Spontaneous cycloidal order mediating a spin-reorientation transition in a polar metal

C. D. Dashwood, L. S. I. Veiga, Q. Fu, J. G. Vale, D. G. Porter, S. P. Collins,
P. Manuel, D. D. Khalyavin, F. Orlandi, R. S. Perry, R. D. Johnson, and D. F. McMorrow

1London Centre for Nanotechnology and Department of Physics and Astronomy, University College London, London, WC1E 6BT, UK
2Diamond Light Source, Harwell Science and Innovation Campus, Didcot, Oxfordshire, OX11 0QX, UK
3ISIS Neutron and Muon Source, STFC Rutherford Appleton Laboratory, Didcot, Oxfordshire, OX11 0QX, UK
4Department of Physics and Astronomy, University College London, London, WC1E 6BT, UK

We show how, in a polar crystal with uniform Dzyaloshinskii-Moriya interaction, modulated order can spontaneously emerge when magnetic anisotropies compete at a spin-reorientation transition. Combining neutron and resonant x-ray scattering, we reveal that the spin-reorientation in Ca$_3$Ru$_2$O$_7$ is mediated by an incommensurate cycloid whose eccentricity evolves smoothly with temperature. Our results suggest that the application of a magnetic field continuously generates higher harmonic modulations, establishing a rich phase diagram and providing a new, unified interpretation of incommensurate structures previously seen under doping and magnetic field.

Thermally-driven spin-reorientation transitions (SRTs) have been a source of enduring interest since the discovery of the Morin transition in hematite [1, 2]. They involve a change in magnetic symmetry between two ordered states, and are generally driven by competing magnetic anisotropies. As well as hematite, they are well studied in the orthoferrites, where they show great promise for magnetic memory applications [3–7].

The bilayer ruthenate Ca$_3$Ru$_2$O$_7$ has recently received much attention as a rich example of a correlated, multiband, magnetic metal [8–19] on the verge of a Mott metal-insulator transition [20, 21]. This richness is exemplified by an SRT which is intricately coupled to the crystal structure and fermiology. It has been reported that at $T_S = 48$ K the collinear Ru moments undergo a reorientation from the b (AFM$_b$, see Fig. 1b) to a axis (AFM$_a$, Fig. 1d) [13, 14]. In both phases the spins are coupled ferromagnetically (FM) within each bilayer and antiferromagnetically (AFM) between the bilayers, with propagation vector $(0, 0, 1)$ [9, 13, 14]. The reorientation coincides with a rapid change in the lattice parameters [9] and an increase in the resistivity caused by a gapping of most of the Fermi surface [11, 16, 18]. It has been proposed that the energy gain from this Fermi surface reconstruction is actually the driver of the SRT, identifying a new “magnetolectric” anisotropy in metals [18]. Crucial to this mechanism are the non-centrosymmetric crystal structure (with polar space group $Bk2_1m$ [9]) and sizeable spin-orbit coupling [15].

In this Letter, we show that these ingredients are responsible for richer physics at this transition than previously thought, resulting in an SRT that is highly distinct from those in centrosymmetric insulators such as hematite or the orthoferrites. Instead of a direct transition between the two collinear magnetic structures, we find that the SRT proceeds via an incommensurate cycloid, that continuously varies between the end states and decomposes into them in the commensurate limits. Symmetry analysis reveals that the cycloid is stabilised by a uniform Dzyaloshinskii-Moriya interaction (DMI), resulting from spin-orbit coupling within the polar crystal structure, which competes with the easy-axis anisotropies through the transition. We demonstrate how the competition that gives rise to the mediating order also makes it highly sensitive to perturbation by a magnetic field, and reinterpret previously observed field-induced incommensurate order [15] as second harmonic modulations of the fundamental cycloid.

High-quality single crystals of Ca$_3$Ru$_2$O$_7$ were grown by the floating zone method, and characterised by x-ray powder diffraction, resistivity measurements and energy dispersive x-ray spectrometry. Twin domains were identified with polarised light microscopy, and single-domain pieces were cut from larger crystals using a wire saw. Measurements were performed on multiple crystals from different growth batches with consistent results. The neutron and x-ray data presented below are all from same crystal, which was aligned by Laue diffraction. Neutron scattering measurements were performed at the WISH instrument of the ISIS Neutron and Muon Source [22], and resonant x-ray scattering measurements at beamline 116 of the Diamond Light Source. Further experimental details can be found in the Supplemental Material.

