Spin Jahn-Teller antiferromagnetism in CoTi$_2$O$_5$

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We have used neutron powder diffraction to solve the magnetic structure of orthorhombic CoTi$_2$O$_5$, showing that the long-range ordered state below 26 K identified in our muon-spin rotation experiments is antiferromagnetic with propagation vector $\mathbf{k} = (\pm \frac{1}{2}, \frac{1}{2}, 0)$ and moment of 2.72(1)µ$_B$ per Co$^{2+}$ ion. This long range magnetic order is incompatible with the experimentally determined crystal structure because the imposed symmetry completely frustrates the exchange coupling. We conclude that the magnetic transition must therefore be associated with a spin Jahn-Teller effect which lowers the structural symmetry and thereby relieves the frustration. These results show that CoTi$_2$O$_5$ is a highly unusual low symmetry material exhibiting a purely spin-driven lattice distortion critical to the establishment of an ordered magnetic ground state.

The Jahn-Teller effect is the spontaneous lowering of symmetry that lifts an orbital degeneracy [1] and involves a coupling of the orbital and lattice degrees of freedom. In some rather rare cases an analogous effect can occur in which spin, rather than orbital, degrees of freedom play a role. This spin Jahn-Teller effect has been identified in pyrochlores in which the large spin degeneracy in the lattice of corner-sharing tetrahedra can be relieved by a distortion in those tetrahedra [2, 3]. In some cubic spinnels an analogous effect can take place in which a tetragonal distortion relieves the frustration [4, 5]. A related effect has also been observed near level-crossing in molecular wheels [6, 7]. In this Letter we demonstrate the existence of spin Jahn-Teller driven antiferromagnetism in CoTi$_2$O$_5$, a compound which has much lower symmetry than either pyrochlores or spinnels, showing that spin-phonon coupling can induce order in a larger class of materials than has previously been appreciated. The site symmetry of the magnetic Co$^{2+}$ (3d$^7$) ion is m2m (C$_{2v}$) and so the orbital levels are already non-degenerate (so no longer susceptible to a conventional Jahn-Teller transition). Nevertheless, we show that long range spin order is only permitted in the presence of the structural distortion that we predict to set in at $T_N = 26$ K.

Cobalt titanates are of interest due to their numerous applications. Co$_2$TiO$_4$ has a complex spinel magnetic structure [8,11], which has found uses in catalysis [12,13], microwave devices [14], and Li-ion cells [15]. CoTiO$_3$ has been used as a photocatalyst [16], gas sensor [17], and also in semiconductor transistors and memory storage [18]. CoTi$_2$O$_5$, however, is less well-studied. It is the only cobalt titanate to melt incongruently [19], and its pseudo-brookite structure [20] is an entropy-stabilized high temperature phase [21] which is susceptible to decomposition below 1414 K [22,23]. Only recently has it become possible to synthesize high-quality single crystals of CoTi$_2$O$_5$ [24].

A polycrystalline CoTi$_2$O$_5$ powder sample was prepared using high purity (> 99.99%) Co$_3$O$_4$ and TiO$_2$ via the solid state reaction technique. Mixed powders were sintered at 1200°C for 48h in air with intermediate grinding. After confirming the phase purity of the powder using x-ray diffraction, a cylindrical rod of diameter 10 mm and length 100 mm was sintered at 1250°C in air for 12h. Finally, the single crystal was grown in a four-mirror optical floating-zone furnace (Crystal System Inc.) in argon/oxygen mixed gas (90:10 ratio) atmosphere with a growth rate of 2–3mm/h.

Magnetic susceptibility and heat capacity data are shown in Fig. 1(a) and (b) respectively and are consistent with a magnetic transition at 26 K. The calculated entropy associated with the transition is 48% of the expected $R\ln(4)$ associated with the spin-only moment, indicative of significant correlations above $T_N$.

Zero field $\mu$SR (ZF-μSR) experiments [26, 27] were performed using a Quantum Continuous Flow Cryostat mounted on the general purpose spectrometer (GPS) at the Swiss Muon Source. All of the $\mu$SR data were analyzed using WiMDA [28].

