Bi$_2$CoO$_2$F$_4$—A Polar, Ferrimagnetic Aurivillius Oxide-Fluoride

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ABSTRACT: Aurivillius oxides are well-known ferroelectrics, but by replacing oxide ions by fluoride, divalent magnetic cations can be introduced, giving Bi$_2$MO$_2$F$_4$ (M = Fe, Co, and Ni). Our combined experimental and computational study on Bi$_2$CoO$_2$F$_4$ indicates a low-temperature polar structure of P2$_1$ab symmetry (analogous to ferroelectric Bi$_2$WO$_6$) and a ferrimagnetic ground state. These results highlight the potential of Aurivillius oxide-fluorides for multiferroic properties. Our research has also revealed some challenges associated with the reduced tendency for polar displacements in the more ionic fluoride-based systems.

INTRODUCTION

Designing and preparing new multiferroic and magnetoelectric phases (with both polar and magnetic order) is an ongoing challenge in materials chemistry and physics. The Aurivillius oxides are well-known ferroelectrics, but it has proved challenging to introduce high concentrations of magnetic ions into these phases. Aurivillius materials, of general formula Bi$_2$A$_{n-1}$BO$_{n+3}$ (with A typically group 2 or lanthanide or Bi, Pb cations; B typically d$^0$ transition metal ions in high oxidation states), adopt layered perovskite-related structures composed of fluoride-like [Bi$_2$O$_4$]$^{2+}$ layers separating perovskite-like blocks n layers thick (Figure 1). The ideal aristotype structure is tetragonal, but Aurivillius phases often adopt lower-symmetry distorted structures, which allow in-plane polarizations and rotations of BO$_6$ octahedra. These distortions occur in part to optimize cation coordination environments and to relieve strain in stacking the slightly wider perovskite-like blocks with the more narrow [Bi$_2$O$_4$]$^{2+}$ layers.

These distortions can be discussed in the context of the n = 1 Aurivillius oxide Bi$_2$WO$_6$. Its aristotype high-symmetry structure would be of I4/mmm symmetry (a$_0$ ≈ 3.8 Å, c$_0$ ≈ 16.4 Å, where the subscript t denotes this ideal I4/mmm structure), although this ideal structure is never observed in practice—Bi$_2$WO$_6$ undergoes a reconstructive phase transition on warming above 950 °C. At intermediate temperatures, Bi$_2$WO$_6$ adopts a polar structure of B2cb symmetry, which allows rotations of WO$_6$ octahedra about an in-plane axis (about [110]$_t$), as well as polar displacements along this same axis (Figure 1). These distortions of odd-layer Aurivillius and Ruddlesden–Popper phases have been tabulated and can also be explored using web-based ISODISTORT software, and key distortions are illustrated in Figure 1 (see also the Supporting Information). The distortions can be described using irrep notation (where the letter denotes the k-point of the distortion, and the superscript indicates whether or not inversion symmetry is preserved), and the rotations of BO$_6$ octahedra can also be described using Glazer notation. The intermediate B2cb structure of Bi$_2$WO$_6$ allows both X$_t$$^+$ ($\alpha$'a$'$c$'$) rotations of WO$_6$ octahedra and X$_s$$^-$ in-plane polar displacements. On cooling below 670 °C, a second WO$_6$ rotation (X$_s$$^+$, a$'$c$'$) occurs, lowering the symmetry further to P2$_1$ab.

The more limited compositional flexibility of the Aurivillius phases (including the difficulties associated with introducing magnetic ions) compared with perovskite and Ruddlesden–Popper systems may relate to steric factors related to stacking strain but could also arise from the polar displacements of the d$^0$ B-site cations in Aurivillius materials, which would be less favorable for magnetic d$^0$ transition metal ions. Replacing some of the oxide ions by fluoride ions in n = 1 Aurivillius materials lowers the B-site oxidation state required for charge balance and may also change the relative significance of polar displacements and rotations of octahedra. This has allowed magnetic n = 1 Aurivillius oxide-fluorides Bi$_5$BO$_2$F$_4$ (B = Fe, Co, and Ni) to be prepared. The report of long-range magnetic order in Bi$_2$WO$_6$ motivated us to investigate it further. Mitoudi Vagourdi et al. were able to use X-ray diffraction to confirm its n = 1 Aurivillius structure, but X-rays are relatively insensitive to the positions of the light O/F anions, making it difficult to investigate possible structural distortions further. We report here the structural character-

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ization of \( \text{Bi}_2\text{CoO}_2\text{F}_4 \) using neutron powder diffraction (NPD) and second-harmonic generation (SHG) experiments, complemented by density functional theory (DFT) calculations. These methods reveal a distorted structure analogous to those adopted by ferroelectric \( \text{Bi}_2\text{WO}_6 \). Low-temperature NPD data allow us to determine the long-range magnetic structure of \( \text{Bi}_2\text{CoO}_2\text{F}_4 \) and explain the field dependence reported by Mitoudi Vagourdi et al.\(^{25}\)

**METHODS**

Pink polycrystalline samples of \( \text{Bi}_2\text{CoO}_2\text{F}_4 \) were prepared hydrothermally, as described in ref \(^{25}\). Variable temperature X-ray powder diffraction (XRPD) data were collected using a PANalytical Empyrean diffractometer with Cu K\(\alpha_1\) radiation (with a Ge monochromator), an X'Celerator detector, and an Oxford Cryosystems Phenix cryostat. 20 min scans were collected at 20 K intervals on warming from 12 to 300 K, with dwell times of 10 min for temperature equilibration before each scan.

NPD data were collected at the ISIS Neutron and Muon Source. One batch (0.84 g) was used to collect medium-resolution NPD data on the GEM diffractometer; the sample was placed in a cylindrical vanadium sample can (diameter of 6 mm) to a height of \( \sim 1\) mm, and data were collected at 50 K and at 5 K. High-resolution NPD data were also collected on a second batch of sample (0.35 g) on the HRPD diffractometer; the sample was placed in a thin-walled vanadium can to a height of 1.9 cm, and data were collected at 5 K. Powder diffraction data were analyzed using Topas Academic software\(^{28,29}\) and ISODISTORT\(^{30}\) was used to explore possible structural distortions and magnetic ordering arrangements. Jana2006 software\(^{31}\) was used for incommensurate refinements.