We first report the discovery of bulk incommensurate order in Ca$_3$Ru$_2$O$_7$ from neutron scattering measurements. Figure 1a shows reciprocal-space maps at temperatures around $T_S$. Well above and below $T_S$ (top and bottom panels) a single peak can be seen at $q = (0, 0, 1)$ reciprocal lattice units (r.l.u.) which arises from the known AFM$_a$ and AFM$_b$ structures. As unpolared neutron scattering is sensitive to the component of the moment perpendicular to $q$, we are sensitive to the full moment in both phases and the lower intensity in the former is indicative of a smaller moment, consistent with previous reports [14]. Strikingly, close to $T_S$ (middle panel) the central peak is strongly suppressed, and satellites can be seen at incommensurate positions $(\pm \delta, 0, 1)$ with $\delta \approx 0.023$ r.l.u. Satellite peaks closely spaced around
FIG. 1. Incommensurate satellites at the spin-reorientation from neutron scattering. (a) Reciprocal space maps showing satellite peaks $(\pm \delta, 0, 1)$ around the $(0, 0, 1)$ magnetic peak over a narrow temperature range around $T_S = 48 \text{ K}$. (b) Crystal and magnetic structure of Ca$_3$Ru$_2$O$_7$ below $T_S$ with collinear spins pointing along the $b$ axis. (c) Integrated intensity of the $(0, 0, 1)$ (blue to red, with blue representing the AFM$_b$ and red the AFM$_a$ phase) and $(\pm \delta, 0, 1)$ (purple) peaks as a function of temperature, plotted alongside the in-plane resistivity $\rho_{ab}$ (black). (d) Crystal and magnetic structure of Ca$_3$Ru$_2$O$_7$ for $T_S < T < T_N$ with spins pointing along the $a$ axis.

In the incommensurate phase, the magnetic structure is intimately linked to the electronic behaviour. The boundaries of the incommensurate phase correspond to changes of slope in $\rho_{ab}$, revealing how the magnetic structure is intimately linked to the electronic behaviour.

Having established the existence of an incommensurate phase in the vicinity of the SRT, we now turn to resonant x-ray scattering to unravel its nature. Tuning the incident x-rays to the Ru $L_2$ absorption edge causes a resonant enhancement of the scattered intensity, which combined with polarisation analysis of the scattered beam results in an element-selective probe of long-range magnetic order. Figure 2a shows rocking scans of the $(0, 0, 5)$ peak in two orthogonal polarisation channels. X-rays polarised in the scattering plane are denoted $\pi$, while those orthogonal to it $\sigma$ (see Fig. 2b). For incident $\sigma$ x-rays, resonant scattering from a magnetic moment occurs only in the crossed $\sigma - \pi'$ polarisation channel [27], so the dominant intensity in this channel verifies the magnetic origin of the peak. The remnant intensity in the $\sigma - \sigma'$ channel is due to leakage through the analyser (see the Supplemental Material).

In contrast to neutron scattering, resonant x-ray scattering in $\sigma - \pi'$ is sensitive to the component of the moment parallel to $k_F$. More information about the magnetic structure can therefore be obtained by rotating the sample through an azimuthal angle $\Psi$ in order to vary the component projected along $k_F$ (see Fig. 2b). Azimuthal dependences of the $(0, 0, 5)$ peak are shown in Fig. 2c. For basal-plane collinear structures, calculation of the resonant cross-section gives an intensity $\propto \cos^2(\Psi + \phi)$ (solid lines in Fig. 2c) where $\phi$ is the rotation of the moments away from the $a$ axis [13]. At 40.4 K it can be seen that $\phi = 90^\circ$ and the moments are along $b$, while at 55.6 K $\phi = 0^\circ$ and the moments are along $a$. The upper and lower panels in Fig. 2d show $h$ scans through $(0, 0, 5)$ as a function of temperature for two azimuths, sensitive to the $(\Psi = -90^\circ)$ and $(\Psi = -180^\circ)$ components of the moments respectively. The spin reorientation is clearly identified by the transfer of commensurate intensity between the azimuths. The satellite peaks are also visible at both azimuths, and intriguingly have subtle temperature dependences to their wavevectors and intensities. We now analyse these satellites in more detail.

Figure 3a shows $h$ scans in both polarisation channels, confirming the magnetic origin of the satellites. In order to determine the structure of the incommensurate phase we performed a detailed investigation of the azimuthal dependence of the satellites. Representative dependences are shown in Fig. 3b. All of the dependences are sinusoidal, but show dramatic changes in peak-to-peak amplitude and phase, evidencing a remarkable evolution of the structure over a small temperature window. Unlike in the commensurate phases where the intensity goes to zero when $k_F$ is perpendicular to $m$, here we see a finite intensity at all $\Psi$. This is a clear indication of a non-collinear rotating structure, with a component of the moment always parallel to $k_F$. We calculated the cross-section for all possible modulated states using the
FIG. 2. Spin reorientation from resonant x-ray scattering. (a) Rocking curves of the (0,0,5) peak at 10.5 K in the \( \sigma - \pi' \) (orange) and \( \sigma - \sigma' \) (green) polarisation channels, confirming its magnetic origin. (b) Experimental geometry, showing incident x-rays with wavevector \( \mathbf{k}_i \) (red arrow) scattering from a magnetic moment \( \mathbf{m} \) (blue arrow) to wavevector \( \mathbf{k}_f \). The incident x-rays are polarised horizontally, normal to the scattering plane (\( \sigma \) polarised, green arrow), and the scattered x-rays are polarised either in the scattering plane (\( \pi' \), orange) or normal it (\( \sigma' \), green). The azimuth \( \Psi \) is varied by rotating the sample around the scattering vector \( \mathbf{q} = \mathbf{k}_f - \mathbf{k}_i \) (black arrow). (c) Azimuthal scans of the (0,0,5) as a function of temperature at \( \Psi = -90^\circ \) (top panel, sensitive to the component of the moment along \( \mathbf{b} \)) and \( \Psi = -180^\circ \) (lower panel, sensitive to the component along \( \mathbf{a} \)). The intensity is plotted on a log scale.

