

## Zero-field magnetic structure and metamagnetic phase transitions of the cobalt chain compound $\text{Li}_2\text{CoCl}_4$

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Exploring the uncharacterized magnetic phases of  $\text{Co}^{2+}$  chain compounds is critical for finding new low-dimensional magnets hosting quantized excitations. We map the unexplored magnetic phases of the  $\text{Co}^{2+}$  chain compound  $\text{Li}_2\text{CoCl}_4$ . Magnetometry reveals magnetic ordering below 7 K with a metamagnetic transition near 16.5 kOe and a gradual transition to a field-aligned paramagnetic state above 31 kOe. Curie-Weiss fits to the high-temperature susceptibility reveal a high-spin ( $\text{spin-}\frac{3}{2}$ ) state for cobalt. Heat capacity data, though, give a magnetic entropy change of 5.46 J/mol, consistent with cobalt effective  $\text{spin-}\frac{1}{2}$  systems. To characterize the zero-field antiferromagnetic ordering, we separately calculated the energy of proposed magnetic structures with density functional theory and collected 3.5 K neutron diffraction data, finding that  $\text{Li}_2\text{CoCl}_4$  has ferromagnetic chains with antiferromagnetic interactions between them. Increasing field rotates these spin chains, producing the antiferromagnetic to intermediate to paramagnetic transition sequence.

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### I. INTRODUCTION

Low-dimensional  $\text{spin-}\frac{1}{2}$  magnets are ideal systems for probing quantum ground and excited states, providing opportunities for realizing Ising and Heisenberg magnetism models and for hosting quantized excitations.  $\text{Co}^{2+}$  in octahedra, notably, can have a low-spin configuration ( $\text{spin-}\frac{1}{2}$ ,  $t_{2g}^6 e_g^1$ ).  $\text{Co}^{2+}$  can also have a high-spin configuration ( $\text{spin-}\frac{3}{2}$ ,  $t_{2g}^5 e_g^2$ ) where spin-orbit coupling leads to a ground-state Kramers doublet ( $J=\frac{1}{2}$ ) that is energetically well-separated from higher-energy states and can dominate low-temperature behavior [1–3], effectively producing  $\text{spin-}\frac{1}{2}$  properties [4–8]. Mapping the magnetic phase regions of unexplored octahedral  $\text{Co}^{2+}$  compounds is thus necessary to assess their applicability for studying low-dimensional  $\text{spin-}\frac{1}{2}$  behavior.

Of interest here are alkali- $\text{Co}^{2+}$ -halide compounds, which often contain one-dimensional cobalt chains. High-spin  $\text{CsCoBr}_3$ ,  $\text{CsCoCl}_3$ , and  $\text{RbCoCl}_3$  have antialigned magnetic moments along their cobalt chains, and experimental data match Ising antiferromagnet behavior [9–12], with  $\text{CsCoCl}_3$  and  $\text{CsCoBr}_3$  experimental data also matching effective  $\text{spin-}\frac{1}{2}$  behavior [13,14]. As a result, these materials have been used to study quantum spin excitations [15,16]. Another material with antialigned intrachain moments,  $\text{Cs}_2\text{CoCl}_4$ , has  $\text{Co}^{2+}$  cations arranged in cobalt-chlorine tetrahedra, and it has an effective  $\text{spin-}\frac{1}{2}$  state [17] that has encouraged its use in studying quantum phase transitions [18] and in developing an entanglement detection protocol [19].

While searching for similar one-dimensional magnetic compounds using a magnetic dimensionality toolkit [20], we found  $\text{Li}_2\text{CoCl}_4$ . The compound is another alkali-cobalt-halide with  $\text{Co}^{2+}$  chains and with octahedral coordination. It has a low-temperature phase with  $Cmmm$  space group symmetry [21], and near 300 °C, differential thermal analysis [22], differential scanning calorimetry, and neutron powder diffraction have shown a transition to a disordered rock-salt structure [21]. The low-temperature phase has nearly regular, edge-sharing cobalt-chlorine octahedra that form chains parallel to the unit cell's  $c$ -axis. Studied only for its electronic transport properties [23,24],  $\text{Li}_2\text{CoCl}_4$  has unexplored magnetic properties. This structure, promisingly, is similar to that of high-spin  $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ , which has field-dependent magnetic phases and experimental results matching effective  $\text{spin-}\frac{1}{2}$  Ising chain behavior [25–31].  $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ , consequently, has observed quantum criticality and spin excitations [32,33], with its magnetic anisotropy, due to polyhedral distortions, influencing magnetic excitations [34] and Bloch oscillations [35]. Therefore, probing the magnetic structure of  $\text{Li}_2\text{CoCl}_4$  will provide further insights into the magnetic behavior of its cobalt chains and their potential for studying quantum phenomena.

### II. MATERIALS AND METHODS

#### A. Synthesis

We ground  $\text{LiCl}$  (99.9%, Alfa Aesar) and  $\text{CoCl}_2$  (99.7%, Alfa Aesar) together under argon in the stoichiometric ratio and placed the mixture in a quartz tube. Highly hygroscopic  $\text{LiCl}$  cannot be exposed to air or moisture. Therefore, we used an Edwards Speedivalve to close the tube under argon and

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transfer it to a vacuum pump line. The vacuum line was then pumped at 45 mTorr for 15 min to clear it before opening the valve to pump argon from the sample tube. We heated the sealed mixture at 10 °C/min to 550 °C, held for 12 h, and then cooled to room temperature at 10 °C/min. Samples were royal blue and solidified in chunks, having been heated above the melting temperature.

### B. Characterization

We used a Bruker D8 Advance equipped with a capillary geometry to collect x-ray diffraction (XRD) data with Mo  $K\alpha$  radiation. We sealed XRD samples under vacuum in a thin glass capillary. This process involved momentary exposure to air.

