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Measuring the Dzyaloshinskii–Moriya interaction in a weak ferromagnet

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Magnetism—the spontaneous alignment of atomic moments in a material—is driven by quantum mechanical exchange interactions that operate over interatomic distances. Some magnetic interactions cause^{1,2}, or are caused by^{3,4}, a twisting of arrangements of atoms. This can lead to the magnetoelectric effect, predicted to play a prominent role in future technology, and to the phenomenon of weak ferromagnetism, governed by the so-called Dzyaloshinskii–Moriya interaction^{5–8}. Here we determine the sign of the latter interaction in iron borate (FeBO₃) by using synchrotron radiation. We present a novel experimental technique based on the interference between two X-ray scattering processes, where one acts as a reference wave. Our experimental results are validated by state-of-the-art *ab initio* calculations. Together, our experimental and theoretical approaches are expected to open up new possibilities for exploring, modelling and exploiting novel magnetic and magnetoelectric materials.

There is considerable mystery behind the origins of complicated structures. Although the dominant short-range interactions that allow the building blocks to grow are well understood, the much more subtle forces that lead to a particular twisting at larger length-scales, such as chiral biological molecules and liquid crystals⁹, and canted magnetic systems³, remain subjects of topical debate. In this Letter we seek to address this question for the case of magnetism. Our main findings are twofold: first, we demonstrate a novel and elegant experimental method for exploring magnetic materials with weak relativistic spin–orbit interactions, and second, we present a state-of-the-art quantum-mechanical many-body approach to the detailed description of such interactions in crystals. As a touchstone example we selected crystalline iron borate (FeBO₃), which is a strongly correlated electron system with a relatively simple crystal structure, nonetheless allowing a non-trivial canted and locally twisted magnetic ordering pattern. Taken together, these two strands demonstrate that modern condensed matter theory is capable of determining the elusive sign of the Dzyaloshinskii–Moriya interaction, and is thus able to elucidate the mechanism for coupling electric and magnetic degrees of freedom in magnetoelectric multiferroics, and to begin to predict the properties of this important class of materials.

The interactions between atomic magnetic moments (or spins) are not direct, but mediated by the intervening matter. Coupling can be diminished through screening¹⁰, or enhanced, for example, by superexchange via oxygen atoms¹¹. Moreover, the coupling is

a property of the material and, according to Neumann's principle, must therefore possess all of its symmetries. The most general form of the bilinear coupling energy between two spins contains a scalar (isotropic) exchange term, exchange anisotropy (which we will neglect for the present discussion) and an antisymmetric term that reverses with permutation of the spin indices. The latter is the Dzyaloshinskii–Moriya interaction, which can be expressed in terms of a Dzyaloshinskii–Moriya vector, \mathbf{D} , and the vector product of spins, leading to a spin-dependent energy (for classical spins),

$$\Delta E = \sum_{m \neq n} J_{mn} \mathbf{S}_m \cdot \mathbf{S}_n + \sum_{m \neq n} \mathbf{D}_{mn} \cdot [\mathbf{S}_m \times \mathbf{S}_n] - \mu_B g S \sum_m \mathbf{H} \cdot \mathbf{S}_m \quad (1)$$

where the summations run over all magnetic atoms. \mathbf{S}_m is a unit vector along the direction of the m th spin of magnitude S , μ_B is the Bohr magneton and $g \approx -2$ is the gyromagnetic ratio. Both the exchange coefficients J_{mn} and the Dzyaloshinskii–Moriya vectors \mathbf{D}_{mn} depend on the relative positions of the magnetic atoms. The dominant first term in equation (1) prefers parallel/antiparallel coupling of spins (depending on the sign of J_{mn}), whereas the second term favours an orthogonal alignment, producing a small twist, or canting, of the atomic moments.

In 3d transition metal oxides it is usually necessary to consider only the nearest neighbours, because these dominate the exchange interactions. The Dzyaloshinskii–Moriya interaction is typically a few per cent of the isotropic term (~ 0.1 meV, compared to ~ 10 meV), producing just a modest canting. Nevertheless, the effect is important. A spontaneous rearrangement of atoms to favour the Dzyaloshinskii–Moriya interaction (often called the inverse Dzyaloshinskii–Moriya effect) can produce a large electric polarization in magnetoelectric materials^{1,2}. In so-called weak ferromagnets, canting of the otherwise collinear antiferromagnetic arrangement leads to a small net ferromagnetic polarization that couples strongly to an external magnetic field¹².

