Two- and three-dimensional magnetic order in the layered cobalt oxychloride $\text{Sr}_2\text{CoO}_3\text{Cl}$

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The temperature dependence of the nuclear and magnetic structure of the cobalt oxychloride $\text{Sr}_2\text{CoO}_3\text{Cl}$ has been studied using neutron powder diffraction. The material crystallizes with a structure related to $\text{K}_2\text{NiF}_4$ and contains two-dimensional (2D) layers of $\text{Co}_2\text{O}_3$ square pyramids that are segregated along $\text{z}$ by alternate rocksalt SrCl and SrO blocks. The development of magnetic Bragg scattering indicates that the compound orders antiferromagnetically with a $T_N=330(5)$ K. The phase adopts a collinear magnetic structure related to the nuclear cell by the propagation vector $\text{k}=(\frac{1}{2}, \frac{1}{2}, 0)$ with the cobalt spins aligned along the $a$ axis of the magnetic cell. The ordered moment $\mu=2.82(3)\mu_B$, refined at 3 K, is consistent with a high-spin ($t_{2g}^2e_g^2$) electron configuration for the Co(III) ions. The onset of long-range magnetic order is characterized by a three-dimensional transition and is accompanied by anomalous behavior in the Co environment with distinct magnetostriction effects observed in the interlayer Co to Co exchange pathways. The transition is preceded by diffuse magnetic scattering arising from short-range in-plane correlations, with significant diffuse intensity observed up to the maximum temperature studied of 378 K. Magnetic susceptibility measurements indicate that the onset of significant 2D interactions occurs at $T\approx500$ K. The diffuse intensity can be fitted using the Warren function to give a maximum in the 2D correlation length $\xi$ of 40(4) Å just above $T_N$. Below $T_N$ diffuse scattering coexists with magnetic Bragg scattering, indicating that the transition to long-range order is hindered most probably due to the presence of stacking disorder between the antiferromagnetic sheets.

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I. INTRODUCTION

The continued investigation of correlated electronic behavior exhibited by $3d$ transition-metal oxides with extended structures has also led to the development of mixed anion materials in which the oxide ion is partially replaced.\textsuperscript{1–3} One such class of compounds is the oxide-halide family. These materials are of particular relevance to studies into cooperative behavior as they offer the potential to both control the transition-metal oxidation state, through variation of the oxide to halide ratio, and influence interlayer and intralayer separations within a particular structure type through variation in halide size. The flexibility afforded by oxyhalides is best exemplified by the wide range of oxide halide superconductors\textsuperscript{4} developed from the $\text{K}_2\text{NiF}_4$ oxychloride $\text{Sr}_2\text{CuO}_2\text{Cl}_2$.\textsuperscript{5} Following the discovery of high-$T_c$ materials, $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ and other lamellar oxyhalide cuprates have been investigated in great detail to probe the behavior of undoped superconductors,\textsuperscript{6,7} and $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ is now viewed as an ideal square lattice Heisenberg antiferromagnet.\textsuperscript{8}

Recently cobalt oxyhalide chemistry has been extended with the report of cobalt (II) $\text{Sr}_2\text{CoO}_2\text{X}_2$ ($\text{X}=\text{Cl}$ and Br) phases,\textsuperscript{9} that are isostructural to $\text{Sr}_2\text{CuO}_2\text{Cl}_2$, and isolation of single crystals of the cobalt (III) Ruddlesden-Popper oxychlorides $\text{Sr}_2\text{CoO}_2\text{Cl}$ and $\text{Sr}_2\text{CoO}_2\text{Br}$ by McGlothlin et al.\textsuperscript{10} In a later study the crystal structures of $\text{Sr}_2\text{CoO}_2\text{Cl}_2$ and $\text{Sr}_2\text{Co}_2\text{O}_2\text{Cl}_3$ were further characterized using neutron powder diffraction at room temperature (RT).\textsuperscript{11} The interest in cobalt oxides and oxyhalides stems from the metal’s ability to adopt a number of electron configurations for a range of oxidation states in the solid state. This relationship between valence and spin state leads to a number of cobalt phases, such as $\text{LaCoO}_3$ (Ref. 12) and Tl$\text{Sr}_2\text{CoO}_3$ (Ref. 13), displaying unusual magnetic and electronic properties.