Zero-field neutron diffraction data were collected on  $\sim 2$  g powder at 3.5 and 15 K on the ECHIDNA beamline [36] at the Australian Centre for Neutron Scattering using neutrons with a 2.4395 Å wavelength. We solved the magnetic structure using FULLPROF [37] and GSAS-II [38], giving the same result. The GSAS-II magnetic structure solution additionally used the Bilbao Crystallographic Server’s  $K$ -SUBGROUPSMAG program [39]. Unit cell images were produced with VESTA [40].

We collected susceptibility and magnetization data with a Quantum Design Magnetic Property Measurement System (MPMS3) on powder samples. For 2–400 K data sets collected at 8, 16, 25, and 45 kOe, we used the vibrating sample magnetometry (VSM) mode. For magnetic phase mapping, which involved fields up to 70 kOe, we used the dc mode since the MPMS3 VSM fitting was poor at the highest moment values. We measured the compound’s zero-field-cooled and field-cooled susceptibility from 2.5 to 15 K at 10, 100, and 1000 Oe before stepping in 5 kOe intervals from 5 to 70 kOe. We also collected isothermal magnetization curves from  $-70$  to 70 kOe at 2.5 K and at 3–9 K at 1 K intervals.

For heat capacity data, we used a Quantum Design Physical Property Measurement System. We attached a 1.1 mg chunk of polycrystalline  $\text{Li}_2\text{CoCl}_4$  to a calibrated puck with Apiezon N-grease and subtracted the grease contribution. We measured the heat capacity from 3 to 145 K at zero field and from 3 to 40 K for applied fields up to 55 kOe.

### C. Computational procedure

We performed spin-polarized density functional theory (DFT) calculations with the Vienna *Ab-initio* Simulation Package (VASP) [41] for 12 proposed magnetic configurations. Total energies for each were calculated using the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) to describe the exchange-correlation energy [42]. We used the cell parameters and atomic positions from our 3.5 K neutron diffraction experiment as a starting point for relaxations [43]. Only the atomic geometry was provided, not the magnetic structure, to avoid biasing our calculations.

Convergence tests found that a plane-wave cutoff of 800 eV with a  $3 \times 2 \times 6$   $\Gamma$ -centered  $\mathbf{k}$ -point grid for single unit cell magnetic configurations converged pressure and energy values well ( $\Delta P < 0.01$  kbar,  $\Delta E < 0.090$  meV/atom). For configurations requiring  $c$ -axis doubling, a  $3 \times 2 \times 3$  grid

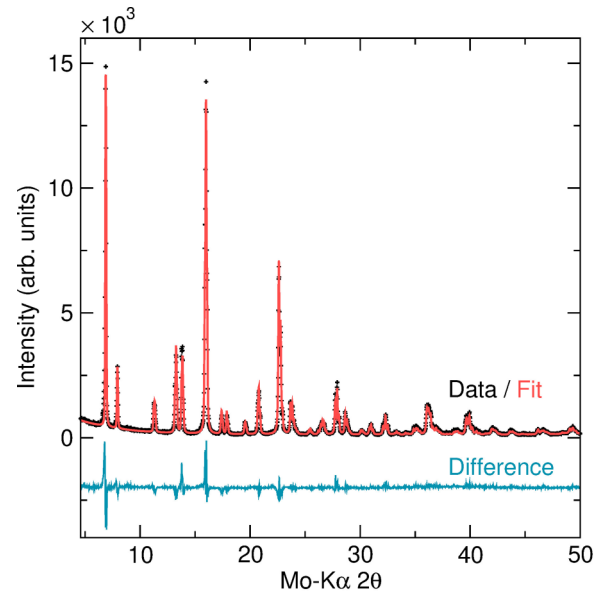


FIG. 1. Room-temperature powder XRD data match the expected low-temperature  $Cmmm$  space-group phase.

was used. We relaxed the atomic positions, cell shape, and cell volume of the 3.5 K cell with a force tolerance of 5 meV/Å, performing a collinear calculation and initializing the cobalt magnetic moments to  $\pm 1 \mu_B$ . Then we performed a noncollinear calculation with spin-orbit coupling. Band structure and density of states calculations for the lowest energy configuration were performed using the SCAN meta-GGA functional without spin-orbit coupling [44].

## III. RESULTS AND DISCUSSION

### A. Phase purity

Powder XRD confirmed sample phase purity (Fig. 1) with Rietveld refinements matching the low-temperature  $Cmmm$  polymorph (Fig. 2). If  $\text{Li}_2\text{CoCl}_4$  is exposed to air, the XRD pattern shows unidentified impurity peaks within minutes, so keeping the samples in an inert environment is critical. Note that though  $\text{Li}_2\text{CoCl}_4$  was originally reported to crystallize in the  $Immm$  space group [45,46], this was corrected [21].

The compound has an order-disorder phase transition, determined previously by differential thermal analysis and

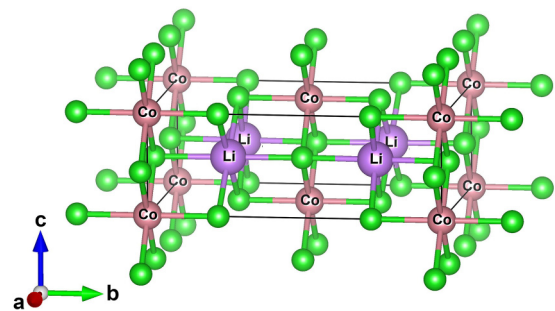


FIG. 2. The low-temperature phase unit cell contains cobalt-chlorine octahedra, forming chains along the  $c$ -axis. Similarly, lithium-chlorine octahedra chains run along the  $a$ -axis.

