Revisiting the ground state of CoAl$_2$O$_4$: Comparison to the conventional antiferromagnet MnAl$_2$O$_4$

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The $A$-site spinel material CoAl$_2$O$_4$ is a physical realization of the frustrated diamond-lattice antiferromagnet, a model in which unique incommensurate or “spin-spiral-liquid” ground states are predicted. Our previous single-crystal neutron scattering study instead classified it as a “kinetically inhibited” antiferromagnet, where the long-ranged correlations of a collinear Néel ground state are blocked by the freezing of domain-wall motion below a first-order phase transition at $T^* = 6.5$ K. This paper provides new data sets from a number of experiments, which support and expand this work in several important ways. We show that the phenomenology leading to the kinetically inhibited order is unaffected by sample measured and instrument resolution, while new low-temperature measurements reveal spin correlations are unchanging between $T = 2$ K and 250 mK, consistent with a frozen state. Polarized diffuse neutron measurements show several interesting magnetic features, which can be entirely explained by the existence of short-ranged Néel order. Finally, and crucially, this paper presents some neutron scattering studies of single crystalline MnAl$_2$O$_4$, which acts as an unfrustrated analog to CoAl$_2$O$_4$ and shows all the hallmarks of a classical antiferromagnet with a continuous phase transition to Néel order at $T_N = 39$ K. Direct comparison between the two compounds indicates that CoAl$_2$O$_4$ is unique, not in the nature of high-temperature diffuse correlations, but rather in the nature of the frozen state below $T^*$. The higher level of cation inversion in the MnAl$_2$O$_4$ sample indicates that this behavior is primarily an effect of greater next-nearest-neighbor exchange.

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The $A$-site spinels $AB_2X_4$, with $A$ magnetic, have seen a surge of interest in the past decade due to a series of interesting experimental observations [1–15] and theoretical predictions of novel spin-liquid ground states [16–20]. Magnetic cations in these materials comprise a bipartite diamond lattice, and novel behavior is argued to be the result of a competition between nearest- ($J_1$) and next-nearest- ($J_2$) neighbor superexchange interactions [2,21]. This is demonstrated explicitly by the calculations of Bergman et al. [16], who have shown for spin-only materials that the collinear Néel structure favored by $J_1$ is progressively destabilized with increasing $J_2$ until a Lifshitz point is encountered at $J_2^* = J_1^* = \frac{1}{8}$. For greater $J_2$, the ground state is predicted to be a “spiral-spin-liquid” (SSL) state characterized by fluctuations between an infinitely degenerate set of incommensurate spin spirals, whose propagation wave vectors form a series of calculable manifolds in reciprocal space (“spiral surfaces”). Further calculations [16–18] predict that these mass degeneracies are lifted by low-lying thermal or quantum fluctuations, driving first-order phase transitions via the order-by-disorder mechanism [22] to either unique spin spiral or Néel ordered states, depending on the specific value of $J_2$.

These ideas have been quite successful in explaining the multiple transitions and incommensurate ground state of the singular material MnSc$_2$S$_4$ [7,8], and very recent work has confirmed key SSL predictions [23]. In oxides, however, the search for SSL physics has focused most intently on the compound CoAl$_2$O$_4$. In this material, the diamond sublattice of the spinel structure is occupied by Co$^{2+}$ cations, which exist in a tetrahedrally coordinated crystal-field environment and have $S = \frac{3}{2}$. Early magnetization and heat capacity measurements by Tristan et al. revealed a high degree of frustration and an “unconventional glasslike” transition at $T_g = 4.8$ K [4]. Neutron powder diffraction (NPD) measurement by the same group revealed significant short-range antiferromagnetic correlations in the glassy state [6], and Bergman et al. immediately listed CoAl$_2$O$_4$ as a candidate SSL material [16]. Subsequent experimental work, however, has not settled the issue. Although Suzuki et al. concluded a spin-liquid ground state with $T^* \sim 10$ K based on results of thermodynamic measurements [9], a detailed NPD and NMR...
study of high-quality powders led Roy et al. to declare the existence of a continuous phase transition to classical Néel state at $T_N = 9.8$ K [13]. Separate NPD [11] and single-crystal neutron [12,14] studies by Zaharko et al. instead concluded an unconventional antiferromagnetic phase below $T_N = 8$ K, with a significant level of microstructural defects and accompanied by diffuse “streaks” of scattering which they suggested was indicative of coexisting SSL correlations.

