

Noncollinear ferrimagnetic structures and spin dynamics in Al-doped lithium ferrites

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The new non-collinear magnetic order, in an Al-doped lithium ferrite (Al-LFO), ($\text{Li}_{0.5}\text{Al}_{0.5}$)($\text{Fe}_{0.75}\text{Li}_{0.25}$) $_2\text{Fe}_3\text{O}_8$ (denoted as Li50Al50), could be determined in the magnetic space group $P4_32'_12'$ using high-resolution neutron powder diffraction (HRNPD) at 3 and 50 K. The largest spin-canting angle of the non-collinear octahedral B-sublattice determined from the structural analysis using 3K-HRNP approaches the Yafet-Kittel angle 21° at 0 K, extrapolated from saturation magnetization. The spin-canting textures shown at 3 and 50 K are thermally averaged at elevated temperatures to reveal collinear spin alignments along [001] at 300 K under zero external fields. The non-collinearity of magnetic spins in Al-LFOs arises from multiple spin-reorientation (SR) processes without magnetic phase transitions below T_c (e.g., 788 K in Li50Al50). The SRs are activated above 100 K, showing Arrhenius behavior, but blocked at 5 K without altering the spontaneous magnetic polarization, as indicated by ac magnetic susceptibility data. The dilute effect of Li^+ replacing Fe^{3+} (20% in Li60Al40 or 25% in Li50Al50) because of the respective Al^{3+} -substitution for 40% and 50% Li^+ in the geometrically frustrated B-sublattice (the hyperkagome lattice) enhances not only the lattice-distortion-induced electric polarization, but also the intrinsic spin dynamics. All SR-related features in both Al-LFOs are effectively quenched above 0.5 kOe, where all magnetic spins of Fe^{3+} are collinearly aligned parallel to the external magnetic fields, independent of frequency and temperature. These findings could be applied to further develop LFO-type multiferroics, e.g., for photovoltaic applications.

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I. INTRODUCTION

Spinel-type compounds encompass a wide class of materials exhibiting diverse and strongly correlated physical phenomena [1–3]. The spinel structure with the general formula AB_2O_4 accommodates a broad range of magnetic and nonmagnetic cations at both A and B sites, offering significant flexibility in tuning the physical properties through compositional modifications [1]. Spinel feature a diamond-like lattice of AO_4 tetrahedra (A-sublattice) coexisting with a pyrochlore-type lattice composed of corner-sharing BO_6 octahedra (B-sublattice). The geometric frustration intrinsic to the B-sublattice is a key driver of complex magnetic ground states in these systems [2]. Variations in the degree of polyhedral distortion and the ordering of A and B cations are critical in lowering the symmetry from the ideal space group

(SG) $Fd\bar{3}m$. These distortions and symmetry breakings at specific atomic sites—whether magnetic or nonmagnetic—are intimately linked to the emergence of magnetoelectric (ME) effects in spinel-type multiferroics (MFs) [1–3]. These structural considerations are especially pertinent in the case of α - LiFe_5O_8 (referred to hereafter as LFO), an inverse spinel that provides a model system for investigating ME coupling and related phenomena. LFO accommodates two Fe^{3+} ions at the tetrahedral A sites and a mixed occupancy of [$\text{Li}^+ + \text{Fe}^{3+}$] at the octahedral B sites, undergoing a symmetry lowering to $P4_332$. The observed collinear ferrimagnetic spin order along the c axis was reported based on *ab initio* calculations restricted in the cubic SG $P4_332$ [4]. Nevertheless, this analysis seems inconsistent with group-theoretical expectations for the LFO-type topology. This suggests that the group-subgroup relationship between the space group and the magnetic space group supports a collinear ferrimagnetic spin arrangement only in $P4_32'_12'$, which is one of the tetragonal magnetic subgroups of $P4_332$. Indeed, the tetragonality of Al-doped LFO-type compounds (Al-LFOs) was experimentally confirmed in our previous work, where results from the group-theoretical classification were graphically presented with all possible cubic and tetragonal magnetic subgroups of $P4_332$ (Fig. A.14 in Supplemental Material in Ref. [5]). In particular, the calculated spin orders in both cubic magnetic space groups (MSG) $P4_332$ and $P4'_332'$ (Fig. A.15 in Ref. [5])

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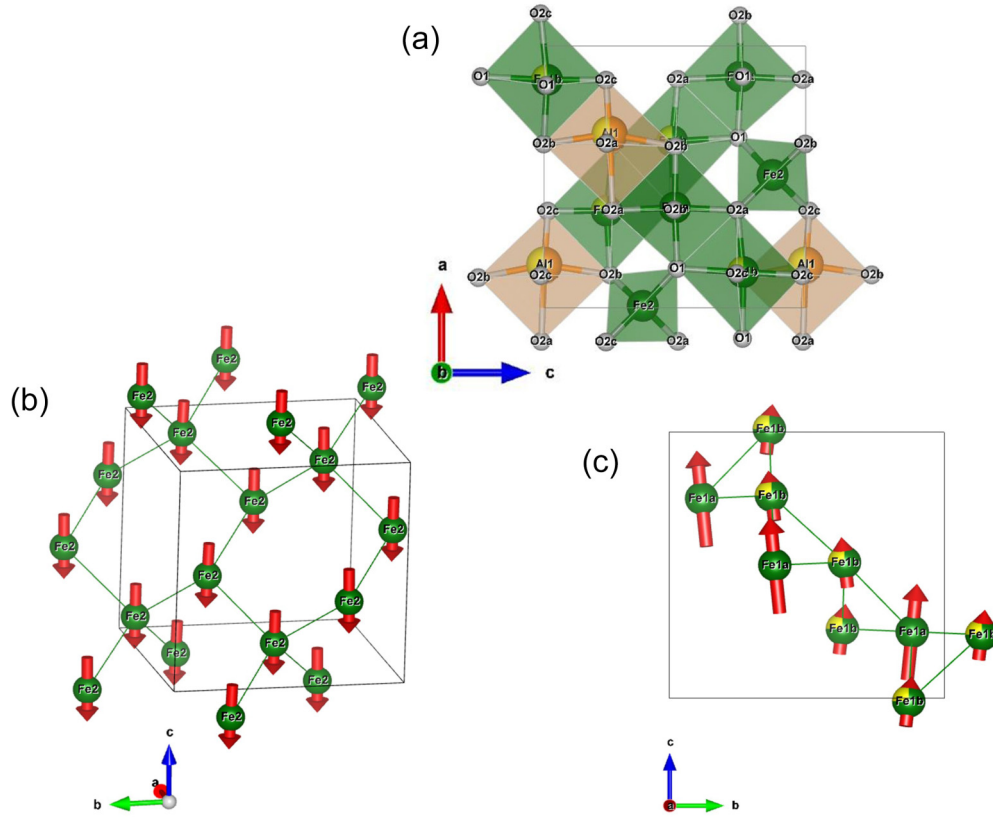


FIG. 1. (a) A polyhedral structure model of $(\text{Li}_{0.5}\text{Al}_{0.5})(\text{Fe}_{0.75}\text{Li}_{0.25})_2\text{Fe}_3\text{O}_8$ (Li50Al50) at 300 K; (b) The A-sublattice in Li50Al50 with Fe^{3+} at a tetrahedral site, Fe2, where magnetic spins are arranged in $[00-1]$; (c) A ferrimagnetic spin order in the B-sublattice of Fe^{3+} at both octahedral sites Fe1a and Fe1b oriented almost in $[001]$ when refining without the constraints $M_x = M_y = 0$ [5].

were unable to match neutron powder diffraction data. The tetragonal MSG $P4_32_12'$ could be unambiguously determined as the true MSG for Al-LFOs at room temperature (RT) [5]. Based on this fact, the present study extends to the discovery of non-collinear order in Al-LFOs below RT.

