Dynamics of a fractal set of first-order magnetic phase transitions in frustrated Lu$_2$CoMnO$_6$

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The axial next-nearest-neighbor Ising model predicts a fractal (infinite) set of phases with incommensurate wave vectors that are separated by first-order phase boundaries. This complexity results from a simple frustration condition between nearest- and next-nearest-neighbor interactions along a chain of Ising spins. Using x-ray photon correlation spectroscopy (XPCS), we investigate the surprising antiferromagnetic dynamics that emerge from such a complex phase diagram over a wide range of temperatures. We present XPCS measurements of the frustrated magnetic chain compound Lu$_2$CoMnO$_6$ and Monte Carlo simulations. Incommensurate magnetic Bragg peaks slide towards commensurate “up-up-down-down” spin order with decreasing temperature and increasing time. Both simulation and experiment support a counterintuitive “upside-down” temperature dependence of the magnetic dynamics: at higher temperatures in the region of first-order phase boundaries, slower dynamics are observed where the speckle maintains its coherence. At the lowest temperatures, where part of the sample adopts commensurate order, the dynamics speed up and result in fast decoherence.

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In frustrated magnets, seemingly simple competition between spin interactions can create profound complexity. The axial next-nearest-neighbor Ising (ANNNI) model is a classic model of frustration in which nearest-neighbor ferromagnetic (FM) interactions and next-nearest-neighbor antiferromagnetic (AFM) interactions compete with each other along chains of Ising spins. As an ANNNI system is cooled below $T_N$, it passes through a fractal set of first-order phase boundaries that separate AFM phases with different incommensurate (ICM) wave vectors, referred to as the “devil’s staircase” or “devil’s flower.” At a lower temperature, a commensurate (CM) wave vector emerges such as “up-up-down-down” spin ordering along the chains of Ising spins.

The existence of such a large number of first-order phase transitions should produce interesting dynamics of the magnetic system. However, historically, the dynamics of antiferromagnets, frustrated or otherwise, has been difficult to study due to their domains having no net magnetization. Thus, the development of x-ray-based techniques at light sources presents unique opportunities to probe AFM domain dynamics. In particular, x-ray photon correlation spectroscopy (XPCS) of Bragg scattering that is resonantly tuned to magnetic ions can detect AFM order and its inhomogeneities in time (seconds to hours) and space (nanometers to microns). This is important since frustrated systems evolve between different, nearly degenerate states, creating slow dynamics and inhomogeneities. XPCS has led to, e.g., observations of the dynamics of spin density waves in Cr [12] and of spin-helix phases in Dy [13,14]. Thus far, XPCS studies of antiferromagnets have found that when samples are cooled slightly below the Néel temperature $T < T_N$, the AFM dynamics become slow or freeze, as would be intuitively expected from thermal activation [12–14].

In this work, however, we use XPCS to observe very slow dynamics over a broad range of temperature down to a quarter of $T_N$ in highly frustrated Lu$_2$CoMnO$_6$ [16–19]. Moreover, we provide a theoretical framework to understand the dynamics using Monte Carlo simulations of the ANNNI model. This compound is known to be a likely ANNNI system based on previous measurements of thermodynamic properties, muon spin resonance ($\mu$sR), and neutron diffraction [20,21]. Co$^{2+}$ and Mn$^{4+}$ with $S = 3/2$ spins occupy oxygen cages, and the two magnetic ions alternate along the $a$, $b$, and $c$ axes [16] with lattice spacing of $a = 5.1638(1)$ Å, $b = 5.5467(1)$ Å, $c = 7.4153(1)$ Å. A powder neutron diffraction study found that the magnetic state at 4 K consists of Co↑→Mn↓→Co↓→Mn↑ with both the spins and wave vector along the $c$ axis and a slight incommensurability with $\vec{k} \approx [0.0223(8), 0.0098(7), 0.5]$ [see Fig. 1(a)] [16]. Since the compound is a type II multiferroic [16–19], previous studies used both the magnetization and electric polarization to determine that this system has slow dynamics, down to hour...
timescales, as well as frequency dependence of the above quantities. These dynamics were observed below $T_N = 48$ K and above $T_{\text{Hyst}} = 30–35$ K, where hysteresis emerges in the magnetization and electric polarization on hour timescales. Dynamics between picosecond and microsecond timescales were also uncovered by measuring $\mu$SR and neutron diffraction [21]. Below $T_{\text{Hyst}}$, hysteresis appears in the magnetization and electric polarization, suggesting that AFM and field-induced FM domains become pinned below this temperature by spin-lattice interactions [16,19].