Our own single-crystal neutron scattering study presented a yet different perspective on the low-temperature state of CoAl$_2$O$_4$ [1]. As with other groups [12,13], we observed short-range antiferromagnetic correlations at moderate temperatures, with growing intensity and correlation length as the system was cooled toward an apparently “glasslike” transition at $T^* = 6.5$ K. Contrary to expectations for a glass, however, we showed that $T^*$ is associated with the sudden emergence of a second, anisotropic contribution to the scattering function with Lorentzian-squared character, and an inelastic spectrum dominated by collective spin-wave excitations. A Lorentzian-squared line shape, we pointed out, is the expected form for scattering from a series of ordered domains separated by sharp walls, as seen during the coarsening step of order formation below a first-order phase transition [24]. Fits of measured spin-wave dispersions in our samples implied that $\frac{\delta}{T} \sim 0.104$, close to the Lifshitz point of $\frac{\delta}{T} = 0.125$ and near where Bergman et al. predicted a first-order transition to a Néel ordered state [16]. In a frustrated spin system, the energy scale of exchange interactions is typically large compared to thermal energies at temperatures below observed magnetic ordering transitions, and one may well expect domain-wall motion below any first-order transition to be “kinetically inhibited”, leading to a frozen short-range ordered state such as the one we have reported [1]. Fundamentally out of equilibrium, such a frozen coarsening picture would also naturally explain the glasslike, but unconventional, characteristics reported for bulk thermodynamic data [4,9].

Nonetheless, the presence of site defects undoubtedly plays a role in determining the material properties of A-site spinels. Calculations by Savary et al. suggest that spiral order in A-site spinels may be induced by relatively small numbers of point defects and that materials close to the predicted Lifshitz point may be predisposed to glassiness, when $\frac{\delta}{T} > \frac{1}{8}$ [25]. Monte Carlo simulations by Zaharko et al. for systems with $\frac{\delta}{T} = 0.1$ predict that Néel order is weakened and diffuse scattering intensified when either systematic absences are introduced on the spinel A-site or impurity moments placed on the B site [14]. In the latter case, the presence of as few as 4% impurity moments was sufficient to suppress Néel order completely [14]. Hanashima et al. highlighted the effects of common cation site inversion through a systematic magnetization study of the series (Co$_{1-x}$Al$_x$)(Al$_{2-x}$Co$_x$)O$_4$. They suggest that either a spin-glass phase with an unvarying $T_N = 4.5$ K or a spin-liquid ground state with $T^* \sim 7-10$ K is favored for $\delta > 0.101$ and $\delta < 0.0643$, respectively, with a sizable coexistence region at intermediate inversion levels [26]. It should be kept in mind, however, that experimentally measured power laws for temperature dependence of heat capacity [1,4,9,13] and frequency dependence of ac susceptibility [26] have consistently shown that CoAl$_2$O$_4$ cannot be described as a canonical spin glass; it is not clear if and how conjectured “unconventional spin-glass” states with strong antiferromagnetic correlations might be distinct from reports of collinear antiferromagnetic order with broader than resolution-limited Bragg peaks [13], “unconventional” Néel order with significant “microstructural effects” [12], or “kinetically inhibited order” characterized by finite-size ordered domains [1].

In this paper, we seek to clarify the nature of magnetic correlations in CoAl$_2$O$_4$ and the greater aluminate family by presenting two complementary sets of experiments. In the first, we provide a comprehensive single-crystal neutron scattering study of the material MnAl$_2$O$_4$, which acts as an unfrustrated analog to CoAl$_2$O$_4$. The two materials have near identical structures, but the larger $S = \frac{3}{2}$ moments and weaker next-neighbor interactions in MnAl$_2$O$_4$ reduce frustration and result in a continuous ordering transition at $T_N \sim 40$ K to a collinear Néel ordered ground state [4,10,21]. Although recent reports of remnant paramagnetism [4] and short-range magnetic correlations [15] in the ordered state have led to speculations about competing states in this compound, our results seem to demonstrate that it acts as a model classical antiferromagnet with resolution-limited Bragg peaks and collective spin-wave excitations. Fits of measured dispersions imply $\frac{\delta}{T} = 0.069 \pm 0.006$, which is consistent with the expectations of Bergman et al. [16] for the known $T_N$. Our measurements were also able to distinguish the critical correlations in this material, which were seen to have a Lorentzian-type character and give rise to distinctive diffuse scattering to temperatures well above $T_N$, but still clearly associated with the Néel ordered state.

