Competing Exchange Interactions in the Multiferroic and Ferrimagnetic CaBaCo$_7$O$_7$

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Competing exchange interactions can produce complex magnetic states together with spin-induced electric polarizations. With competing interactions on alternating triangular and kagome layers, the swedenborgite CaBaCo$_7$O$_7$ may have one of the largest measured spin-induced polarizations of $\sim 1700$ nC/cm$^2$ below its ferrimagnetic transition temperature at 70 K. Upon rotating our sample about $c = [0, 0, 1]$ while the magnetic field is fixed along $[1, 0, 0]$, the three-fold splitting of the spin-wave frequencies indicates that our sample is hexagonally twinned. Magnetization measurements then indicate that roughly 20% of the sample is in a domain with the $a$ axis along $[1, 0, 0]$ and that 80% of the sample is in one of two other domains with the $a$ axis along either $[-1/2, \sqrt{3}/2, 0]$ or $[1/2, -\sqrt{3}/2, 0]$. Powder neutron-diffraction data, magnetization measurements, and THz absorption spectroscopy reveal that the complex spin order in each domain can be described as a triangular array of bitetrahedral $c$-axis chains ferrimagnetically coupled to each other in the $ab$ plane. The electric-field dependence of bonds coupling those chains produces the large spin-induced polarization of CaBaCo$_7$O$_7$.

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I. INTRODUCTION

Competing exchange interactions produce complex magnetic states with a wide range of interesting behavior found in spin glass [1], spin ice [2], and magnetic skyrmions [3]. In multiferroic materials, complex spin states can exhibit a spin-induced electric polarization $P$ due to either the spin current, $p$-$d$ orbital hybridization, or magnetostriction [4]. Because the coupling between the electrical and magnetic properties in multiferroic materials is both scientifically and technologically important, the effects of competing exchange interactions have been investigated in a wide range of multiferroic materials such as $\text{RMnO}_3$ [5], $\text{CoCrO}_2$ [6], $\text{CuCrO}_2$ [8], $\text{CuFeO}_2$ [9], and $\text{MnWO}_4$ [10]. While the first four materials [6–9] are geometrically frustrated due to competing interactions on a triangular lattice, $\text{MnWO}_4$ [10] exhibits long-range competing interactions [11] on a highly-distorted monoclinic lattice.

Compounds in the “114” swedenborgite family [12] $\text{RBaM}_x\text{O}_7$ ($M = \text{Co or Fe}$) contain alternating triangular and kagome layers, both of which are geometrically frustrated when undistorted. The “114” cobaltites [13–15] were initially studied to find charge ordering among the $\text{Co}^{2+}$ and $\text{Co}^{3+}$ ions. An important member of this family, $\text{YBaCo}_7\text{O}_7$ exhibits antiferromagnetic ordering [15–17] below 110 K and diffuse scattering [13–14] indicative of spin disorder below 60 K. The magnetic state between 110 K and 60 K is stabilized by a structural transition [18] that relieves the geometric frustration. Both structural and magnetic transitions are quite sensitive to excess oxygen and no magnetic order [19,20] appears in $\text{YBaCo}_7\text{O}_{7+\delta}$ for $\delta \geq 0.12$. Another family member, $\text{YbBaCo}_7\text{O}_7$ undergoes a structural transition at 175 K that stabilizes an antiferromagnetic state below 80 K [21].

A particularly interesting “114” cobaltite, $\text{CaBaCo}_7\text{O}_7$ undergoes an orthorhombic distortion [22,23] that relieves the geometric magnetic frustration on both the kagome and triangular layers sketched in Fig. 1 above the magnetic transition temperature $T_c = 70$ K. Below $T_c$, $\text{CaBaCo}_7\text{O}_7$ develops a very large spin-induced polarization $\sim 1700$ nC/cm$^2$ [24], second only to the conjectured [25] spin-induced polarization $\sim 30000$ nC/cm$^2$ of $\text{BiFeO}_3$. Also unusual, $\text{CaBaCo}_7\text{O}_7$ displays a substantial ferrimagnetic moment of about 0.9 $\mu_B$ per formula unit (f.u.) [26], which could allow magnetic control of the

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FIG. 1: (Color online) (a) and (b) The predicted spin configuration for layers 1 and 2 in zero field. Spins 1 and 5 lie on a triangular layer above the first kagome layer in (a); spins 1' and 5' lie on a triangular layer above the second kagome layer in (b). Layers are arranged so that spins 1' and 5' lie directly above spins 1 and 5.

angular array of ferrimagnetically aligned, bitetrahedral c-axis chains with net moment along b. Competing interactions within each chain produce a non-collinear spin state. The strong electric polarization of CaBaCo$_4$O$_7$ below $T_c$ is induced by the displacement of oxygen atoms surrounding bonds that couple those chains.