The present study describes the results of a variable-temperature neutron powder diffraction investigation of $\text{Sr}_2\text{CoO}_3\text{Cl}$ which has revealed the presence of antiferromagnetic order within the material. The evolution of the cobalt spin correlation has been monitored through the growth of magnetic Bragg and diffuse scattering in the temperature range $2\leq T \leq 378$ K. The diffraction results are interpreted alongside susceptibility measurements and provide insight into the interplay between short-range two-dimensional (2D) and long-range three-dimensional (3D) order within the material.

II. EXPERIMENT

The synthesis of polycrystalline $\text{Sr}_2\text{CoO}_3\text{Cl}$ reported by Louerio et al.\textsuperscript{11} was achieved through reaction of $\text{SrO}_2$, $\text{SrCl}_2$, and $\text{Co}_3\text{O}_4$ and is reliant on oxidation of cobalt through the presence of excess oxygen from the decomposition of $\text{SrO}_2$ during phase formation to give stoichiometric $\text{Sr}_2\text{CoO}_3\text{Cl}$. This approach yielded a phase of reasonable purity; however, appreciable quantities of $\text{Sr}_2\text{Co}_3\text{O}_{15}$ (Ref. 14) (7.5 wt %) and $\text{Sr}_2\text{Co}_2\text{O}_5\text{Cl}_4$ (Ref. 15) (5.6 wt %) were also present along with an unidentified impurity phase. In an effort to improve phase purity we first synthesised the $\text{Co}_3^+$ precursor $\text{Sr}_2\text{Co}_2\text{O}_5$ by reaction of $\text{SrCO}_3$ and $\text{Co}_3\text{O}_4$ at 1000°C (Ref. 16) and then reacted $\text{Sr}_2\text{Co}_3\text{O}_5$ with high-purity $\text{SrCO}_3$ and $\text{SrCl}_2$ in the molar ratios 1:1:1 at 850°C for a period of 24 h. The heating was interrupted once to regrind the sample. The sample obtained was a black highly crystalline material. Long-scan powder x-ray diffraction data
in the 2θ range 10° – 100° were collected on a Bruker D8 Advance diffractometer operating with Cu Kα1 radiation and a SOLEX detector to filter the fluorescence associated with Co-containing materials. The only impurities detected were Sr4OCl6 (Ref. 17) and Sr4Co3O15 (Ref. 14) estimated at a level of ~2%–3% from the ratio of most intense Sr2CoO3Cl and impurity reflections.

Constant-wavelength neutron powder diffraction (NPD) were collected on a 5-g sample at 3 K on the high-resolution diffractometer D2B at the Institut Laue Langevin (ILL), France, for a period of 6 h. The sample was placed inside a 10-mm vanadium container and cooled using a Displex refrigerator. The optimum wavelength of the instrument (λ = 1.5943 Å) was utilized to obtain high-quality crystallographic data. Further scans in the temperature range 2–378 K were then obtained using the high-flux diffractometer D20 to monitor the evolving crystal and magnetic structure. The machine was operating in high-resolution mode with Soller collimators set at 10°, a vertical 10-mm-wide monochromator window, and λ = 2.4178 Å. Scans below RT (298 K) were performed in a standard ILL cryostat and data at 298 K and above collected using a dedicated furnace. Approximate scan times of 30 min were utilized for each temperature. Analyses of the crystal and magnetic structure were then performed using the GSAS package.18

Magnetic susceptibility data were collected on a powder sample of Sr2CoO3Cl. Data in the temperature range 1.8–400 K were collected on warming using a Quantum Design MPMS-5S superconducting quantum interference device (SQUID) magnetometer in an applied field of 1 kOe. Further data were then collected using an Oxford Instruments VSM on heating from 360 K to 850 K with the sample mounted inside a furnace insert and in the same applied field.

