t_{2g} \)-derived bands (Fig. 3C, Inset). The details of the low-energy DFT band structure are sensitive to the precise degree of exchange splitting, which varies with the choice of exchange-correlation functional and is larger when using a generalized gradient approximation functional than using a local density approximation (LDA) one (see SI Appendix, Fig. S2 for a comparison). We find that the LDA calculation better describes the experimental data, with the large hole-like pocket present at \( \Gamma \), although the electron pocket there is not clearly seen in the dispersions measured above \( T_s \) (Fig. 2A), and the experimental situation may in fact be best reflected by an exchange splitting that is between the results of these two calculations. We stress, however, that both functionals show qualitatively the same behavior (SI Appendix, Fig. S2), namely a hybridization of zone-center electron and hole-like bands below \( T_s \). This hybridization is mediated by spin–orbit coupling (Fig. 3C), with a gap that opens throughout the Brillouin zone (Fig. 1D and cf. Fig. 2C) and develops gradually as the spin moment is rotated away from the \( a \) axis (Fig. 3D), but is almost invariant when the moment is rotated between the \( b \) and \( c \) axes (SI Appendix, Fig. S3).

We attribute this spin moment-dependent gapping to a local breaking of inversion symmetry driven by the \( X^\alpha \) tilt mode of the RuO\(_6\) octahedra (14, 15). The vertically stacked octahedra of the perovskite bilayer develop hinge-like distortions about the shared apical oxygen, which reverse in direction between neighboring in-plane sites as shown schematically in Fig. 3. Each pair of outer apical oxygens is displaced in the opposite direction to the shared central apical oxygen. This leads to a local polarization oriented along the tilt direction (the \( a \) axis here) with an antiferro-type ordering within the \( ab \) plane. No net polarization is generated along \( a \). Locally, however, an asymmetric spin–orbit coupling of the Rashba type (31–33), \( \mathcal{H}_R \propto \mathbf{p} \cdot (\mathbf{S} \times \mathbf{E}) \), can generically be expected, where \( \mathbf{p} \) is the electron momentum, \( \mathbf{E} \) is an effective internal electric field along the \( a \) axis representing the local inversion asymmetry, and \( \mathbf{S} \) is the electron spin of the itinerant states, which are fixed along one of the in-plane crystallographic axes by the magnetic moment orientation. This provides a natural explanation for the hybridization of intraband spin-majority and -minority bands observed here. For the spin moment aligned along the \( a \) axis (Fig. 3A and B, \( \mathbf{S} \times \mathbf{E} = 0 \)), the Rashba-type term cannot act and thus no hybridization would be expected from this form of spin–orbit coupling. In contrast, at the spin reorientation transition where the moment aligns along the \( b \) axis (Fig. 3C), the Rashba-like spin–orbit interaction becomes active (\( \mathbf{S} \times \mathbf{E} \neq 0 \)), enabling the band hybridization.

When the hybridization is allowed, the large hole-like Fermi surface thus becomes gapped. The corresponding hybridization energy scale in our DFT calculations is on the order of 50 meV. In reality, however, the true hybridization gap is renormalized to significantly smaller values due to the strong electronic correlations of this system. We estimate that the true gap magnitude in the low-temperature phase is \( \approx 10 \) to 15 meV, comparable to a 13-meV gap (originally attributed to a pseudogap) which was seen to open in optical spectroscopy measurements upon cooling through \( T_s \) (34). The gap size is thus comparable to thermal energy scales at \( T_s \). We propose that at the Néel transition, the fluctuating moments of the paramagnetic state above \( T_s \) develop a long-range order, with the spin orientation fixed along the \( a \) axis by conventional magnetocrystalline anisotropy effects. There is no electronic incentive for orienting the moment along the \( b \) axis (as found experimentally for \( T < T_s \)), the electron and hole bands at the zone center develop a strong hybridization. The hybridization develops gradually as the moment is rotated away from the \( a \) axis in both \( ab \) and \( ac \) planes (Fig. 3D). This demonstrates that it is the moment orientation and not the structural changes at \( T_s \) that mediates the opening of a band gap at the Fermi level observed here experimentally (Figs. 1E and 3C).

*The relative spin orientation is reversed from bilayer to bilayer, due to the antiferromagnetic coupling between bilayers. Nonetheless, the interbilayer hopping is small, and so an effective ferromagnetic description is a good starting point for considering local interactions that can hybridize these states.*
Materials and Methods

Single-Crystal Growth. Single crystals of Ca$_2$Ru$_2$O$_7$ were grown using a floating-zone method in a mirror furnace (Canon Machinery; model SCI-MDH) (38). The crystal growth was performed in an atmosphere of a mixture of Ar and O$_2$ (Ar : O$_2$ = 85 : 15). In general, antiphase domains can be expected and are visible via contrast in polarized-light optical microscopy (SI Appendix, Fig. S4). We used this to select samples which are single domain over a scale of at least 500 × 500 μm$^2$. The monodomain nature of our resulting samples is further evident in our measured Fermi surfaces, which show a clear twofold symmetry with no signatures of rotated features coming from different domains.

Angle-Resolved Photoemission. ARPES measurements were performing using the Bloch beamline of the MAX IV synchrotron and the I05 beamline of Diamond Light Source. Measurements were performed using p-polarized 22-eV synchrotron light. Additional data measured using s-polarized light are shown in SI Appendix, Fig. S1. The samples were cleaved in situ and measured at temperatures between 6 and 70 K, as specified in Figs. 1 and 2. Temperature-dependent datasets were repeated on multiple samples and via both warming and recooling cycles, confirming that the changes shown in Fig. 2 are intrinsic and are not a result of sample aging upon temperature cycling.

Density-Functional Theory. DFT calculations were performed using the local spin density approximation (LSDA) exchange-correlation functionals, as implemented in the full-potential local-orbital minimum-basis code (39–41). Additional calculations were performed with the Perdew–Burke–Emzerhof (PBE) functional (42) and are shown in SI Appendix, Fig. S2. The experimental crystal structures were used in all cases (11), and spin–orbit coupling was included throughout. The Brillouin zone sampling employed a $k$ mesh of at least 16 × 16 × 6 $k$ points. Additional calculations were performed using WIEN2K (43) and gave consistent results. We employed spin–orbit magnetic calculations, neglecting the antiferromagnetic coupling between neighboring bilayers. Given the ferromagnetic ordering within the bilayer and the weak coupling between bilayers, this does not affect any of the key conclusions drawn from our calculations, as confirmed by the broad agreement between our calculations and the experimentally measured electronic structure shown in Fig. 1E.

Data Availability. The data that underpin the findings of this study are available from the University of St Andrews research portal: https://doi.org/10.17636/eb89b8e0e-a6f3-4117-87c7-b1df1607dcb1 (44).

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