Chiral spin structures in globally centrosymmetric crystals can be determined by using polarized neutron scattering^{13,14} or circularly polarized X-rays¹⁵. Although such structures are of topical interest owing to the presence of skyrmion lattices, the magnetoelectric effect and so on, the underlying exchange coupling is identical to the classical problem of weak ferromagnetism. Moreover, the latter is a particularly attractive test case for developing new theoretical techniques, as the magnetic structures do not exhibit long (or infinite) magnetic periodicities. Unfortunately, standard

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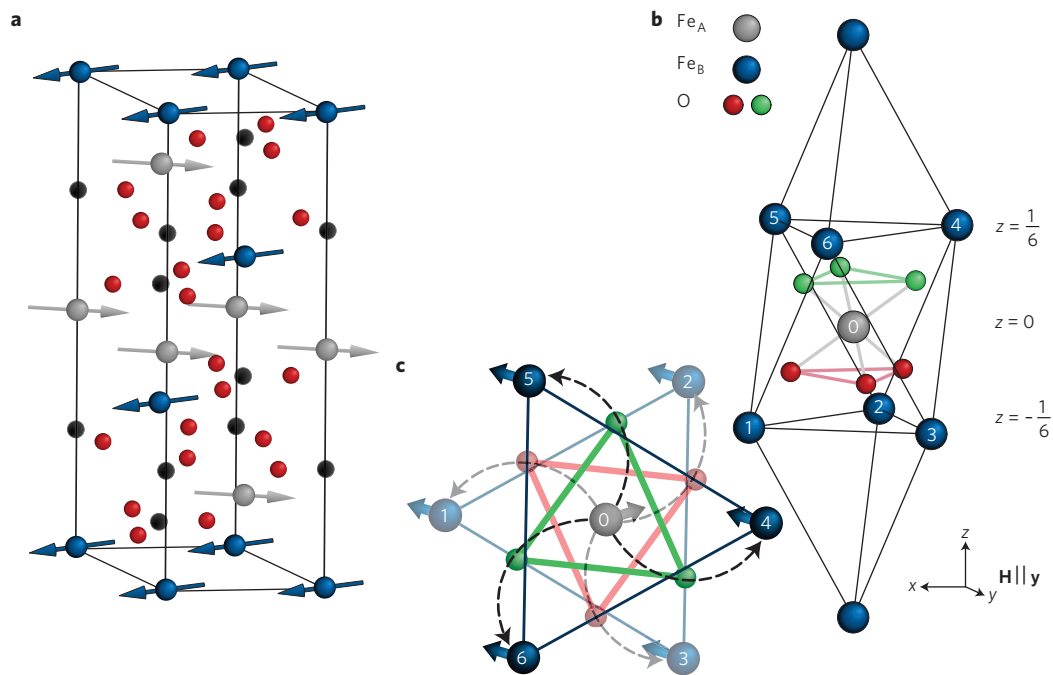


Figure 1 | Atomic and magnetic order in FeBO₃. **a**, A magnetic (hexagonal) unit cell, showing oxygen atoms (red), boron atoms (black), and two symmetry-related magnetic iron sublattices (blue and grey) with moments tilted between the two. **b**, The local environment of one of the grey (A-site) Fe atoms, showing neighbouring B-site Fe atoms (blue). The upper and lower oxygen triangles are coloured green and red, and boron atoms are removed for clarity. **c**, The same structure viewed from the top, highlighting the twisted superexchange paths from the A-site Fe atom to the upper Fe layer (dark blue) and the lower layer (pale blue) via the oxygen triangles.

techniques do not reveal the phase of the magnetic structures with respect to the twisting of the atomic arrangement and so the direction of magnetic twist in weak ferromagnets cannot be determined and has remained an unsolved problem.