MAGNETIX package [28] and found that a cycloid with moments rotating in the \( \mathbf{a} - \mathbf{b} \) plane, maintaining the FM coupling within bilayers and AFM coupling between bilayers, is uniquely consistent with our data.

To understand the temperature evolution of the magnetic structure, we developed a model in which the cycloid is decomposed into two spin-density wave components \( \pi/2 \) out-of-phase, that in the commensurate limits are equivalent to the AFM\(_b\) and AFM\(_a\) structures. The only free parameters are the amplitudes of these components, \( M_b \) and \( M_a \), which describe the elongation of the envelope of the cycloid along the \( \mathbf{b} \) and \( \mathbf{a} \) axes respectively. We fit the azimuthal dependences using MAGNETIX (solid lines in Fig. 3b) and found that this simple model provides a remarkably accurate description of the data at all temperatures. The fits can be intuitively understood by neglecting the small \( h \) component of the wavevector, which simplifies the dependence to \( \propto (M_b \sin \Psi)^2 + (M_a \cos \Psi)^2 \). It can then be seen that the peak-to-peak amplitude of the oscillations, \( M_b^2 - M_a^2 \), is directly related to the eccentricity of the cycloid, while the phase depends on whether \( M_b \) or \( M_a \) is larger. The fitted values of the amplitudes are shown in Fig. 3c (including fits to the commensurate dependences like those in Fig. 2c). In the commensurate phases only one of the components is present, as expected. In the incommensurate phase, by contrast, both amplitudes are finite and vary with temperature. This describes the magnetic structure shown schematically in Fig. 3d, where the envelope of the cycloid transitions from elongated along \( \mathbf{b} \), to circular, to elongated along \( \mathbf{a} \). Our x-ray data has therefore revealed a complex and evolving cycloidal magnetic structure which mediates the SRT.

Theoretical justification of this model is provided by a symmetry analysis of terms in the free energy (full details can be found in the Supplemental Material). The AFM\(_b\) and AFM\(_a\) phases can each be associated with a one-dimensional order parameter, \( \mu \) and \( \rho \). The polar structure of \( \text{Ca}_3\text{Ru}_2\text{O}_7 \) allows the Lifshitz-type invariant \( \mu(\partial \mu/\partial y) - \rho(\partial \rho/\partial y) \) in the free energy. Such invariants describe instabilities towards incommensurate modulated states [26, 29, 30] including the cycloid observed here. The microscopic origin of the Lifshitz invariant lies in the DMI, which competes with the easy-axis anisotropies to select the ground state of the system. Away from \( T_S \), the easy-axis anisotropies dominate and preclude the formation of a modulated state, leading to the AFM\(_b\) or AFM\(_a\) phase. In the vicinity of the SRT, however, the easy-axis anisotropies gradually change to \( \mathbf{a} \) to \( \mathbf{b} \), possibly due to a spin-orbit mediated gapping of the Fermi surface [18]. In this region, we expect minimal or easy-plane anisotropy, allowing the uniform DMI to dominate and stabilise the cycloidal phase.

The competition that gives rise to the mediating cycloid should make it highly sensitive to perturbation. To demonstrate this, we performed a neutron scattering experiment on \( \text{Ca}_3\text{Ru}_2\text{O}_7 \) with a magnetic field applied along the \( \mathbf{b} \) axis. The resulting phase diagram is shown in Fig. 4, revealing that the field rapidly increases the temperature region over which the incommensurate phase is stabilised. Our data also provides a new interpretation of incommensurate peaks at \( (\pm \Delta, 0, 0) \) measured with small angle neutron scattering (SANS) under magnetic fields [15], which can now be readily understood as field-
induced second harmonics of the fundamental cycloidal order. The connection to the magnetic satellites that we observe can be seen by doubling our wavevector \((\delta,0,1)\) and then projecting it back into the first Brillouin zone through subtraction of the lattice vector \((0,0,2)\), giving \((2\delta,0,0) \approx (\Delta,0,0)\) [31]. We did not directly observe the second harmonic satellites in our experiment, as the incident long-wavelength neutron flux was insufficient to measure at such high d-spacing. However, the appearance of second harmonics under magnetic fields is naturally explained by a phase-modulation of the cycloid stabilised by symmetry-allowed terms in the free energy (see the Supplemental Material), avoiding the need for higher-order Lifshitz-type terms which couple AFM and field-induced FM order parameters [15]. This phase modulation corresponds to the spins bunching along the field direction in order to reduce their Zeeman energy, shown schematically by the purple arrows in Fig. 4. In our scenario, a net magnetisation thus develops as higher harmonics are generated continuously from the zero-field cycloid, in the absence of any metamagnetic transition. Such behaviour is reminiscent of the highly robust, tuneable soliton lattices seen in chiral helimagnets under field [32].