X-ray absorption near-edge structure data was obtained on the \( \text{Bi}_2\text{CoO}_2\text{F}_4 \) material using the B18-CORE XAS instrument at Diamond Light Source at the Harwell Science and Innovation Campus in Oxfordshire. XANES measurements of the Co K-edge were performed, and data was analyzed qualitatively to look at the oxidation state of the Co metal. Calibration of the energy scale was ensured by simultaneously collecting XANES data from a Co foil using a third ionization chamber.

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Figure 1. Illustration of (a) an ideal \( I4/mmm \) structure for an \( n = 1 \) Aurivillius oxide and (b) schematic showing key structural distortions (order parameter directions for the irreps are given in parentheses) for this structure (and resulting space group symmetries); panel (c) shows the intermediate \( B2cb \) structure of \( \text{Bi}_2\text{WO}_6 \) and panel (d) shows the low-temperature \( P2_1ab \) model of \( \text{Bi}_2\text{WO}_6 \). Bi, B/W, and O ions are shown in purple, blue, and red, respectively.
Bi$_2$CoO$_4$F$_4$ was tested for an SHG signal using the experimental setup described in ref 32; Bi$_2$CoO$_4$F$_4$ powder was placed in a fused silica tube (with an outer diameter of 4 mm). Relevant comparisons with a known SHG material, α-SiO$_2$, were made under the same conditions. A 1064 nm pulsed Nd:YAG laser (Quantel Laser, Ultra 50) generated the fundamental light, and the SHG intensity was recorded at room temperature using an oscilloscope (Tektronix, TDS3032).

Calculations were performed within DFT$^{33}$ using the ABINIT package.$^{34,35}$ The projected augmented waves (PAW) approach$^{36}$ was used to represent the valence and core electrons. The exchange correlation energy functional was evaluated within both the local density approximation (LDA) and the generalized gradient approximation (GGA).$^{37}$ The atomic data set was taken from the JTH table$^{38}$ where 15 valence electrons were used for Bi (5d$^{10}$ 6s$^2$ 6p$^3$), 17 for Co (3s$^2$ 3p$^6$ 3d$^7$ 4s$^2$), 6 for O (2s$^2$ 2p$^4$), and 7 for F (2s$^2$ 2p$^3$). The wave functions were expanded up to a maximum kinetic energy cutoff of 22 hartrees. Integrals over the Brillouin zone were performed in LDA and GGA until the absolute values of the forces on atoms were converged to less than 10$^{-6}$ Ha/bohr. The 3d electrons were corrected through the DFT + U approximation$^{39,40}$ where different values of on-site Coulomb interaction $U$ and site exchange interaction $J$ were used to check the energy differences between spin configurations. Phonons were calculated using density functional perturbation theory within GGA-JTH.$^{41,42}$

**RESULTS**

**XANES.** XANES is a useful tool for determining oxidation states of transition metals by comparison of the absorption edge position with that from standards containing the transition metal in known oxidation states. The energy of the absorption edge increases with the oxidation of state of the transition metal since more energy is required to remove electrons from ions with higher charge. In this case, CoO, Co$_2$O$_4$, Ba$_2$CoO$_4$, and BaCoO$_3$ were chosen as standards with Co oxidation states of +2, +2.67, +4, and +4, respectively.

Figure 2 shows the absorption edges of these reference materials and the Bi$_2$CoO$_4$F$_4$ sample. As expected, the energy of the absorption edges of the standards increases with oxidation state. The energy of the absorption edge of the Bi$_2$CoO$_4$F$_4$ sample, measured half way up the edge, is the same as that from CoO, indicating that the Co oxidation state in Bi$_2$CoO$_4$F$_4$ is close to +2. We note that the Co site in Bi$_2$CoO$_4$F$_4$ is thought to be coordinated by the more electron-negative F$^-$ anions rather than O$^2-$ ions (see below and Mitoudi Vagourdi et al.$^{25}$), which may shift the Co K-edge position to slightly higher energies. The observed edge position could therefore indicate a slightly lower cobalt oxidation state in our sample, but further work involving comparison with stoichiometric cobalt fluoride references is needed to confirm this.

**Second Harmonic Generation.** SHG measurements using 1064 nm radiation gave a signal for Bi$_2$CoO$_4$F$_4$ (about 0.4 times that of α-SiO$_2$) (Figure 2); no laser damage was observed for the sample. This measurement indicates that Bi$_2$CoO$_4$F$_4$ must adopt an acentric structure at room temperature.

**Preliminary Characterization Using XRPD Data.** XRPD data were collected between 20 and 300 K to monitor unit cell parameters as a function of temperature. The data were fitted reasonably well by orthorhombic models considered for analysis of NPD data (see below), and the unit cell volume increased smoothly on warming (see the Supporting Information). There is a change in slope in the unit cell $c$ parameter below 190 K (see the SI). This may indicate a structural change (e.g., a tilt transition) below this temperature as suggested from phonon analysis from Raman data,$^{25}$ but further structural analysis as a function of temperature is needed to confirm this.

**Crystal Structure Determination from NPD Data.** The main reflections observed in 50 K NPD data are consistent with an $n = 1$ Aurivillius phase, but additional reflections were also observed that cannot be indexed by the high-symmetry $I4/mmm$ ($a_0 \approx 3.8 \text{ Å}, c_0 \approx 16.3 \text{ Å}$) cell. These additional reflections are consistent with a larger $2a_0 \times \sqrt{2}a_0 \times c_0$ unit cell. These superstructure reflections also rule out the non-centrosymmetric disordered model of $I4$ symmetry ($a_0 \approx 3.8 \text{ Å}; c \approx 16.3 \text{ Å}$) reported by Mitoudi Vagourdi et al. from X-ray diffraction work.$^{25}$ The observation of superstructure reflections from neutron scattering data (with relatively stronger sensitivity to the positions of the light anions)$^{43}$ and not from careful X-ray studies (in which the scattering is dominated by the electron-rich Bi$^{3+}$ sites) suggested that structural distortions involving displacements of the anion sites (such as rotations of the CoX$_6$ octahedra) should be considered. (Given the similar neutron scattering lengths of oxygen and fluorine ($0.803(4)$ and $0.65(1)$ fm, respectively),$^{44}$ no attempt was made at this stage to determine the anion distribution over the three sites, and all were modeled as fully occupied by oxide ions.) ISODISTORT was used to explore possible distortions that might give rise to such a supercell. Mode inclusion analysis$^{45}$ (see the Supporting Information) suggested that the lower-symmetry structure results from rotation of CoX$_6$ octahedra about an in-plane axis (described by irrep $X_1$); see Figure 1 and the Supporting Information, giving a model of Bnab symmetry (a,b,c) of space group 54, Cnma).
Table 1. Details from Rietveld Refinement Using 50 K NPD Data Collected for Bi₂CoO₂F₄ Using the P2₁/a Setting of Space Group 41, with Anion Vacancies and mF₂ Magnetic Model