This paper has six sections. Section II proposes a microscopic model for CaBaCo$_4$O$_7$. New magnetization and optical measurements are presented in Section III. Fitting results are discussed in Section IV. In Section V, we predict the spin-induced electric polarization. Section VI contains a conclusion.

II. MICROSCOPIC MODEL

Each magnetic unit cell of CaBaCo$_4$O$_7$ contains 16 Co ions on two kagome and two triangular layers with orthorhombic lattice constants $a = 6.3$ Å, $b = 11.0$ Å, and $c = 10.2$ Å. Four crystallographically distinct Co ions have three different valences $^{22,28}$. Triangular layers contain mixed-valent Co$^{3+}$/Co$^{2+}$ with ligand hole (L) spins 1, 5, 9, and 13 with moments $M_1 = 2.9$ µB. Kagome layers contain Co$^{2+}$ spins 2, 3, 6, 7, 10, 11, 14, and 15 with moments $M_2 = M_3 = 2$ µB and mixed-valent Co$^{3+}$/Co$^{2+}$ spins 4, 8, 12, and 16 with $M_4 = 2.4$ µB.

Because adjacent kagome or triangular layers are related by symmetry, $S_i = S_{i+8}$ on layer two is identical to $S_i$ on layer one. With $S_i = S_i{(cos \phi_i, sin \phi_i, 0)}$ constrained to the ab plane, the ferrimagnetic moment lies along b if $\phi_{i+4} = \pi - \phi_i$ ($i = 1, \ldots, 4$).

The 12 different nearest-neighbor exchange couplings $J_i$ are drawn in Figs. 1(a-b) and 2. Six of these ($J_1$ through $J_6$) couple the kagome and triangular layers as shown in Fig. 2; the other six ($J_7$ through $J_{12}$) couple the spins within a kagome layer as shown in Figs. 1(a) and (b). The dominance of nearest-neighbor exchange over next-nearest neighbor exchange justifies setting the exchange interactions between spins on the triangular layers to zero. Our model also includes easy-plane anisotropies $D$, easy-axis anisotropies $C$ within both kagome and triangular layers, and hexagonal anisotropy $A$ on the triangular layers.

With magnetic field $\mathbf{B}$ along $\mathbf{m}$, the Hamiltonian is

$$
\mathcal{H} = -\sum_{\langle i,j \rangle} J_{ij} S_i \cdot S_j + D^{\text{tri}} \sum_{i, \text{tri}} S_{ic}^2 + D^{\text{kag}} \sum_{i, \text{kag}} S_{ic}^2
$$

$$
- C^{\text{kag}} \sum_{i, \text{kag}} (\mathbf{o}_i \cdot \mathbf{S}_i)^2 - C^{\text{tri}} \sum_{i, \text{tri}} (\mathbf{n}_i \cdot \mathbf{S}_i)^2
$$

$$
- A^{\text{tri}} \text{Re} \sum_{i, \text{tri}} (S_{ia} + iS_{ib})^6 - g\mu_B B \sum_i \mathbf{m} \cdot \mathbf{S}_i, \quad (1)
$$

where $\mathbf{S}_i$ is a spin $S$ operator on site $i$. For simplicity, we set $g = 2$ for all spins.

The easy-axis anisotropy terms proportional to $C^{\text{kag}}$ and $C^{\text{tri}}$ involve unit vectors $\mathbf{o}_i$ along the “bowtie” directions $\phi_i = \pi/2$ (spins 2 and 6), $5\pi/6$ (spins 3 and 8)
and \(7\pi/6\) (spins 4 and 7) for the kagome layers and \(n_i\) along the \(\phi_i = \pi/6\) (spin 1) and \(-\pi/6\) (spin 5) directions for the triangular layers. The hexagonal anisotropy on the triangular layers has expectation value

\[-A^{\text{tri}} S_i^6 \sum_{i,\text{tri}} \sin^6 \theta_i \cos 6\phi_i.\]

All anisotropy terms may act to constrain the spins to the \(ab\) plane.