Within this framework, we can also explain previous observations of incommensurate structures in doped \(\text{Ca}_3\text{Ru}_2\text{O}_7\) [33–35]. Here, a reduced anisotropy from the introduction of magnetic dopants should allow an easier turning of the moments away from their easy-axis by the DMI, stabilising cycloidal structures with shorter repeat distances and over larger temperature ranges.

Our analysis therefore unifies previously disparate behaviours of this correlated, multi-band, polar metal, revealing a highly rich phase diagram and providing vital information for the development of a conclusive microscopic theory. Further, our work stimulates the search for other modulated magnetic textures stabilised by the DMI in non-centrosymmetric crystals when magnetic anisotropies compete. This search may prove especially fruitful in systems with chiral crystal structures, where the DMI is responsible for the formation of topological skyrmion lattices [36–38], or in insulating ferroelectrics, where it is responsible for multiferroic behaviour [39–41]. We have also shown how magnetic fields can be used to finely control the cycloidal structure. Given the strong coupling between the structural, electronic and magnetic degrees of freedom in correlated oxides, one might imagine the possibility of using mechanical or electrical stimuli as tuning parameters, with profound applications in magnetic memory and spintronics.

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FIG. 4. Phase diagram for a magnetic field along the $b$ axis from neutron scattering. The colour scale is the integrated intensity of the $(\delta, 0, 1)$ peak, with the AFM$_b$, AFM$_a$ and phase-modulated incommensurate cycloid (PM-ICC) phases marked. The black dashed line encloses the region over which peaks at $(\Delta, 0, 0) \approx (2\delta, 0, 0)$ were seen in a previous SANS measurement [15]. The offset in the lower phase boundaries is most likely due to the low intensity of the satellites in this region and the difficulty resolving them from the direct beam in the SANS measurement. The purple arrows are a cartoon of the spin distribution in the $a - b$ plane in the PM-ICC phase, depicted with a circular envelope for clarity.

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* cameron.dashwood.17@ucl.ac.uk
† d.mcmorrow@ucl.ac.uk

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Supplemental Material for
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C. D. Dashwood,1,* L. S. I. Veiga,1 Q. Faure,1 J. G. Vale,1
D. G. Porter,2 S. P. Collins,2 P. Manuel,3 D. D. Khalyavin,3
F. Orlandi,3 R. S. Perry,1 R. D. Johnson,4 and D. F. McMorrow1,†

1London Centre for Nanotechnology and Department of Physics and Astronomy,
University College London, London, WC1E 6BT, UK
2Diamond Light Source, Harwell Science and Innovation Campus,
Didcot, Oxfordshire, OX11 0DE, UK
3ISIS Neutron and Muon Source, STFC Rutherford Appleton Laboratory,
Didcot, Oxfordshire, OX11 0QX, UK
4Department of Physics and Astronomy,
University College London, London, WC1E 6BT, UK
FIG. S1. Sample characterisation. (a) Polarised light microscope image of the Ca$_3$Ru$_2$O$_7$ single crystal used in this study. Twin domains, corresponding to swapped $a$ and $b$ axes, are visible as light and dark stripes running diagonally along $(1, \bar{1}, 0)$ down the sample. The red outline marks the single-domain region that was cut out with a wire saw and used in the neutron and x-ray experiments. The crystallographic axes are marked. (b) Powder x-ray diffraction pattern of a ground crystal from the same batch as that in a, showing single-phase Ca$_3$Ru$_2$O$_7$ with no impurities. Rietveld refinement was performed in the $B\bar{6}2_1m$ space-group setting using the PROFEX software [1] and yielded lattice parameters $a = 5.3836(3)$ Å, $b = 5.5174(4)$ Å, $c = 19.5629(8)$ Å, with $R_{wp} = 4.12\%$ and $R_{exp} = 1.74\%$.