III. RESULTS

A. Crystal and magnetic structures

The nuclear structure of Sr2CoO3Cl was initially determined from Rietveld analysis of the higher-resolution D2B data collected at 3 K using the atomic coordinates reported by Loureiro et al. as the starting model.11 The analysis proceeded with refinement of global parameters such as background and lattice constants to give a reasonable fit to the data; however, discrepancies in the calculated intensity were apparent for certain reflections. This effect was attributed to a preferred orientation arising from the platelike morphology of the crystallites within the sample and was corrected satisfactorily using the March-Dollase function.19 The positional and atomic displacement parameters for the individual atoms were then varied. In the closing stages of the refinement the occupancy of each site was permitted to vary and no significant site deficiencies were detected, indicating that the minor impurity levels of Sr6Co3O15 (2.6 wt %) and Sr4OCl6 (1.5 wt %) have no effect on the stoichiometry of the main phase. Table I summarizes the structural parameters derived from the refinement and the fit achieved to the data is shown in Fig. 1. Analysis of the lower-resolution D20 data employed the atomic coordinates determined from the D2B analysis in initial cycles and followed the same refinement procedure.

Additional Bragg reflections were observed in the NPD scans that could not be accounted for by the nuclear model of Sr2CoO3Cl. The low-angle position of the peaks indicated that they might be magnetic in origin and this was confirmed by variable-temperature scans performed on D20, which showed that the reflections vanished above T = 338 K (Fig. 2). The reversibility of the magnetic transition was then established on cooling back to RT. The magnetic intensities could be indexed on the basis of an orthorhombic magnetic cell related to the nuclear cell by \( a_{\text{mag}} = b_{\text{mag}} = \sqrt{2} a_{\text{nuc}} \) and \( c_{\text{mag}} = c_{\text{nuc}} \). For a collinear magnetic structure this implies a propagation vector \( k = (\frac{1}{2}, \frac{1}{2}, 0) \). The most intense magnetic peaks were identified as the (101), (102), and (103) reflections analogous to the behavior observed for the K2NiF4

![Image](174407-2)

**FIG. 1.** The NPD pattern obtained for Sr2CoO3Cl on D2B (λ = 1.5943 Å) at 3 K. Crosses are observed data; lines are calculated and difference plots. Vertical tick marks indicate the position of allowed reflections for the nuclear structure of Sr2CoO3Cl (bottom) and magnetic structure (top). Reflections for the minor impurities Sr4OCl6 (lower middle) and Sr6Co3O15 (upper middle) are also shown.
phases La$_2$NiO$_4$ (Ref. 20) and PrCaCrO$_4$ (Ref. 21). The magnetic form factor of Co$^{3+}$ was used$^{22}$ and an excellent fit to the data (Fig. 3) achieved with the cobalt spins aligned along the $x$ direction to form antiferromagnetic layers within the $ab$ plane and nearest moments in neighboring layers stacked to form antiferromagnetic sheets in the $ac$ plane. Alternatively the spin direction could be chosen to lie along the $y$ direction with $A$-type centering to yield an equivalent result. Models with a component of the moment along $z$ were tested; however, this led to a deterioration of the fit and any experimentally significant canting of the spins out of the basal plane can be discounted. The temperature dependence of the $T_{\text{N}}$ and $T_{\text{N}}^\perp$ magnetic reflections allows the $T_{\text{N}}$ to be estimated as 330(5) K.

FIG. 2. The temperature dependence of the magnetic scattering exhibited by Sr$_2$CoO$_3$Cl in the $T$ range 298–378 K. The positions of the two most intense magnetic Bragg reflections are labeled.

FIG. 3. The NPD pattern obtained for Sr$_2$CoO$_3$Cl on D20 at 2 K. The plot follows the same labeling style as in Fig. 1. Also indicated are the (101) and (102) magnetic reflections of Sr$_2$CoO$_3$Cl.

B. Two-dimensional correlation length

In addition to the coherent Bragg scattering a broad asymmetric feature centered at $2\theta \sim 25.5^\circ$ ($d$ spacing $\sim 5.5$ Å) was also apparent. The shape of this feature, which is evident even at the highest experimental temperature of 378 K, is seen to sharpen on cooling until the $T_{\text{N}}$ is reached. Cooling below $T_{\text{N}}$ sees the growth of magnetic Bragg peaks at the expense of the asymmetric diffuse peak (Fig. 2). Remarkably there is a wide temperature range below $T_{\text{N}}$ where both coherent magnetic Bragg scattering and diffuse scattering coexist. Even at 200 K there appears to be a weak diffuse peak underneath the strong (101) magnetic reflection. This diffuse magnetic scattering arises from short-range 2D spin-spin correlations and its position corresponds to the (10) reflection of a short-range-ordered system. The intensity was fitted using the Warren function$^{23}$ [Eq. (1)] to obtain an estimate of the 2D spin-spin correlation length $\xi$ for temperatures at and above 298 K. The scattered power is given by