| atom  | site | x     | y     | z     | occupancy | U_iso × 100 (Å²) |
|-------|------|-------|-------|-------|-----------|------------------|
| Bi(1) | 4a   | 0.004(6) | 0.011(2) | 0.0776(7) | 1         | 1.7(2)          |
| Bi(2) | 4a   | 0.505(6) | 0.009(2) | 0.5771(7) | 1         | 1.4(1)          |
| Co    | 4a   | 0*     | 0.976(4) | 0.747(1) | 1         | 0.6(2)          |
| O/F(1) (eq) | 4a | 0.208(7) | 0.290(3) | 0.7865(7) | 0.75 | 1.5(2) |
| O/F(2) (eq) | 4a | 0.806(7) | 0.199(4) | 0.2700(9) | 0.76 | 2.7(4) |
| O/F(3) (ap) | 4a | 0.027(7) | 0.929(4) | 0.874(1) | 1      | 2.3(3) |
| O/F(4) (ap) | 4a | 0.517(7) | 0.933(4) | 0.373(1) | 0.81 | 2.0(4) |
| O/F(5) (fl) | 4a | 0.255(7) | 0.243(3) | 0.994(6) | 1      | 1.7(3) |
| O/F(6) (fl) | 4a | 0.749(7) | 0.256(3) | 0.4996(6) | 1    | 1.4(2) |

The refinement was carried out using NPD data from the 91 and 35° banks and included BiF₃O₂ impurity (14(1)% by mass). The Bi₂CoO₂F₄ main phase (86(1)% by mass) had unit cell parameters a = 5.4343(5) Å, b = 5.4339(6) Å, c = 16.350(1) Å and volume = 482.81(8) Å³; Rwp = 6.32%, Rp = 4.64%, and χ² = 2.90%. (Abbreviations “ap”, “eq”, and “fl” refer to “apical”, “equatorial”, and “fluorite”, respectively.)

The SHG activity observed (Figure 2) indicates that Bi₂CoO₂F₄ must adopt a non-centrosymmetric crystal structure, and so non-centrosymmetric, polar models (including those of B2cb and P2₁/a symmetry, analogous to Bi₂WO₄) were considered. This was consistent with mode inclusion analysis, which suggested a further improvement in fit if in-plane polar displacements (described by the Γ₂⁻ irrep), or rotation of CoX₆ octahedra about the long axis ([001]), described by the X₇⁺ irrep, were allowed (see the Supporting Information).

The model of B2cb symmetry (cab setting of space group 41, Aba2) allows displacements along the polar a axis ([110]₀, where the subscript t denotes the high-symmetry I4/mmm unit cell), as well as rotation of CoX₆ octahedra about this axis (described by the X₇⁺ irrep). Lowering the symmetry further to P2₁/a (cab setting of space group 29, Pca₂₁) allows an...
additional rotation of Co$_x$ octahedra about the long axis ([001]) described by the X$_a$ irrep.

Both B2cb and P2$_1$ab models give good fits to the data at 50 K ($R_{wp}$ of 6.64% (61 parameters) and 6.28% (79 parameters) for B2cb and P2$_1$ab models, respectively) (see the Supporting Information) but surprisingly high atomic displacement parameters for the equatorial anion site(s). In Rietveld refinements, atomic displacement parameters are often correlated with site occupancies, and so this could indicate vacancies on this site or a problem with the model in terms of the position of the site. For both models, refinements were carried out using a single global atomic displacement parameter and allowing occupancies of anion and cobalt sites to refine, while the bismuth site occupancies were fixed at unity. These refinements suggested significant vacancies on equatorial anion sites (other site occupancies refined to unity with two esds and so were fixed as fully occupied), similar to reports for LaSrCoO$_{3.5}$+$\alpha$ (Site occupancies refined to values of 0.75(4), 0.76(4), and 0.81(1) for X(1), X(2), and X(4) sites, respectively.) Site occupancies were fixed at these values for subsequent refinements, and refining atomic displacement parameters for each site gave more physically reasonable values, and so it is likely that there are some anion vacancies in this sample of Bi$_2$CoO$_4$F$_{4}$. Allowing the atomic displacement parameter to refine anisotropically for this site in the B2cb model did suggest some increased displacement (either static or dynamic) in the ab plane, which may indicate some further rotation of Co$_x$ octahedra (e.g., about the long axis). Refinement details for P2$_1$ab refinements using 50 K data are shown in Figure 3 and Table 1 and below (Table 2 and Figures 5 and 6) for refinements using 5 K data.

Bond valence sum calculations were used as a simplistic way to determine the likely anion distribution using 50 K bond lengths. (Bond valence sum parameters calculated for this low-temperature model should not be interpreted quantitatively as the parameters are determined from room temperature structures, but can be instructive for comparing between different ordering models.) Calculating apparent valences for equatorial and apical sites gave valences close to 1 (assuming either F or O occupancy), while higher valences closer to 2 were calculated for anion sites in the fluorite-like layers (full details are given in the Supporting Information). These values suggest that anion sites in the perovskite layers might be favored by F$^-$ ions giving CoF$_6$ octahedra, while O$^{2-}$ ions occupy sites in the fluorite-like [Bi$_2$O$_4$]$^{2-}$ layers. Taking into account the anion vacancies noted above, this suggests an approximate composition of Bi$_2$CoO$_4$F$_{3.32}$ compared with the target stoichiometry of Bi$_2$CoO$_4$F$_{4}$.  