CRYSTAL GROWTH AND BULK CHARACTERISATION

High-quality single crystals of Ca$_3$Ru$_2$O$_7$ were grown using the floating zone method in a Crystal System Corporation FZ-T-10000-H-VI-VPO-I-HR-PC mirror furnace. The crystal structure was checked using a Rigaku Miniflex 600 x-ray powder diffractometer, with the resulting diffraction pattern shown in Fig. S1b. The resistivity shown in Fig. ??c of the main text was measured in a standard four-probe configuration using a Quantum Design PPMS. The stoichiometry was confirmed with an Oxford Instruments energy dispersive x-ray spectrometer on a JEOL JEM-2100 electron microscope, yielding a Ca:Ru ratio of 3:1.97±0.06. A polarised light microscope was used to identify twin domains, and single-domain pieces were cut from larger crystals using a wire saw (see Fig. S1a).
NEUTRON SCATTERING

Neutron scattering measurements were performed at the WISH instrument of the ISIS Neutron and Muon Source [2]. WISH is a time-of-flight cold neutron instrument, allowing measurement of closely spaced magnetic peaks with high \(d\)-spacing. The sample was mounted on the end of an aluminium pin with aluminium tape. For the detector images shown in Fig. ??a of the main text, the sample was mounted in a closed-cycle refrigerator with the \(a\) axis vertical so that the satellites lie along the vertical \(^3\)He detector banks. For the data in Fig. ??c and Fig. ?? of the main text the sample was mounted in a 10T cryomagnet with the \(b\) axis vertical, along the field direction. In this geometry only the \((+\delta,0,1)\) satellite was accessible. In both cases, the sample was rotated such that the peak being measured (satellite or commensurate) was located close to forward scattering where the flux at the relevant \(d\)-spacing (around 19.5 Å) is highest. Data analysis was performed with the MANTID software package [3]. All data is normalised to the cumulative current and a beam monitor. The intensities were obtained by diffraction focusing a small area on the detector around the peak, and then integrating the resulting time-of-flight spectra.

RESONANT ELASTIC X-RAY SCATTERING

Resonant elastic x-ray scattering measurements were performed at beamline I16 of the Diamond Light Source, where a six-circle kappa diffractometer allows a wide range of reciprocal space to be accessed. The horizontally (\(\sigma\)) polarised incident beam was tuned to the Ru \(L_2\) edge (2.967 keV) by a double-bounce on a channel-cut Si (1,1,1) monochromator. Polarisation analysis of the scattered beam, shown in Fig. ??a and ??a of the main text, was achieved by a combination of in-vacuum graphite (0,0,2) analyser and avalanche photodiode detector. Measurement of the direct beam showed leakage between the polarisation channels of \(\sim\)10%. The total scattered intensity, shown in the remainder of Fig. ?? and ?? of the main text, was measured using an in-vacuum Pilatus 100K area detector in ultrahigh gain mode. An extended in-vacuum beam pipe was used to reduce air absorption of the beam. The diffractometer was operated in fixed-azimuth mode with a vertical scattering geometry, as indicated in Fig. ??b of the main text. The sample was mounted to a copper holder with GE varnish to ensure good thermal contact and no thermally-induced strain, and was cooled...
FIG. S2. Additional x-ray data. (a) Energy scans of the $(0,0,5)$ peak at 10.5 K in the $\sigma - \pi'$ (orange) and $\sigma - \sigma'$ (green) polarisation channels, showing the resonant nature of the peak. The small signal in the $\sigma - \sigma'$ channel is due to leakage through the analyser. (b) Energy scans of the $(\delta,0,5)$ peak at 48 K in the two polarisation channels. (c) Azimuthal scans of the $(0,0,5)$ peak at temperatures not shown in the main text. (d) Azimuthal scans of the $(\delta,0,5)$ peak at temperatures not shown in the main text.

with an Advanced Research System closed-cycle cryocooler. Data analysis was carried out using the Py16 program written by D.G.P. [4]. All data is normalised to the ring current and corrected for self-absorption (this has minimal effect on the azimuthal dependences as the beam-footprint is nearly constant so close to the specular condition). Intensities in the azimuthal dependences are obtained from summation over a region-of-interest on the area detector, and then fitting of the resulting rocking curves with pseudo-Voigt profiles plus a constant background. This provides full three-dimensional integration of the peaks with virtually zero background contribution.

FREE ENERGY INVARIANTS

In this section, we categorise the symmetry of the high temperature (AFM$_a$) and low temperature (AFM$_b$) collinear commensurate antiferromagnetic structures, and the inter-
mediate incommensurate cycloidal (ICC) antiferromagnetic structure found in Ca$_3$Ru$_2$O$_7$.

We then present a Lifshitz-type free energy invariant in terms of the AFM$_a$ and AFM$_b$ magnetic order parameters, which describes an incommensurate instability originating in Dzyaloshinskii-Moriya antisymmetric exchange that stabilises the spontaneous cycloidal order. Finally in this section, we give free energy invariants that generate cycloidal harmonics when an in-plane magnetic field is applied to the cycloid, transverse to the direction of propagation. These harmonics combine to form a phase-modulated cycloid described in the next section.