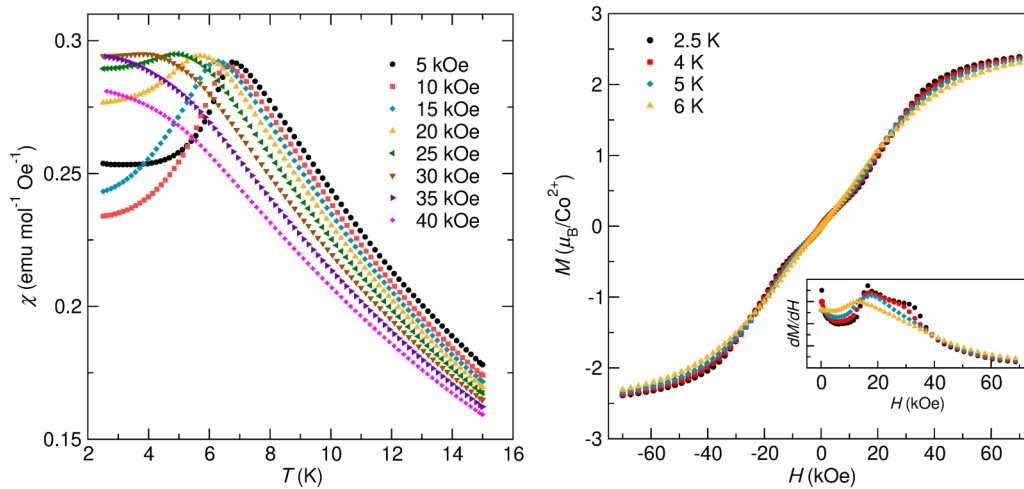


FIG. 3. Left: zero-field-cooled magnetic susceptibility data collected at  $5 \leq H \leq 40$  kOe show observable transition temperatures used to construct the magnetic phase diagram. Data below 5 kOe had a tail at low temperature, presumably from impurity spins, that was suppressed at higher fields [43]. Data above 30 kOe continue to decrease in susceptibility, indicating a saturated paramagnetic state [43]. Right: magnetization curves show slope changes associated with metamagnetic phase transitions. The shifts appear as peaks in the derivative plot inset.

differential scanning calorimetry, between 270 and 316 °C [21,22,45]. We collected *in situ* XRD data up to 480 °C, which showed the transition near 330 °C. Upon cooling, the compound transformed back into the low-temperature phase at the same temperature [43]. We could not stabilize the high-temperature phase at room temperature by quenching 430 °C powder in ice water; quenching resulted in a pure low-temperature phase product. The high-temperature phase, therefore, prevents simple single-crystal growth by slow cooling the melt. After confirming phase purity, we performed basic magnetic measurements to map the magnetic phase diagram.

### B. Magnetic susceptibility and magnetization

The magnetic susceptibility at low temperature shows a distinct peak and downturn, indicating antiferromagnetic (AFM) order. At 1 kOe, the Néel temperature ( $T_N$ ) is 6.8 K. The transition peak broadens with increasing field until above 30 kOe the susceptibility no longer decreases at lower temperatures. As the field increases above 30 kOe, the moment begins to saturate, leading to a decrease in susceptibility. Moment saturation along with the absence of a sharp transition in the susceptibility indicates a paramagnetic state with field-induced moment alignment. Representative spectra are shown in Fig. 3 with additional data in the supplemental material [43]. In the magnetization curves, we observe no sharp transitions; rather, we see gradual transitions that we identify with derivative curve peaks (Fig. 3). It is, of course, unclear how sharp these transitions may be for single-crystal measurements along specific axes. The derivative peaks indicate three magnetic ordering regions. Combining the peaks with susceptibility derived transition temperatures gives the magnetic phase diagram boundaries in Fig. 4. The boundaries between the low-field (AFM), intermediate-field, and high-field regions are not sharp. The magnetization derivative peaks separating the regions, likewise, broaden with increasing temperature. At 70 kOe and 2.5 K, the measured  $2.38 \mu_B/\text{Co}^{2+}$

magnetization appears close to saturation, and at the proposed transition from the AFM phase to the intermediate-field phase, the magnetization is  $0.76 \mu_B/\text{Co}^{2+}$ , roughly one-third the saturated moment.  $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ , noted before because of its similar structure to  $\text{Li}_2\text{CoCl}_4$ , has an antiferromagnetic to ferrimagnetic (FiM) transition followed by a FiM to paramagnetic (PM) transition with increasing field [29,30,32]. At low fields,  $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$  has ferromagnetic (FM) chains with antiferromagnetic interactions between them, and with increasing field, one-third of the moments rotate to form the FiM phase.

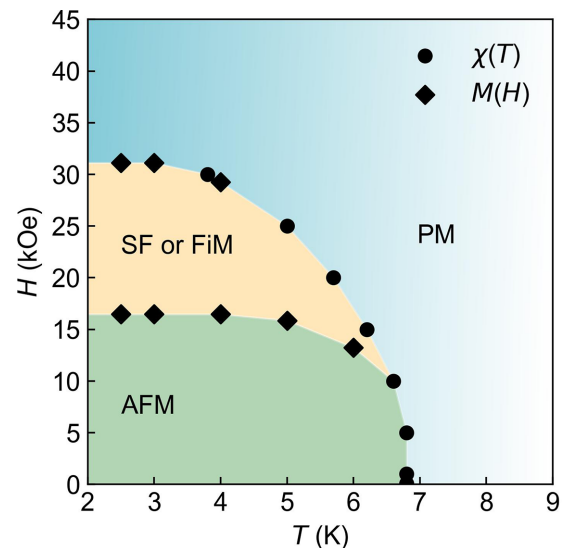


FIG. 4. The magnetic phase regions of  $\text{Li}_2\text{CoCl}_4$  are derived from susceptibility transition temperatures and from isothermal magnetization curve derivatives. At 2.5 K, an antiferromagnetic phase transitions to an intermediate phase (spin-flop or possibly ferrimagnetic) around 16.5 kOe and from the intermediate phase to a nearly saturated paramagnetic phase around 31 kOe. The powder data indicate gradual changes during the field-driven transitions. Data point shapes correspond to their origin.