In Al-LFOs, the partial ordering of cations in the B-sublattice makes the tetragonality decisive in the LFO topology with Al^{3+} (Fig. 1). In particular, both solid-solution compounds $(\text{Li}_{0.5}\text{Al}_{0.5})(\text{Fe}_{0.75}\text{Li}_{0.25})_2\text{Fe}_3\text{O}_8$ (denoted as Li50Al50) and $(\text{Li}_{0.6}\text{Al}_{0.4})(\text{Fe}_{0.8}\text{Li}_{0.2})_2\text{Fe}_3\text{O}_8$ (denoted as Li60Al40) crystallize in the tetragonal space group $P4_32_12$, as confirmed in our recent study using high-resolution powder diffraction (HRNPD) at 300 K [5]. This previous study demonstrated that partial substitution of Al^{3+} exclusively at the Li^+ site and Li^+ replacing Fe^{3+} only at one of the two octahedral Fe sites significantly enhances polyhedral distortion within the B-sublattice. This geometrical distortion acts as a driving force for magnetoelastically induced electric polarization. Its nonpolar point group 422 and its direct cubic supergroup 432 do not support spontaneous electric polarization but allow second-order ME effects. Indeed, the ME coupling coefficient, $\alpha_{\text{ME}} \approx 2$ mV/Oe-cm, has been measured with LFO at 120 K [6]. This effect persists up to 250 K with α_{ME} of 0.2 mV/Oe-cm [6,7]. Thus, the LFO-type compounds have been investigated for integration into RT-operable composite MFs [7–9]. The ME response in LFO arises from the magnetic-field-induced dipole moments of high-spin Fe^{3+} ($3d^5$, $S = 5/2$) ions situated in distorted BO_6

octahedra, within a ferrimagnetically ordered background below the Curie temperature, $T_C \approx 900$ K [10]. The magnetic modulation of the resulting polarization is enabled through spin ordering of Fe^{3+} at polar atomic sites (C2), facilitating a field-responsive spin-orbital interaction [11]. For studying MFs, a subtle elucidation of magnetic spin order-disorder features is essential. Regarding this relevant aspect, HRNPD data of Li50Al50 and Li60Al40 were pivotal in accurately resolving the ferrimagnetic structures of these materials in a tetragonal magnetic SG, $P4_32_12'$, conclusively establishing the true atomic SG as $P4_32_12$ [5].

The aim of our prior investigation on Al-LFOs was to enhance electric polarization by inducing chemical stress via Al^{3+} for Li^+ substitution within the LFO topology and consequently promoting polyhedral distortion. This approach was intended to realize second- and higher-order ME coupling coefficients near RT. However, a key trade-off observed was the reduction in net magnetization compared to LFO as the enhanced electric polarization via distortion was accompanied by magnetic dilution due to Li^+ partially replacing Fe^{3+} at one of the octahedral sites. Further investigation is needed to increase geometric distortion-induced electric polarization without reducing magnetization saturation in LFO-type compounds. On the other hand, their structural and physical behaviors at low temperatures (LT) are rarely known. Particularly, it is interesting to observe how static and dynamic disorders of magnetic spins interact with fundamental physical properties. In contrast to the geometric frustration often

observed in spinel-type compounds, where spin alignments within magnetic cation triangles in the B-sublattice are imperfectly antiparallel, LFO-type compounds exhibit parallel spin alignment along [001] in the B-sublattice, suppressing such frustration. Nevertheless, geometric frustration can still emerge in Al-LFOs, particularly under external perturbations that promote competing ferromagnetic and antiferromagnetic interactions in the resulting hyperkagome lattice. In fact, the apparent collinear ferrimagnetic spin alignments along the crystallographic c axis of Al-LFOs at RT seemed due to thermally averaged spin reorientations. As given in Supplemental Material in [5], our preliminary ac magnetic susceptibility acquired with Li60Al40 at 1 Hz clearly resolved the nonzero third harmonic term. This indicated spin reorientations (SRs) which are not associated with a change in spontaneous magnetization. Within the experimental resolution in our HPNPD data at RT [5], standard deviations of both magnetic moment components, M_x and M_y , of all Fe^{3+} are too large to claim a non-collinear spin order. Accordingly, the constraints $M_x = M_y = 0$ were imposed, leading to the conclusion that, at room temperature, this ferrimagnetic spin configuration is thermally averaged into a collinear ferrimagnetic order aligned along the c axis. However, the LT-HRNPd data sets of Li50Al50 (3 and 50 K) unambiguously confirm the non-collinear nature of the ferrimagnetic order, which is the primary focus of the current study. Another compelling avenue for investigation lies in the spin dynamics within and between magnetic domains in these Al-doped LFO-type solid solutions. Their relatively small tetragonality suggests a propensity to form ferrodistorive and ferromagnetic domains, accompanied possibly by stressed domain boundaries. Motivated by these considerations, the second part of the present study involves magnetic field-dependent heat capacity measurements on Li50Al50, acquired from 0.35 to 300 K. A detailed investigation of the magnetic spin dynamics of Li50Al50 and Li60Al40 was carried out by means of ac magnetic susceptibility measurements across a wide temperature range from 5 to 300 K.

Overall, the motivation for this study is to provide a fundamental basis for atomic and magnetic spin order, enabling the design of multiferroic materials for photovoltaic (PV) applications. In particular, the magnetic noncollinearity arises from competing magnetic interactions induced by the significant geometric distortion in Al-LFOs. This magnetostriction effect is relevant for enhancing the magnetoelectric effect in MF-PVs. Our recent theoretical studies show that the band gap of pure LFO (2.05 eV) decreases to 1.70 eV upon substituting Al for 50% Li in the B-sublattice of Li50Al50 (Results from these theoretical studies will be reported elsewhere). We believe the findings from the current experimental study are indispensable fundamentals for the design of alternative materials for photovoltaic applications based on LFO-type MFs.

II. MATERIALS AND METHODS

A. High-resolution neutron powder diffraction (HRNPD)

The identical powder samples of both Li50Al50 and Li60Al40 described in [5] were used for HRNPD on the neutron powder diffractometer *ECHIDNA* [12] at the Australian Neutron Source OPAL at ANSTO, Sydney. For LT-HRNPd

TABLE I. Experimental parameters in neutron powder diffraction data analysis of an Al-doped lithium ferrite, $(\text{Li}_{0.5}\text{Al}_{0.5})(\text{Fe}_{0.75}\text{Li}_{0.25})_2\text{Fe}_3\text{O}_8$ (Li50Al50) in the magnetic space group $P4_32'_12'$ at 3 and 50 K (wavelength: 1.6215 Å).

Temperature		3 K	50 K
Lattice metric	a [Å]	8.2584(5)	8.2598(3)
	c [Å]	8.2453(9)	8.2415(6)
	V [Å ³]	562.34(4)	562.27(3)
R_p [%]		5.80	5.28
R_{wp} [%]		7.57	6.92
GOF		1.95	1.80
$R_p = \frac{\sum_i y_i(\text{obs}) - y_i(\text{calc}) }{\sum_i y_i(\text{obs})} \cdot 100$; $R_{wp} = \sqrt{\frac{\sum_i [w_i(y_i(\text{obs}) - y_i(\text{calc}))^2]}{\sum_i w_i y_i(\text{obs})^2}} \cdot 100$; $w_i = \frac{1}{\sigma^2(y_i(\text{obs}))}$; $R_{\text{exp}} = \sqrt{\frac{\sum_i w_i y_i(\text{obs})^2}{n-p}} \cdot 100$; $GOF = \frac{R_{wp}}{R_{\text{exp}}}$; $y_i(\text{obs})$, $y_i(\text{calc})$ = observed and calculated intensity at i^{th} measuring point, respectively; n = number of observations; p = number of profile points			

data collection, 0.9 g of Li50Al50 was packed within a vanadium sample can and located in a closed-cycle helium cryostat. HRNPd data sets were acquired at 50 and 3 K at cooling from 300 K using a constant wavelength of 1.6215 Å with a Ge(335) monochromator with a step size of 0.05° in a range of 4°–164°(2 θ).