We employ the standard setting of the paramagnetic space group, $Cmc_2_1$, throughout. To transform between the non-standard space group setting $Bb_2_1m$ used in the literature and the standard setting one can simply rotate the direct lattice basis:

\[
a(Bb_2_1m) \rightarrow b(Cmc_2_1) \\
b(Bb_2_1m) \rightarrow c(Cmc_2_1) \\
c(Bb_2_1m) \rightarrow a(Cmc_2_1)
\]

Both AFM$_a$ and AFM$_b$ magnetic structures have Y-point propagation vector $\mathbf{k} = (1, 0, 0)$. The full Y-point magnetic representation for the Ru Wyckoff site $8b$ decomposes into four one-dimensional irreducible representations (irreps): $mY_1$, $mY_2$, $mY_3$, and $mY_4$. Symmetry-adapted modes of $mY_4$ correspond to the AFM$_a$ magnetic structure, and symmetry-adapted modes of $mY_2$ correspond to AFM$_b$.

Consider two, one-dimensional magnetic order parameters, $\mu$ and $\rho$, that transform by the $mY_2$ and $mY_4$ irreps, respectively. These two order parameters can be combined into a Lifshitz-type free energy term that is symmetry allowed by the non-centrosymmetric $Cmc_2_11'$ space group:

\[
\mu \frac{\partial \rho}{\partial y} - \rho \frac{\partial \mu}{\partial y}
\]

where the component of the gradient operator, $\frac{\partial}{\partial y}$, transforms as a polar vector $\parallel y$ ($\Gamma_3$ irrep). The symmetry invariance of this term can be appreciated by inspection of the matrix form of the $Cmc_2_11'$ generators (Tables S1 and S2), which demonstrate the transformational properties of order parameters associated with the $mY_2$, $mY_4$, and $\Gamma_3$ irreps. It is well known that the presence of Lifshitz type invariants in the free energy implies an instability of the system towards inhomogeneous modulated states [5]. For instance, this instability is responsible for the formation of a long-period cycloidal magnetic structure in polar BiFeO$_3$ [6,
TABLE S1. Irreducible representation (irrep) matrices for rotation and mirror generators of the \( Cmc_{211}' \) space group and \( T \), the time reversal operator (\( \Gamma \)-point, \( \mathbf{k} = (0,0,0) \); Y-point, \( \mathbf{k} = (1,0,0) \); \( \Delta \)-line of symmetry, \( \mathbf{k} = (0,k_y,0) \)).

| \( \mu \) | \( \rho \) | \( \frac{\partial}{\partial y} \) | \( H_z \) | \( (\eta,\eta^*) \) |
|---|---|---|---|---|
| \( \{1|0,0,0\} \) | \( \{2z|0,0,1/2\} \) | \( \{m_x|0,0,0\} \) | \( \{m_y|0,0,1/2\} \) | \( T \) |
| \( \{1|0,0,0\} \) | \( \{2z|0,0,1/2\} \) | \( \{m_x|0,0,0\} \) | \( \{m_y|0,0,1/2\} \) | \( T \) |
| \( \mu \) | \( \rho \) | \( \frac{\partial}{\partial y} \) | \( H_z \) | \( (\eta,\eta^*) \) |
| \( mY_2 \) | \( mY_4 \) | \( \Gamma_3 \) | \( m\Gamma_2 \) | \( m\Delta_2 \) |
| \( \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \) | \( \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \) | \( \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix} \) | \( \begin{pmatrix} 0 & -1 \\ -1 & 0 \end{pmatrix} \) | \( \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix} \) |

TABLE S2. Irreducible representation (irrep) matrices for translation generators of the \( Cmc_{211}' \) space group.

| \( \mu \) | \( \rho \) | \( \frac{\partial}{\partial y} \) | \( H_z \) | \( (\eta,\eta^*) \) |
|---|---|---|---|---|
| \( \{1|1/2,1/2,0\} \) | \( \{1|1,0,0\} \) | \( \{1|0,1,0\} \) | \( \{1|0,0,1\} \) |
| \( \{1|1/2,1/2,0\} \) | \( \{1|1,0,0\} \) | \( \{1|0,1,0\} \) | \( \{1|0,0,1\} \) |
| \( \mu \) | \( \rho \) | \( \frac{\partial}{\partial y} \) | \( H_z \) | \( (\eta,\eta^*) \) |
| \( mY_2 \) | \( mY_4 \) | \( \Gamma_3 \) | \( m\Gamma_2 \) | \( m\Delta_2 \) |
| \( \begin{pmatrix} e^{-\pi i k_y} & 0 \\ 0 & e^{\pi i k_y} \end{pmatrix} \) | \( \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \) | \( \begin{pmatrix} e^{-2\pi i k_y} & 0 \\ 0 & e^{2\pi i k_y} \end{pmatrix} \) | \( \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \) |

The free energy term specified above describes an incommensurate instability away from the commensurate order of AFM\(_a\) and AFM\(_b\), and promotes a cycloidal order propagating along the \( b \)-axis with propagation vector \( \mathbf{k} = (1,\delta,0) \).