Our second set of experiments might be thought of as a confirmation and expansion of our original study on single-crystalline CoAl$_2$O$_4$ [1], with which we provide several new insights about this material. Whereas our previous study demonstrated Lorentzian-type Néel correlations in CoAl$_2$O$_4$ suddenly giving way to anisotropic Lorentzian-squared correlations at transition temperature $T^* = 6.5$ K, this paper shows that these experimental results depend on neither the exact sample measured nor on the instrument resolution, and further that neither scattering line shape nor correlation length changes with temperature below $T = 2$ K down to $T = 250$ mK. This lack of low-temperature evolution is particularly striking, as it seems to favor a frozen ground-state picture over one which invokes a role for low-lying thermal excitations. New inelastic measurements again confirm that the inelastic spectrum is dominated by collective spin-wave excitations consistent with Néel order, but improved energy resolution in our measurements allows us to extract a more precise value for $\frac{\delta}{T} = 0.110 \pm 0.003$, even closer to the first-order transition region predicted by Bergman et al. Finally, we present polarized neutron diffraction measurements of the significant magnetic diffuse scattering in this material, and show it to be isotropic with no measurable chirality. Simple simulations demonstrate that diffuse features are largely accounted for by the Lorentzian-type Néel correlations mentioned above.

Perhaps most crucial of all, direct comparison of results on CoAl$_2$O$_4$ and MnAl$_2$O$_4$ make clear the origin of the Lorentzian scattering in both compounds is simply critical correlations, and show that the cobalt material is unique, not in the nature of diffuse correlations at intermediate temperatures, but in the unusual character of the frozen state below $T^*$. As the
FIG. 1. Magnetization (closed symbols) of (a) CoAl₂O₄ and (b) MnAl₂O₄ single crystals, scaled by the applied fields of H = 10 and 2 kOe, respectively. Also shown is the inverse susceptibility (open symbols) of each, and the lines of best fit of high-temperature data to a linear dependence. Data for CoAl₂O₄ have been scaled by a factor of 2 to facilitate comparison with MnAl₂O₄ on the same scale. Effective moments and Weiss parameters listed were extracted from inverse fits.

MnAl₂O₄ has the greater level of cation inversion, our results further reinforce the primary role of $\frac{T_c}{2}$ and not disorder in determining the magnetic ground state in these materials.

I. CRYSTAL GROWTH AND CHARACTERIZATION

The single-crystal samples explored in this study were grown using 2-mirror NEC optical image furnaces, at the National High Magnetic Field Laboratory (NHMFL) in Tallahassee, FL, and at Oak Ridge National Laboratory (ORNL), in Oak Ridge, TN. X-ray powder diffraction (XPD) was performed on crushed portions of the crystals to ensure sample purity and to quantify the level of cation site inversion. Bulk magnetization was subsequently measured using Quantum Design MPMS SQUID magnetometers, with main results shown in Fig. 1.

The CoAl₂O₄ crystals were grown at ORNL, and representative characterization data can be found in the Supplementary Information for Ref. [1]. As reported previously, XRD refinements suggest a cation inversion $x = 0.02 \pm 0.04$, among the lowest in the literature. Our previous fits of magnetization to a Curie-Weiss temperature dependence also yielded an effective moment $\mu_{\text{eff}} = 4.89 \pm 0.03 \mu_B$ and Weiss constant $\Theta = -109 \pm 1$ K. The large effective moment for Co⁴⁺ in a tetrahedral crystal-field environment can be understood as an effect of spin-orbit coupling [27,28], but it has recently been pointed out that this value is also larger than many other reports in the literature [13]. On this last issue, we note that these other publications typically extract moments and Weiss constants from fits to inverse susceptibility, rather than magnetization itself with a background term and used a different temperature range. For more direct comparison to these studies, we reproduce the data from Ref. [1] in Fig. 1(a) and fit the inverse susceptibility over the range 100 K < $T$ < 300 K, neglecting the possible existence of temperature-independent background contributions. These fits yield the lower values $\mu_{\text{eff}} = 4.63 \pm 0.01 \mu_B$ and $\Theta = -98 \pm 1$ K. Although these results put our samples more in line with other reports in the literature [13], the strong dependence of fit parameters on details of fitting procedure should preclude one from drawing strong conclusions from such an analysis. A more reliable aspect of the data in Fig. 1(a) is the sharp cusp at $T^* = 6.5 \pm 1$ K, which is above the universal glass temperature reported by Hanashima for materials with larger $x$ [26], and which we have shown from neutron diffraction is consistent with a kinetically inhibited first-order phase transition [1].