Spin amplitudes \(S_n\) are fixed at their observed values \(M_{n,2}\) after performing a 1/2 expansion about the classical limit. Alternatively, the spins \(S_n\) could all have been taken as 3/2 but with different \(g\)-factors for different sets of spins. As discussed below, that would reduce the estimated exchange coupling \(J_{ij}\) by a factor of 4\(S_i S_j/9\).

Static properties are obtained by minimizing the classical energy \(\mathcal{H}\) (the zeroth-order term in this expansion) with respect to the 16 spin angles. The eigenvalues and eigenvectors of a 32 \(\times\) 32 equations-of-motion matrix \([29]\) produced by the second-order term in the 1/2 expansion give the optical mode frequencies and absorptions, respectively.

**III. MAGNETIZATION AND OPTICAL MEASUREMENTS**

Perhaps due to excess or deficient oxygen \([31]\) or different domain populations (see below), previous magnetization measurements \([22,26,31-33]\) on CaBaCo\(_4\)O\(_7\) are rather scattered. Consequently, new magnetization measurements were performed at 4 K on hexagonally-twinned crystals with a common \(c = [0,0,1]\) axis. In domain I, \(a\) lies along the laboratory direction \(x = [1,0,0]\) and \(b\) lies along \(y = [0,1,0]\); in domain II, \(a = [-1/2,\sqrt{3}/2,0]\) and \(b = [-\sqrt{3}/2,-1/2,0]\); and in domain III, \(a = [-1/2,-\sqrt{3}/2,0]\) and \(b = [\sqrt{3}/2,-1/2,0]\). If \(p_l\) are the domain populations, then the magnetizations \(M_x\) and \(M_y\) measured with fields along \(x\) and \(y\) only depend on \(p_1\) and \(p_2 + p_3 = 1 - p_1\). Of course, \(M_z\) measured with field along \(z\) is independent of \(p_l\). Fig. 3 indicates that all three magnetizations increase monotonically up to at least 32 T.

Previous optical measurements \([34]\) at the ordering wavevector \(Q\) found two conventional spin-wave modes that couple to the ground state through the magnetization operator \(M = 2\mu_B \sum_i S_i\). These magnetic-resonance (MR) modes are degenerate in zero field with a frequency of 1.07 THz and split almost linearly with increasing field along \(y\), as shown in Fig. 4. For \(m = y\), the MR modes are excited in two geometries: \((i)\) with THz fields \(E_\omega||x\) and \(B_\omega||z\) and \((ii)\) with \(E_\omega||z\) and \(B_\omega||x\). Those measurements also found an electromagnon (EM) that couples to the ground state through the polarization operator \(P\). The EM with zero-field frequency 1.41 THz is only excited in geometry \(ii\).

Because the exchange couplings already break every degeneracy in the unit cell, the 16 predicted modes for a single domain are non-degenerate. Therefore, the split MR modes must come from different domains. This was verified by measuring \([35]\) the MR mode frequencies as a function of the rotation angle \(\theta\) for field \(B = B(\cos \theta, \sin \theta, 0) = B(x \cos \theta + y \sin \theta)\) in the laboratory reference frame. In practice, this is accomplished by rotating the sample about \(c\) while keeping the field fixed.
TABLE I: Exchange and anisotropy parameters in meV.

| $p_1$ | $J_1 = J_5$ | $J_2 = J_6$ | $J_3 = J_7$ | $J_4$ | $J_9$ | $J_{10}$ | $J_{11} = J_{12}$ | $D^{\text{kag}}$ | $D^{\text{tri}}$ | $C^{\text{kag}}$ | $C^{\text{tri}}$ | $S_1^4 A^{\text{tri}}$ |
|-------|-------------|-------------|-------------|-------|-------|---------|----------------|-------------|-------------|-------------|-------------|-------------|
| 0.185 | -91.5       | -10.8      | 41.4        | -29.9 | 79.8  | 108.0   | -6.7          | -0.67       | -1.24       | 3.70        | 0.77        | 0.0064     |

error ±0.071 ±3.6 ±0.5 ±0.7 ±1.9 ±7.5 ±0.1 ±4.5 ±0.1 ±0.06 ±0.03 ±0.15 ±0.09 ±0.0004

FIG. 4: (Color online) The predicted MR (solid) and EM (dashed) modes for domain I (thick) and domains II and III (thin). Measured modes are indicated by solid points.