B. Rietveld analysis with HRNPD of Li50Al50

Atomic and magnetic structures of Li50Al50 at 3 and 50 K were determined by Rietveld analysis with HRNPd data using the software package *Jana2020* [13], starting with the refined model for Li50Al50 at 300 K in the tetragonal SG $P4_32'_12$, as reported in [5]. Rietveld refinements were carried out, excluding two data regions in each LT-HRNPd data set: below 10°(2 θ) due to extremely high background, where there were no Bragg reflections from atomic and magnetic spin arrangements; and above 145°(2 θ) due to intense reflections from the Al cryostat. There are no extra magnetic Bragg reflections over the entire HRNPd patterns of Li50Al50. This implies no structural phase transition down to 3 K while retaining the ferrimagnetic order in the magnetic space group (MSG) $P4_32'_12'$. After refining atomic parameters, this tetragonal MSG was applied to calculate intensities from magnetic contributions with the propagation vector $k = (0, 0, 0)$ to each LT-HRNPd pattern. The refined atomic and magnetic structures were visualized using the program, *VESTA* [14]. Details of experimental parameters are given in Table I.

C. Polyhedral distortion and electric moments in Li50Al50

Using interatomic distances and angles in Li50Al50 at 3 and 50 K (Supplemental Material Table I [15]), polyhedral distortions and electric dipole moments were calculated according to Song *et al.* [16,17]. More details on polyhedral distortion calculations were reported, along with results from the analysis of 300K-HRNPd data [5]. The electric dipole moment induced in a distorted polyhedron can be expressed by $p(r_{cm}) = q_i(r_i - r_{cm})$, where p is the electric dipole moment of a distorted polyhedron; r_{cm} is its center position; r_i

and q_i are the ligand positions and their charge, respectively. The electric dipole moments of polyhedra in the refined structure models were calculated using the software *Atomsk* [18].

D. Heat capacity (C_p) data acquisition

To gain deeper insight into the spin degrees of freedom in these materials, heat capacity (C_p) measurements were performed on Li50Al50. Heat capacity data can reveal structural and magnetic phase transitions and provide information on the spin contribution to thermodynamic properties and thus complementing the structural and magnetic characterization of these complex ferrite systems.

The heat capacity as a function of temperature, ranging from 300 down to 0.3 K, was measured at zero applied field and 10 kOe on a pressed powder pellet fixed with Apiezon N grease, using a Quantum Design PPMS equipped with a ^3He refrigerator.

E. Alternating current magnetic susceptibility measurements

Alternating current susceptibility (χ_{AC}) measurements were performed to study spin dynamics phenomena in Li50Al50 at varying frequencies (f) as a function of temperature and magnetic field. To see the dilute effect, χ_{AC} of Li60Al40 was probed for comparison. The χ_{AC} data acquisitions of powdered samples of both Al-LFOs were conducted within a frequency window of $10\text{ Hz} < f < 10\text{ kHz}$, under an excitation field of $H_{AC} = 1\text{ Oe}$, at temperatures ranging from 5 to 350 K using a Quantum Design PPMS susceptometer. Additionally, ac measurements were carried out using a Superconducting Quantum Interference Device (SQUID) magnetometer in the frequency range $1\text{ Hz} < f < 1\text{ kHz}$. Second and third harmonics were obtained in the experiments. To gain deeper physical insight into the nature of the observed spin-relaxation processes, we investigated the influence of an applied polarizing magnetic field (H) between 0 and 1 kOe on the spin dynamics.

III. RESULTS AND DISCUSSION

A. Results from Rietveld analysis

Rietveld refinements with HRNPD data of the Al-rich compound Li50Al50 at 3 and 50 K were conducted after refining all profile parameters, including the lattice metrics. As given in Table I, the lattice metrics conserve tetragonality with $c < a$ from 3 up to 300 K. However, there is an anomalous lattice volume contraction owing to the reduction of the lattice parameter c from 3 to 50 K. This unusual discontinuity in the thermal expansion of Li50Al50 will be further considered in terms of magnetic response to temperature.

All atomic positions at 3 K were refined while calculating all atomic displacement parameters (ADPs) site-independently over all cationic sites due to their extremely small magnitudes, i.e., the site-averaged ADP value is $0.0028(4)\text{ \AA}^2$. All occupation parameters (OCCs) at four independent sites for oxygen were fixed to full occupation while refining their group-specific isotropic ADPs (U_{iso}), $0.0023(4)\text{ \AA}^2$. These constraints were reasonable to determine the OCCs at cationic sites to prevent high correlation with their ADPs.

The refined OCC ratio of Li: Al was 0.24(2): 0.26(2) at a special atomic site ($4a$), Li1(Al1). The refined OCCs of Fe at an octahedral site, Fe1a ($4a$), and at a tetrahedral site, Fe2 ($8b$), indicated exclusively full occupation by Fe. Hence, their OCCs are fixed to 1 in the subsequent refinement cycles to reduce the number of parameters. In contrast, the refined OCC of Fe at another octahedral site, Fe1b ($8a$), was far from full occupation when refining OCC with Fe as the only scatterer type. For compensating the excess positive charge at Li1(Al1) with Al^{3+} replacing 50% Li^+ , the only possible co-occupant at Fe1b might be Li for its negative coherent neutron scattering length, where an atomic ratio of Li: Fe = 0.25: 0.75 was readily estimated. Indeed, the respective OCC values of 0.25(1) and 0.75(1) for Li and Fe at Fe1b matched the estimate exactly. The refined OCCs at all cationic sites exhibit a selective partial ordering in the B-sublattice only, resulting in $(\text{Li}_{0.25}\text{Al}_{0.25})(\text{Fe}_{0.75}\text{Li}_{0.25})_2\text{Fe}_3\text{O}_8$.

All atomic positions at 50 K were refined simultaneously, where their ADPs were refined with constraint: $U_{iso}[\text{Li1(Al1)}] = U_{iso}(\text{Fe1a}) = U_{iso}(\text{Fe1b}) = U_{iso}(\text{Fe2})$ while fixing their OCCs to the values refined at 3 K. U_{iso} for all four oxygen sites at 50 K were group-specific refined in the same way as those at 3 K. The respective refined ADPs, $0.0042(3)\text{ \AA}^2$ and $0.0056(4)\text{ \AA}^2$, for all cationic sites and O sites at 50 K are approximately twice those at 3 K (Table II).

Finally, all magnetic moments M were refined in the tetragonal $\text{MSG } P4_32'_12'$ simultaneously without any constraints on magnetic moments (Table III). Like 300 K, the magnetic moment component M_z in $[001]$ is significantly larger than the other components M_x and M_y in $[100]$ and $[010]$, respectively, at all Fe sites in Li50Al50. However, at Fe1a occupied by Fe only, M_x and M_y are sizeable, with M_y (with a symmetrical restriction $-M_x = M_y$) equals to $1.0(2)\mu_B$ and $0.9(1)\mu_B$ with the spin-canting angle 16° and 14° with respect to $[001]$ at 3 and 50 K, respectively. Such spin canting is less distinctive at Fe1b (8° at 3 K), possibly due to the site-averaged magnetic moment of Fe^{3+} statically disordered with Li^+ . The magnetic spin alignment at Fe2 in the A-sublattice is considered collinear, given the negligible values for M_x and M_y within the limit of experimental resolution. The qualities of the atomistic and magnetic models of Li50Al50 at 3 and 50 K (Table II) are graphically demonstrated in Fig. 2.