The MnAl₂O₄ crystal was grown and characterized at the NHMFL, and the inversion parameter was determined from XRD to be $x = 0.05 \pm 0.02$. This value is equal or higher than in the cobalt sample. Magnetization measurements were performed using an applied field $H = 2$ kOe in a field-cooled (FC) configuration, and the resultant data are shown in Fig. 1(b). As with CoAl₂O₄, high-temperature data are well described by a Curie-Weiss temperature dependence, and were fit in an analogous way. The best fit yielded parameters $\mu_{\text{eff}} = 5.89 \pm 0.01 \mu_B$ and $\Theta = -139 \pm 1$ K. These values are comparable to the results of Tristan et al. [4]. A local maximum in susceptibility reveals an ordering temperature of $T_N \sim 40$ K, consistent with neutron results [5]. Below $T_N$, there is a significant level of remnant paramagnetism, and a similar fitting procedure yields $\mu_{\text{eff}} = 2.8 \pm 0.1 \mu_B$ and $\Theta' = -17 \pm 1$ K. These results are also in line with previous results [4].

II. NEUTRON SCATTERING

A. Experimental methods

Neutron scattering measurements presented in this work were performed using instruments at the High Flux Isotope Reactor (HFIR) at ORNL and the Heinz Maier-Leibnitz Zentrum (MLZ) at Garching, Germany. MnAl₂O₄ was explored using the HB1 spectrometer at HFIR, with a 3-g single crystal mounted in the (H H L) scattering plane, and collimation set to 48°-40°-40°-120°. Elastic and inelastic measurements were performed with fixed final energies of $E_f = 13.5$ and 14.7 meV, respectively.

New elastic measurements of CoAl₂O₄ were performed first using the HB1a triple-axis instrument with $E_i = 14.6$ meV neutrons and collimation 48°-48°-40°-68°, which are identical to conditions employed in Ref. [1]. One crystal was wired to a copper mounting plate in the (H H L) scattering plane, and mounted to the cold finger of a He3 cryostat insert to achieve lowest temperatures. Subsequent measurements used 48°-20°-20°-68° collimation, which reduced the resolution width by 25% in $Q$ and 11% in energy. Both HB1a and HB1 measurements employed pyrolytic graphite (PG) monochromators and analyzers, and further PG filters were used to remove higher-order contamination in the neutron beam. Inelastic measurements were performed using the PANDA [29] cold triple-axis spectrometer at MLZ, using a configuration...
with a double-focusing analyzer and monochromator and fixed $E_f = 5$ meV. Higher-order contamination was removed using a cooled beryllium filter. Also at MLZ, diffuse scattering measurements were carried out using the polarized neutron spectrometer DNS [30,31], with a neutron wavelength of 4.75 Å.

**B. MnAl₂O₄**

We begin by presenting the results of our neutron scattering study of a single-crystal of MnAl₂O₄, in which NPD measurements have long implied the existence of collinear Néel order below $T_N \sim 40$ K [6,21]. Our measurements confirm the same ordered state in crystals. Significant magnetic scattering intensity is seen at $T = 8$ K above measured intensity at $T = 50$ K at the positions of $(H K L) = (0 0 2), (1 1 1), (1 1 1), (2 2 0)$, and $(3 3 3)$ Bragg peaks, but not at $(0 0 4)$ or $(2 2 0)$, in line with expectations for the Néel state. Here, $(H K L)$ are the reciprocal lattice indices of the cubic unit cell. To track the evolution of magnetic correlations with temperature, we performed a series of radial and transverse scans across $(0 0 2)$ and $(1 1 1)$ magnetic Bragg positions, with the main results for the $(0 0 2)$ peak illustrated in Fig. 2.

Plots of representative radial [Figs. 2(a) and 2(b)] and transverse [Figs. 2(c) and 2(d)] scans across the $(0 0 2)$ position demonstrate that the Néel correlations in this compound are nearly isotropic at all temperatures, and consist of two distinct forms of scattering. Intense, resolution-limited Gaussian peaks dominate the scattering at temperatures below $T_N$ [Figs. 2(a) and 2(c)], and a two orders-of-magnitude weaker Lorentzian component is also present, which is clearest at temperatures directly above $T_N$ [Figs. 2(b) and 2(d)]. Radial and transverse scans across the $(0 0 2)$ peak were fit simultaneously to a sum of a Gaussian and a Lorentzian convolved with instrument resolution, and fit parameters are shown in Figs. 2(e) and 2(f). Although not presented here, inspection of scattering at the $(1 1 1)$ peak position leads to similar plots.