Important symmetry restrictions on the Dzyaloshinskii–Moriya vector have been discussed since it was initially introduced more than fifty years ago^{5–8}. In the case of FeBO₃, with crystal symmetry $R\bar{3}c$, there are two iron atoms at the $2b$ inversion centres, two boron atoms at the $2a$ positions, and six oxygens at $6e$ sites. If the oxygen atoms were absent, or positioned exactly between two neighbouring iron atoms, the symmetry would be $R\bar{3}m$, which does not allow for the Dzyaloshinskii–Moriya interaction. It is therefore the small displacement of oxygen atoms, striving towards a close-packed structure, that drives iron borate into the observed complex magnetic ordering pattern shown in Fig. 1. Iron atoms form ferromagnetic layers with their magnetic moments aligned in plane, with the layers stacked in alternating but not exactly opposite directions. (The antiferromagnetic pattern produces weak pure magnetic diffraction at points in reciprocal space that are otherwise forbidden by spacegroup symmetry.) A closer examination of the FeBO₃ crystal structure reveals that each Fe atom is connected to six equivalent nearest Fe neighbours: three in the plane above and three below. The six Dzyaloshinskii–Moriya vectors linking these Fe atoms are related by symmetry and, when summed, lead to a resultant vector along z . It follows from equation (1) that the Dzyaloshinskii–Moriya vector of this type induces a twist between A and B spins in the xy plane, but the symmetry alone cannot say whether this twist will be left-handed or right-handed. The absolute sign of the local twist can be found both experimentally and theoretically using the techniques described here.

The present experimental technique relies on the fact that the weak ferromagnetic moment is perpendicular to the opposing antiferromagnetic components (Fig. 1). As the former can be turned

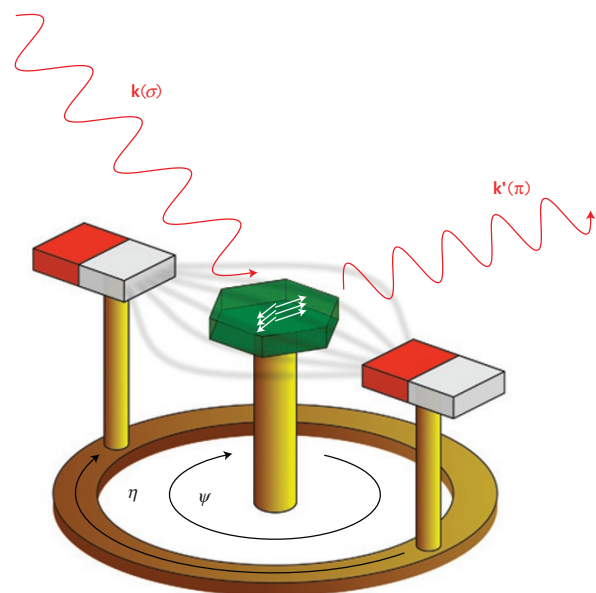


Figure 2 | A schematic view of the experiment carried out on FeBO₃. The incident and scattered X-ray beams are shown, along with the FeBO₃ crystal, indicating weak ferromagnetic moments aligned with the applied magnetic field. The sample and field were rotated about a common axis so that $\psi = 0$ and $\eta = 0$ correspond to the crystallographic $(100)_{\text{hex}}$ axis and the field direction (from south to north pole of the magnet assembly), directed along $\mathbf{k} + \mathbf{k}'$, respectively.

with a small external field (Fig. 2), the dominant antiferromagnetic structure is ‘dragged’ around to follow it, providing an elegant alternative to rotating the entire crystal, thus avoiding experimental artefacts such as multiple X-ray diffraction.