The incommensurate propagation vector \( \mathbf{k} = (1,\delta,0) \) is equivalent to \( \mathbf{k} = (0,\delta-1,0) \) located on the \( \Delta \)-line of symmetry. The reducible \( \Delta \)-line magnetic representation for the Ru Wyckoff site decomposes into two two-dimensional irreps, \( m\Delta_1 \), and \( m\Delta_2 \). The compatibility relationships for \( m\Delta_1 \), \( m\Delta_2 \), and the Y-point irreps,

\[
m\Delta_1 = mY_1 \oplus mY_3
\]
\[
m\Delta_2 = mY_2 \oplus mY_4
\]
indicate that the modulated states that transform by the m\(\Delta_2\) irrep decompose into m\(Y_2\) and m\(Y_4\) order parameters in the commensurate limit. Hence, the magnetic cycloid stabilised by the Lifshitz invariant, which is expected to be a small perturbation of the commensurate magnetic structures associated with the m\(Y_2\) and m\(Y_4\) irreps, transforms according to the m\(\Delta_2\) irrep (listed in Tables S1 and S2).

In the zero magnetic field scattering experiments the spontaneous cycloidal order was found to have a single (fundamental) propagation vector, \(\pm k_1 \approx (0, \pm 0.97, 0)\), where the subscript denotes that this is the fundamental (1\text{st} order) propagation vector. We write the general complex order parameter of the fundamental cycloidal modulation as \((\eta_1, \eta_1^*)\), where \(\eta_1\) and \(\eta_1^*\) are complex and complex conjugate components corresponding to \(+k_1\) and \(-k_1\), and their appropriate linear combination provides real values for the ruthenium magnetic moments.

We now consider the effect of applying a magnetic field in the plane of the cycloid, and transverse to the direction of propagation \((H_z)\). \(H_z\), and the \(\Gamma\)-point magnetisation it creates, transform by the m\(\Gamma_2\) irrep, as listed in Tables S1 and S2. The presence of the field implies a coupling of additional magnetic order parameters, with the lowest order coupling invariant that is linear in \(H_z\) being

\[
H_z(\eta_2^*\eta_1^2 + \eta_2\eta_1^{*2})
\]

where \((\eta_2, \eta_2^*)\) is a second harmonic cycloidal component with propagation vector \(k_2 = 2k_1\), which also transforms as m\(\Delta_2\). This invariant dictates that, when \(H_z\) is finite, the energy of the system is lowered through the creation of a second harmonic modulation. More generally, this invariant can be written to higher orders as

\[
H_z(\eta_n^*\eta_1^n + \eta_n\eta_1^{*n})
\]

where \((\eta_n, \eta_n^*)\) is the two-dimensional order parameter of the \(n\)\text{th} harmonic cycloid, and \(n = 2, 4, 6, \ldots\) \(i.e.\) an infinite series of even harmonics with propagation vector \(k_n = nk_1\) are created by this free energy invariant.

Similarly, odd order harmonics can be expected to occur in the field-modulated cycloid, and they are accounted for by invariants that are quadratic rather than linear in the field:

\[
H_z^2(\eta_n^*\eta_1^n + \eta_n\eta_1^{*n})
\]
where \( n = 3, 5, 7, \ldots \)

These field-induced harmonics combine to form a phase modulated cycloid, described in the following section.

**PHASE MODULATED CYCLOID**

In this section, we provide an analytical model of a phase modulated cycloid and its Fourier decomposition, valid for small phase modulations. We consider a cycloid with moments rotating in the \( x - y \) plane, propagating along \( x \), and with an external magnetic field applied along \( y \). For simplicity, we take a single atom in the unit cell, which is sufficient to demonstrate the general Fourier decomposition of the cycloid, but not sufficient for structure factor calculations of the neutron and x-ray diffraction intensity from the real material which has eight Ru atoms in the conventional unit cell.

We can write the magnetic moment, \( \mathcal{M} \), of a given atom as

\[
\mathcal{M}^r = m_x^r \hat{x} + m_y^r \hat{y}
\]

where \( \mathbf{r} \) is a direct lattice vector that relates the atom’s unit cell to the origin. For a phase modulated cycloid with phase modulation periodicity the same as that of the fundamental cycloid (as expected for a \( \Gamma \)-point field induced modulation), we define

\[
m_x^r = M_x \cos (\phi_r + 2\pi A \cos (\phi_r)) \tag{8}
\]

\[
m_y^r = M_y \sin (\phi_r + 2\pi A \cos (\phi_r)) \tag{9}
\]

where \( \phi_r = 2\pi \mathbf{k}_1 \cdot \mathbf{r} \), \( M_x \) and \( M_y \) are the moment magnitudes along \( x \) and \( y \) that define an elliptical envelope for the rotating moments, and \( A \) is the amplitude of the phase modulation. Figure S3 illustrates \( \mathcal{M} \) with a circular envelope for different values of \( A \). One can observe the magnetisation of the cycloid parallel to the applied field that is established via the phase modulation (changing the sign of \( A \) corresponds to the opposite field direction).