The temperature dependence of the Gaussian component clearly confirms that it acts as an order parameter for the collinear antiferromagnetic phase. Fits near the transition to a mean-field power law yield $T_N = 39.1 \pm 0.4$ K, in line with the value gleaned from magnetization measurements. The ordered moment size extracted from the integrated Bragg peak intensity at lowest temperature was $M_{\text{Mn}} = 5.2 \pm 0.2 \mu_B$, higher than originally reported by Roth [21] but within error equal to the full moment expected for $S = \frac{5}{2}$ spins. The weak Gaussian contribution to the scattering at highest temperatures is consistent with scattering from the $(0 0 4)$ nuclear Bragg peak by $\lambda/2$ neutrons, imperfectly filtered from the incident beam. The Lorentzian component is evident at all temperatures, but masked by the much stronger Gaussian component below $T_N$. At higher temperatures, it is the dominant contribution to the scattering, and the peak height and correlation length (inverse of width) diverge with power-law dependencies as the temperature approaches $T_N$ from above. This is the exact behavior expected for scattering above a second-order phase transition, and clearly associates the Lorentzian component with classical Ornstein-Zernicke critical correlations [32].

At low temperatures, inelastic neutron scattering measurements reveal the emergence of collective spin-wave excitations out of the Néel ordered state. Figure 3(a) shows a comparison of several energy scans at reciprocal lattice positions along the line $(0 0 L)$, and demonstrates a variation of the excitation energy from $E = 0$ to $6$ meV as reciprocal lattice vector $\mathbf{Q}$ is varied from the magnetic zone center $(0 0 2)$ to the zone boundary $(0 0 3)$. There was no indication of an excitation gap in MnAl₂O₄ within the sensitivity of our measurements. Using similar constant-$\mathbf{Q}$ scans, we tracked the spin-wave excitations along five different paths in reciprocal space, indicated by solid red lines in Fig. 3(b), and fit the results to predictions of classical spin-wave theory broadened to account for instrument resolution effects. Results are plotted in Figs. 3(c)–3(g).

Spin-wave calculations assumed the Hamiltonian

$$\mathcal{H} = J_1 \sum_{\langle i,j \rangle} \mathbf{S}_i \cdot \mathbf{S}_j + J_2 \sum_{\langle i,j \rangle} \mathbf{S}_i \cdot \mathbf{S}_j,$$

where the first (second) sum is over nearest (next-nearest) neighbors on the Mn²⁺ sublattice. Simultaneous fits of all five dispersion curves led to the determination that $J_1 = 0.87 \pm 0.02$ meV and $J_2 = 0.059 \pm 0.004$ meV. These give the ratio.
were made using only a single free and for MnAl.

represent a second set of measurements performed using and points along the line \([0 0 L]\) in reciprocal space, presented on a logarithmic scale. (b) Schematic of the \([H H L]\) scattering plane, where diamonds (circles) represent the positions of nuclear (magnetic) Bragg peaks for a material with the spinel structure and Néel antiferromagnetism. Solid red lines represent the loci of the first-order phase transition. Within this interpretation, the presence of intense Lorentzian scattering at lowest temperatures is a signature of remnant fluctuations below \(T^*\), due to the incomplete nature of the transition.

In Fig. 4, we show data from different experiments which reproduce our original experimental results in a single-crystal sample, and under more stringent experimental conditions. Using the same instrument and collimation choices as our previous work [1], we first measured elastic neutron scattering intensity in the vicinity of the magnetic \((0 0 2)\) Bragg reflection, while crossing the peak in \([0 0 L]\) and \([H H 0]\) directions in reciprocal space and while decreasing temperature to \(T = 0.25 K\). The resultant data are plotted in Figs. 4(a) and 4(b), revealing the same evolution of Lorentzian to Lorentzian + Lorentzian-squared line shape reported previously, and were fit the same way. Fit parameters are plotted in Figs. 4(c) and 4(d), alongside data from our original measurements [1] (dashed lines), and confirm the reproducibility of our results between different samples in the same temperature range. Figures 4(e)–4(h) represent a second set of measurements performed using tighter instrument collimation (25% reduction in momentum resolution), and demonstrate the independence of our main conclusions from exact instrument resolution. Specifically, we have directly confirmed that the isotropic Lorentzian plus anisotropic Lorentzian-squared line shape remains far superior to any single-component scattering function, regardless of the instrument configuration.