XPCS data were collected on a millimeter-sized single crystal of Lu$_2$CoMnO$_6$ [18] at the Coherent Soft X-ray Scattering (CSX, 23-ID-1) beamline at the National Synchrotron Light Source-II (NSLS-II) [15] during three different beam times. This beamline has previously demonstrated sufficient stability for XPCS studies over multiple hours [15]. All data presented here are for one beam time and one sample, while data for two additional beam times and one additional sample are presented in the Supplemental Material [22] (see also Refs. [23–25] therein). The crystal was polished on the (001) face upward on a copper sample holder with silver paint. Coherent x rays passed through a 10-$\mu$m pinhole, then resonantly Bragg scattered off the Co or Mn ions in the geometry shown in Fig. 1. Speckle in the Bragg peak was detected using a two-dimensional (2D) detector and serves as a measure of AFM inhomogeneities. The autocorrelation function of this speckle can be analyzed to extract statistical information. Each speckle pattern was recorded at a fixed $T$ every 3.25 s for up to 3 h, after verifying thermalization (see the Supplemental Material (SM) [22]). The dynamics of the speckle pattern and thus the domain patterns which they encode are analyzed by computing the autocorrelation function $g^{2}(\vec{q}, \tau)$ of the speckle intensity $I(\vec{q}, t)$: $g^{2}(\vec{q}, \tau) = \langle I(\vec{q}, t)I(\vec{q}, t + \tau) \rangle / \langle I(\vec{q}, t) \rangle^2$. Here, the intensities $I(\vec{q}, t)$ and $I(\vec{q}, t + \tau)$ are extracted for a particular momentum vector $\vec{q}$ at times $t$ and $t + \tau$, with $\tau$ being a delay time and angle brackets denoting time averaging.

We investigate the two satellite ICM Bragg peaks $\vec{k} = \lbrack \pm \delta, \mp \delta, 1/2 \mp \epsilon \rbrack$ and a CM Bragg peak $\vec{k} = \lbrack 0, 0, 1/2 \rbrack$, where the CM peak corresponds to the up-up-down-down ordering. $\delta$ and $\epsilon$ are in the range of 0.01 or lower and decrease with $T$ [22]. Data were taken at Co and Mn edges for $\sigma$ and $\pi$ x-ray polarization, and a complete XPCS data set was taken at the Co edge with $\pi$ polarization since it had the largest magnitude.

We find that above $T_{\text{Hyst}}$ (the region where physical properties have no hysteresis in $T$ or magnetic field) the nominal CM $\lbrack 0, 0, 1/2 \rbrack$ Bragg peak has no resolvable energy dependence near the Co or Mn $L_3$ edges, showing that this peak is not at a magnetic resonance. We conclude that it is dominated by the second harmonic of the x-ray beam diffracting off the $\lbrack 0,0,1 \rbrack$ lattice peak. However, below $T_{\text{Hyst}}$ this Bragg peak acquires a strong resonance at the Co and Mn $L_3$ edges. Thus, this Bragg peak becomes dominated by the $\lbrack 0, 0, 1/2 \rbrack$ magnetic peak. The predominance of the spin rather than the charge scattering channel at the lowest temperature is also confirmed by comparing $\sigma$ and $\pi$ polarizations (see the SM [22]). Meanwhile, the ICM peak can be observed only at the Co and Mn $L_3$ edges at all $T < T_N$, both above and below $T_{\text{Hyst}}$, proving its magnetic character. The fact that the CM peak abruptly acquires a magnetic component below $T_{\text{Hyst}}$ may indicate that part of the sample evolves all the way to the CM order as $T$ is lowered, while another part of the sample remains trapped in a state described by an ICM wave vector. Evidence for this is also found in intermittent pinning of parts of the ICM peak as the temperature is lowered (see Fig. 1 and the movie in the SM). The wave vectors of the CM and ICM peaks were reproducible at different locations on the sample, although the ICM peaks were not always visible.