Magnetic Structure Determination from 5 K NPD Data. NPD data collected (on the GEM diffractometer) at 5 K were similar to those observed at 50 K, with some additional low-intensity peaks observed at long d-spacing (see the Supporting Information). Most of these peaks could be indexed by the same size unit cell as the nuclear structure, although a shoulder to the 102 peak ($\sim$12,700 $\mu$s, 4.52 Å) was not indexed by this unit cell. Attempts to index this peak using larger or lower-symmetry unit cells were unsuccessful.

High-resolution NPD data were also collected at 5 K, and although the strong reflections were consistent with those observed in the GEM data, some additional reflections on either side of some strong reflections were also observed. Attempts were made to fit these satellite reflections, but the reflections were fairly broad and low intensity, and our attempts were not successful (stable refinements were not achieved). It is likely that they indicate an incommensurate modulation of the crystal structure, but their relatively broad nature may indicate a shorter correlation length of this modulation compared with the long-range average (commensurate) structure. Evidence for an incommensurate modulation in the crystal structure of another sample of Bi$_2$CoO$_4$F$_{4}$ has also been observed in electron diffraction data, but the possibility of vacancies on the anion sublattice, and slight differences in the O:F ratio, means that this incommensurate modulation could be quite sample-dependent. Our subsequent analysis is based on the average commensurate structure as determined from our NPD data collected on the GEM diffractometer.

ISODISTORT was used to explore possible magnetic structures to fit the 5 K (GEM) NPD data, assuming a P2$_1$ab nuclear structure. Mode inclusion analysis (see the Supporting Information) suggested that models with an antiferromagnetic arrangement of moments in-plane gave good fits to the data. Two almost collinear models, m$_1$ and m$_2$ (see Figure 4a,b), give comparable fits to the data, and it is difficult to differentiate between these models from NPD data. The m$_1$ model has Co$^{3+}$ moments along the polar $a$ axis, which is the axis about which CoF$_6$ octahedra rotate, similar to the intermediate-temperature magnetic model reported for La$_2$CoO$_4$ (with nuclear symmetry Bmnab). The m$_2$ model is similar but with Co$^{3+}$ moments predominantly along the in-plane axis perpendicular to this (see Figure 4a,b). Given the

![Figure 4](https://doi.org/10.1021/acs.chemmater.2c02745)

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tiny orthorhombic distortion observed, it is not surprising that these models give similar fits to our NPD data, and it is likely that these models are of similar energies. Interestingly, the m\text{f}_2 model allows an FM in-plane component (perhaps consistent with the low-field magnetic behavior evidenced by magnetization vs field measurements reported by Mitoudi Vagourdi et al.). Further diffraction studies on single crystals (e.g., susceptibility measurements on single crystals or polarized neutron diffraction experiments) might allow these two models to be distinguished. Allowing this FM in-plane component to refine the m\text{f}_2 model gave a stable refinement (although only small improvement in fit; \( R_{wp} \) decreased from 5.826 to 5.825% for this additional parameter), and a small nonzero FM moment per Co\({}^{2+}\) site of 2.5(1) \( \mu_B \) (further refinement details are given in the Supporting Information). Refinement details are given in Table 2 and profiles in Figure 5, with the final magnetic and nuclear structure illustrated in Figure 4c.

**Density Functional Theory Calculations.** Initial phonon calculations on the parent 14/mmm model were used to determine key structural instabilities (to identify structural models for further spin-polarized calculations). Six unstable modes (which are all doubly degenerate) were identified: \( X_3^\ast \) and \( X_3 \) rotations, \( \Gamma_5 \), and \( M_6 \),\( \ast \) polar and antipolar in-plane displacements (Figure 1), as well as another rotation mode \( X_4^\ast \) \( (a^\ast - a^\ast c^0/(a - a c^0)) \) and \( X_5^\ast \) in-plane antipolar displacements (see the Supporting Information). It is striking that the “rigid-layer” modes \( \Gamma_5 \) and \( M_6 \),\( \ast \), which describe in-plane displacements of [Bi\text{O}_2] layers relative to the perovskite-like blocks (along \([110]_j\)), are harder than often observed in perovskite-related Aurivillius phases.

Spin-polarized calculations were therefore carried out for the aristrotype 14/mmm model and for lower-symmetry models that allow these distortions (and are common ground states for \( n = 1 \) Aurivillius phases):

\[
Pbca \ (X_3^\ast \oplus X_3 \oplus M_6^\ast)
\]

\[
B2cb \ (X_3^\ast \oplus \Gamma_5^\ast)
\]

\[
P2_1ab \ (X_3^\ast \oplus X_3 \oplus \Gamma_5)
\]

Three arrangements of Co\text{2+} magnetic moments (Figure 6) were considered for each of the three nuclear structures: FM with all moments ferromagnetically aligned; AFM1 with ferromagnetic alignment within Co\text{F}_4 layers and antiferromagnetic coupling between layers; and AFM2 with antiferromagnetic Co\text{F}_4 layers. Preliminary calculations using LDA-JTH were inconclusive, being very sensitive to geometry optimization and giving results inconsistent with the experiment (see the Supporting Information).

Calculations using GGA-JTH gave the FM ground state for the 14/mmm nuclear structure, but AFM2 ground states (with AFM1 next lowest in energy) for all the orthorhombic nuclear structures (for \( U = 4 \) and 6 eV; \( J = 0.2, 0.4, \) and 0.6 eV), consistent with experimental results. Having established AFM2 as the ground state magnetic structure, it is interesting to compare the three nuclear models with the aristrotype 14/mmm model (with AFM2 spin order) (Table 3).

These results from DFT calculations are largely consistent with the experimental results discussed above, in terms of both the nuclear and magnetic structures.

