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The magneto-structural relationship in the tetrahedral spin chain oxide CsCoO$_2$

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We have investigated the structural and magnetic transitions in CsCoO$_2$ using calorimetric measurements, neutron powder diffraction (NPD), density functional theory (DFT) calculations and muon-spin relaxation ($\mu$SR) measurements. CsCoO$_2$ exhibits three-dimensional long-range antiferromagnetic (AFM) order at 424 K, resulting in antiferromagnetic alignment of chains of ferromagnetically ordered Co-Co spin dimers. Although there is no change in magnetic structure around a structural transition at $T^*=100$ K, the resulting bifurcation of corner sharing Co–O–Co bond angles causes a weakening of the AFM interaction for one set of bonds along the chains. Consequently, the system undergoing a complex freezing out of relaxation processes on cooling.

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Cobalt-based multinary oxides continue to attract significant interest due to their complex phase diagrams and the richness of their magnetic and electronic properties, induced by strong correlation between spin, charge, and orbital degrees of freedom. Together with chemical composition and synthesis conditions, the spin states in oxocobalates are sensitive to external physical parameters such as temperature and pressure. A subtle energy balance between the crystal field splitting and Hund’s rule exchange energy in the 3d states ultimately regulates the spin state of individual Co ions, offering new potential for tuning materials properties.\textsuperscript{1–3} The most commonly encountered coordination geometry in multinary oxocobalates(III), (3d$^6$), is octahedral, resulting in the low-spin electron configuration ($S=0$; $e_g^6\bar{e}_g^0$). The less commonly observed tetrahedral coordination geometry, with the weaker crystal field splitting, favours the high-spin state ($S=2$; $e_g^4\bar{e}_g^2$).\textsuperscript{4–8} Within the AMO$_2$ family of ternary oxides, the recently discovered CsCoO$_2$ features a singular crystal structure.\textsuperscript{9} Here Co$^{3+}$ is again in a tetrahedral coordination with edge-linked CoO$_4$ tetrahedra forming ‘bow-tie’ shaped Co$_2$O$_6^{2–}$ dimers which are then connected via corner-shared oxygen ions to form spin chains, creating an overall butterfly motif.

The special connectivity engendered by this architecture leads to very strongly coupled antiferromagnetism. According to the Goodenough-Kanamori-Anderson (GKA) rules the interdimer superexchange interaction (mediated via corner-shared oxygen ions, denoted O2) the Co–O2–Co bonding angle between neighboring Co atoms lies close to 180°; hence the subsequent interaction between partially filled $d$ orbitals is strongly antiferromagnetic (AFM). Conversely, intradimer Co–Co neighbors are coupled through the intervening edge-shared oxygen ions (denoted O1) with bonding angles close to 90°, and hence the superexchange interaction is expected to be ferromagnetic (FM). Measurements of the magnetic susceptibility\textsuperscript{9} show that the consequence of the connectivity between Co$^{3+}$ ions in such a structure is canted antiferromagnetic order below the remarkably high temperature of $T_N = 430$ K. Above the ordering temperature the susceptibility becomes temperature independent, suggesting the persistence of very strong exchange coupling. Despite the progress made in understanding this system, the magnetic behaviour that accompanies a structural transition that occurs around 100 K (hereafter denoted $T^*$), involving a monoclinic distortion resulting from a tilting of the edge-sharing tetrahedra, remains poorly understood. We have therefore carried out a detailed investigation into the magnetism of this system, whose aim is to determine the low energy model of spin interactions and to elucidate both the nature of the ordering transition and the magnetic effects that result from the low temperature structural transition.

Thermodynamic measurements confirm the presence of the reported magnetic transition around $T_N = 424$ K.\textsuperscript{9}

![FIG. 1: Peaks within the heating (a) and cooling (b) curves in the DSC measurements indicate an enthalpy of transition $\Delta H$ associated with the magnetic phase transition around $T \approx 421$ K. (c) The clear feature in the Fisher heat capacity at $T_N \approx 421$ K verifies the magnetic origin of the transition.](image-url)
observed as the temperature is reduced, producing a set
of monoclinic temperature model proposed in our earlier work.
try and can be correctly fitted employing the structural
NPD patterns collected between 100-
raction (NPD) measurements were
and the details of the structural transition around
ing the Fisher heat capacity method we have calculated
mal hysteresis (\(a\)) substantial change in magnetic entropy and large ther-
doesn’t alter the transition temperature range. There is
The refinement of the crystal structures above and below
\(T_N \approx 430\) K (within the paramagnetic and magnetically ordered phases respectively) reveals no significant modifi-
cation in the nuclear structure, indicating this transition is of solely magnetic origin.