FIG. 5: (Color online) The measured (solid circles) and predicted (blue, red, and green curves for domains I, II, and III, respectively) angular dependence of the MR mode frequencies for 12 and 15 T. The inset to (a) sketches the angular dependence of $B_{SF}$ (dashed curve), which separates low-field (LF) and high-field (HF) states. The inset to (b) shows the net magnetization of any domain for angles $\psi$ on either side of 0. Flips of the $b$-axis spin at $\psi = 0$ and $\pi$ produce cusps in the mode frequencies.

IV. FITTING RESULTS

Fits for the coupling parameters utilize the field dependence of $M$, the zero-field powder-diffraction data \[22\], the field dependence of the MR and EM modes at $\theta = \pi/2$ \[34\], and the MR mode frequencies at $\theta = 0$ and $\pi/3$ for 7, 12 and 15 T. The resulting exchange and anisotropy constants are provided in Table I and the corresponding zero-field spin state is plotted in Figs. 1(a-b). In contrast to the previously proposed \[22\] spin state with zig-zag chains in the $ab$ plane containing spins 2, 3, 6, and 7, our spin state can be better described as an array of $c$-axis chains or connected bitetrahedra \[12,36\] containing spins $\{1, 2, 3, 4\}$ (chain $\alpha$) or $\{5, 6, 7, 8\}$ (chain $\beta$) as sketched in Fig. 2. Chains are coupled by exchanges $J_9$, along $x$. As shown in Fig. 5 for 12 and 15 T, each hexagonal domain then contributes one MR branch with a period of $\pi$.

With field $\mathbf{B}_{\text{loc}} = B(\cos \psi, \sin \psi, 0) = B(a \cos \psi + b \sin \psi)$ in the domain reference frame, the upper MR mode in Fig. 4 corresponds to the $\psi = \pi/2$ mode for domain I while the lower MR mode corresponds to the degenerate $\psi = \pm \pi/6$ modes for domains II and III. Previously measured MR frequencies plotted in Fig. 4 at 12 T correspond to the diamond and triangular points in Fig. 5(b) at $\theta = \pi/2$. Cusps in the MR curves for each domain at $\psi = 0$ and $\pi$ are caused by flipping the $b$ component of the magnetization (see inset to Fig. 5(b)).
J_{10}, and J_{12} in the ab plane.

What explains the wide range of J_i values? An orthorhombic distortion $a' = \frac{2a + b}{3} + c' = 0.018$ as $T \to 0$ breaks the hexagonal symmetry of the ab plane and explains the difference between the pairs $\{J_1, J_2\}$, $\{J_5, J_{11}\}$, and $\{J_{10}, J_{12}\}$. The difference between couplings like $\{J_7, J_8\}$ is caused by charge ordering: whereas $J_7$ couples moments 2 and 3 with $M_2 = M_3$, $J_8$ couples moments 2 and 4 with $M_2 \neq M_4$. Charge ordering also explains the difference between the pairs $\{J_2, J_3\}$ and $\{J_6, J_{10}\}$. Although not demanded by symmetry, we set $J_1 = J_5$, $J_2 = J_4$, $J_3 = J_6$, and $J_{11} = J_{12}$ because the spin state and excitations at $Q$ only depend on their averages.

Given other conditions, our fit chooses the spin state that matches the powder-diffraction data $\{\phi\}$ as closely as possible. At zero field, the predicted spin state has angles $\phi_1 = -0.83\pi$, $\phi_2 = 0.40\pi$, $\phi_3 = -0.23\pi$, and $\phi_4 = 0.62\pi$. Based exclusively on powder-diffraction data and symmetry constraints, the previously proposed spin state $\{\phi\}$ had $\phi_1 = -0.24\pi$, $\phi_2 = \phi_3 = 0.67\pi$, and $\phi_4 = -0.44\pi$. In both cases, $\phi_{i+4} = \pi - \phi_i$ ($i = 1, \ldots, 4$) so that the moment $M_b$ lies along the b axis. As shown in Table II, our spin state does not satisfy the powder diffraction data quite as well as the earlier state, primarily because it underestimates the powder diffraction peak I(112).

For the previous spin state, $\chi^2$ is minimized by Lorentzian form factors with $Q_1/4\pi = 0.088$ Å$^{-1}$, $Q_2/4\pi = Q_4/4\pi = 0.095$ Å$^{-1}$, and $Q_3/4\pi = 0.088$ Å$^{-1}$ for spins $S_n$. For the new spin state, $Q_1/4\pi = 0.052$ Å$^{-1}$, $Q_2/4\pi = Q_3/4\pi = 0.224$ Å$^{-1}$, and $Q_4/4\pi = 0.102$ Å$^{-1}$. All are smaller than the scale $Q_0/4\pi \approx 0.3$ Å$^{-1}$ measured by Khan and Erickson for Co$^{2+}$ in CoO.