Significantly, the data in Fig. 4 also reveal that both scattering line shape and peak width remain unchanged in the temperature region \(T = 0.25–2 K\). This is a direct contradiction to expectations from Monte Carlo calculations, which predict resolution-limited (Gaussian) Bragg scattering at lowest temperatures and ascribe the finite scattering widths at \(T = 2 K\) to the presence of low-lying thermal excitations [12]. In passing, we note that our low-temperature results would also seem to rule out the existence of a second magnetic transition to a competing ordered state, as one might expect if the \(T^* = 6.5 K\) transition was driven by the order-by-disorder mechanism [16]. Temperature independence below 2 K is perfectly in line with expectations for a glassy or kinetically frozen state, both of which are inherently out of thermal equilibrium. By considering the integrated weight under the \((0 0 2)\) Bragg reflection, we estimate the frozen moment size to be \(m_{Co} = 1.09 \pm 0.08 \mu_B\).

\[
\frac{J_1}{J_2} = 0.069 \pm 0.006,
\]

which reproduce the measured ordering parameter within the predictions of Bergman et al. [16]. Intensities were not fit, and lines in the five plots on the right side of Figs. 3(c)–3(g) were made using only a single free scaling parameter, after assuming the above-determined values for \(J_1\) and \(J_2\).

\[
J_1 = 0.069 \pm 0.006,
\]

\[
J_2 = 0.098 \pm 0.008.
\]
FIG. 4. Thermal triple-axis elastic measurements of magnetic correlations in CoAl$_2$O$_4$. (a), (b) Representative plots of neutron scattering intensity as $Q$ is scanned across the magnetic (0 0 2) Bragg peak in the [0 0 L] (a) and [H H 0] (b) directions. Solid lines represent simultaneous fits to an isotropic Lorentzian plus anisotropic Lorentzian-squared fit function. (c), (d) Heights (c) and widths (d) of fitted Lorentzian and Lorentzian-squared components. For direct comparison, dashed lines represent data from Ref. 1, taken on a different crystal with identical instrument resolution conditions. (e)–(h) Equivalent data presented in (a)–(d), but taken with the instrument in a higher resolution configuration. Specifics are given in main text. Vertical arrows in these plots denote the position of $T^*$, as determined by magnetization measurements.

To search for mode splitting, novel excitations, or other signatures of a competing ground state, we accompanied our high-resolution elastic measurements with new inelastic scattering measurements using a cold neutron triple-axis spectrometer, with a significant improvement in energy resolution ($\Delta E \sim 0.1$ meV versus 0.6 meV in previous experiments). As with previous measurements, however, the resultant data, shown in Fig. 5, failed to reveal any overt signature of order beyond the long-range collective spin-wave excitations associated with the Néel ordered state. Typical inelastic scans are shown in Fig. 5(a), which demonstrates dispersion of the single gapped excitation along the line [0 0 L] in reciprocal space. Figure 5(b) shows the mode disappear as temperature is increased. Figures 5(b)–5(f) show the variation of excitation energy with momentum transfer along five different paths in reciprocal space. As with previously reported data 1,12, these dispersions are perfectly captured by classical spin-wave theory, using the Hamiltonian

$$
\mathcal{H} = J_1 \sum_{\langle i,j \rangle} S_i \cdot S_j + J_2 \sum_{\langle\langle i,j \rangle\rangle} S_i \cdot S_j - g \mu_B H_A \sum_i \| S_i \|, 
$$

where again the first (second) sum is over nearest (next-nearest) neighbors on the Co$^{2+}$ sublattice.

The best fit of the collective dispersions gives values $J_1 = 0.94 \pm 0.01$ meV, $J_2 = 0.103 \pm 0.002$ meV, and $g \mu_B H_A = 0.015 \pm 0.001$ meV for nearest-neighbor exchange, next-nearest-neighbor exchange, and anisotropy field, respectively. This gives a ratio of $J_2 / J_1 = 0.110 \pm 0.003$, more precise but equal within error to our previous results 33. The spin gap is observed to be $0.50 \pm 0.06$ meV, also consistent with our original work 1. We have previously argued that this gap is a signature of spin-orbit coupling on the cobalt site, but it is interesting to note that a gap on the order of 0.2 meV is predicted from finite-size effects if one considers the measured $\sim 150$ Å domain-wall separation in the cubic [1 1 0] direction. Thus, the observed gap may be another signature of a frozen domain structure. Notably, the width of the excitation at the...
magnetic zone center ($\Delta E = 0.43 \pm 0.08$ meV) also remains much broader than energy resolution; this indicates that the line broadening at the zone center is inherent, consistent with the failure of the material to achieve true long-range order.