$$P(\theta) = K m F^2_{hk} \frac{(1 + \cos^2 2\theta)}{2 \sin^2 \theta} \left( \frac{\xi}{\lambda \sqrt{\pi}} \right)^{1/2} F(a),$$

where

$$a = 2 \frac{\xi \sqrt{\pi}}{\lambda} (\sin \theta - \sin \theta_0)$$

and $K$ is a scale factor, $\lambda$ is the neutron wavelength, and $m$ is the multiplicity of the 2D reflection $(hk)$ centered at $\theta_0$ with structure factor $F_{hk}$. The function $F(a)$ was evaluated numerically as described previously.$^{24}$

All diffraction patterns collected at and above 298 K were fitted between $20^\circ < 2\theta < 38^\circ$ with data in the vicinity of the impurity nuclear reflection at $29.6^\circ$ being excluded. For measurements performed at 318 K and below it was necessary to also exclude data in the vicinity of the (101) and (102) magnetic Bragg peaks. In the absence of a full spin polarization analysis the diffuse magnetic scattering was estimated to be at most only $\sim 25\%$ of the background at the peak maximum and qualitatively good fits (Fig. 4) to the Warren function.
were achieved by subtracting a simple linear background function. The thermal dependence of the correlation length $\xi$ through the long-range-ordering transition is shown in Fig. 5a. Also shown in Fig. 5b are the temperature dependence of the diffuse intensity and the behavior of the total magnetic scattering in the same 2θ region.

C. Magnetic susceptibility

The temperature dependence of the magnetic susceptibility of Sr$_2$CoO$_3$Cl in the temperature range 10–850 K is plotted in Fig. 6. The molar susceptibility passes through a broad maxima centered at $T=500$ K (see inset) and then drops slowly on cooling, reaching a minimum at $\approx 200$ K. At very low temperatures $\chi$ shows a rise attributed to the Sr$_6$Co$_{3}O_{15}$ impurity. The increase in scatter observed for the high-temperature data reflects the decreased sensitivity and greater level of background signal associated with the vibrating-sample-magnetometer (VSM) measurement. Imperfect background subtraction for the VSM data accounts for the small discrepancy in the measured susceptibility between the two data sets.

IV. DISCUSSION

The presence of magnetic Bragg scattering in all neutron powder data sets collected below 328 K for Sr$_2$CoO$_3$Cl reveals the presence of antiferromagnetic long-range order (AFLRO) of the cobalt spins in the material. The original room-temperature neutron diffraction study by Loureiro et al. did not report this behavior and concluded from susceptibility measurements that no magnetic order was present in the compound. Initially, differences in the synthetic method and phase purity of the respective samples seemed to be the most likely reason for this contrasting behavior. For example any small oxygen deficiency within the material could significantly affect the chances of observing magnetic order, particularly the long-range correlation required for coherent Bragg scattering. However, from inspection of the low-angle neutron data presented in Ref. 11 we now conclude that the three additional peaks observed in the region 16° –30° were wrongly identified as an impurity and were in fact of magnetic origin. Possibly the poorer phase purity and the absence of variable-temperature scans contributed to the magnetic scattering being overlooked.

The crystal and magnetic structures of Sr$_2$CoO$_3$Cl are shown in Fig. 7 in which the close structural analogy between the phase and the K$_2$NiF$_4$ structure is apparent. The large chloride ion effectively replaces one of the terminal apical oxygen positions of the perovskite block of the K$_2$NiF$_4$ phase LaSrCoO$_4$ (Ref. 26). Ordering of the chloride ion along $z$, rather than random replacement of oxide, leads to a reduction of the cell symmetry from the I$4/mmm$ of ideal K$_2$NiF$_4$ phases to P$4/nmm$. Significantly the presence of the chloride ion results in alternate CoO$_2$ layer separations of 5.85 Å and 8.42 Å along the $c$ direction rather than the regular $c/2$ stacking of K$_2$NiF$_4$. A further structural subtlety is that the cobalt ions are shifted along $z$ away from the basal plane of the CoO$_3$ square pyramids and this gives rise to a high level of buckling—in i.e., a O(1)-Co-O(1) bond angle $\approx 162$° compared with the flat 180° planes observed in standard 0201 phases.