Our results indicate that the exchange coupling $J_8 \approx 188$ meV between moments 2 (Co$^{2+}$, $S_2 = 1$) and 4 (Co$^{3+}$/Co$^{2+}$, $S_4 = 1.2$) is strongly ferromagnetic and larger in magnitude even than the 155 meV antiferromagnetic coupling found in the cuprate Nd$_2$CuO$_4$.

The strength of this coupling might be explained by the double-exchange mediated hopping of ligand holes $L$ from site 4 to 2. Bear in mind, however, that the estimated exchange parameters would be significantly reduced if the fits were performed with $S = 3/2$ for all Co spins. In particular, $J_8$ would then fall from 188 to 100 meV.

Except for $J_{10}$, the five largest exchange couplings $J_1 = J_5 \approx -92$ meV, $J_3 = J_6 \approx 41$ meV, and $J_8 \approx 188$ meV lie within connected tetrahedral, $c$-axis chains. Inside each chain, competing interactions between spins 1, 2, and 4 produce a non-collinear spin state.

Although occupying a triangular lattice, chains $\alpha$ and $\beta$ are magnetically ordered with moments $M^{\alpha} = (\pm 1.18, 1.33, 0)\mu_B$/f.u.. These chains are primarily coupled by the strongly ferromagnetic interaction $J_{10} \approx 108$ meV between nearly parallel spins $\{4, 6\}$ ($\phi_4 = 0.62\pi$, $\phi_6 = 0.60\pi$) and $\{2, 8\}$ ($\phi_2 = 0.40\pi$, $\phi_8 = 0.38\pi$). Above $T_c = 70$ K, the short-range order within each chain may be responsible for the large, negative Curie-Weiss temperature $\Theta_{CW} \approx -1720$ or $-890$ K, larger than expected Curie constant, and the susceptibility anomaly at 360 K suggestive of short-range magnetic order far above $T_c$.

Comparison between the theoretical and experimental results for the magnetization in Fig. 3 suggests that roughly 20% of the sample is in domain I. Different domain populations or even orthorhombic twinning in other samples may explain the discrepancies between the reported magnetization measurements $\{22,20,31,53\}$.

Easy-axis anisotropies $A$ and $C$ favor ferrimagnetic alignment along $b$ rather than $a$. The spin-flip (SF) field required to flip the spins towards the $a$ direction must increase as the field along $b$ increases. As shown in the inset to Fig. 5(a), $B_{SF}(\psi)$ then increases with $\psi$. If $B_{SF}(\psi = 0) < 15$ T, then the MR spectrum for 15 T would show a discontinuity at the transition from a low-field (LF) to a high-field (HF) state below some critical value of $\psi$. Since the MR mode frequencies in Fig. 5(a) do not exhibit any discontinuities as a function of $\psi$, we conclude that $B_{SF}(\psi = 0)$ exceeds 15 T and probably, based on the smooth dependence of the magnetizations on field, exceeds 32 T as well. The apparent small size of $B_{SF}$ must reflect the net magnetization of all three domains.

Predicted modes below 5 THz are plotted in Fig. 4. The Goldstone modes for all three domains are lifted by in-plane anisotropies to become the MR modes with zero-field frequencies of 1.07 THz. As remarked earlier, the lower MR mode comes from domains II and III while the upper MR mode comes from domain I. Below 3.5 THz, one EM mode is produced in domain I and another in domains II and III. The degenerate EM modes from domains II and III dominate the optical absorption. The predicted field dependence of the upper MR mode is quite close to the observed dependence. But the predicted curvatures of the lower MR mode and the EM mode, both from domains II and III, is not observed.

V. SPIN-INDUCED ELECTRIC POLARIZATION

Below the ferrimagnetic transition, CaBaCo$_4$O$_7$ is reported to develop a very large spin-induced polarization $\sim 1700$ nC/cm$^2$, which is surpassed in type I multiferroics only by the conjectured spin-induced polarization $\sim 3000$ nC/cm$^2$ of BiFeO$_3$. Other measurements indicate that the spin-induced polarization of CaBaCo$_4$O$_7$ ranges from 320 nC/cm$^2$ to 900 nC/cm$^2$.