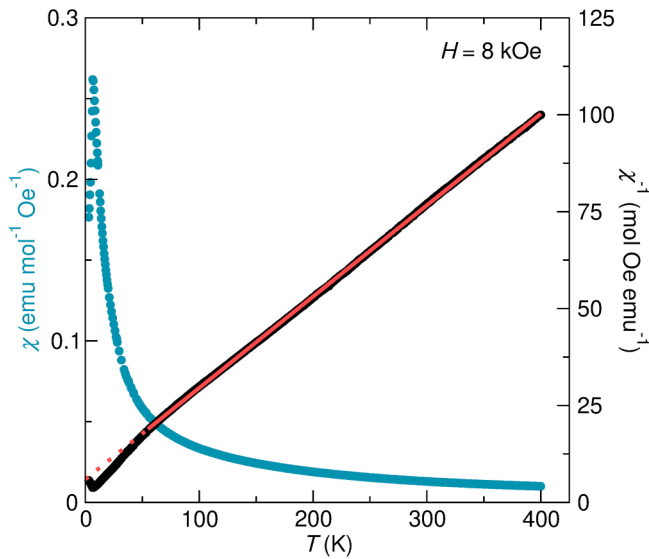


FIG. 5. Field-cooled magnetic susceptibility data collected at 8 kOe follow Curie-Weiss paramagnetism above 55 K ( $R^2 = 0.99992$ ) with  $\theta_{CW} = -25.3$  K indicating antiferromagnetic order.

Consequently, the FiM phase magnetization is one-third that of the saturated moment. The similar magnetization behavior of  $\text{Li}_2\text{CoCl}_4$  indicates that it may transition with increasing field from AFM to FiM to PM behavior. Our data, though, are also consistent with an intermediate field spin-flop (SF) phase [47]. Therefore, further neutron diffraction experiments with applied field are needed to confirm the intermediate field phase ordering.

Figure 5 shows a Curie-Weiss fit to susceptibility data from 55 to 400 K at 8 kOe. This gives  $\theta_{CW} = -25.3$  K and an effective moment of  $5.83 \mu_B$ , indicating dominant antiferromagnetic interactions and a large, unquenched orbital moment. The frustration index of 3.8 ( $|\theta_{CW}|/T_N = |-25.3|/6.7$ ) also indicates mild frustration. The moment magnitude is consistent with other spin- $\frac{3}{2}$   $\text{Co}^{2+}$  compounds with regular or nearly regular octahedra (frequently double perovskites) [5,48–50]. At higher fields, linear fits to data from 55 to 400 K also give negative Curie-Weiss parameters; however, deviations from linear behavior indicate competing ferromagnetic and antiferromagnetic interactions [43]. Also, the inverse susceptibility shifts slightly below 55 K at all fields, no longer obeying Curie-Weiss paramagnetism. For  $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ , a temperature-independent term accounted for curvature in the inverse susceptibility, changing the fitted Curie-Weiss temperature from  $-29$  K along the  $c$  axis [25] to 1 K [26]. However, we could not account for the curvature with a temperature-independent term.

Similar low-temperature deviations from Curie-Weiss behavior are observed for FM [51,52] and AFM [53,54] chains of high-spin  $\text{Co}^{2+}$  in octahedral environments. At low temperatures, for isolated  $\text{Co}^{2+}$  in a regular octahedral environment with weak crystal field, spin-orbit coupling and Zeeman splitting of the  $^4T_1$  ground term are predicted to produce a similar temperature-dependent slope change in the inverse susceptibility, which follows Curie-Weiss behavior at high

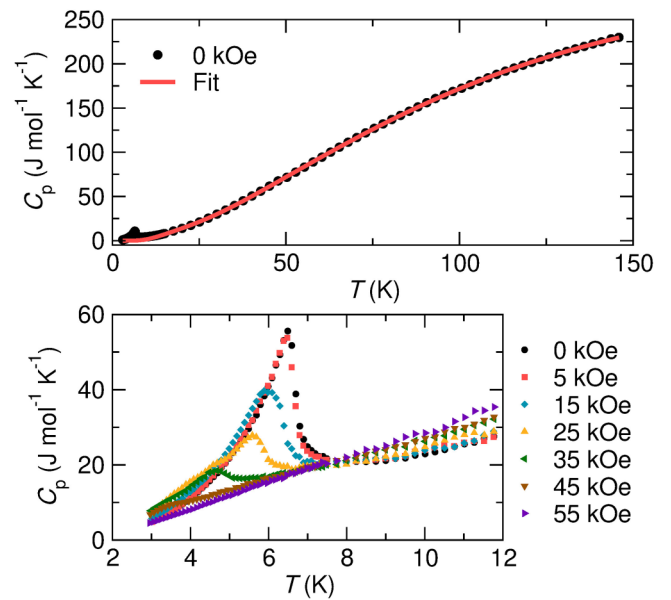


FIG. 6. Top: the zero-field heat capacity is plotted along with a Debye-Einstein fit to data above 15.5 K. The Néel temperature appears as a peak. Bottom: low-temperature heat-capacity data are plotted for increasing field. The zero-field and 5 kOe data are nearly identical. Above the intermediate phase to PM transition found with magnetometry, there remains a peak until around 55 kOe, where the low-temperature heat capacity is linear.

temperatures [55].  $\text{Li}_2\text{CoCl}_4$  and the other chain compounds with this behavior are high-spin (weak crystal field) with octahedrally coordinated  $\text{Co}^{2+}$  and significant orbital contributions, making it likely that these effects account for the temperature-dependent deviations. Curie-Weiss fits, therefore, are approximations but can still indicate the spin state and dominant interaction type.