We find that for the ICM peak, there is a small $T$ dependence of $\delta$ and $\epsilon$ (see the SM [22]) such that the ICM peaks approaches the CM $\vec{k} = \lbrack 0, 0, 1/2 \rbrack$ position as $T$ is lowered from $T_N$ to $T_{\text{Hyst}}$, as predicted for the ANNNI model. We also noted a significant drift in the magnetic ICM Bragg peak position over time for $T > T_{\text{Hyst}}$. This drift is shown in Fig. 2 over a roughly 2-h period, with a lack of drift in CM peak shown for comparison. A similar drift of the ICM peak towards the CM peak was observed in the potential ANNNI spin chain compound Ca$_3$Co$_2$O$_6$ [20,26,27], where it was attributed to the inability of the system to reach its stable ICM wave vector after a decrease in $T$ due to very slow dynamics.

Figures 3(a) and 3(b) show the dynamics of speckle in the ICM peak at the Co edge at 778 eV at $T = 35$ K and 24 K, just above and below $T_{\text{Hyst}} = 30$ K. On the right are waterfall plots, showing an average over a vertical stripe through the center of the Bragg peak $1.4 \times 10^{-4}$ Å$^{-1}$ wide (2 pixels) vs time. The ICM speckle pattern is relatively unchanged at 35 K over the 3 h, whereas at 25 K the speckle shifts and decorrelates on this timescale.

In Figs. 3(c) and 3(d) the normalized intermediate scattering function $g^{2} - 1$ (the autocorrelation function between the signal at different times) is shown at $T = 25$, 35, and 55 K. The CM peak resonates at the Co and Mn edges for 25 K, while the ICM peak resonates at 25 and 35 K. The
temperature 55 K is above $T_N$, and therefore, no magnetic signal is present in the data, while the reported signal in the CM position at this $T$ is attributed to the lattice, as already discussed. The autocorrelation is normalized to the average of $g^{(2)} - 1$ within the first 30 s of integration, serving as a representative baseline. The non-normalized autocorrelation also showed a clear decrease in speckle contrast with decreasing $T$, consistent with the emergence of fast (microsecond) relaxation timescales observed in other work [21]. Non-normalized autocorrelations as well as the exact regions of interest (ROIs) used can be found in the SM [22]. Autocorrelation functions for other subregions of the CM Bragg peak were unable to discern notably separate dynamics between the central and outer portions of the Bragg peak (see the SM [22]).

Therefore, by means of XPCS we determine that the speckle from domains in the magnetic ICM and CM peaks at 25 K (below $T_{Hyst}$) decorrelate significantly more rapidly than at 35 K. This result is reproduced in an additional data set shown in the SM [22]. While this observation is counterintuitive since dynamics usually freeze at low $T$, it is, in fact, a prediction of the ANNNI model due to the presence of a devil’s staircase of first-order phase transitions at intermediate temperatures [1–3]. These dense first-order phase boundaries can lead to an effective pinning of ICM wave fluctuations within each domain.

In the following, we calculate the dynamics in an ANNNI Monte Carlo model. Monte Carlo simulations of the dynamic behavior of the ANNNI model were performed to compare with the experimental data. We note that in Lu$_2$CoMnO$_4$, there are two magnetic ions instead of one, which is a deviation from the classic single-ion ANNNI model. We perform simulations for the two-ion ANNNI model (here) and compare the results to the single-ion model (see the SM [22]) to confirm that the dynamics are similar. Moreover, we perform calculations for 2D and three-dimensional (3D) models (see the SM [22]) and find similar dynamics.