### DISCUSSION

Analysis of NPD data collected at 50 K suggests that “Bi\text{II}_{2}Co\text{II}_{2}O_{6.5}\text{F}_{4}” may be slightly nonstoichiometric with anion vacancies. If these vacancies involve only F\text{−} ions, the refined
occupancies would suggest a composition closer to Bi$_2$CoO$_2$F$_3$-2. This is reminiscent of reports on La$_3$CoO$_2$S$_6$ (prepared by the floating zone method under controlled atmosphere), suggesting that cobalt ions may adopt an oxidation state <2. This contrasts with a recent report on “Bi$_2$MO$_2$F$_6$” (M = Fe and Ni) analogues in which the stability of the +2 oxidation state for nickel gives stoichiometric Bi$_2$NiO$_2$F$_6$ while the iron analogue is Bi-deficient with Fe$^{2+}$/Fe$^{3+}$ cations. Given that the XANES data suggest a cobalt oxidation state close to +2 (Figure 2), the possibility of some excess oxygen and a small degree of O–F anti-site disorder (O$^{2−}$ ↔ 2F$^−$, giving compositions Bi$_2$CoO$_2$Fe$_{2+}$/Fe$_{1−}$) seems likely (i.e., for the sample described in Table 1, the site occupancies would suggest x ≈ 1.38, Bi$_2$CoO$_2$Fe$_{2+}$/Fe$_{1−}$). This would result in partial occupancy of some nominally “F−” sites by vacancies and O$^{2−}$ ions, consistent with site occupancies from NPD analysis (Table 1). The anion vacancies are largely concentrated on the equatorial sites, consistent with LaSrCoO$_{5+x}$ in which equatorial oxygen vacancies occur to maintain the expected Co$^{2+}$ oxidation state. This illustrates the difficulty in preparing pure, stoichiometric Aurivillius oxyfluorides containing d$^9$-B-site cations. It is possible that the precise composition varies from sample to sample (and between batches) and may depend on the synthetic route.

The 50 K (above $T_N$) crystal structure of Bi$_2$CoO$_2$F$_4$ is orthorhombic, but it is striking that the unit cell is metrically very close to tetragonal ($a = 5.4343(5)$ Å, $b = 5.4339(6)$ Å), as reported for other n = 1 Aurivillius oxyfluorides (including Bi$_2$NbO$_2$F$_5$, Bi$_2$FeO$_2$F$_5$, and Bi$_2$NiO$_2$F$_3$). The orthorhombic crystal structure of Bi$_2$CoO$_2$F$_4$ of P2$_1$ab symmetry can be described in terms of rotations of CoF$_6$ octahedra about the a axis (X$^+_a$, irrep $a^6c^0$ in Glazer notation relative to the parent structure of I4/mmm symmetry) and about the long axis (X$^+_a$, irrep $a^6c^0$ in Glazer notation), as well as small polar displacements of cations relative to anions along the polar a axis, as mapped out in the Supporting Information. Our analysis of diffraction data and the observed SHG activity indicate that Bi$_2$CoO$_2$F$_4$ adopts a crystal structure allowing both polar $Γ_5^−$ displacements as well as rotation of CoF$_6$ about an in-plane axis (X$^+_a$ rotations).

Results from DFT calculations (Table 3 and the Supporting Information) are consistent with the experimental models described above, with lower-symmetry models calculated for all magnetic models dominated by X$^+_a$ (a$^6$ c$^0$) rotations of CoF$_6$ octahedra, with some further stabilization (and smaller contributions) from polar displacements ($Γ_5^−$) and X$^+_a$ (a$^6$ c$^0$) rotations.

If the only long-range ordered distortions are X$^+_a$ rotations and polar $Γ_5^−$ displacements, then the model of B2cb symmetry would seem most appropriate to describe the average long-range structure. It is difficult to confirm the P2$_1$ab structure (with long-range order of X$^+_a$ rotations) over a disordered model of B2cb symmetry from our powder diffraction data, and a larger sample of higher purity would be needed for high-resolution NPD data or complementary electron diffraction studies. DFT results (Supporting Information) indicate that the X$^+_a$ model is significantly softer than the polar $Γ_5^−$ instability, and so the P2$_1$ab ($X^+_a$ ⊕ $X^+_a$ ⊕ $Γ_5^−$) model seems the best description of the ground state. The difficulty in distinguishing between the disordered B2cb and ordered P2$_1$ab models experimentally is perhaps explained by their similar energies calculated by DFT (Table 3 and Supporting Information). It is possible that the second rotation mode, X$^+_a$, condenses in on cooling, consistent with the disorder-order transition on cooling noted from Raman spectroscopy.

The Ruddlesden–Popper phase La$_2$CoO$_4$ (and related analogues) adopts a closely related structure of Bmnb symmetry (for 135 K < T < 408 K) with rotation of CoO$_6$ octahedra about the in-plane axis (X$^+_a$, rotations) but without further rotations or polar displacements. Models of P4$_2$/ncm symmetry were also considered for Bi$_2$CoO$_2$F$_4$ but gave fairly poor fits to the data (there was no clear change in peak widths from data at 50 K and at 5 K that might indicate a similar orthorhombic—tetragonal distortion for Bi$_2$CoO$_2$F$_4$). La$_2$CoO$_4$ contrasts with the Aurivillius oxide Bi$_2$WO$_6$ that adopts a polar ground state of P2$_1$ab symmetry (allowing X$^+_a$ and X$^+_a$ rotations as well as $Γ_5^−$ polar displacements). The comparison between polar Bi$_2$WO$_6$ and Bi$_2$CoO$_2$F$_4$ with nonpolar Ruddlesden–Popper La$_2$CoO$_4$ perhaps highlights the role of the fluorite-like [BiO$_2$] layers in the n = 1 Aurivillius phases that contain 6$^2$ Bi$^{3+}$ cations, known to favor lower-symmetry coordination environments. However, while the Bi$^{3+}$ cations may help stabilize these further distortions (X$^+_a$ tilts and polar displacements), the dominant contribution to the polarization is from the perovskite-like layers (apical F$^−$ displacements and, to a lesser extent, Co$^{2+}$ and equatorial F$^−$ displacements), consistent with theory work on analogous Bi$_2$WO$_6$. Polar displacements of d$^9$ cations are often ascribed to the pseudo-Jahn–Teller effect, and this electronic driving force is lessened for d$^9$ cations such as Co$^{3+}$ here. Morita et al. explored the change in polarization with F$^−$ content in the series Bi$_2$(W,B)(O,F)$_6$ (B = Ta, Nb, and Ti) and noted that the polarization decreased noticeably with increasing F$^−$ content. This is likely explained by reduced cation–anion hybridization for more ionic fluoride-based systems, increasing the importance of geometric drivers for distortions over electronic (pseudo-Jahn–Teller effect) factors. This is consistent with polar $Γ_5^−$ distortions being the softest instability for Bi$_2$WO$_6$ (and making similar contributions as X$^+_a$ and X$^+_a$ rotations to the ground state), while the X$^+_a$ rotations are dominant for Bi$_2$CoO$_2$F$_4$ and $Γ_5^−$ distortions make a much diminished contribution (Table 3 and Supporting Information). The reduced polarization as oxide ions are replaced by fluoride might also be a factor in the smaller orthorhombic distortion of the oxide-fluorides.