Finally, to learn more about the nature of diffuse scattering in this material and search for signatures of SSL correlations, we performed a series of polarized neutron diffraction measurements using the DNS instrument at MLZ. This instrument uses the XYZ method of polarization analysis, which allows one to extract information about diffuse magnetic correlations over a wide range of reciprocal space, including the directionality of ordered spins and possible existence of spin chirality [34]. Diffuse scattering correlations were explored in the [H H L] scattering plane of CoAl$_2$O$_4$ with two sets of measurements, and main results are plotted in Figs. 6 and 7.

Correlations were first explored over a 180° range of scattering angles using $\lambda = 4.75$ Å neutrons and only investigating the polarization direction perpendicular to the scattering plane, which mixes magnetic and nonmagnetic contributions. The results, shown in Fig. 6 on a logarithmic scale, demonstrate that scattering in these materials is dominated by short-range antiferromagnetic correlations, in the form of Lorentzian-type peaks centered at Bragg positions associated with Néel order. Even at lowest temperatures, these peaks are far broader than resolution limits, resulting in significant diffuse scattering away from the Brillouin zone centers. As temperature is raised, the Lorentzian heights decrease and widths increase, until distinguishable features are lost by $T = 25$ K. These observations are consistent with previously published results by Zaharko et al. [12], and essentially as expected from the observation of Lorentzian scattering in our own triple-axis measurements [1]. In Fig. 6(d), we demonstrate this explicitly by simulating the expected diffuse scattering pattern from assuming isotropic Lorentzian scattering at Néel Bragg positions, with heights and widths extracted from Fig. 4. All major features of the diffuse scattering data are accounted for by this basic model, with no need to assume a second contribution to the scattering. Notably, among these reproducible features are the apparent “streaks” of scattering connecting peak positions [Figs. 6(e) and 6(f)] which arise from overlapping Lorentzian tails from different Brillouin zones.

Our second set of polarized measurements employed the full XYZ polarization analysis over a smaller region of reciprocal space that encompasses (002) and (111) Bragg positions. From the resultant data, we extracted correlations associated with spins within (i.e., the $y$ direction) and perpendicular to ($z$ direction) the [H H L] scattering plane at two temperatures,
and plot the results in Fig. 7. In addition to confirming the magnetic origin of diffuse correlations, our results show that spin directions are largely isotropic. Following the analysis of Schweika [34], we also compared spin-flip polarization in the $x$ direction to scattering taken with polarization reversed to search for signatures of chirality in this direction, but failed to see anything of note. Magnetic correlations are qualitatively similar above and below the temperature $T = T^\ast$, consistent with our claim that diffuse scattering is largely the result of Lorentzian-type correlations, which we have shown exist at all temperatures.

III. DISCUSSION

The data presented in this paper provide a clear picture of how magnetic correlations develop in the spinel aluminates. Lower than expected ordered moment notwithstanding, the observed correlations in MnAl$_2$O$_4$ adhere extremely closely to expectations for a classical antiferromagnet. Bragg peaks are resolution limited at low temperatures and have the symmetry of the predicted Néel state for this material. Both energies and intensities of collective excitations in the ordered state are well explained by classical spin-wave theory, and the $J_1$ and $J_2$ implied by fits reproduce the measured ordering temperature. At all temperatures, but especially near $T_N$, the system also exhibits significant short-range Lorentzian-type correlations about Bragg positions, which can be completely understood within the context of classical critical fluctuations associated with the second-order phase transition.

Given the strong similarities between the two systems, it is very difficult then to associate the Lorentzian-type correlations in CoAl$_2$O$_4$ as a signature of anything but critical correlations heading towards a similar ordered state. Indeed, as shown in Fig. 8, the variation of the correlation widths (inverse of correlation length) with temperature is identical between the two samples when well above $T^\ast$. The distinction comes at lower temperatures, approaching and below the putative ordering transitions. In MnAl$_2$O$_4$, the magnetic correlation length diverges as the Néel temperature is approached from above, as expected for a second-order transition; below this temperature, resolution-limited Gaussian Bragg peaks emerge. The antiferromagnetic correlation length in CoAl$_2$O$_4$ plateaus instead of diverging, indicative of a freezing transition; this is despite the lower density of defects in this compound when compared to MnAl$_2$O$_4$. At temperatures $T < T^\ast$, the magnetic scattering peaks remain broader than resolution and have an anisotropic Lorentzian-squared character. This empirical description is successful in describing the data, regardless of sample or instrument resolution, and remains unchanged to temperatures as low as $T = 0.25$ K. The inelastic spectrum is dominated by collective spin-wave excitations, indicative of an ordered state. As discussed thoroughly above, we believe the best explanation of these collective results is the freezing out of domain-wall motion below a first-order phase transition, whose thermodynamic signatures are presumably suppressed due to the close proximity to the known Lifshitz point. This is an effect of increased $\frac{\tau}{T}$ in CoAl$_2$O$_4$, however, the conditions which led to this unusual state were sufficiently general that we expect similar phenomenology might arise in any number of frustrated spin systems with first-order phase transitions or unconventional glass phases at low temperature.