ZF-μSR asymmetry spectra $A(t)$ are shown in Fig. 1(c). At low $T$, we observe an oscillatory beating pattern of $A(t)$, along with two peaks in the Fourier transform spectra [Fig. 1(d)]. This is indicative of long-range magnetic order and two inequivalent muon stopping sites. The data can be fitted either in the time domain [29] or in the field domain.

Below $T_N$, the spectral intensity $I(B)$ in the field domain can be modelled with a sum of three Lorentzian distributions:

$$I(B) = I_1 L(B; B_1, \lambda_1) + I_2 L(B; B_2, \lambda_2) + I_3 L(B; 0, \lambda_3),$$

(1)

where $L(B; B_i, \lambda_i)$ is a Lorentzian distribution centred on $B_i$ with a width $\lambda_i/\gamma_\mu$ ($\gamma_\mu = 2\pi \times 135.5$ MHz T$^{-1}$ is
The fitted values from Eq. 1 for the $T$ evolution of $\lambda_i$ and $B_i$ are presented in Figs. 2(b) and (c) respectively. As $T$ increases towards $T_N$, the two peaks broaden and merge, while their centers move towards 0 T as the long-range-ordered magnet transitions to the paramagnetic regime. The data in Fig. 2(c) were fitted with the phenomenological formula $B = B_0 (1 - (T/T_N)^{\alpha})^{\beta}$ [25], giving $T_N = 26.0(11)$ K for both components. We also find values of the internal fields at the muon sites as $T \to 0$: $B_1 = 330(3)$ mT and $B_2 = 276(6)$ mT. There appears to be an additional small feature in the data at low $T$ at $\approx$ 400 mT (marked by the asterisk in Fig. 1(d)), which may arise due to the site disorder and is discussed below.

Neutron powder diffraction (NPD) measurements were performed on the WISH time-of-flight diffractometer [29] at ISIS, the UK Neutron and Muon Source. A highly pure, single crystal sample was ground to a fine powder and loaded into a cylindrical vanadium can, which was mounted within a $^4$He cryostat. Data were collected with high counting statistics at 1.5 K, deep into the long-range ordered magnetic phase, and at 100 K in the paramagnetic phase. All diffraction data were refined using FULLPROF [30].

NPD data collected at 100 K (well above any anomalies in $\chi$) were fitted with a nuclear model based upon the published crystal structure [20]. The goodness-of-fit was excellent, the data and fit are shown in Fig. 3(a), and the refined structural parameters are given in [25]. There was no evidence of impurity phases in these data. There is a small amount of site mixing whereby 2.8% of Co sites are occupied by Ti, and 1.4% of Ti sites are occupied by Co.

When compared to the NPD pattern at 100 K, data collected at 1.5 K showed more than 10 new diffraction peaks (Fig. 3(b)). Based on bulk properties measurements [25] and the results of our ZF-$\mu$SR experiments, we could robustly assign the origin of the new intensities to long-range magnetic order. The observation of such a large number of magnetic diffraction peaks allowed us to unambiguously determine the magnetic propaga-

**FIG. 1.** (a) Magnetic susceptibility of CoTi$_2$O$_5$ measured in an applied field of $\mu_0 H = 0.1$ mT. The asterisk marks a kink at $T_N$. (b) Molar heat capacity. (c) ZF-$\mu$SR spectra above and below $T_N$. Fits to Eq. 1 of [25] are also plotted. (d) The Fourier transform of these spectra with fits with Eq. 1. The asterisk indicates an additional feature, discussed in the main text.
The magnetic order parameter can take one of three distinct directions in the space spanned by the irreducible representation: $(\eta, \eta)$, $(\eta, 0)$, or $(\eta, \epsilon)$. In all cases, the respective magnetic structures involve moments oriented strictly parallel to the orthorhombic $c$ axis. As all of the Co ions in the lattice are structurally equivalent, and therefore have the same chemical environment, all of the moments on these ions are constrained to be equal in magnitude. The only order parameter direction consistent with this constraint is $(\eta, 0)$.