At temperatures below 440 K, in both the \(\alpha\) and \(\beta\) phases, the NPD patterns of CsCoO\(_2\) also contain mag-
etic diffraction peaks due to the long range order (LRO) of the magnetic Co\(^{3+}\) ion spins. At the structural phase boundary (\(T^{*} \approx 100\) K), the extra (magnetic) intensities follow the trend of lowering the symmetry, for instance the magnetic intensity contained in the position of the \((1,1,1)\) peak of the crystal structure in the \(\beta\) phase is split into the extra intensity in the \((-1,1,1)\) and \((1,1,1)\) peaks in the patterns of the \(\alpha\) phase below \(T^{*}\), in a similar fashion to the nuclear intensities. However, no magnetic diffraction pattern changes are observed upon cooling below the structural transition, indicating that the magnetic ordering type and pattern is common to both structural phases. (It is possible that this tempera-
ture independence of the average Co–O bond distances and of the Co–O bond angles via the edge-sharing
of the magnetic Co
ion spins. At the structural phase
boundary (\(T^{*} \approx 100\) K), the extra (magnetic) intensities
all the magnetic diffraction peaks have been in-
dexed with the propagation vector \(k = (0,0,0)\), for both the \(\alpha\) and \(\beta\) phases. The symmetry analysis for this
propagation vector and Co ion locations within both the
\(C2/c\) and \(Cmca\) symmetries, has been carried out with the
program SARAh-2K\(^{12}\) and all symmetry-reasonable magnetic ordering schemes have been verified against the
Rietveld refinements. For both the \(\beta\) orthorhombic and the \(\alpha\) monoclinic phase, just one irreducible represen-
tation is compatible with the magnetic ordering model, satisfactorily explaining the observed magnetic intensity patterns. The magnetic ordering is essentially identical for both the \(\alpha\) and \(\beta\) phases and is illustrated in Fig. 2(c) for one buckled CoO\(_2\) layer. This spin order consists of ferromagnetically ordered Co-Co dimers, which are them-
selves antiferromagnetic ordered. The intradimer Co-Co
interatomic distance is significantly shorter than the cor-

FIG. 2: The behavior of the NPD refined nuclear structure for CsCoO\(_2\) associated with the structural phase transition (\(T^{*} \approx 100\) K): (a) Temperature dependence of the average Co-O2-Co bond angle involving corner-shared oxygen ions, (b) the \(c\)-axis lattice constant and the monoclinic angle \(\beta\) within \(\alpha\)-CsCoO\(_2\), (c) Illustration of the magnetic structure of a single CoO\(_2\) layer within \(\alpha\)-CsCoO\(_2\),

The results of differential scanning calorimetry (DSC\(^{10}\)) and the Fisher heat capacity method,\(^{11}\) are shown in
Fig. 1. The DSC thermogram measured on heating dis-
plays an endothermic peak centered around 421 K cor-
responding to the onset of long range AFM ordering, in good agreement with the Neel temperature observed by other methods (see below). The rate of tempera-
ture change only slightly affects the enthalpy change but
doesn’t alter the transition temperature range. There is
a substantial change in magnetic entropy and large ther-
mal hysteresis (\(\Delta T \approx 15\) K) at \(T_N\) between the heating and cooling scans of the DSC plot. In addition, employing
the Fisher heat capacity method we have calculated
d(\(\chi\))\(dT\) vs. \(T\) from our magnetic susceptibility data\(^{9}\) as shown in Fig. 1(c), displaying a sharp spike consistent with the onset of long range AFM ordering.

In order to elucidate the magnetic structure below \(T_N\)
and the details of the structural transition around \(T^{*}\),
neutron powder diffraction (NPD) measurements were
performed. The NPD patterns collected between 100-
700 K are consistent with orthorhombic \(Cmca\) symme-
try and can be correctly fitted employing the structural
model proposed in our earlier work.\(^9\) Below \(T^{*} \approx 100\) K a
displacive structural phase transition from the high tem-
perature \(Cmca\) space group (hereafter the \(\beta\) phase) to
monoclinic \(C2/c\) space group (hereafter the \(\alpha\) phase) is
observed as the temperature is reduced, producing a set
responding interdimer Co-Co junctions. In the directions of the closest interdimer distances in the ac-planes (along the diagonal \(a + c\) and \(a - c\) directions), the ordering between the Co moments in the adjacent dimers is antiferromagnetic, thus leading to the overall compensation of the total magnetization. In the adjacent CoO\(_2\) layer, the magnetic ordering repeats, being naturally offset by a \((0.5, 0.5, 0)\) translation. We find that the direction of the Co\(^{3+}\) magnetic moments is along the \(c\)-axis of the crystal lattice. The irreducible representations leading to this magnetic ordering type are \(\Gamma_1\) and \(\Gamma_5\) for the \(\alpha\) monoclinic and \(\beta\) orthorhombic phases of CsCoO\(_2\) correspondingly, which in principle do not preclude Co magnetic moment components along the other crystal axes. In the \(\alpha\) phase, an admixture of the \(a\)-component with identical ordering type as for the actual \(c\)-direction could be possible, while for both the \(\alpha\) and \(\beta\) phases, an admixture of the ferromagnetic ordering with the \(b\)-component could also be symmetrically reasonable. We are unable to assign any significantly meaningful values to the magnitudes of these two ordering types. This means that at all temperatures \(T \leq T_N\) where CsCoO\(_2\) exhibits magnetic LRO, the only definitely confirmed moment direction is along the \(c\)-axis of the unit cell. We have determined unusually low magnitudes for the ordered magnetic moments of 3.089 (2 K) and 2.628 (300 K)\(\mu_B/\text{Co}^{3+}\) for \(\alpha\)- and \(\beta\)-CsCoO\(_2\), respectively. The suppression of the Co\(^{3+}\) magnetic moment can be attributed to strong Co(3d)O(2p) hybridization.