### C. Heat capacity

Figure 6 contains the heat capacity data. The heat capacity is similar at zero field and 5 kOe, showing a transition at the Néel temperature. In the intermediate-field region at 25 kOe, there is a small kink in the transition peak at 4.9 K, reflecting the destabilization of the antiferromagnetic behavior with increasing field. There is also a peak at 4.6 K with an applied field of 35 kOe and a small hump at 3.5 K with a 45 kOe field.

To isolate the magnetic heat capacity contribution, we fit the lattice contribution of the zero-field data above 15.5 K to a Debye-Einstein equation with one Debye term and two Einstein terms (Fig. 6). Based on diffraction and published computational data [56,57], we estimated that the difference between  $C_p$  and  $C_v$  is negligible. Fit information is in the supplemental material [43], and Fig. 7 shows the isolated magnetic heat capacity. At 25 kOe applied field, a hump in the magnetic heat capacity above the susceptibility transition temperature appears. This hump is characteristic of one-dimensional systems with short-range order [50,58–60]. At 55 kOe, only the hump remains. This corresponds with the high-field susceptibility data where at low temperature the curve no longer decreases and appears paramagnetic with a saturated moment [43]. Integrating  $C_{p,\text{mag}}/T$  over temperature

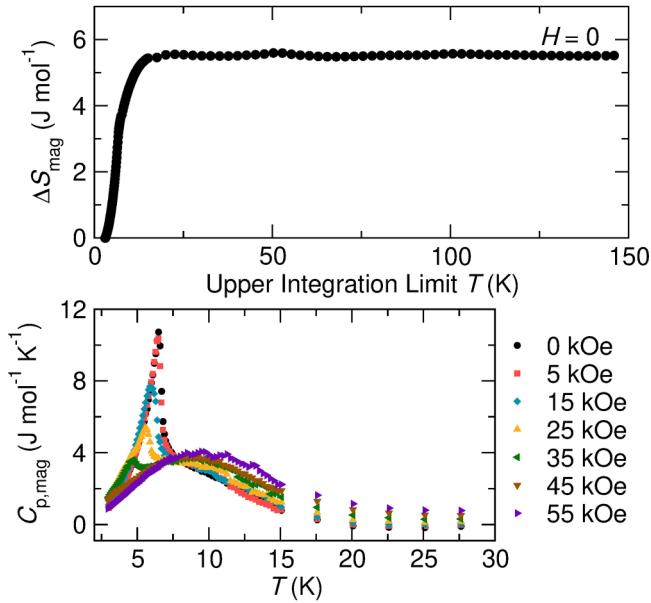


FIG. 7. Top: the magnetic entropy change is calculated over a range of integration intervals, showing a total change of 5.46 J/mol. Bottom: the magnetic contribution to the heat capacity is plotted, showing a transition from long-range to short-range order with increasing field.

gives the magnetic entropy change during these transitions. For the zero-field data, the entropy change reaches 5.46 J/mol (Fig. 7). This is 94.7% of the expected value of  $R\ln(2)$  for spin- $\frac{1}{2}$  systems. Since the value reflects the configuration multiplicity, which depends on spin-orbit coupling effects, the observed entropy change suggests a Kramers doublet ground state with effective spin- $\frac{1}{2}$  ( $J = \frac{1}{2}$ ), consistent with behavior seen in other high-spin cobalt materials [4,5,60].

#### D. DFT magnetic structure and spin state

To probe the magnetic ordering, we performed DFT total energy calculations on 12 potential magnetic configurations without consulting neutron diffraction results. Each configuration was defined by its cobalt intrachain and interchain interactions as well as its moment direction. A-C had ferromagnetic chains with antiferromagnetic interactions between them; D-F had antiferromagnetic chains with ferromagnetic interactions between them; G-I had antiferromagnetic chains with antiferromagnetic interactions between them; and J-L were ferromagnetic. Each set of interaction types included a configuration with moments along the  $a$ -axis (A, D, G, J),  $b$ -axis (B, E, H, K), and  $c$ -axis (C, F, I, L). Unit cells for all 12 and their relaxed volumes are in the supplemental material [43].

As expected, differences between the total energies are small, but trends are apparent (Fig. 8). For each set of interaction types, the configuration with moments along the  $a$ -axis had the highest energy, indicating that the  $a$ -axis should be the hard axis. The differences between  $b$ -axis and  $c$ -axis configurations, on the other hand, were much smaller. Regarding average energies for each interaction type set, the ferromagnetic chain with antiferromagnetic

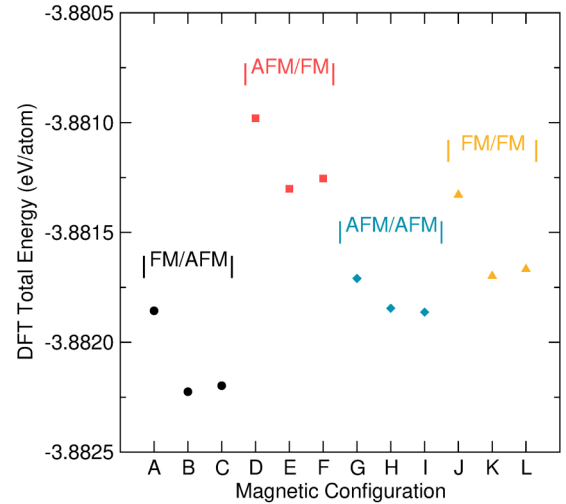


FIG. 8. DFT-calculated total energies (GGA) are shown for each magnetic configuration. The four groups are labeled by their intrachain/interchain interactions. Generally, FM/AFM configurations were the most stable, and AFM/FM ones the least. Moments along the  $a$ -axis were considerably less favorable than along  $b$  or  $c$ .

interactions between chains set (A-C) had the lowest energy while the inverse antiferromagnetic intrachain paired with ferromagnetic interchain interactions (D-F) had the highest.