The cobalt spins within Sr$_2$CoO$_3$Cl are aligned in an antiparallel manner in the $ab$ plane of the magnetic cell. This arrangement leads to two possibilities for the relative orientation of the nearest-neighbor layers as illustrated by the re-
labeled $K_2NiF_4$ phases $La_2NiO_4$ (Ref. 20) and $La_2CuO_4$ (Ref. 27). The absence of the (100) reflection for $Sr_2CoO_3Cl$ enables the spin arrangement shown in Fig. 7 to be identified in which an antiferromagnetic (AF) relationship between neighboring spins located in the $ac$ plane is favored. In comparison a ferromagnetic arrangement is observed for both $La_2CuO_4$ and $Sr_2CuO_2Cl_2$ (Ref. 6). It is noteworthy that for $2D$ antiferromagnets such as $K_2NiF_4$ itself$^{20}$ and the manganese oxychloride $Sr_2MnO_3Cl$ (Ref. 29), with spin directions confined to the tetragonal axis this subtlety does not arise. In their paper on the magnetism of $Sr_2CuO_2Cl_2$ Vaknin et al.$^6$ have shown that for purely dipolar interactions the magnetic structure observed for $La_2CuO_4$ is favored rather than the spin arrangement adopted by $La_2NiO_4$ and now observed for the cobalt oxychloride. Therefore it seems likely that interlayer exchange coupling, rather than through-space dipolar interactions, governs both the spin structure and the transition to LRO within $Sr_2CoO_3Cl$.

The refined moment of $2.82(3)\mu_B$ obtained at $3\,K$ from the D2B data is in agreement with the presence of high-spin $Co^{3+}$ ($S=2$) once the expected reductions commonly observed for the static moment in related $2D$ systems due to zero-point fluctuations and covalency effects are taken into account. The magnitude of the moment, however, does not preclude the presence of a level of the intermediate, $S=1$, spin state that is known to occur in distorted chemical environments.$^{13}$ Furthermore, determination of the spin state may be complicated by partially quenched orbital interactions for the cobalt ion, a conclusion that is supported by the $\mu_{Cll}=6.8\mu_B$ obtained from the high-temperature susceptibility data ($600–850\,K$), and further studies are required for a definitive assignment of the cobalt electronic configuration.

The temperature dependence of the normalized moment in the temperature range $2–340\,K$ along with a fit to the power law given in Eq. (3) below is shown in Fig. 8. Also shown is the expected behavior for a $2D$ Ising model (dashed line). The inset shows the fit to the power law in the critical region.

\[
\frac{M(T)}{M(0)} = C(1-T/T_N)^\beta.
\]

A reasonable fit over the whole temperature range was obtained with $C=1.08(4)$, $T_N=328(4)\,K$, and $\beta=0.28(3)$. If the fit is instead limited to the critical region (see inset), then excellent agreement is obtained with $C=1.2(2)$, $T_N=328(1)\,K$, and $\beta=0.33(5)$ consistent with a $3D$ transition. This behavior contrasts with that exhibited by classical $2D$ systems such as $K_2NiF_4$ (Ref. 28) and $K_2FeF_4$ (Ref. 30) which display $2D$ Ising-type transitions with $\beta \sim 0.15$. The transition from $2D$ correlations to long-range order in $K_2NiF_4$ occurs within a $1\,K$ window either side of $T_N$ as LRO is established essentially in two dimensions and $3D$ order follows parasitically. In contrast the behavior of $Sr_2CoO_3Cl$ is characterized by a more gradual transition that is consistent with interlayer coupling playing a significant part in the growth of LRO in the material. In this respect $Sr_2CoO_3Cl$ is similar to $La_2CuO_4$ (Ref. 31).