B. Polyhedral distortion and electric moments in Li50Al50

Individual interatomic distances and angles in Li50Al50 between 3 and 50 K showed no systematic variations (Supplemental Material Table I [15]). However, we can identify certain trends in polyhedral distortions and electric dipole moments, which were calculated using interatomic distances in the refined models of Li50Al50. The calculated polyhedral distortion degrees and dipole moments at 3 and 50 K were compared with those at 300 K in Supplemental Material Table II [15].

In Figs. 3 and 4, polyhedral distortion degrees from the respective ideal polyhedron and the resulting modulus of electric dipole moments at each polyhedron are graphically demonstrated for easy comparison. At 3 K, $(\text{Al}, \text{Li})\text{O}_6$ is the most distorted among all polyhedra in Li50Al50, but becomes relaxed around 50 K and then again increasingly distorted

TABLE II. Atomic parameters refined using HRNPD data at 3 and 50 K. ADPs (U_{iso}) at 3 K were site-independently refined over all cationic sites to determine their occupancy parameters (OCCs) without significant correlation with their ADPs. ADPs at 50 K were refined with the constraints $U_{\text{iso}}[\text{Li1(Al1)}] = U_{\text{iso}}(\text{Fe1a}) = U_{\text{iso}}(\text{Fe1b}) = U_{\text{iso}}(\text{Fe2})$ while fixing their OCCs to the values refined at 3 K. U_{iso} at all four oxygen sites at 3 K as well as 50 K were group-specific refined.

T	Site	Type	Coordinates			Occupancy	U_{iso} [$\text{\AA}^2$]	Wyckoff site
			x	y	z			
3 K	Li1(Al1)	Li	0.174(7)	0.174(7)	0	0.24(2)	0.0028(4)	4a
		Al				0.26(2)	0.0028(4)	
	Fe1a	Fe	0.611(1)	0.611(1)	0	0.5	0.0028(4)	4a
	Fe1b	Fe	0.878(2)	0.369(2)	0.006(2)	0.75(1)	0.0028(4)	8b
		Li				0.25(1)	0.0028(4)	
	Fe2	Fe	0.751(1)	0.995(1)	0.119(1)	1	0.0028(4)	8b
	O1	O	0.146(2)	0.388(2)	0.508(1)	1	0.0023(4)	8b
	O2a	O	0.878(1)	0.129(2)	0.512(1)	1	0.0023(4)	8b
	O2b	O	0.122(1)	0.109(1)	0.251(1)	1	0.0023(4)	8b
	O2c	O	0.874(2)	0.381(2)	0.235(1)	1	0.0023(4)	8b
50 K	Li1(Al1)	Li	0.153(8)	0.153(8)	0	0.24(2)	0.0042(3)	4a
		Al				0.26(2)	0.0042(3)	
	Fe1a	Fe	0.617(1)	0.617(1)	0	0.5	0.0042(3)	4a
	Fe1b	Fe	0.873(2)	0.362(2)	0.009(1)	0.75(1)	0.0042(3)	8b
		Li				0.25(1)	0.0042(3)	
	Fe2	Fe	0.752(1)	0.994(1)	0.123(1)	1	0.0042(3)	8b
	O1	O	0.146(2)	0.384(2)	0.509(2)	1	0.0056(4)	8b
	O2a	O	0.870(2)	0.131(2)	0.510(1)	1	0.0056(4)	8b
	O2b	O	0.129(2)	0.117(2)	0.254(1)	1	0.0056(4)	8b
	O2c	O	0.871(2)	0.378(3)	0.238(2)	1	0.0056(4)	8b

at 300 K. Its electric dipole moment modulus nonlinearly increases from 3 up to 300 K. The polyhedral distortion of (Fe, Li) O_6 slightly increases along with dipole moments at elevated temperatures. At 3 K, FeO_6 shows the highest polyhedral distortion among all Fe-containing polyhedra and the highest electric dipole moments in $\text{Li}_5\text{OAl}_5\text{O}_{15}$. However, the distortion degree of FeO_6 and its electric dipole drops faster from 3 up to 50 K and then decreases more slowly up to 300 K. FeO_4 tetrahedron is rigid, as shown by a quasi-temperature-independent distortion degree of about 3% in a wide temperature range of 3–300 K.

TABLE III. The magnetic moment components (M_x , M_y , M_z), the modulus M [μ_B] at three independent Fe sites in $\text{Li}_5\text{OAl}_5\text{O}_{15}$, and the spin-canting angles [$^\circ$] about the c axis, resulting from Rietveld analysis with LT-HRNPD data sets in the tetragonal MSG $P4_32_12'$. The spin canting of Fe^{3+} at the octahedral site Fe1a in the B-sublattice is noticeable below RT. In the analysis of 300K-HRNPD data, all M_x and M_y were constrained to zero as their refined magnitudes were negligibly small within the experimental resolution [5].

T	Site	M_x	M_y	M_z	M	Canting angle
3 K	Fe1a	-1.0(2)	1.0(2)	4.9(2)	5.1(2)	16(2)
	Fe1b	0.1(3)	-0.5(3)	3.5(2)	3.5(2)	8(5)
	Fe2	0.1(2)	0.1(3)	-4.2(1)	4.2(1)	2(4)
50 K	Fe1a	-0.9(1)	0.9(1)	5.1(1)	5.3(1)	14(1)
	Fe1b	-0.4(2)	-0.2(2)	3.2(2)	3.2(2)	3(4)
	Fe2	0.0(2)	0.2(2)	-4.0(1)	4.0(1)	3(3)
300 K [5]	Fe1a	0	0	4.7(1)	4.7(1)	
	Fe1b	0	0	2.4(2)	2.4(2)	
	Fe2	0	0	-3.8(1)	3.8(1)	

A high polyhedral distortion of (Al, Li) O_6 at 300 K can be understood with a high flexible geometry around Li^+ as the central cation [19], i.e., LiO_6 octahedra are geometrically flexible with longer interatomic distances to oxygens and narrow bonding angles (Supplemental Material Table I [15]) when comparing to Al^{3+} and Fe^{3+} . Similarly, the presence of Li^+ and Fe^{3+} at Fe1b is associated with a strong increase in geometrical distortion-induced electric dipole moments of (Fe, Li) O_6 at elevated temperatures. In contrast, at 3 K, the dipole moment modulus of FeO_6 is about four times larger than that of (Al, Li) O_6 , even though the latter is almost four times more distorted than the former. Similarly, at 3 K, (Fe, Li) O_6 is five times less distorted than (Al, Li) O_6 , but its dipole moment magnitude is about twice as high as that of (Al, Li) O_6 . Moreover, the reduction of the distortion degree and the dipole moment modulus in FeO_6 with increasing temperatures, particularly in the range of 3–50 K, could be a sign of a strong spin-lattice correlation in $\text{Li}_5\text{OAl}_5\text{O}_{15}$. The fashion and dynamics of magnetic spins appear to interact profoundly with polyhedral distortion and electric dipole moments. In the following sections, we discuss more about the non-collinearity in Al-LFOs, followed by their spin-reorientation transitions.