Other alkali-cobalt-halide materials have antiferromagnetic chains [9–12], matching the D-I configurations, while  $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$  has ferromagnetic chains with antiferromagnetic interactions between [26], matching the A-C configurations. For  $\text{Li}_2\text{CoCl}_4$ , the B and C configurations are the lowest in energy, with B only 0.028 meV/atom lower in energy than C, less than the energy convergence from convergence tests. This adds more evidence that the  $\text{Li}_2\text{CoCl}_4$  magnetic phases match that of  $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ . The highest- and lowest-energy configurations are shown in Fig. 9. For the 12 configurations, the calculated cobalt moment ranged from 2.442 to 2.455  $\mu_B$ . The lowest-energy interaction type is the same for the unrelaxed cell as well. In the unrelaxed case, the C configuration becomes the lowest-energy configuration, but still by less than the convergence threshold (only 0.062 meV/atom lower in energy than B), and the hard and easy axis trends change for the D-F and G-I interaction sets [43].

The density of states (DOS) for the lowest-energy configuration, B, was calculated using the parameter-free SCAN functional to determine if DFT predicts electronic spin- $\frac{1}{2}$  or spin- $\frac{3}{2}$  for  $\text{Li}_2\text{CoCl}_4$ . The total DOS and one cobalt atom's  $d$  electron projected DOS are shown in Fig. 10. Each cobalt atom's  $d$  electron projected DOS looks similar. The spin-up states are fully occupied (see the bottom panel of Fig. 10), as expected for the high-spin configuration. One would also expect the spin-up minus spin-down occupation of cobalt  $d$  electrons to be 1 for spin- $\frac{1}{2}$  and 3 for spin- $\frac{3}{2}$  if the system were fully ionic. Integrating the states below the Fermi energy gives 4.60 spin-up electrons and 2.04 spin-down electrons. The difference, 2.56, is closer to the expected value for spin- $\frac{3}{2}$ . The corresponding band structure is in the supplemental material [43].

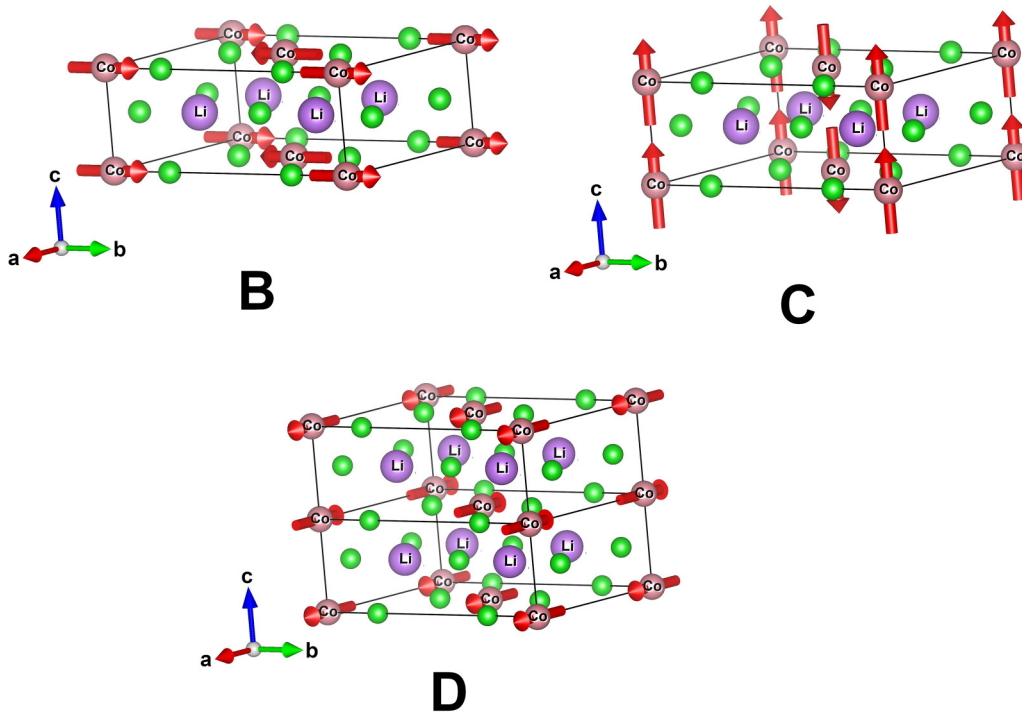


FIG. 9. The DFT-calculated highest-energy configuration (D) and the two lowest-energy configurations (B and C) for the relaxed  $\text{Li}_2\text{CoCl}_4$  cell are shown. B and C have ferromagnetic chains with antiferromagnetic interactions between them while D reverses this with antiferromagnetic intrachain and ferromagnetic interchain interactions. C is 0.028 meV/atom higher in energy than B, and D is 1.245 meV/atom higher in energy than B.