When analyzing the 5 K NPD data, we have tentatively described possible magnetic structures, assuming the P2$_1$ab nuclear structure (on the assumption that the second tilt mode condenses in on cooling), but similar magnetic models can be derived for the B2cb nuclear structure (see the Supporting Information).
Information). Our analysis of the 5 K NPD data suggests that Co\(^{2+}\) moments are close to collinear (in zero applied magnetic field) with antiferromagnetic nearest-neighbor interactions, consistent with the negative Weiss temperature (\(\theta \approx -142\) (2 K) determined by Mitoudi Vagourdi et al. for \(T > 150\) K in 7 T applied field).\(^{25}\) The magnetic peaks are slightly broadened (particularly those with large \(l\) index) compared with the magnetic Bragg peaks, and this was fitted using a model to describe antiphase boundaries.\(^{26,27}\) In the magnetic structure perpendicular to the \(c\) axis, with a magnetic correlation length \(\xi \approx 60(10)\) Å at 5 K. This suggests that the in-plane magnetic exchange interactions are noticeably stronger than the interlayer exchange interactions. This is unsurprising given the layered crystal structure and is consistent with the largely XY-like magnetic behavior to the Ruddlesden–Popper oxides and perovskite-like layers is likely to remain diminished. Future analysis for \(n\) = 1 Aurivillius phases, additional distortions involving \([\text{Bi}_2\text{WO}_6]\) layers (although the polarization contribution from the perovskite-like layers is likely to remain diminished). Further work to explore the relative energies of the exchange interactions and sources of anisotropy in \([\text{Bi}_2\text{CO}_3\text{F}_4]\) as well as characterization using single crystals, would give further insights into this.

## CONCLUSIONS

Our combined experimental and computational studies on \([\text{Bi}_2\text{CoO}_3\text{F}_4]\) have given insight into its structural and magnetic properties. The ground state structure is best described by polar \(P_2_1/ab\) symmetry, analogous to the Aurivillius oxide ferroelectric \([\text{Bi}_2\text{WO}_6]\).\(^{13,19}\) The magnetic ground state of \([\text{Bi}_2\text{CoO}_3\text{F}_4]\) is ferrimagnetic, arising from a small canting of otherwise collinear AFM arrangement of moments. This combination of polarity and FM component highlights the potential of Aurivillius oxide-fluorides for multiferroics and magnetoelectrics, particularly given the magnetostriective effects observed at \(T_\text{k}\) in capacitance data for \([\text{Bi}_2\text{FeO}_3\text{F}_4]\).\(^{27}\) However, our work has also identified some challenges: while replacing \(\text{O}^{2-}\) by \(\text{F}^-\) ions allows more magnetic ions to be accommodated by the perovskite-like layers (and gives similar magnetic behavior to the Ruddlesden–Popper oxides such as \([\text{La}_2\text{CoO}_3]\)),\(^{25,26,67}\) the increased ionic character of the fluorides compared with oxides tends to reduce the stability of polar distortions, reducing the polarization.\(^{24}\) It would be interesting to study the effect of concentrating \(\text{F}^-\) ions in the equatorial sites in the perovskite-like layers, leaving the apical sites fully occupied by \(\text{O}^{2-}\).\(^{76}\) This may give similar energies for the polar distortions involving \([\text{Bi}_2\text{O}_3]\) layers to those observed in \([\text{Bi}_2\text{WO}_6]\) (although the polarization contribution from the perovskite-like layers is likely to remain diminished). Future work to explore the optimum O:F ratio and ordering for designing multiferroic and magnetoelectric Aurivillius oxide-fluorides would be valuable.

## ASSOCIATED CONTENT

* Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.chemmater.2c02745.

Analysis of variable temperature XRPD data, symmetry analysis for \(n = 1\) Aurivillius phases, additional refinements (Rietveld and Pawley) using different models for 50 K and 5 K NPD data, selected bond lengths (and bond valence sum analysis) and angles from Rietveld refinements using NPD data, details of the magnetic structure investigation, and details from DFT calculations (PDF)
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REFERENCES

(1) Hill, N. A. Why are there so few magnetic ferroelectrics? J. Phys. Chem. B 2000, 104, 6694–6709.

(2) Spaldin, N. A.; Ramesh, R. Advances in magnetoelectric multiferroics. Nat. Mater. 2019, 18, 203–212.

(3) Fang, P. H.; Robbins, C. R.; Aurivillius, B. Ferroelectricity in Compound Bi2TiO3. Phys. Rev. 1962, 126, 892.

(4) Deearujo, C. A. P.; Cuchiaro, J. D.; McMillan, L. D.; Scott, M. C.; Scott, J. F. FATTIGUE-FREE FERROELECTRIC CAPACITORS WITH PLATINUM-ELECTRODES. Nature 1995, 374, 627–629.

(5) McCabe, E. E.; Greaves, C. Structural and magnetic characterisation of Bi2Sn3.3La0.6 Nb5 MnO13 and its relationship to Bi2Sn3.3Nb5MnO13. J. Mater. Chem. 2005, 15, 177–182.

(6) McCabe, E. E.; Greaves, C. Structural and magnetic characterisation of Aurivillius material Bi2Sr2Nb2.5Fe0.5O12. J. Solid State Chem. 2008, 181, 3051–3056.

(7) Giddings, A. T.; Stennett, M. C.; Reid, D. P.; McCabe, E. E.; Greaves, C.; Hyatt, N. C. Synthesis, structure and characterisation of the n=4 Aurivillius phase Bi5TFSrCrO15. J. Solid State Chem. 2011, 184, 252–263.

(8) Keeney, L.; Colfer, L.; Schmidt, M. Probing Ferroelectric Behavior in Sub-10 nm Bismuth-Rich Aurivillius Films by Piezoresponse Force Microscopy. Microsc. Microanal. 2022, 28, 1396–1406.