C. Non-collinear ferrimagnetic spin arrangements in $\text{Li}_5\text{OAl}_5\text{O}_{15}$ below RT

As given in Table III, the nonzero spin-canting angles against the c axis in $\text{Li}_5\text{OAl}_5\text{O}_{15}$ at 3 and 50 K could be obtained from HRNPD data analyses. This finding demonstrates new non-collinear ferrimagnetic orders in spinel-type MFs (Fig. 5). The non-collinearity is due to nonzero M_x and M_y

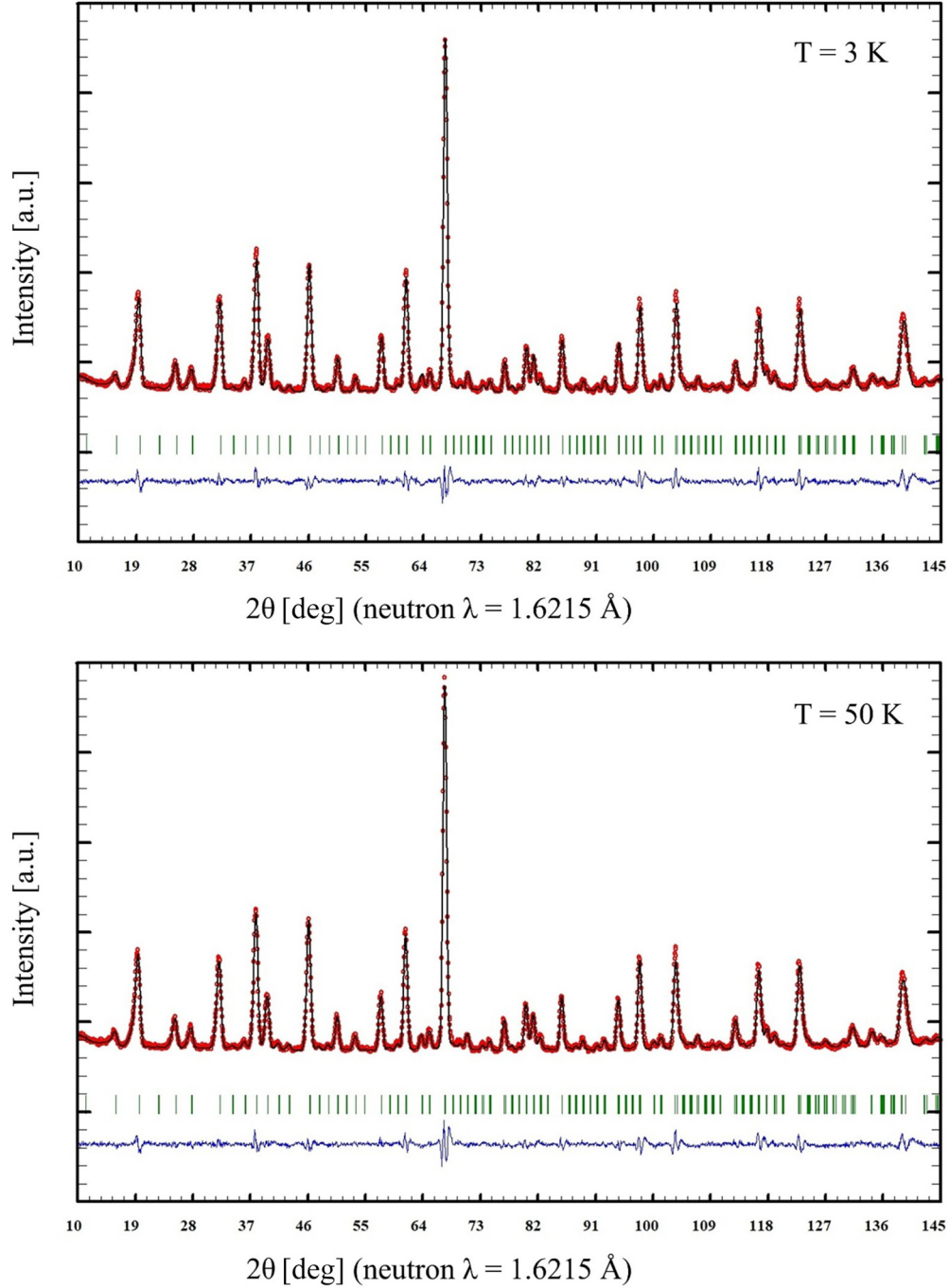


FIG. 2. Graphical presentation of results from Rietveld analysis in the MSG $P4_32'_12'$ with LT-HRNP data of Li50Al50 at 3 K (top) and at 50 K (bottom). Bragg peak positions from the ferrimagnetic spin order and the atomic order are superimposed (green bars). The weighted profile residual (R_{wp}) values of 0.0757 for 3 K and 0.0692 for 50 K reflect the agreement factors, corresponding to the respective difference profiles (blue lines) between the observed (red circles) and the calculated (black lines) profiles.

components of Fe^{3+} mainly at the site Fe1a within FeO_6 . Its spin canting decreases at elevated temperatures, suggesting a pronounced spin reorientation process (see the next sections). At 300 K, as already reported, the obtained values for M_x and M_y at Fe1b are smaller than their standard deviations [5], and those of Fe^{3+} at Fe1b within $(\text{Fe}, \text{Li})\text{O}_6$ and Fe2 within FeO_4 are very small even at 3 K with large standard deviations (Fig. 6). Hence, magnetic moments at Fe1b and Fe2 seem to be oriented almost collinear without much contribu-

tion to SR phenomena from 3 to 300 K. It can be inferred that thermally averaged Fe^{3+} spins are aligned in [001] at octahedral sites (B-sublattice) or in [00-1] at tetrahedral sites (A-sublattice) at ambient conditions (Supplemental Material Fig. 1 [15]). The expected T -dependent decrease of magnetic moments from 3 to 300 K was observed at all Fe sites, except for a slight increase (within the error bars) of the magnetic moment modulus at Fe1a from 3 to 50 K (Fig. 6). Over the temperature range 3–300 K, the highest M_z value was found at

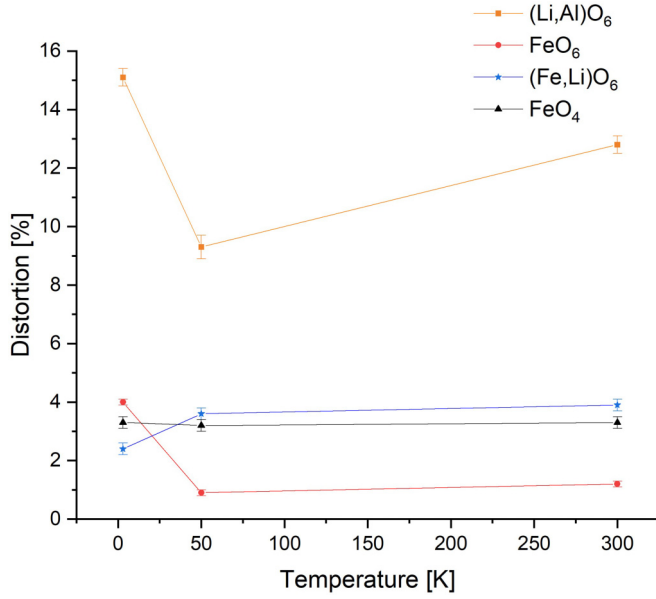


FIG. 3. Changes of polyhedral distortion against temperature in Li50Al50.

Fe1a at 50 K. This anomaly can be linked to negative thermal expansion along the c axis from 3 to 50 K (Table I), suggesting a correlation between the lattice and magnetic interactions. The tetragonality $c < a$ in Al-LFOs predicts subtle changes of the space-diagonal next-nearest magnetic interactions in the B-sublattice (J'_{BB}) against the face-diagonal nearest magnetic interaction (J_{BB}), which is sensitive to SRs. Hence, the SR process at Fe1a is considered as the driving force for the non-collinear ferrimagnetic order in Li50Al50.