**E. Zero-field magnetic structure**

While collecting zero-field neutron diffraction data, we observed several magnetic peaks after cooling from 15 to

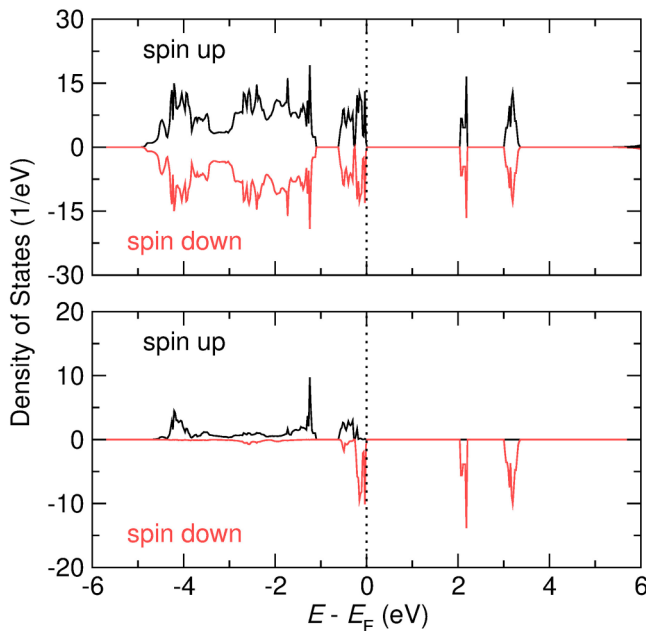


FIG. 10. Top: the total density of states for the B configuration of  $\text{Li}_2\text{CoCl}_4$ , calculated with the SCAN functional. Bottom: the density of states for a single cobalt ion's  $d$  electrons. The Fermi energy is set as the energy of the highest occupied state.

3.5 K. These peaks could be indexed to the nuclear unit cell parameters with a loss of  $C$ -centering. Therefore, we used a  $\mathbf{k} = (1,0,0)$  magnetic propagation vector to find the magnetic space group  $P_2\text{-bam}$  (BNS no. 55.363). The neutron diffraction data refinement at 3.5 K is in Fig. 11, and the magnetic unit cell is in Fig. 12. The 15 K data are in the supplemental material [43]. The refined moments are parallel to the  $c$ -axis by symmetry with ferromagnetic chains and antiferromagnetic interactions along the cell diagonal. This matches the DFT-calculated C configuration and the interaction behavior of the  $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$  low-field, antiferromagnetic phase but with a different moment axis. The interaction types further support that  $\text{Li}_2\text{CoCl}_4$  transitions from AFM to SF or FiM with increasing field. As the field increases, additional ferromagnetic chains can flip throughout a powder sample, leading to the gradual transitions observed with magnetic susceptibility and magnetization measurements as well as the short-range order behavior of the magnetic heat capacity.

The zero-field structure is also consistent with the low-field Curie-Weiss fit that gives a negative  $\theta_{\text{CW}}$ . At 3.5 K, each  $\text{Co}^{2+}$  is separated by 3.59 Å from its two nearest neighbors along the chain (Co-Cl-Co pathway) and 6.21 Å from its four next nearest neighbors along the cell diagonal (Co-Cl-Li-Cl-Co pathway). Additionally, each  $\text{Co}^{2+}$  has two antialigned next next nearest neighbors in each neighboring chain (Co-Cl-Li-Cl-Co pathway) at the same distance, 7.18 Å, as the two aligned  $\text{Co}^{2+}$  ions at the end of the Co-Cl-Co-Cl-Co pathway along the chain. Therefore, even if the ferromagnetic exchange interaction is stronger than the antiferromagnetic one, the higher number of antiferromagnetically coupled neighbors can produce a negative Curie-Weiss temperature.

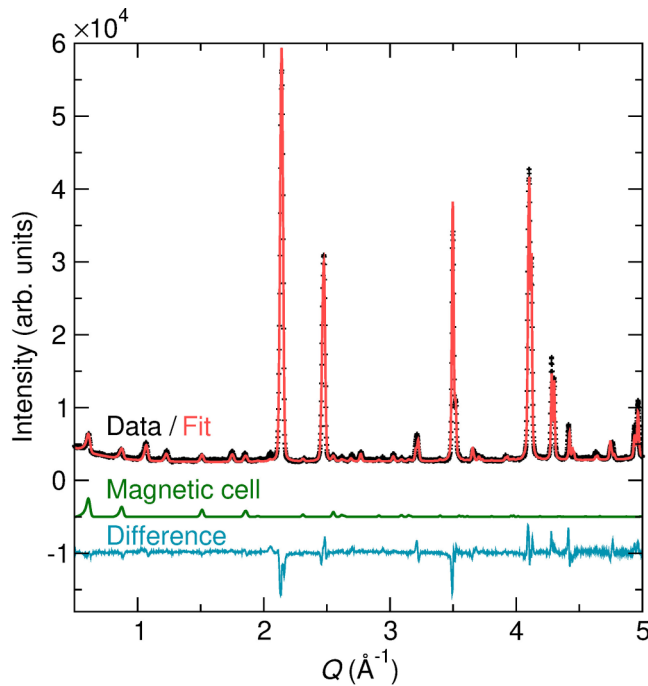


FIG. 11. Zero-field neutron powder diffraction data collected on the ECHIDNA beamline at 3.5 K are refined, and the magnetic contribution is plotted.

The refined moment is  $2.19(4) \mu_B$ . Since neutron diffraction measures  $M_{\text{sat}} = gS \mu_B$ , we would expect a  $3 \mu_B$  moment for  $\text{spin-}\frac{3}{2}$  assuming  $g = 2$ . The observed reduced moment can be explained by local defects disrupting the cobalt chains. A similar neutron diffraction refined moment has been observed in high-spin  $\text{Co}^{2+}$  double-perovskite oxides with regular octahedra, which have neutron diffraction refined moments ranging from 2 to  $2.43 \mu_B$  [5,48–50]. The cell refinement to the neutron data shows no significant distortion of the cobalt octahedra at 3.5 K, indicating no spin-crossover from high-spin to low-spin has occurred.