The appearance of coherent magnetic Bragg scattering is preceded by diffuse scattering arising from short-range $2D$ correlations confined to the basal $CoO_2$ planes. The sharpening of the Warren peak on cooling from $378$ to $338\,K$ (Fig. 2) is clearly associated with a steady increase in the $2D$ correlation length which reaches a maximum of $40\,\AA$ at $338\,K$ just above $T_N$ (Fig. 5). In theory for such a second-order phase transition we expect a divergence of $\xi$ to infinity at $T_N$, followed by a crossover to long-range $3D$ ordering, whereupon the Warren feature should disappear as magnetic Bragg peaks are formed. We do not observe such an abrupt transition. Instead both diffuse scattering and magnetic Bragg peaks coexist over a large thermal region. This behav-
ior indicates that the transition to 3D LRO is hindered in some areas of the sample and the most likely explanation for this lies with the microstructure of the sample used in the current study. For example, the presence of stacking faults along c will severely affect the 3D correlation within the material. Physically, the occurrence of stacking disorder within \( \text{Sr}_2\text{CoO}_3\text{Cl} \) is likely given the presence of an easy plane of cleavage along the relatively weakly bonded double \( \text{SrCl} \) layers. The significant preferred orientation observed for the diffraction patterns of the finely ground sample provides strong evidence that such a cleavage plane is present in the material. In addition it is possible that occasional intergrowths of the closely related double- and triple-layer phases \( \text{Sr}_x\text{Co}_y\text{O}_z\text{Cl}_w \) (Ref. 10) and \( \text{Sr}_x\text{Co}_y\text{O}_z\text{Cl}_w \) (Ref. 15) occur. These would also significantly disrupt the interlayer coherence required for 3D Bragg intensity.

The maximum in correlation length, \( \xi = 40(4) \ \text{Å} \), corresponds to a coherence length that extends within the \( xy \) plane for ca. 10 unit cells before diminishing to approximately half that value at 378 K (Fig. 5). In comparison a value of \( > 200 \ \text{Å} \) has been determined for \( \text{La}_2\text{CuO}_4 \) above \( T_N \) (Ref. 31) and a recent study of the \( \text{K}_2\text{NiF}_4 \) manganite family \( \text{Ba}_x\text{Sr}_{1-x}\text{LaMnO}_4 \) \( (0 < x < 0.30) \) reported a \( \xi = 21(3) \ \text{Å} \) for the \( x = 0.06 \) member.\(^{32}\) The values obtained below \( T_N \) remain static at around 30 Å and this may provide an estimate of the size of the two-dimensionally correlated domains that persist below \( T_N \) due to static disorder.

The temperature dependence of the magnetic susceptibility of \( \text{Sr}_2\text{CoO}_3\text{Cl} \) (Fig. 6) provides further evidence of the 2D magnetic character of the material at temperatures above \( T_N \). The broad transition observed between 400 and 600 K is a signature of short-range AF correlations in a planar system and indicates the onset of significant 2D order at \( T_{x\text{max}} \approx 500 \text{ K} \). Between 500 K and 330 K the strength of these in-plane correlations grows until \( \xi \) reaches a critical point at \( T_N \) as defined by Eq. (4) and 3D ordering becomes energetically favorable:\(^{33}\)

\[
T_N = \frac{\xi}{a} J_x S^2 / k_B .
\] (4)

Taking \( \xi = 40 \ \text{Å} \), the cell parameter \( a = 3.9 \ \text{Å} \), and \( S = 2 \) allows the value of the interlayer exchange \( J_x = 0.78 \ \text{K} \) to be estimated. The strength of the intraplanar \( J_{xy} \) interaction can also be evaluated using Line’s formula\(^{34}\) and taking \( T_{x\text{max}} = 500 \text{ K} \) yields a \( J_{xy} = 74.3 \ \text{K} \):

\[
\frac{k_B T_{x\text{max}}}{J_{xy}} = 1.12 S(S + 1) + 0.10 ,
\] (5)

indicating that the \( J_x \) interaction within \( \text{Sr}_2\text{CoO}_3\text{Cl} \) is approximately two orders of magnitude weaker than the in-plane superexchange coupling.