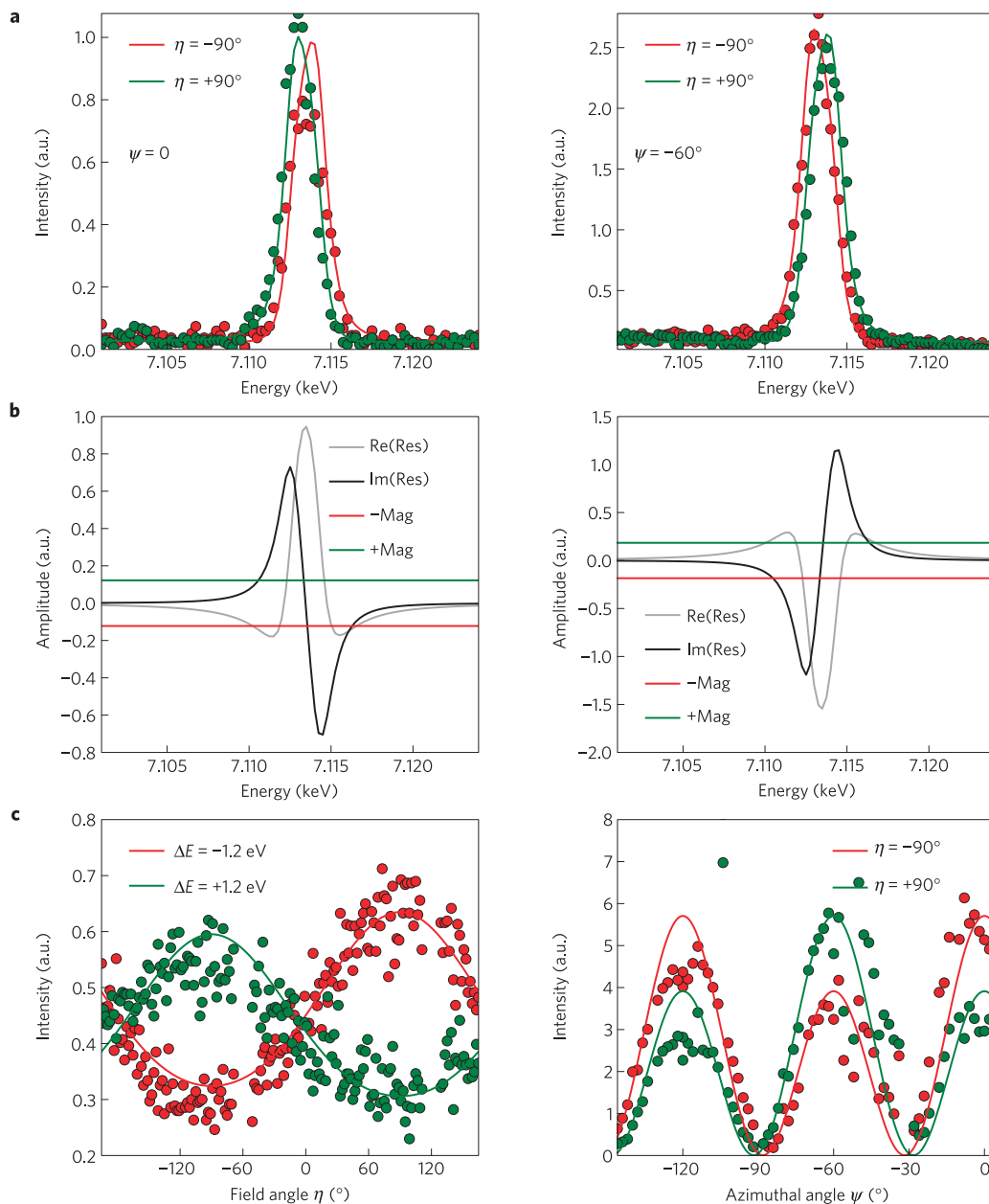


Figure 3 | The major experimental results and simulations for FeBO_3 . Fits are derived from the coherent sum of the magnetic and resonant amplitudes, with the latter based on a ‘double-resonance’ model (see Supplementary Information). **a**, A remarkable shift in the X-ray resonance energy is observed on rotation of the magnet ($\eta = \pm 90^\circ$). The shift reverses as the sample azimuth is rotated from $\psi = 0$ to $\psi = -60^\circ$ (reversing the phase of the resonant amplitude), as is evident in both experimental data and model calculations. **b**, The resonant and magnetic amplitudes used to fit the data in **a**. The origin of the energy jump can be understood by considering interference between the constituent amplitudes. The magnetic amplitude is in phase or antiphase with the imaginary part of the resonance amplitude (black lines), causing constructive: (destructive) interference on the low: (high) energy side of the resonance, depending on the relative phase of the magnetic and resonant scattering amplitudes. **c**, The same phase of the magnetic scattering gives very good agreement with intensity measurements versus field angle (left), with the resonance amplitude reversed by shifting the energy above and below the resonant centre ($\Delta E = \pm 1.2$ eV). Right: the intensity variation with azimuthal angle and opposite magnetic amplitudes ($\eta = \pm 90^\circ$). In **(a)** and **(c)**, circles represent experimental data and solid lines are fits.