To further resolve a microscopic picture of the possible static magnetic structures of CsCoO\(_2\), we performed a sequence of density functional theory (DFT) total energy calculations. The density functional plane wave pseudopotential method within the generalized gradient approximation was used as implemented in the CASTEP code. A systematic search was performed to categorize the possible AFM structures. In agreement with the NPD results, the lowest energy configuration for both the \(\alpha\)- and \(\beta\)-phases of CsCoO\(_2\) is the spin quantum number of the dimer triplet \(S\) = 2 equal to the continuous step from high- (low-) spin density transferred onto the edge-shared oxygen ions (1.2\(\mu_B\) per ion), in good agreement with the low-\(T\) value obtained through NPD refinements.

To probe the local magnetism on a timescale distinct from that measured by NPD, muon-spin relaxation (\(\muSR\)) measurements\(^{15}\) were made on CsCoO\(_2\). For asymmetry spectra obtained in ZF measurements, spontaneous oscillations are clearly visible for temperatures below around 420 K [Fig. 4(a)]. This constitutes unambiguous evidence of quasi-static magnetic LRO throughout the bulk of the material. A clear indication of the transition temperature is given by considering the time-averaged \((t \leq 9.5 \mu s)\) asymmetry data, which drops abruptly upon cooling, where asymmetry is lost as the material enters the magnetically ordered state. Fig. 4(b) shows this drop in average asymmetry, which may be fitted with a Fermi-like step function \(\langle A(T) \rangle = A_2 + \frac{A_1 - A_2}{1 + \exp(-T/T_c)}\), providing a method for extracting the transition temperature\(^{16}\) by parametrising the continuous step from high- (low-) \(T\) asymmetry \(A_2\) \((A_1)\) with midpoint \(T_c\) and width \(w\). The fit yielded values of \(T_c = 423.7(2)\) K and \(w = 1.57(2)\) K, in agreement with the value previously obtained.\(^9\)

Asymmetry spectra below \(T_N\) were best fitted with the single-frequency oscillatory relaxation function \(A(t) = A_1 \cos(2\pi\nu t)e^{-\lambda_1 t} + A_2e^{-\lambda_2 t} + A_0\), where the oscillating amplitude \(A_1\) was fixed to its average value of 5.7%. The non-relaxing baseline contribution \(A_0\) is attributable to muons which stop in the Ti sample holder, and, more importantly, to the non-precessing component of muon spins which lie parallel to the local magnetic field. Parameters resulting from this fit are displayed in Fig. 4(c,d). The Larmor precession frequency of the muon ensemble is related to the average magnitude of the static magnetic field \(B\) at the muon site via \(2\pi\nu = \gamma B\). Here \(B\), and hence \(\nu\) serves as an effective order parameter for
the LRO.

Upon cooling below $T_N$, the precession frequency $\nu$ increases in the expected manner, and the relaxation rates $\lambda_i$ peak, as is typical for an AFM phase transition (Fig. 4). Frequencies in the critical region $400 \, \text{K} < T < T_N$ were fitted to $\nu(T) = \nu(0) \left(1 - T/T_N\right)^{\beta}$, where $T_N = 424 \, \text{K}$ was fixed [see Fig. 4(b) inset]. The fit yielded a value for the critical parameter $\beta = 0.35(2)$, which is consistent with that expected for a 3D Heisenberg antiferromagnet. Moreover, dipole field simulations were performed on CsCoO$_2$ using the proposed magnetic spin structure and crystal parameters obtained from x-ray diffraction at 50 K and 296 K. A Bayesian analysis of this calculation shows that the observed muon precession frequencies are fully consistent with a moment size of 2.63$_{\pm 1}$M$_{\mu B}$ from the neutron measurement and further suggests a muon stopping site approximately 1 Å from the corner-sharing oxygen ions.