$(\eta, 0)$ corresponds to a magnetic structure that low-

ers the symmetry of the system to monoclinic (magnetic space group $P_n2_1/m$ [31]). Magnetic moments on the Co1, Co2 and Co4 sites are parallel, but with the moment on the Co3 sites aligned antiparallel. A second domain exists with order parameter $(0, \eta)$, in which Co1, Co3, and Co4 sites are aligned parallel to each other, with Co2 antiparallel. Inspection of the $mS^m$ matrices given in Table S.II [25] shows that the $(\eta, 0)$ and $(0, \eta)$ magnetic domains are interchanged by the symmetry operator \{m$_s$[0,0,0]$, which is indeed broken below the magnetic phase transition. Furthermore, the $(\eta, 0)$ and $(0, \eta)$ domains are described by single propagation vectors, $k_1$ and $k_2$, respectively, which are also related by $m_s$. The two domains are shown in Fig. 4 with the schematic in the right hand panes illustrating the two propagation vector directions. We note that the two domains are indistinguishable in our powder diffraction data. The magnitude of the Co moment was refined against the diffraction data and found to be 2.72(1)$\mu_B$ at 1.5 K (see Fig. 3(b)).

The only nearest neighbour, super-exchange interactions between cobalt atoms (Co–O–Co) connect magnetic moments along the $a$-axis in Co1–Co1 chains. All other nearest-neighbour interactions are mediated by super-exchange (Co–O–O–Co). One can assume that the super-exchange interactions are dominant and, by the
exponentially determined magnetic structure, are antiferromagnetic. All exchange interactions between the (Co1,Co4) and (Co2,Co3) sites, coloured dark and light blue in Fig. [4] respectively, are exactly frustrated by the $m_x$ symmetry element. This frustration will likely lead to one dimensional ordering of the $a$-axis chains above $T_N$, but below the mean field energy of the dominant super-exchange interaction, consistent with the missing entropy evidenced in the heat capacity. For long range order to develop in CoTi$_2$O$_5$, the $m_x$ mirror symmetry must be broken either at a structural phase transition above $T_N$, or through the spin Jahn-Teller effect, in which the primary magnetic order parameter couples to a secondary, symmetry breaking structural order parameter spontaneously at $T_N$ [2, 3]. In the absence of any experimental evidence for a higher $T$ structural phase transition, we discuss possible magneto-structural coupling schemes.

The lowest order, free energy invariant that can couple the magnetic order to symmetry breaking crystallographic distortions must be quadratic in the magnetic moments (to be time-reversal even), and linear in the structural order parameter. On traversing the crystal in the direction of the propagation vector, magnetic moments change sign from one unit cell to the next. However, in the square of the moments each unit cell is the same. Hence, the square of the order parameter components, $\eta^2$ and $\epsilon^2$, must couple to a $k_s = (0,0,0)$, $\Gamma_1$ point structural distortion if the coupling term is to be invariant by translation, as required. Through exhaustive searches performed using the ISOTROPY suite [32, 33], the only linear-quadratic invariant that can couple a non-trivial $\Gamma_1$ point structural distortion to the magnetic order is $\delta (\eta^2 - \epsilon^2)$, where the irreducible representation of the structural order parameter, $\delta$, is $\Gamma_2^+$. For completeness, we should also consider the trivial coupling invariant $\xi (\eta^2 + \epsilon^2)$, where the structural order parameter $\xi$ transforms according to the totally symmetric $\Gamma_1$ irreducible representation, i.e. structural distortions that were already allowed within the $Cmcm$ parent symmetry can also occur at $T_N$. The atomic displacements of $\Gamma_1^+$ and $\Gamma_2^+$ are tabulated in [25]. High resolution laboratory based x-ray powder diffraction experiments yielded no evidence of these distortions below $T_N$. We therefore assume that any structural distortion in CoTi$_2$O$_5$ will be small, and the following calculations utilize the undistorted unit cell.

In order to establish the potential muon stopping sites in CoTi$_2$O$_5$, we employed Density Functional Theory (DFT) calculations to map out the electrostatic Coulomb potential of CoTi$_2$O$_5$ throughout its unit cell [26], plotted using the VESTA software [34] in Fig. 5(a). The maxima of such a potential map are a reliable approximation to the muon sites as they correspond to low energies needed to add a positive charge, such as the muon [35, 36]. We also carried out relaxation calculations [25], which allow for local distortions of the lattice caused by the muon’s presence. These gave a single symmetry-invariant muon stopping site at the general position $[0.322, 0.03, 0.151]$ with a 1.0 Å O–H-like bond with the nearest oxygen. This is in line with the approximate position we identified from the electrostatic potential.