By writing Equations 8 and 9 as

\[
m_x^r = M_x [\cos (\phi_r) \cos (2\pi A \cos (\phi_r)) - \sin (\phi_r) \sin (2\pi A \cos (\phi_r))] \tag{10}
\]

\[
m_y^r = M_y [\sin (\phi_r) \cos (2\pi A \cos (\phi_r)) + \cos (\phi_r) \sin (2\pi A \cos (\phi_r))] \tag{11}
\]
and expanding the factors dependent on the phase modulation amplitude $A$ as a Taylor series (in the following we expand $\cos(x)$ up to $x^4$ and $\sin(x)$ up to $x^3$), one can show that

\[ m_{x}^r = M_x[\alpha_1 \cos (\phi_r) + \alpha_2 \sin (2\phi_r) + \alpha_3 \cos (3\phi_r) + \alpha_4 \sin (4\phi_r) + ...] \] (12)

\[ m_{y}^r = M_y[\beta_0 + \beta_1 \sin (\phi_r) + \beta_2 \cos (2\phi_r) + \beta_3 \sin (3\phi_r) + \beta_4 \cos (4\phi_r) + ...] \] (13)

where

\[ \alpha_1 = 1 - \frac{3}{2}(\pi A)^2 + \frac{5}{12}(\pi A)^4 \] (14)

\[ \alpha_2 = \frac{1}{3}(\pi A)^3 - (\pi A) \] (15)

\[ \alpha_3 = \frac{5}{24}(\pi A)^4 - \frac{1}{2}(\pi A)^2 \] (16)

\[ \alpha_4 = \frac{1}{6}(\pi A)^3 \] (17)
TABLE S3. Fourier coefficients $\psi_n$ and $\chi_n$ and their relationship to $\alpha_n$ and $\beta_n$. The amplitudes and intensities have been evaluated for $A = 0.1$.

| Fourier coefficient | Amplitude | Intensity |
|---------------------|-----------|-----------|
| $\psi_0 = \alpha_0$ | 0         | 0         |
| $\psi_1 = \alpha_1$ | 0.856     | 0.733     |
| $\psi_2 = -i\alpha_2$ | 0.304 $i$ | 0.092     |
| $\psi_3 = \alpha_3$ | -0.047    | 0.002     |
| $\psi_4 = -i\alpha_4$ | -0.005 $i$ | $\sim 0$ |
| $\chi_0 = \beta_0$ | 0.299     | 0.089     |
| $\chi_1 = -i\beta_1$ | -0.951 $i$ | 0.905     |
| $\chi_2 = \beta_2$ | 0.293     | 0.086     |
| $\chi_3 = -i\beta_3$ | 0.048 $i$ | 0.002     |
| $\chi_4 = \beta_4$ | -0.005    | $\sim 0$ |

and

$$\beta_0 = (\pi A) - \frac{1}{2}(\pi A)^3$$  \hspace{1cm} (18)

$$\beta_1 = 1 - \frac{1}{2}(\pi A)^2 + \frac{1}{12}(\pi A)^4$$ \hspace{1cm} (19)

$$\beta_2 = (\pi A) - \frac{2}{3}(\pi A)^3$$ \hspace{1cm} (20)

$$\beta_3 = \frac{1}{8}(\pi A)^4 - \frac{1}{2}(\pi A)^2$$ \hspace{1cm} (21)

$$\beta_4 = -\frac{1}{6}(\pi A)^3$$ \hspace{1cm} (22)

If $A = 0$, only the $\alpha_1$ and $\beta_1$ coefficients of the fundamental modulation are non-zero, as expected. $M_y\beta_0$ is exactly the magnetisation of the cycloid parallel to the field direction, $y$, which, to first order, is directly proportional to the phase modulation amplitude $A$. Furthermore, we note that the coefficients of the odd harmonics are in terms of only even powers of $A$, and the coefficients of the even harmonics are in terms of only odd powers of $A$. This is fully consistent with the free energy invariants given in Equations 5 and 6, by which the even and odd harmonics couple linearly and quadratically to the magnetic field, respectively.

Finally, we consider the Fourier transform of the phase modulated cycloid. Equation 7
can be recast as the sum over Fourier components, $S_k$.

$$\mathcal{M}^r = \sum_k S_k e^{2\pi i k \cdot r} \quad (23)$$

where

$$S_k = \frac{1}{2}(\psi_n M_x \hat{x} + \chi_n M_y \hat{y}) \quad (24)$$

The sum in Equation 23 must be taken over $\pm k$, and $S_k = S_k^*$. The Fourier coefficients $\psi_n$ and $\chi_n$ are related to $\alpha_n$ and $\beta_n$, as shown in Table S3. We also tabulate numerical values for the Fourier coefficients (evaluated for $A = 0.1$) and their modulus squared, which gives an indication of the expected, relative diffraction intensities.