To determine the sign of the Dzyaloshinskii–Moriya interaction, we must determine whether the rotation of the spins is in the same sense as the rotation of the oxygen triangles, or opposite. Unfortunately, the standard techniques for characterizing antiferromagnetic structures—polarized neutron or X-ray diffraction—do not help: the sign of the twist appears in the phase of the diffracted wave, which is lost in an intensity measurement—an aspect of the famous ‘phase problem’ of crystallography. Borrowing from the ideas behind holography, it was recently suggested by some of

us¹⁶ that the sign of the Dzyaloshinskii–Moriya vector could be measured with resonant X-ray diffraction by observing interference between the resonant¹⁷ and magnetic¹⁸ scattering amplitudes. The resonant scattering process adopted is a rather exotic one, involving pure electric quadrupole events (that is, beyond the usual dipole approximation). However, in recent years, such phenomena have been studied in detail and are now extremely well understood^{19,20}. Its phase and amplitude vary rapidly with photon energy, being significant only very close to the Fe K X-ray absorption pre-edge

energy of 7.11 keV, and it has a complex dependence on both photon polarization and the azimuthal rotation of the sample about the normal to the diffracting planes (ψ -angle). Moreover, both the resonant and magnetic scattering signals appear at the same Bragg reflection positions— $(hkl) = (0, 0, 6n + 3)$ —that are ‘forbidden’ for the vastly stronger charge scattering processes, and have comparable amplitudes to each other, maximizing the effects of interference. The sign and amplitude of the magnetic scattering signal depends on the spin direction, which can be rotated with a magnetic field, whereas those of the resonant scattering depend on the precise X-ray energy and azimuthal orientation of the crystal. We thus expect control of the amplitude and phase of both the magnetic scattering and resonant reference wave, allowing the phase of the magnetic scattering to be determined. Details of the magnetic and resonant scattering amplitudes are given in Supplementary Information.

Three types of measurement are presented. The first shows a remarkable effect: an apparent jump in the energy of the resonant scattering peak as the magnetic motif is rotated by 180° —the result of constructive (destructive) interference on the low (high) energy side of the resonance (Fig. 3). The opposite jump was observed when the phase of the resonant scattering was reversed by changing the sample ψ angle. Both jumps are reproduced by our *ab initio* calculations, which make a definite prediction for the sign of the Dzyaloshinskii–Moriya interaction, the phase of the magnetic scattering amplitude, and thus the direction of the jump. The second measurement shows the intensity, measured as a continuous rotation of the field angle, for the low and high energy side of the resonance. For the final measurement, the sample azimuthal angle was varied continuously, with a fixed photon energy and field applied in two opposite directions, transverse to the incident beam. In all cases, the phase of the magnetic scattering whose reversal would convert red to green lines and vice versa were consistent, completely unambiguous, and in agreement with the calculations.

One of the main goals of the present work was to demonstrate that the sign of the Dzyaloshinskii–Moriya interaction can be determined reliably not only by experiment but also theoretically. To this end we have performed first-principles calculations by using the local density approximation incorporating the on-site Coulomb interaction U and the spin–orbit coupling^{21,22} (LDA + U + SO). Our calculations predict (see Supplementary Information) that the lowest energy stable magnetic structure is precisely the one observed experimentally and shown in Fig. 1. Furthermore, we predict that the magnetic twist between adjacent layers is in the same direction as the twist of the oxygen triangles. This is the basis of the calculated curves in Fig. 3, and is thus very clearly confirmed by experiment.

Because the vector product $[\mathbf{S}_A \times \mathbf{S}_B]$ in equation (1) is parallel to the z axis, and the corresponding Dzyaloshinskii–Moriya interaction must reduce the energy of the system, we can deduce that D_{AB}^z is negative. The absolute value of the Dzyaloshinskii–Moriya interaction energy is readily estimated from the measured canting angle (0.9°) and isotropic exchange interaction: $|D_{AB}^z| = 2J|S_y/S_x| = 0.33$ meV. Here J is approximately 10.3 meV.

The determination of the J_{mn} and \mathbf{D}_{mn} parameters taking into account hybridization, correlation, temperature and spin–orbit coupling effects is a complex methodological and computational problem requiring a whole arsenal of numerical techniques^{8,23–25}. Here, we outline a second, and very general next-generation method that has a simple formulation and captures all the important electronic and magnetic excitation effects²⁶. The resulting expression for the correlated band Dzyaloshinskii–Moriya interaction can be applied to a wide range of materials and is given by

$$\mathbf{D}_{mn} = -\frac{i}{2} \text{Tr}_{L,o} \left\{ N_{nm} [\hat{\mathbf{J}}, \hat{t}_{mn}]_+ \right\} \quad (2)$$

where N_{nm} is the energy-integrated inter-site Green’s function describing the propagation of an electron from site n to m , $\hat{\mathbf{J}}$ is the total moment operator, t_{mn} is the hopping matrix and $[\cdot, \cdot]_+$ represents an anticommutator (see Supplementary Section IV for details). The method is developed in a many-body form, thus, state-of-the-art numerical approaches such as dynamical mean-field theory can be used to take into account temperature and dynamical Coulomb correlations effects.