The in-plane ordering wave vector is small; thus, we assume a simple nearest-neighbor FM interaction in the $a$-$b$ plane. The spin Hamiltonian is expressed as

$$\mathcal{H} = -J_1 \sum_{NN} \sigma_i \sigma_j - J_2 \sum_{NNN} \sigma_i \sigma_j - J'_2 \sum_{NNN} \mathbf{S}_i \cdot \mathbf{S}_j - A \sum_{i} \langle S_i^z \rangle^2,$$

where $\sigma_j = \pm 1$ is the Co$^{2+}$ Ising spin and $|\mathbf{S}_j| = 1$ is the Mn$^{4+}$ Heisenberg spin with an easy-axis anisotropy, $A > 0$. $\mathbf{S}_i$ and $\sigma_j$ form two sublattices of the square lattice, as shown in Fig. 4(a). $J_1 > 0$ is the nearest-neighbor FM interaction, and $J_2 < 0$ and $J'_2 < 0$ are the next-nearest-neighbor AFM interaction along the $c$ axis. We choose $J_2 = J'_2 = -0.6J_1$ and $A = J_1$. We employ a 2D model corresponding to the $a$-$c$ plane of Lu$_2$CoMnO$_4$ and perform Monte Carlo simulations of $\mathcal{H}$ with the standard Metropolis algorithm.

The calculated ordering wave vector $Q$ vs $T$ is shown in Fig. 4(a). Because of the finite-size effect, $Q$ changes stepwise with $T$. There are peaks in the calculated specific heat when $Q$ changes which correspond to the first-order phase transition.
transition between different \( Q \) states. The first-order phase transition implies slow dynamics in the ICM phase. For increasing system size, \( Q \) changes quasicontinuously through many weak first-order transitions. To capture the dynamics, we compute the autocorrelation function \( A(t) \) at fixed \( Q = 0.25 \times 2\pi / c \) vs time for varying \( T \). Time \( t \) is shown in units of Monte Carlo sweep (MCS).

The simulations of the dynamics are qualitatively consistent with the XPCS results. The theory and experiment both show “inverted” dynamics, where the speckle decorrelates faster below \( T_{\text{Hyst}} \) than above it.

In conclusion, we observed dynamics of speckle in CM and ICM peaks over a very broad range of temperature down to a quarter of \( T_N \). Surprisingly, these dynamics are inverted in temperature from ordinary magnets, with fast decorrelation at low \( T \) and slow decorrelation at high \( T \). Monte Carlo simulations showed that these unusual dynamics are predicted by the ANNNI model for both one and two types of magnetic ions. Above \( T_{\text{Hyst}} \), the ANNNI model predicts many (theoretically infinite) first-order phase transitions occurring at closely spaced temperatures whose domain boundaries pin the ICM wave vectors, creating slow dynamics. This manifests as a lack of decorrelation in the speckle measured. Though the ICM wave vectors do not decorrelate, they drift in the direction of the CM wave vector for at least 3 h after a change in \( T \), as has been seen in other similar ANNNI systems [27]. Below \( T_{\text{Hyst}} \), the system has stable pinned domains, and so the dynamics are dominated by fast fluctuations within each domain and rapid decorrelation of the speckle. Previous XPCS investigations of Dy and Cr also showed ICM order due to frustration between nearest and next-nearest neighbors [12,14]. However, these systems do not have Ising spins and are thus not examples of the ANNNI model. In these compounds, dynamics were observed only in the immediate vicinity of \( T_N \).

Our work demonstrates that magnetic frustration can produce unexpected dynamics over a wide range of temperatures detectable by XPCS. Though the ANNNI model of frustration was first developed in the 1980s, we can now investigate its ramifications for the dynamics of antiferromagnetic inhomogeneities using both simulation and experiments.

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FIG. 4. (a) Monte Carlo simulations of the ICM AFM wave vector \( Q \) vs \( T \), obtained by slowly cooling to \( T = 0 \) and then heating. The inset shows the magnetic model with nearest- and next-nearest-neighbor magnetic interactions. (b) Calculated spin autocorrelation function \( A(t) \) at fixed \( Q = 0.25 \times 2\pi / c \) vs time for varying \( T \). Time \( t \) is shown in units of Monte Carlo sweep (MCS).