#### F. Cobalt spin state

We have presented several indicators for the spin state of  $\text{Co}^{2+}$  in  $\text{Li}_2\text{CoCl}_4$ . High-temperature data unambiguously point to a high-spin state. Curie-Weiss fits give effective moments much too large to be low-spin. DFT results, which predicted the correct interaction types, show a  $2.442$ – $2.455 \mu_B$  moment, similar to the refined moment of  $2.19 \mu_B$  and the saturation magnetization of  $2.38 \mu_B$ , and the DFT projected DOS for the cobalt  $d$  orbitals points to the high-spin arrangement. The system, therefore, has an electronic  $\text{spin-}\frac{3}{2}$  configuration.

It is less clear whether the system transitions to an effective  $\text{spin-}\frac{1}{2}$  state at low temperature by preferentially populating the  $J = \frac{1}{2}$  ground-state doublet. The strongest evidence is the magnetic entropy change. The entropy value of  $5.46 \text{ J/mol}$ , following  $\Delta S = R \ln(2S + 1)$ , is much closer to the  $\text{spin-}\frac{1}{2}$  case of  $\Delta S = 5.76 \text{ J/mol}$  than to the  $\text{spin-}\frac{3}{2}$  case of  $\Delta S = 11.5 \text{ J/mol}$ . Others have tried to infer an effective  $\text{spin-}\frac{1}{2}$  state from high-temperature data, extracting  $g$ , assuming it

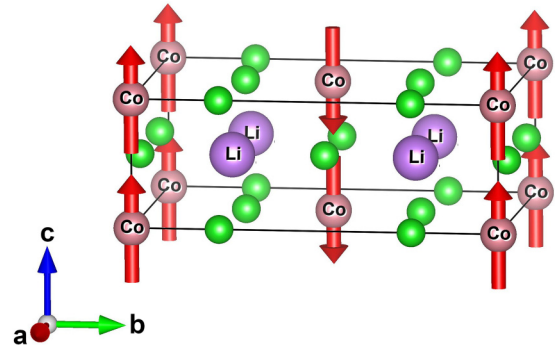


FIG. 12. The zero-field magnetic unit cell of  $\text{Li}_2\text{CoCl}_4$  is commensurate with the nuclear cell with a loss of  $C$ -centering.  $\text{Co}^{2+}$  magnetic moments with a magnitude of  $2.19(4) \mu_B$  are aligned along the cobalt chains.

is a constant scalar quantity, from Curie-Weiss fits when orbital contributions were significant [7,8,61,62]. Using our 8 kOe susceptibility data gives  $gS \mu_B = 3.37 \mu_B$  ( $g = 6.73$ ) for  $S = \frac{1}{2}$  and  $gS \mu_B = 4.52 \mu_B$  ( $g = 3.01$ ) for  $S = \frac{3}{2}$ . Our low-temperature refined moment is, in that case, closer to the  $\text{spin-}\frac{1}{2}$  value though still  $\sim 1 \mu_B$  different. Without spectroscopic data, neither of these effective  $\text{spin-}\frac{1}{2}$  indicators is conclusive. A more complete verification of the ground-state doublet's importance would require direction-dependent data, as seen for  $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ , where modeled effective  $\text{spin-}\frac{1}{2}$  behavior matches magnetometry, inelastic neutron scattering, and far-infrared transmission data [63].

#### IV. CONCLUSIONS

We mapped the magnetic phase regions of  $\text{Li}_2\text{CoCl}_4$  by combining susceptibility, magnetization, and heat capacity data. The material has a low-field antiferromagnetic phase, an intermediate-field spin-flop or ferrimagnetic phase, and a high-field paramagnetic phase. The field-driven transitions between each phase are gradual as the ferromagnetic cobalt chains rotate throughout the powder samples with increasing applied field. This leads to short-range order observed as humps in the magnetic heat capacity.

DFT calculations provided predictions for the zero-field magnetic structure within narrow energy windows. The DFT structure gave a ground state of ferromagnetic cobalt chains with antiferromagnetic interactions between them, matching the interaction types of the zero-field antiferromagnetic structure found with neutron powder diffraction. Interestingly, this behavior deviates from other alkali-cobalt-halides, which have antialigned intrachain moments. Further neutron diffraction studies are planned for probing the intermediate- and high-field magnetic structures.

$\text{Li}_2\text{CoCl}_4$  has a high-spin ( $\text{spin-}\frac{3}{2}$ ) arrangement based on calculated and refined moments, as well as susceptibility data. But since the cobalt chain moment structure matches that of  $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$  and since its magnetic entropy change is near  $R \ln(2)$ ,  $\text{Li}_2\text{CoCl}_4$  may exhibit effective  $\text{spin-}\frac{1}{2}$  behavior at low temperatures, such as a quantum critical point. Using neutron scattering with a transverse field, a quantum critical point and quantized excitations have been observed in effective  $\text{spin-}\frac{1}{2}$

(electronic spin- $\frac{3}{2}$ )  $\text{Co}^{2+}$  chain materials with weakly coupled ferromagnetic intrachain interactions paired with antiferromagnetic interchain interactions [7,33,64,65]. These measurements would require a single crystal of  $\text{Li}_2\text{CoCl}_4$ . With the magnetic phases of  $\text{Li}_2\text{CoCl}_4$  mapped, it can now be studied in more detail as a one-dimensional magnetic material.

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