The current study aims to further understand the spin-canting phenomena of Al-LFOs in relation to the T -dependent magnetization. The saturation magnetization (M_s [emu/g]) curves of Li60Al40 and Li50Al50 were reported in our previous study (Supplemental Material Fig. 2 [15]) with the

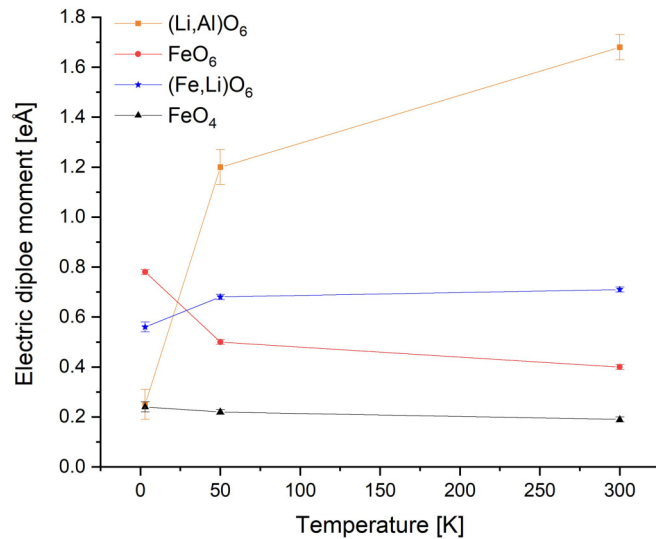


FIG. 4. Moduli of geometrical distortion-induced electric dipole moments of all polyhedra in Li50Al50.

estimated magnetic moment per formula unit (M/pfu) 2.29 and $1.65 \mu_B$ at 0 K, respectively [5]. To comprehend the compositional dependence of M_s , it is worth mentioning that M_s and the magnetic interaction J_{AB} between the A- and the B-sublattice increase with the doping content x at low doping levels but exponentially decrease at x larger than 0.4 in spinel-ferrites, e.g., $\text{Cu}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ [20] and 0.25 in $\text{Ni}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$ [21]. The doping content-dependent M_s in these Cu-Zn and Ni-Co spinel-ferrites has been understood by the dilute-induced spin canting in the B-sublattices. An average spin-canting angle at 0 K can be estimated by the so-called Yafet-Kittel angle α_{Y-K} [22] using experimental estimation of M/pfu at 0 K [23]. At high doping levels, the doping content x gave rise to high spin canting in Cu-Zn, Ni-Co, and further spinel ferrites [20,21,23]. For example, Cu-Zn ferrites have nonzero α_{Y-K} enlarging with increasing x . This is obvious at high doping levels as α_{Y-K} increases from 35° at $x = 0.4$ fast up to 90° at $x = 1.0$. At the same time, M_s decreases with increasing the Zn-doping content from 200 emu/g down to zero. This reflects a correlation of the spin canting with M_s . Therefore, the observations of M_s with increasing α_{Y-K} proportional to the doping content at high doping levels in Cu-Zn and Ni-Co spinel-ferrites can explain the weakening of the magnetic exchange interaction J_{AB} and the strengthening of J_{BB} . The dilute effect, mainly with Li^+ for Fe^{3+} in the B-sublattice on M_s , was also observed in Al-LFOs. A M_s value of 23.0 emu/g for Li50Al50 (Li substitution for Fe: $x = 0.25$) measured at 5 K under an external magnetic field of 10 kOe is lower than a M_s value of 31.8 emu/g for Li60Al40 ($x = 0.20$) (Supplemental Material Fig. 2 [15]) [5]. The α_{Y-K} values at 0 K were estimated for both Al-LFOs according to the following formulas:

$$\begin{aligned} \text{Li60Al40 : } M/pfu &= (1 + 2 \cdot 0.80) \cdot 5\mu_B \cdot \cos \alpha_{Y-K} \\ &\quad - 2 \cdot 5\mu_B \\ &= (2.6 \cdot \cos \alpha_{Y-K} - 2) \cdot 5\mu_B \end{aligned}$$

$$\begin{aligned} \text{Li50Al50 : } M/pfu &= (1 + 2 \cdot 0.75) \cdot 5\mu_B \cdot \cos \alpha_{Y-K} \\ &\quad - 2 \cdot 5\mu_B \\ &= (2.5 \cdot \cos \alpha_{Y-K} - 2) \cdot 5\mu_B. \end{aligned}$$

The calculated α_{Y-K} values of 19° and 21° for Li60Al40 and Li50Al50, respectively, cannot be explained by the Néel collinear model, confirming the spin arrangements in the tetragonal MSG with nonzero M_x and M_y components, which are obviously present at Fe1a (16° at 3 K). We already mentioned that the less significant spin canting at Fe1b (8° at 3 K) is explained by the site-averaged magnetic moment of Fe^{3+} statistically disordered with Li^+ . Overall, however, the angle α_{Y-K} appears to increase with x in two Al-LFOs, as compared so far, even at relatively low doping levels ($x \leq 0.25$). In conclusion, Al-LFOs exhibit 33% – 46% M_s of LFO for non-collinear spin arrangements because of the dilute effect. More interestingly, the spin canting angle of 16° at 3 K, as evaluated from the structural analysis at Fe1a in Li50Al50, approaches the value of 21° for the overall canting angle α_{Y-K} , as determined from the extrapolated M_s value at 0 K. More simply, the angle between three magnetic spins at Fe1a-Fe2-Fe1b is 51.1° , i.e., the spin orientation angle at Fe1a is about 25° with

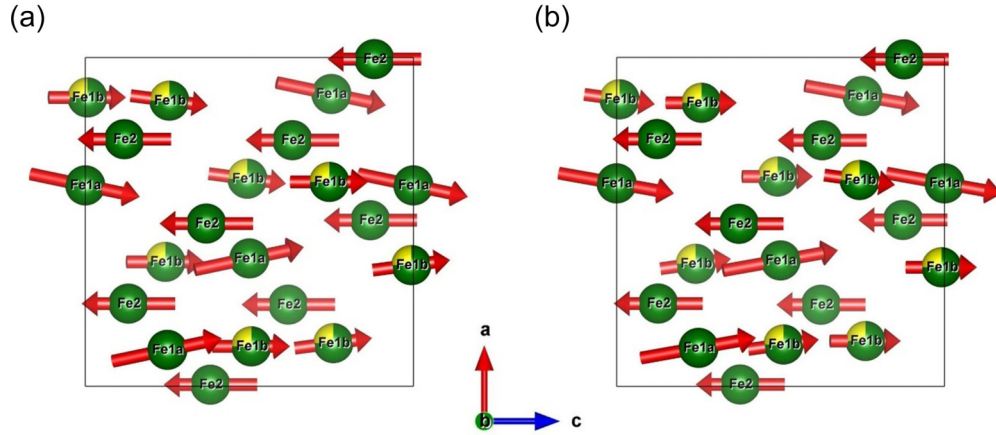


FIG. 5. Comparison of non-collinear spin arrangements in Li50Al50 between 3 K (a) and 50 K (b).

respect to that at Fe2 at 3 K (Fig. 7). These estimations of magnetic spin orientation at Fe1a could unambiguously confirm new non-collinear ferrimagnetic arrangements in Li50Al50 below RT. This finding predicts a weakening of the magnetic interaction J_{AB} due to SRs of Fe^{3+} in the B-sublattice.

D. Heat capacity of Al-LFOs

Recall that both Al-doped lithium ferrites, Li50Al50 and Li60Al40, were investigated to understand the structural consequences of aluminum substitution. The partial substitution of Al^{3+} for Li^+ and Li^+ for Fe^{3+} in the B-sublattice fosters a symmetry-lowering in these materials, as aforementioned.

The resulting structural distortion was interpreted as chemically induced lattice stress, which could promote electric polarization through polyhedral distortion within the LFO framework.