In addition to the behavior observed around $T_N$ described above, which is quite typical for an AFM transition, we find that on cooling though the region $T < T_N$, there are a number of additional, notable features in the $\mu$SR data. Most noticeably, we find that on cooling below $\approx 190 \, \text{K}$ the muon precession frequency $\nu$ is smoothly suppressed [Fig. 4(c)]. This is accompanied by a steady increase in $\lambda_1$, such that $\lambda_1$ is larger by a factor of about 2 below $T^*$ than in the region 200 K $< T < 300$ K [Fig. 4(d)]. Below $T^* \approx 100 \, \text{K}$, $\lambda_1$ and $\nu$ both level off at constant values. The decrease of $\nu$ below 200 K indicates a reduced value of average magnetic field strength experienced at the muon stopping sites. In the fast fluctuation limit we expect that the relaxation rate $\lambda \propto (\langle B^2 \rangle - \langle B \rangle^2)\tau$ (i.e. the second moment of the magnetic field distribution multiplied by the correlation time $\tau$) and so the additional dephasing indicates a broadening of the distribution of static magnetic field strengths experienced by the muon ensemble, or an increased correlation time as relaxation channels freeze out on the muon time scale. It is possible that this behaviour reflects the system exploring some of the energetically similar magnetic states predicted by the DFT calculations described above. These states are realized by flipping the overall spin of a dimer, while preserving their FM intradimer spin configuration [Fig. 3(b)]. Although this could conceivably lead the muon ensemble to experience a broader static magnetic field distribution, with a lower mean field strength, one would expect this to occur below $T^*$ rather than above it. Moreover, the refined cobalt moment sizes from NPD data (shown in the SI) do not show this suppression below 200 K, suggesting that the effect could be dynamic and related to the issue of timescale. Such effects are therefore not seen in the neutron measurements as these effectively take a ‘snapshot’ of the spin distribution, when compared to the muon GHz timescale.

Additional evidence for the influence of dynamics comes from the baseline asymmetry $A_b$, which increases abruptly at around 250 K and upon further cooling below $T^*$ gradually increases further [Fig. 4(c)]. Since relaxation of those muon spins that initially point along the direction of the local magnetic field can only be achieved by dynamic relaxation processes, the increase of such a non-relaxing signal is usually indicative of a freezing of relaxation processes. We therefore have evidence for an initial, abrupt freezing of some relaxation channels around 250 K, prefiguring the suppression of the precession frequency $\nu$, followed by a further, smooth increase that seems to be reminiscent of the size of the monoclinic distortion as indicated by both the change in unit cell angle $\beta$ and the splitting of the corner-shared bond angle Co–O2–Co (Fig. 2). This monoclinic distortion leads to a disproportionation of the corner-sharing

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**FIG. 4:** (a) $A(t)$ spectra, showing the clear single-frequency oscillations in the ordered regime with a fit described in the text (the 210 K data are offset by 10% for clarity). (b) Time-averaged asymmetry near the critical region, displaying an abrupt drop in asymmetry $\Delta A = A_2 - A_1$. The dashed line is the fit described in the text. Inset: scaling plot for the order parameter $\nu$. The linear fit indicates the region where the behaviour is critical. (c) Fitted parameters to the oscillatory relaxation function for all asymmetry data ($t \leq 9.5 \mu s$) for temperatures $T < T_N$; frequency $\nu$ and baseline asymmetry $A_b$, and (d) transverse relaxation rate $\lambda_i$. The Neel temperature $T_N = 424 \, \text{K}$ and the anomalous temperature region $100 \lesssim T \lesssim 190 \, \text{K}$ (including the approximate structural transition temperature $T^* \approx 100 \, \text{K}$) are indicated.
the increase in non-relaxing asymmetry

allows some relaxation channels to freeze out, leading to a

equivalent in the monoclinic phase it is possible that this

values. When these superexchange pathways become in-

interaction strengths pertaining to the weaker AFM in-

terdimer interactions, result in a complicated freezing of

relaxation processes on the muon timescale.

This work is partly based on the results of experiments carried out at the Swiss spallation neutron source SINQ and Swiss muon source SμS, Paul Scherrer Institut, Vülligen, Switzerland. We are grateful for the provision of beamtime, and to Alex Amato for muon experimental assistance. We also wish to thank UKCP and the Archer HPC facility for computer time. This work is supported by the EPSRC (UK).

10. The Supplemental Information contains further experimental details of synthesis, DSC, NPD and μSR measurements. Full structural details obtained from Rietveld refinements of NPD data are also provided.
17. The value of the critical parameter $\beta$ for a given fitted frequency $\nu$ was found to be sensitive to the time range over which the asymmetry spectra were fitted. The quoted value of 0.35 was obtained for fits over early times only ($t \leq 1 \mu s$), which are most sensitive to the behavior of the oscillations.