(9) Halpin, J. C.; Schmidt, M.; Main, T.; Pembel, M. E.; Keeney, L. Compositional Tuning of the Aurivillius Phase Material Bi5Tis–2xFe1–xNb5O15 (0 ≤ x ≤ 0.4) Grown by Chemical Solution Deposition and its Influence on the Structural, Magnetic, and Optical Properties of the Material. IEEE Trans. Ultrason. Ferroelectr. Freq. Control 2021, 68, 303–313.

(10) Snedden, A.; Herweches, C. H.; Lightfoot, P. Ferroelectric phase transitions in SrBi2Nb2O9 and Bi5Ti3FeO15: A powder neutron diffraction study. Phys. Rev. B 2003, 67, No. 092102.

(11) Guo, Y.-Y.; Gibbs, A. S.; Perez-Mato, J. M.; Lightfoot, P. Unexpected phase transition sequence in the ferroelectric Bi4Ti3O12. J. Solid State Chem. 2019, 263, 438–446.

(12) Armstrong, R. A.; Newnham, R. E. Bismuth titinate solid solutions. Mater. Res. Bull. 1972, 7, 1025–1034.

(13) McDowell, N. A.; Knight, K. S.; Lightfoot, P. Unusual high-temperature structural behaviour in ferroelectric Bi2WO6. Chemistries a European Journal 2006, 12, 1493–1499.

(14) Knight, K. S. THE CRYSTAL STRUCTURE OF FERROELECTRIC Bi2WO6 AT 961 K. Ferroelectrics 1993, 150, 319–330.

(15) Hatch, D. M.; Stokes, H. T.; Aleksandrov, K. S.; Misyul, S. V. Phase transitions in the perovskitelike A2B2X4 structure. Phys. Rev. B 1989, 39, 9282–9288.

(16) Hatch, D. M.; Stokes, H. T. Classification of octahedral tilting phases in the perovskite-like A2B2X4 structure. Phys. Rev. B 1987, 35, 8509–8516.

(17) Stokes, H. T.; Hatch, D. M.; Campbell, B. J.; Tanner, D. E. ISODISPLACE: a web-based tool for exploring structural distortions. J. Appl. Crystallogr. 2006, 39, 607–614.

(18) Glazer, A. The classification of tilted octahedra in perovskites. Acta Crystallogr., Sect. B: Struct. Sci. 1972, 28, 3384–3392.

(19) Knight, K. S. THE CRYSTAL-STRUCTURE OF RUSSELL-LITE - A REDETERMINATION USING NEUTRON POWDER DIFFRACTION OF SYNTHETIC Bi2WO6. Mineral. Mag. 1992, 56, 399–409.

(20) Džani, H.; Bouquet, E.; Kellou, A.; Ghosez, P. First-principles study of the ferroelectric Aurivillius phase Bi2WO6. Phys. Rev. B 2012, 86, No. 054107.

(21) Aurivillius, B. The structure of Bi2Nb2O5F and isomorphous compounds. Ark. Kemi 1952, 4, 39–47.

(22) Needs, R. L.; Dann, S. E.; Weller, M. T.; Cherryman, J. C.; Harris, R. K. The structure and oxide/fluoride ordering of the ferroelectrics Bi2TiO4F2 and Bi2Nb2O5F. J. Mater. Chem. 2005, 15, 2399–2407.
density-functional perturbation theory. Phys. Rev. B 1997, 55, 10355–10368.
(43) Berry, F. J.; Moore, E.; Mortimer, M.; Ren, X.; Heap, R.; Slater, P.; Thomas, M. F. Synthesis and structural characterisation of a new oxide fluoride of composition Ba$_3$Sn$_2$O$_6$F$_3$H$_2$O ($x=0.5$). J. Solid State Chem. 2008, 181, 2185–2190.
(44) Sears, V. F. Neutron news 1990, 3, 29–37.
(45) McCabe, E. E.; Free, D. G.; Mendis, B. G.; Higgins, J. S.; Evans, J. S. O. Preparation, Characterization, and Structural Phase Transitions in a New Family of Semiconducting Transition Metal Oxycalogenides $\beta$-La2O2MSe2 (M=Mn, Fe). Chem. Mater. 2010, 22, 6171–6182.
(46) Tuxworth, A. J.; McCabe, E. E.; Free, D. G.; Clark, S. J.; Evans, J. S. O. Structural Characterization and Physical Properties of the New Transition Metal Oxyselenide La2O2ZnSe2. Inorg. Chem. 2013, 52, 2078–2085.
(47) McCabe, E. E.; Stock, C.; Rodrigues, E. E.; Wills, A. S.; Taylor, J. W.; Evans, J. S. O. Weak spin interactions in Mott insulating La2O2Fe2OSe2. Phys. Rev. B 2014, 89, 100402.
(48) Hayward, M. A.; Rosseinsky, M. J. Anion Vacancy Distribution and Magnetism in the New Reduced Layered Co11/Co(1) Phase LaSrCoO3.5-x. Chem. Rev. 2000, 12, 2182–2195.
(49) Brown, I. D.; Altermatt, D. Bond-valence parameters obtained from a systematic analysis of the inorganic crystal structure database. Acta Cryst. 1985, B41, 244–247.
(50) Brese, N. E.; O’Keefe, M. Bond-valence sum parameters for solids. Acta Cryst. 1991, B47, 192–197.
(51) Huvé, M.; Mentre, O.; Arevalo-Lopez, A., Incommensurate structural modulation in Bi$_2$CoO$_3$F$_8$ private communication, 2022.
(52) Yamada, K.; Matsuda, M.; Endoh, Y.; Keimer, B.; Birgeneau, R. J.; Onodera, S.; Mizusaki, J.; Matsuura, T.; Shirane, G. Successive antiferromagnetic phase transitions in single-crystal La$_2$CoO$_4$. Phys. Rev. B 1989, 39, 2336.
(53) Perez-Mato, J. M.; Orobengoa, D.; Aroyo, M. I. Mode crystallography of distorted structures. Acta Crystallogr., Sect. A: Found. Adv. 2010, 66, 558–590.
(54) Orobengoa, D.; Capillas, C.; Aroyo, M. I.; Perez-Mato, J. M. AMPLOMODES: symmetry-mode analysis on the Bilbao Crystallographic Server. J. Appl. Crystalllogr. 2009, 42, 820–833.
(55) Furukawa, Y.; Wada, S.; Kaji, T.; Hosoya, S. 59Co Zero-Field NMR Study of Antiferromagnetism in Low-Temperature Tetragonal Phase of La$_2$CoO$_4$. J. Phys. Soc. Jpn. 1999, 68, 346–349.
(56) Birgeneau, R. J.; Chen, C. Y.; Gabbe, D. R.; Jensen, H. P.; Kastner, M. A.; Peters, C. J.; Picone, P. J.; Thurston, T. R.; Fuller, H. L.; Aaje, J. D.; Bönì, P.; Shirane, G. Soft-phonon behavior and transport in single-crystal La$_2$CuO$_4$. Phys. Rev. Lett. 1987, 59, 1329–1332.
(57) Bönì, P.; Aaje, J. D.; Shirane, G.; Birgeneau, R. J.; Gabbe, D. R.; Jensen, H. P.; Kastner, M. A.; Peters, C. J.; Picone, P. J.; Thurston, T. R.; R. Lattice instability and soft phonons in single-crystal La$_2$Sr$_x$CuO$_4$. Phys. Rev. B 1988, 38, 185–194.
(58) Heger, G.; Mullen, D.; Knorr, K. On the importance of hydrogen bonding for the structural phase transitions in (CH$_3$NH)$_3$B$_2$Mo$_8$O$_{24}$A. Phys. Rev. Lett. 2011, 106, 246801.
(59) Walsh, A.; Payne, D. J.; Eg dell, R. G.; Watson, G. W. Stereochemistry of post-transition metal oxides: revision of the classical lone pair model. Chem. Soc. Rev. 2011, 40, 4455–4466.
(60) Ok, K. M.; Halasymami, P. S.; Casanova, D.; Llunell, M.; Alemay, P.; Alvarez, S. Distortions in Octahedrally Coordinated d0 Transition Metal Oxides: A Continuous Symmetry Measures Approach. Chem. Mater. 2006, 18, 3176–3183.
(61) Eng, H. W.; Barnes, P. W.; Auer, B. M.; Woodward, P. M. Investigations of the electronic structure of d0 transition metal oxides belonging to the perovskite family. J. Solid State Chem. 2003, 175, 94–109.
(62) Kang, S. K.; Albright, T. A.; Eisenstein, O. THE STRUCTURE OF D0$_5$ML6 COMPLEXES. Inorg. Chem. 1989, 28, 1611–1613.
(63) Woodward, P. M.; Karen, P.; Evans, J. S. O.; Vogt, T., Solid state materials chemistry. Cambridge University Press: 2021, DOI: 10.1017/9781139025348.