From a magnetic perspective, the presence of nonmagnetic Li^+ partially replacing Fe^{3+} in the B-sublattice leads to a dilution effect in the ferrimagnetic ordering characteristic of the parent lithium ferrite structure and ensures the electrostatic charge compensation, consequently, from the incorporation of Al^{3+} at the site for Li^+ . This substitutional fashion is hypothesized to disrupt spin alignment and possibly promote spin canting within the B-sublattice, where, in the LFO system, magnetic moments are aligned parallel to the [001] direction

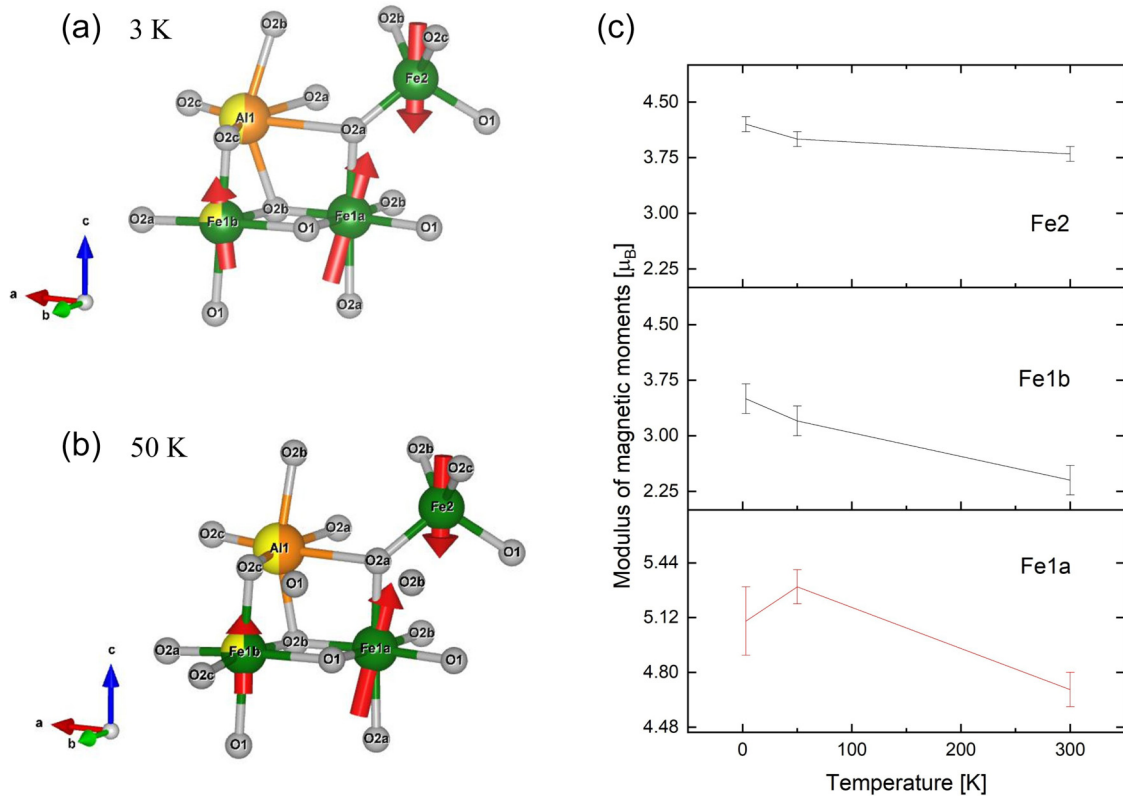


FIG. 6. Spin arrangements of unique polyhedral units in Li50Al50: (a) 3 K; (b) 50 K; (c) Temperature-dependent modulus of magnetic moments at three independent sites for Fe^{3+} in Li50Al50.

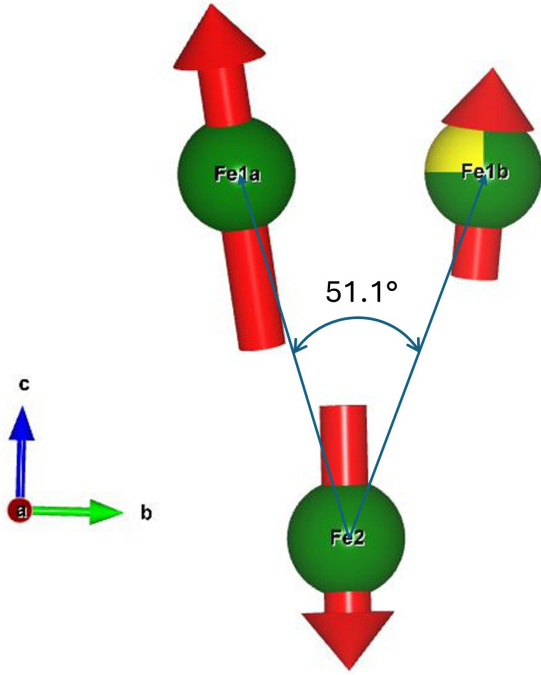


FIG. 7. The spin-canting angle of the B-sublattice against the collinear A-sublattice, determined by the structural analysis using 3K-HRNP data of Li50Al50, is about 25° ($51.1^\circ/2$). This value is in close agreement with the α_{Y-K} value of 21° , estimated from M_s at 0 K.

at ambient conditions. In the case of Li50Al50, strong competition between antiferromagnetic and ferromagnetic interactions could lead to significant geometric frustration due to the hyperkagome lattice, a possibility supported by various simulations [2,24]. An additional point of interest is the study of spin dynamics within and between domains in these Al-LFO compounds. This motivates the investigation of the structural and magnetic properties of LFO-type compounds under external stimuli. For this purpose, we have performed a study of the specific heat data, $C_p(T)$ of Li50Al50.

As seen in Fig. 8(a), the $C_p(T)$ data probed at the zero-field and 10 kOe, exhibit a smooth, featureless curve across the entire temperature range from 0.4 to 300 K, indicating the

absence of long-range magnetic ordering transitions. However, the presence of magnetic contributions, such as featureless spin fluctuations or short-range magnetic correlations, cannot be ruled out. Notably, a broad and shallow anomaly near 1 K may be associated with a spin-fluctuation freezing temperature, T_f . This subtle feature is accompanied by a field-dependent behavior below 2 K, where the zero-field and 10 kOe heat capacity curves begin to diverge. The slight enhancement of the low-temperature heat capacity with increasing magnetic field suggests a magnetic origin for this contribution, potentially indicative of field-enhanced spin fluctuations or localized magnetic excitations.

At 300 K, the obtained C_p of Li50Al50 remains significantly below the Dulong–Petit limit ($C_p \cong 3NR = 42R$) expected for a fully thermally populated lattice at high temperatures [$T \gg T_D$ (Debye temperature)]. This behavior is consistent with a stiff lattice. For the parent LFO, the Debye temperature is reported to be approximately 549 K [25], corresponding to the temperature at which maximum lattice vibrations are thermally excited. In both Al-LFOs, T_D is likely even higher due to increased lattice rigidity introduced by Al^{3+} substitution for Li^+ , as explained ahead. However, accurate determination of T_D for both Al-LFOs is not feasible from heat-capacity data because significant magnetic contributions obscure purely phononic behavior.

This limitation is clearly reflected in the Debye-reduced heat capacity plot (C_p/T^3 vs T). In a system governed solely by lattice contributions, the Debye model predicts a plateau in C_p/T^3 at low temperatures, with $C_p \cong AT^3$, where $A = 12\pi^4NR/5T_D^3$. For LFO, this corresponds to a theoretical value of $C_p/RT^3 = A/R = 1.98 \times 10^{-5} K^{-3}$, indicated by a dotted red reference line in Fig. 8(b). However, the experimental data did not approach this expected plateau. Instead, a noticeable increase in C_p/RT^3 is observed below ~ 40 K, indicating the presence of substantial magnetic contributions. This upturn strongly suggests the activation of magnetic excitations and fluctuations at this low-temperature range, highlighting that the lattice contribution is not dominant.

The next section demonstrates the timescale range of the SR process in both Al-LFOs, as significantly shown above 100 K in ac magnetic susceptibility measurements.