The calculated Dzyaloshinskii–Moriya vector equation (2) linking iron atoms 0 and 1 (Fig. 1), for example, is $\mathbf{D}_{01} = (-0.25, 0, -0.24)$ meV. By symmetry, it lies in the xz plane, perpendicular to the two-fold axis that passes through the oxygen atom⁸. All six symmetrically equivalent vectors have the same z component, but the xy components average to zero. Our calculated canting angle of 0.7° is only slightly smaller than the experimental value of 0.9° , used for the self-consistent calculation.

Crucially, the sign of the Dzyaloshinskii–Moriya interaction, which we have predicted by two theoretical methods, determines the direction of twist of the magnetic structure, which affects the phase of the magnetic scattering and the sign of the interference term in Fig. 3. It is thus confirmed unambiguously by the experimental data.

In conclusion, we show that a new interference technique in which measurements are carried out with precise control of the amplitude and phase of a reference wave gives an unambiguous result for the sign of the Dzyaloshinskii–Moriya interaction. We find that the twist in the magnetic structure is in the same direction as that of the oxygen atoms. The results prove the efficacy of state-of-the-art electronic structure calculations, able to predict the magnetic ground state and both the direction and strength of the Dzyaloshinskii–Moriya interaction. These findings take us a step closer to realising the prediction of complex non-collinear magnetic structures and the associated properties of an important class of materials that includes weak ferromagnets and multiferroics. Finally we note that, although the current technique would seem to be applicable to a very specific class of materials where the symmetry allows coincidence of magnetic and resonant forbidden scattering, in fact such a coincidence is not particularly rare and includes, among others, all three of the classical weak ferromagnets highlighted by Moriya⁸, α - Fe_2O_3 , MnCO_3 and CoCO_3 , and the high- T_C superconductor parent compound La_2CuO_4 (refs 23,26).

Methods

The experiments were mostly carried out at beamline BM28 (XMaS), European Synchrotron Radiation Facility²⁷, with preliminary investigations of the pure magnetic and pure resonant scattering carried out at beamline I16, Diamond Light Source²⁸ (see Supplementary Information). Both beamlines provide intense X-ray beams covering the required energy range (≈ 7 keV), focussed onto a 10–800 K cryofurnace, mounted at the centre of large six-circle diffractometers. The sample—a single crystal of $\text{FeBO}_3 \sim 4 \times 3 \times 0.05$ mm³ in size—was attached with its 001 surface normal to the diffractometer ϕ rotation axis²⁷, which was parallel to the azimuthal rotation axis, ψ (Fig. 2). Two small rare-earth magnets provided a magnetic field of 0.011 T, sufficient to saturate the weak ferromagnetism within the crystal xy plane, with an orientation determined by the motorized rotation angle of the magnets around the ϕ axis. Scattering was in the vertical plane, perpendicular to the linearly (σ)-polarized incident beam, and a linear polarization analyser, based on a Cu 220 Bragg reflection, selected just the rotated ($\sigma \rightarrow \pi$) polarization channel. Most measurements were carried out at temperature $T = 200$ K, where the moments are close to saturation, with subsidiary measurements performed at $T = 400$ K (well above the magnetic ordering temperature of ~ 348 K), where the magnetic scattering is absent. The real and imaginary parts of the resonant amplitudes were calculated using FDMNES (Finite Difference Method for Near Edge Structure) package²⁹ (see Supplementary Information for details).

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Author contributions

V.E.D. and E.N.O. proposed the project. G.B., S.P.C. and G.N. carried out experimental work at BM-28. S.P.C. carried out experimental work at I16. Y.O.K., V.V.M., A.I.L., M.I.K. performed *ab initio* calculations. V.E.D. carried out FDMNES calculations. G.B. performed least-squares fitting of model functions to experimental data. G.N. carried out multiple scattering simulations. S.P.C., V.E.D. and V.V.M. wrote the majority of the text.

Additional information

Supplementary information is available in the [online version of the paper](#). Reprints and permissions information is available online at www.nature.com/reprints. Correspondence and requests for materials should be addressed to S.P.C.

Competing financial interests

The authors declare no competing financial interests.