(64) Garcia-Castro, A. C.; Spaldin, N. A.; Romero, A. H.; Bousquet, E. Geometric ferroelectricity in fluoroperovskites. Phys. Rev. B 2014, 89, No. 104107.

(65) Djani, H.; Hermet, P.; Ghosez, P. First-Principles Characterization of the P21ab Ferroelectric Phase of Aurivillius Bi$_2$WO$_6$. J. Phys. Chem. C 2014, 118, 13514–13524.

(66) Her, J.-H.; Stephens, P. W.; Gao, Y.; Soloveichik, G. L.; Rijssenbeek, J.; Andrus, M.; Zhao, J.-C. Structure of unsolvated magnesium borohydride Mg(BH$_4$)$_2$. Acta Cryst. 2014, 89, No. 104107.

(67) Babkevich, P.; Prabhakaran, D.; Frost, C. D.; Boothroyd, A. T. Magnetic spectrum of the two-dimensional antiferromagnet La$_2$CoO$_4$ studied by inelastic neutron scattering. Phys. Rev. B 2010, 82, No. 184425.

(68) Matsumoto, Y.; Nambu, Y.; Honda, T.; Ikeda, K.; Otomo, T.; Kageyama, H. High-pressure Synthesis of Ba$_2$CoO$_2$Ag$_2$Te$_2$ with Extended CoO$_2$ Planes. Inorg. Chem. 2020, 59, 8121–8126.

(69) Qureshi, N.; Ulbrich, H.; Sidis, Y.; Cousson, A.; Braden, M. Magnetic structure and magnon dispersion in LaSrFeO$_4$. Phys. Rev. B 2013, 87, No. 054433.

(70) Jung, M. H.; Alsmadi, A. M.; Chang, S.; Fitzsimmons, M. R.; Zhao, Y.; Lacerda, A. H.; Kawanaka, H.; El-Khatib, S.; Nakotte, H. Magnetic ordering in single-crystalline SrLaFeO$_4$ and Sr$_{1.1}$La$_{0.9}$FeO$_4$. J. Appl. Phys. 2005, 97, 10A926.

(71) Rodriguez-Carvajal, J.; Fernandez-Diaz, M. T.; Martinez, J. L. Neutron diffraction study on structural and magnetic properties of La$_3$NiO$_4$. J. Phys.: Condens. Matter 1991, 3, 3215–3234.

(72) Le Dréau, L.; Prestipino, C.; Hernandez, O.; Schefer, J.; Vaughan, G.; Paofta, S.; Perez-Mato, J. M.; Hosoya, S.; Paulus, W. Structural Modulation and Phase Transitions in La$_2$CoO$_{4.14}$ Investigated by Synchrotron X-ray and Neutron Single-Crystal Diffraction. Inorg. Chem. 2012, 51, 9789–9798.

(73) Yosida, K., Theory of Magnetism. 1 ed.; Springer Berlin: Heidelberg, 1996.

(74) Moskvin, A. Dzyaloshinskii–Moriya Coupling in 3d Insulators. Condensed Matter 2019, 4, 84.

(75) Crawford, M. K.; Subramanian, M. A.; Harlow, R. L.; Fernandez-Baca, J. A.; Wang, Z. R.; Johnston, D. C. Structural and magnetic studies of Sr2IrO4. Phys. Rev. B 1994, 49, 9198–9201.

(76) Wang, J.; Shin, Y.; Paudel, J. R.; Grassi, J. D.; Sah, R. K.; Yang, W.; Karapetrova, E.; Zaidan, A.; Stroev, V. N.; Klewe, C.; Shafer, P.; Gray, A. X.; Rondinelli, J. M.; May, S. J. Strain-Induced Anion-Site Occupancy in Perovskite Oxylfluoride Films. Chem. Mater. 2021, 33, 1811–1820.