The electric-field dependence of any interaction term in the spin Hamiltonian $\mathcal{H}$ can induce an electric polarization below $T_c$. However, the electric-field dependence of the easy-plane anisotropy $D$ cannot explain the spin-induced polarization along $c$ because the expectation value of $P_z = \kappa S_z c^2$ with $\kappa = -\partial D/\partial E_c$ would vanish in zero magnetic field when all the spins lie in the
ab plane. Easy-axis anisotropy A or C in the ab plane could produce a spin-induced electric polarization perpendicular to c. But the EM mode would then become observable for a THz electric field in the ab plane, contrary to measurements.

As conjectured previously, the spin-induced polarization in CaBaCoO₇ must then be generated by the dependence of the exchange interactions Jₙₙ on an electric field, called magnetostriction. Coupling constant λₙₙ = ∂Jₙₙ/∂Eᵥ for bond {i, j} is associated with a spin-induced polarization 0 per site of Pᵢᵢ = λᵢᵢSᵢ · Sⱼ/4, which accounts for the four equivalent bonds per unit cell. Expanding in the electric field Eᵥ yields an interaction term −EᵥλᵢᵢSᵢ · Sⱼ, linear in the electric field and quadratic in the spin operators.

Taking {0} as the ground state and |n⟩ as the excited spin-wave state, the MR matrix element ⟨n|Mₙ|0⟩ mixes with the EM matrix element ⟨n|P₀|0⟩ for domains II and III but not for domain I. Therefore, our model can explain the strong asymmetry 44 ~ Re{⟨n|M·B₀|0⟩⟨0|P·E₀|n⟩} in the absorption of counter-propagating light waves 24 for the lower observed MR mode in geometry ii with E₀⊥c. But it cannot explain the observed asymmetry of this mode in geometry i with E₀∥c if only ⟨0|P₀|n⟩ is significant.

Can we estimate the coupling constants λᵢᵢ and the spin-induced electric polarization? The optical absorption of any mode in domain l is proportional to p₁² because each matrix element is separately proportional to p₁. At nonzero field, the EM mode absorption is proportional to p₂² + p₃² while the upper MR mode absorption is proportional to p₁². At zero field, all domains have the same mode spectrum so that both the MR and EM mode absorptions are proportional to p₁² + p₂² + p₃². Experimentally, the ratio r of the absorption of the EM mode to the absorption of the upper MR mode rises from r = 7.5 at 0 T to r = 35 at 10 T. This growth is explained by the B > 0 ratio (p₂² + p₃²)/p₁² ≈ 10±5 for p₁ = 0.185±0.071 and p₂ = p₃ = (1 − p₁)/2.

At both 0 and 10 T, the only sets of bonds that generate spin-induced polarizations of the right magnitude are {2, 7} and {3, 4}. Each of those bonds couples adjacent c-axis chains through pairs of spins that are almost anti-parallel. From the relative absorptions r at 0 or 10 T, we estimate that ⟨P₀²⟩ ≈ 2350 or 1960 nC/cm² and ⟨P₃⁴⟩ ≈ 2110 or 1730 nC/cm². However, results for both of these sets of bonds are consistent with the recently observed polarization of 1700 nC/cm². By contrast, density-functional theory 27 predicts that the spin-induced polarization along c is 460 nC/cm². The spin-induced polarization should remain fairly constant with applied magnetic field, decreasing by about 1% for a 10 T field along b.

**VI. CONCLUSION**

We have presented a nearly complete solution for the magnetization, spin state, and mode frequencies of the swedenborgite CaBaCoO₇. An orthorhombic distortion above Tᵢ partially relieves the geometric frustration on the kagome and triangular layers and allows ferrimagnetism and ferroelectricity to coexist below Tᵢ. Although occupying a triangular lattice, bitetrahedral c-axis chains are ferrimagnetically ordered in the ab plane. Competing interactions within each chain produce non-collinear spin states. Sets of bonds coupling those chains are responsible for the large spin-induced polarization of CaBaCoO₇.

Despite its fixed permanent electric polarization, this swedenborgite may yet have important technological applications utilizing the large changes 24 in the spin-induced polarization when a modest magnetic field < 1 T is applied along b just below Tᵢ. A big jump in the polarization should also be produced just below Tᵢ by rotating a fixed magnetic field about the c axis. Above all, our work illuminates a pathway to develop other functional materials with sizeable magnetic moments and electrical polarizations.

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