Having characterized the thermal behavior of the magnetic correlations within \( \text{Sr}_2\text{CoO}_3\text{Cl} \) our attention now focuses on the phase’s crystal structure. The temperature dependences of the lattice parameters and cell volume derived from analysis of the D20 data over the complete temperature range of study are shown in Fig. 9. From these data it is clear that the onset of LRO at the \( T_N \approx 330 \text{ K} \) is not accompanied by a gross structural transition. Strictly, the symmetry is reduced from tetragonal to orthorhombic at the magnetic phase transition. This lowering of symmetry is expected to relieve the degeneracy associated with the interlayer exchange pathways of the tetragonal cell and stabilize the observed spin structure. Indeed the related double-layer Ruddlesden-Popper phase \( \text{Sr}_x\text{Y}_{0.8}\text{Ca}_{0.2}\text{Co}_2\text{O}_6 \) (Ref. 35) has recently been shown to undergo a large orthorhombic distortion at the onset of LRO, emphasizing the link between spin and structural degrees of freedom. However, no detectable peak splitting was observed in the D20 data on crossing \( T_N \). To further test for a reduction in symmetry below \( T_N \) the high-resolution D2B data collected at 3 K were analyzed using an orthorhombic cell. A stable refinement could be obtained with parameters \( a = 3.88556(8) \ \text{Å} \) and \( b = 3.88875(8) \ \text{Å} \), and a small improvement in the agreement statistics, \( \chi^2 = 5.25, R_{wp} = 4.74\% \), and \( R_p = 3.44\% \) compared with 5.43, 4.83\%, and 3.51\%, respectively, in \( P4\text{mm} \text{m} \), was obtained. However, the refined distortion \( b/a \approx 1.0005 \) lies on the limit of the resolution of D2B and the enhancement in the least-squares fit may merely reflect the additional complexity of the structural model. Therefore from our diffraction data the average nuclear structure of \( \text{Sr}_2\text{CoO}_3\text{Cl} \) is best described as tetragonal throughout the measured temperature range.

Figure 10 shows the cobalt bond distances and the in-plane \( \text{Co-O(1)-Co} \) bond angles obtained at 298 K and above. The plots provide evidence of anomalous behavior in the temperature region close to the onset of LRO. Both the \( \text{Co-O(1)} \) in-plane and \( \text{Co-Cl} \) apical separations remain constant between 380 K and 340 K before contracting on cooling below 340 K. Coincidentally the \( \text{Co-O(1)-Co} \) basal bond angle appears to undergo a weak change, flattening out and reducing the extent of buckling. The structural response can be related to the possible AF exchange pathways within \( \text{Sr}_2\text{CoO}_3\text{Cl} \). As \( T_N \) is associated with the onset of 3D order in the material the pathways between adjacent Co ions separated along \( z \) by the rocksalt \( \text{Sr-O} \) and \( \text{Sr-Cl} \) layers are of particular interest. Figure 11 shows the two shortest possible exchange pathways across these layers, with a four-bond link.
mediated through the Sr(1)-O(2) bond and a four-bond pathway through the Cl-Sr(2) bridge. For the sake of clarity only one of the equivalent possibilities for each pathway has been highlighted. Both distances show significant changes close to the onset of LRO, with distance \( J_1 \) passing through a distinct minimum and \( J_2 \) showing a sharp decrease [Fig. 12(a)], suggesting that these interactions play a critical role in the interlayer magnetic propagation. This behavior leads to a reduction in the separation of Co ions across the rocksalt SrCl layers of approximately 0.06 Å between 338 K and 298 K [Fig. 12(b)] and represents a small magnetostriction associated with \( T_N \). The structural response, although discernible, is weak and compatible with the magnetic transition involving a crossover from strong existing 2D interactions to longer-range 3D correlations in the material.

V. CONCLUSION

The magnetism of the layered oxychloride \( \text{Sr}_2\text{CoO}_3\text{Cl} \) exhibits a transition from short-range two-dimensional correlations to long-range three-dimensional order. The crossover occurs at \( T_N = 330(5) \) K and is characterized by a 3D transition rather than the 2D Ising-like behavior that may have been expected given the material’s highly anisotropic structure. In the AFLRO state the cobalt spins are confined to the tetragonal plane and align with a spin structure analogous to that previously described for \( \text{La}_2\text{NiO}_4 \). Both the spin arrangement and the nature of the transition indicate that exchange-mediated interactions are responsible for the Co ordering, an interpretation that is further supported by the weak magnetostriction observed in the interlayer exchange pathways at the onset of LRO. Two-dimensional correlations persist below \( T_N \) and it is believed that stacking disorder of the antiferromagnetic sheets restricts extended 3D correlation. In this respect further measurements on a high-quality single crystal would be beneficial to accurately gauge the effect such structural disorder has on the magnetic correlation within \( \text{Sr}_2\text{CoO}_3\text{Cl} \).
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