The largest remaining question then is whether this system displays any definite signature of SSL correlations coexisting with the confirmed Néel ordered state. Insomuch as the predicted signature of SSL order is a buildup of incommensurate diffuse correlations tracing out a well-defined manifold in reciprocal space, the firm answer to this question is no: in neither this nor any previous study of CoAl$_2$O$_4$ has such a state been observed. One interesting feature in the diffuse scattering patterns of CoAl$_2$O$_4$, reported previously [12] and confirmed in Figs. 6 and 7, is the existence of apparent “streaks” of scattering along crystallographic (1 1 1) directions when connecting the antiferromagnetic Bragg positions (but not otherwise). It has previously been suggested that these streaks are a signature of coexisting SSL correlations [12], and Monte Carlo simulations argue that this scattering eventually evolves into the predicted spiral surface when $J_2$ is increased [14]. We caution against such an exotic interpretation, however. We have pointed out that the overlap of Lorentzian tails between neighboring Brillouin zones would also create apparent streaks of scattering, and explicitly demonstrate in Figs. 6(e) and 6(f) that both the qualitative shape and magnitude of these features along line scans similar to Ref. [12] can be reproduced within this simplest of pictures. We expect more careful modeling which includes slight anisotropic (Lorentzian-squared) spin correlations, nonspherical magnetic form factors, and finite instrument resolution width would only improve agreement with experiment. If simply the result of overlapping Lorentzian tails, this implies that the diffuse streaks are yet another signature of the known short-range antiferromagnetic correlations, and further explains why they evolve with the same temperature dependence, opposite the expected behavior for a competing state. In fact, similar diffuse streaks might be expected between Bragg centers due to any mechanism which destabilizes long-range order, regardless of the associated local picture, and would only become more distinct if a “line Lorentzian” or comparably sophisticated scattering model

![FIG. 8. Direct comparison of antiferromagnetic correlations in MnAl$_2$O$_4$ and CoAl$_2$O$_4$ single crystals. (a) Plots of scattering intensity across the (0 0 2) magnetic Bragg peaks at base temperature for the two materials, and (b) plots showing the temperature dependence of the antiferromagnetic correlation length, derived from the width of observed Lorentzian scattering peaks. In panel (a), data for CoAl$_2$O$_4$ have been scaled along the intensity axis to allow for a more direct comparison of the two materials. In panel (b), data for CoAl$_2$O$_4$ have been scaled along both width and temperature axes.](image-url)
was employed to properly account for microscopic defect structures [35].

IV. CONCLUSIONS

In conclusion, we have performed a series of neutron scattering measurements which shed light on the nature of magnetic correlations in two comparable aluminne spinel systems, MnAl$_2$O$_4$ and CoAl$_2$O$_4$. Results on MnAl$_2$O$_4$ are unequivocal, and paint this material as a classical antiferromagnet whose behavior is in line with expectations for a weakly frustrated diamond-lattice system. This includes observations of a second-order transition to a collinear Néel ground state with restricted diamond-lattice system. This includes observations of a second-order transition to a collinear Néel ground state with 2nd order. This is in direct contrast to measurements of CoAl$_2$O$_4$ which, despite the material having a lower level of disorder, reveal that long-range antiferromagnetic correlations are arrested at a freezing transition $T^* = 6.5$ K. Below this temperature, we show that the scattering function develops a second, anisotropic Lorentzian-squared contribution, an empirical analysis that we confirm is independent of sample, independent of instrument resolution, and persists to temperatures as low as $T = 0.25$ K. We argue that this is a signature of a frozen coarsening state, where the movement of domain walls is inhibited below a first-order phase transition, in turn preventing the formation of true long-range order. The stark contrast between CoAl$_2$O$_4$ and MnAl$_2$O$_4$ emphasizes that the novel physics in CoAl$_2$O$_4$ is driven primarily by frustration associated with an increased $\frac{J_1}{J_2}$ ratio.

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[33] The factor of 2 difference between the current values of $J_1$ and $J_2$ and those reported in Ref. [1] simply reflects the use a different convention for the summation in the Hamiltonian over spins rather than bonds.