There are 16 symmetry equivalent muon sites in the $Cmcm$ parent structure, which are split into two groups of eight in the magnetic unit cell, related by the broken $m_x$ symmetry, and are denoted by $\mu_A$ and $\mu_B$ in Fig. 5(b). The muon stopping probability is dependent upon the electrostatic potential local to the stopping sites, and under a small structural distortion induced at the phase transition, $\mu_A$ and $\mu_B$ become structurally inequivalent, and are therefore associated with different muon stopping probabilities. Changing from one magnetoelastic domain to another swaps the stopping probabilities of the two subgroups [25]. The symmetry of the magnetic structure also dictates that $\mu_A$ and $\mu_B$ will have different local magnetic fields: we calculate these to be 335(1) mT and 277(1) mT, in excellent agreement with our experimental observations at low $T$. As the area under the higher-field peak in Fig. 1(d) is larger than that of the lower-field peak, this suggests that the muon site experiencing this field is preferentially occupied. By comparing the energies at the muon sites under small distortions, we present a possible coupling between a shear distortion and the magnetic domains in [25] that could explain this.

Finally we consider the additional feature marked by an asterisk in Fig. 1(d) at $\approx 400$ mT. This feature likely arises due to a Co ion occupying the nearest Ti site so that a small fraction of muons stopping close to this defect experience a slightly larger field. Indeed, modelling this disorder gives a field at the muon site of $\approx 410$ mT, consistent with the experimental value.
To conclude, we have identified long range magnetic order in CoTi$_2$O$_5$, which is antiferromagnetic with $k = (\pm \frac{1}{3}, \pm \frac{1}{3}, 0)$. Frustration in the super-super-exchange interactions, along with the absence of a structural distortion above $T_N \approx 26$ K, indicate that the magnetic transition must be coupled to a structural transition at $T_N$ in order to relieve the frustration. This coupling occurs due to the spin Jahn-Teller effect, which has so far only been identified in higher-symmetry crystal structures [2-5]. Our results show that magnetic order driven by spin-phonon coupling can be extended to lower-symmetry systems. While the predicted distortion in CoTi$_2$O$_5$ was not resolvable in high resolution laboratory based x-ray powder diffraction experiments, it may be possible to resolve using higher-resolution synchrotron x-ray powder diffraction experiments.

The study of compounds structurally related to CoTi$_2$O$_5$ may provide further insight into the conditions required for the spin Jahn-Teller effect to, or not to, occur.

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1. G. A. Gehring and K. A. Gehring, Rep. Prog. Phys. 38, 1 (1975).
2. Y. Yamashita and K. Ueda, Phys. Rev. Lett. 85, 4960 (2000).
3. O. Tchernyshyov, R. Moessner, and S. L. Sondhi, Phys. Rev. Lett. 88, 067203 (2002).
4. M. Onoda and J. Hasegawa, J. Phys. Condens. Matter 15, L95 (2003).
5. T. Watanabe, S. I. Ishikawa, H. Suzuki, Y. Kousaka, and K. Tomiyasu, Phys. Rev. B 86, 144413 (2012).
6. O. Waldmann, C. Dobe, S. T. Ochsenheim, H. U. Güdel, and I. Sheikin, Phys. Rev. Lett. 96, 027206 (2006).
7. O. Waldmann, Phys. Rev. B 75, 174440 (2007).
8. S. Ogawa and S. Waki, J. Phys. Soc. Jpn. 20, 540 (1965).
9. J. K. Srivastava, S. Ramakrishnan, V. R. Marathe, G. Chandra, R. Vijayaraghava, J. A. Kulkarni, V. S. Darsheane, and S. Singh, J. Phys. C 20, 2139 (1987).
10. G. Gavoille, J. Hubsch, and S. Koutani, J. Magn. Magn. Mater. 102, 283 (1991).
11. S. Nayak, S. Thota, D. C. Joshi, M. Krautz, A. Waske, A. Behler, J. Eckert, T. Sarkar, M. S. Andersson, R. Mathieu, V. Narang, and M. S. Seehra, Phys. Rev. B 92, 214434 (2015).
12. D.-C. Kim and S.-K. Ihm, Environ. Sci. Technol. 35, 222 (2001).
13. J. Zhu and Q. Gao, Micropor. and Mesoporous Mater. 124, 144 (2009).
14. V. G. Harris, A. Geiler, Y. Chen, S. D. Yoon, M. Wu, A. Yang, Z. Chen, P. He, P. V. Parimi, X. Zuo, C. E. Patton, M. Abe, O. Acher, and C. Vittoria, J. Magn. Magn. Mater. 321, 2035 (2009).
15. C. P. Sandhya, B. John, and C. Gouri, Ionics 20, 601 (2014).
16. R. Ye, H. Fang, Y.-Z. Zheng, N. Li, Y. Wang, and X. Tao, ACS Appl. Mater. Interfaces 8, 13879 (2016).
17. X. Chu, X. Liu, G. Wang, and G. Meng, Mater. Res. Bull. 34, 1789 (1999).
18. T. S. Chao, W. M. Ku, H. C. Lin, D. Landheer, Y. Y. Wang, and Y. Mori, IEEE Trans. Electron Devices 51, 2260 (2004).
19. B. Brezny and A. Muan, J. Inorg. Nucl. Chem. 31, 649 (1969).
20. H. Müller-Buschbaum and M. Waburg, Monatsh. Chem. 114, 21 (1983).
21. A. Navrotsky, Am. Mineral. 60, 249 (1975).
22. A. Yankin, O. Vikhreva, and Y. Balakirev, J. Phys. Chem. Solids 60, 139 (1999).
23. K. T. Jacob and G. Rajitha, J. Chem. Thermodyn. 42, 879 (2010).
24. A. M. Balbashov, A. A. Mukhin, V. Y. Ivanov, L. D. Ishkhakova, and M. E. Veronchikhina, Low Temp. Phys. 43, 965 (2017).
25. See Supplemental Material at [URL will be inserted by publisher] for further data fitting and measured parameters, details of the DFT calculations, and a discussion of structural order parameters and lattice distortions.
26. S. J. Blundell, Contemp. Phys. 40, 175 (1999).
27. A. A. Yaouanc and P. D. de. Réotier, Muon spin rotation, relaxation, and resonance : applications to condensed matter (Oxford University Press, 2011) p. 486.
28. F. L. Pratt, Physica B 710, 289 (2000).
29. L. C. Chapon, P. Manuel, P. G. Radaelli, C. Benson, L. Perrott, S. Ansell, N. J. Rhodes, D. Raspino, D. Duxbury, E. Spill, and J. Norris, Neutron News 22 (2011).
30. J. Rodriguez-Carvajal, Physica B 192, 55 (1993).
31. The $P_{21}/m$ magnetic unit cell has a $\{[-2, 0, 0], [0, 0, 1], [\frac{1}{3}, \frac{1}{3}, 0]\}$ change of basis with respect to the $C_{mcm}$ parent structure, plus an origin shift of $[\frac{1}{3}, \frac{1}{3}, 0]$. N.B. The orthorhombic $C_{mcm}$ c-axis is parallel to the $P_{21}/m$ b-axis in the standard setting.
32. B. J. Campbell, H. T. Stokes, D. E. Tanner, and D. M. Hatch, J. Appl. Crystallogr. 39, 607 (2006).
33. B. T. Stokes, D. M. Hatch, and B. J. Campbell, ISOTROPY Software Suite (2007).
34. K. Momma and F. Izumi, J. Appl. Crystallogr. 41, 653 (2008).
35. J. S. Möller, P. Bonfà, D. Ceresoli, F. Bernardini, S. J. Blundell, T. Lancaster, R. De Renzi, N. Marzari, I. Watanabe, S. Sulaiman, and M. I. Mohamed-Ibrahim, Phys. Scripta 6, 068510 (2013).
36. F. R. Foronda, F. Lang, J. S. Möller, T. Lancaster, A. T. Boothroyd, F. L. Pratt, S. R. Gibling, D. Prabhakaran, and S. J. Blundell, Phys. Rev. Lett. 114, 017602 (2015).
37. A. Richards, https://doi.org/10.5281/zenodo.22558 (2015).