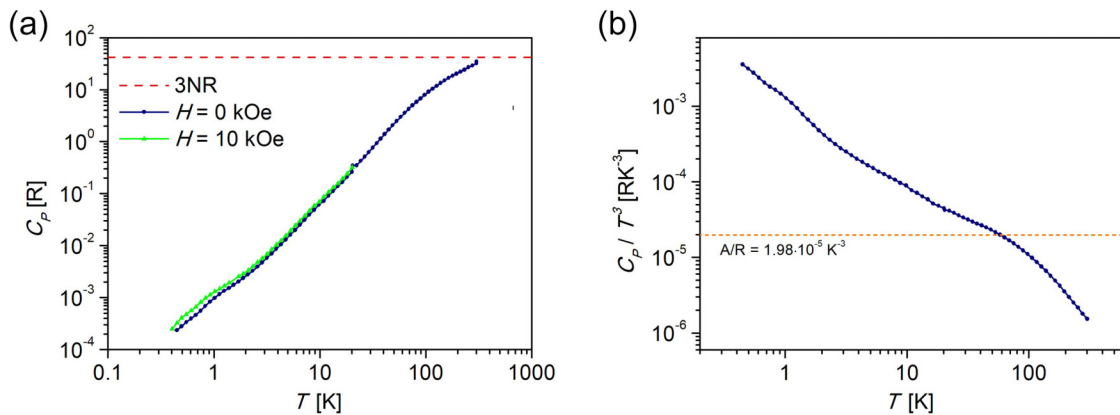


FIG. 8. Specific heat (C_p) characterization for Li50Al50. (a) Temperature variation of $C_p(T)$, in units of R , at two different magnetic fields $H = 0$ and 10 kOe. The bold red line indicates the Dulong–Petit limit; (b) Debye-reduced specific heat C_p/T^3 at the zero-field.

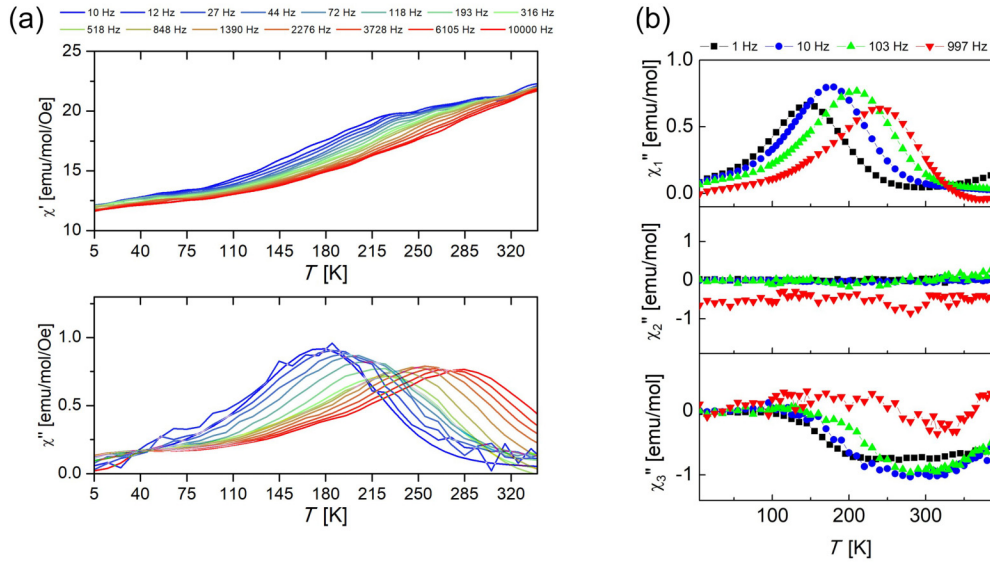


FIG. 9. Alternating current magnetic susceptibility of Li60Al40. (a) χ' and χ'' as a function of T for different frequencies between 10 Hz and 10 kHz; (b) Harmonic analysis, showing the out-of-phase component of the first (top), second (middle), and third harmonics (bottom) for selected frequencies 1, 10, 103, and 997 Hz.

E. Dynamic magnetic properties

The experimental technique of ac susceptibility provides a sensitive probe of magnetic dynamics in condensed matter systems [26,27]. Results from ac magnetic susceptibility (χ_{AC}) measurements on Li60Al40 (Fig. 9) show evidence of a pronounced temperature-induced spin reorientation (SR) process, which results in a significant decrease in the real part of the ac magnetic susceptibility (χ'), from 22 emu/mol at 300 K to 12 emu/mol at 12 K, i.e., a reduction by a factor of approximately 1.8 (Fig. 9(a), top). At low temperatures, approximately 45% of the magnetic susceptibility is suppressed, consistent with the blocking of magnetic dynamics.

The assignment of the observed dynamic behavior to a SR process is validated by the analysis of nonlinear components of susceptibility. In particular, the third harmonic component (χ_3) provides information on the character of the magnetic ordering associated with the phase transition. Under applied magnetic fields, this component is sensitive to the breaking of time-reversal symmetry and provides insight into perturbations of the local spin environment. In contrast, even harmonics, such as the second harmonic (χ_2), are indicative of symmetry-breaking internal magnetic fields and are typically associated with spontaneous magnetization [28]. As shown in Fig. 9(b), our nonlinear analysis revealed a clear divergence in the out-of-phase third harmonic (χ''_3) at the onset of the SR transition across all measured frequencies, primarily manifested in the imaginary component χ'' . In contrast, no such divergence or correlation is observed between the out-of-phase susceptibility and the second harmonic (χ''_2). This absence of χ''_2 response suggests that the observed dynamics are not associated with spontaneous magnetization but rather arise from spin reorientation processes.

The primary SR process occurs over a wide temperature range, from approximately 100 to 350 K, displaying thermal activation. The T dependence of χ_{AC} was further analyzed using a Debye relaxation model with Arrhenius-type thermal ac-

tivation. While this model does not fully capture the system's complexity, it provides a reasonable basis for interpreting the thermally activated SR dynamics in the non-collinear ferromagnetic state. Analyzing the maximum in χ'' as a function of temperature for the different frequencies allows extracting the SR timescale as a function of temperature $\tau(T)$. The thermal dependence of the relaxation time is described by the equation $\tau(T) = \tau_0 \exp(E/k_B T)$ with the following parameters: $\tau_0 = 2.0 \pm 1.810^{-10}$ s and $E/k_B = 3279 \pm 195$ K. The prefactor τ_0 represents the effective intrinsic attempt time of the spin system to reorient with typical values of 10^{-9} to 10^{-12} s for collective spin dynamics. The obtained τ_0 and energy barrier are similar to those from previous measurements on the dynamics of domain walls [29]. This simple analysis assumes a single relaxation time, while the broadness of the susceptibility curves indicates a distribution of relaxation times and activation energies. While the dominant SR process is well resolved in this HT range, an additional LT dynamic process is suggested at 10 kHz, although it remains less clearly defined.

In Li50Al50, we observed similarly complex spin dynamics across a broad temperature range from 5 to 350 K. A main T -induced SR process is evident, with the real part of the ac magnetic susceptibility (χ'), decreasing significantly from 21 emu/mol at 350 K to 9 emu/mol, at 5 K: a reduction by a factor 2.3 [Fig. 10(a)]. This corresponds to approximately 57% of the magnetic susceptibility. This behavior can be ascribed to T -induced SR processes that are blocked at 5 K. This substantial drop of the magnetic susceptibility is attributed to thermally driven spin reorientation processes that affect a major fraction of the system's magnetic response.

The imaginary component of the ac magnetic susceptibility (χ'') enables a Debye-type fit, revealing an additional low-temperature SR process in Li50Al50 [Fig. 10(b)]. At least two distinct SR processes can be resolved: (i) the primary one occurring above 100 K (SR1), and (ii) a secondary,

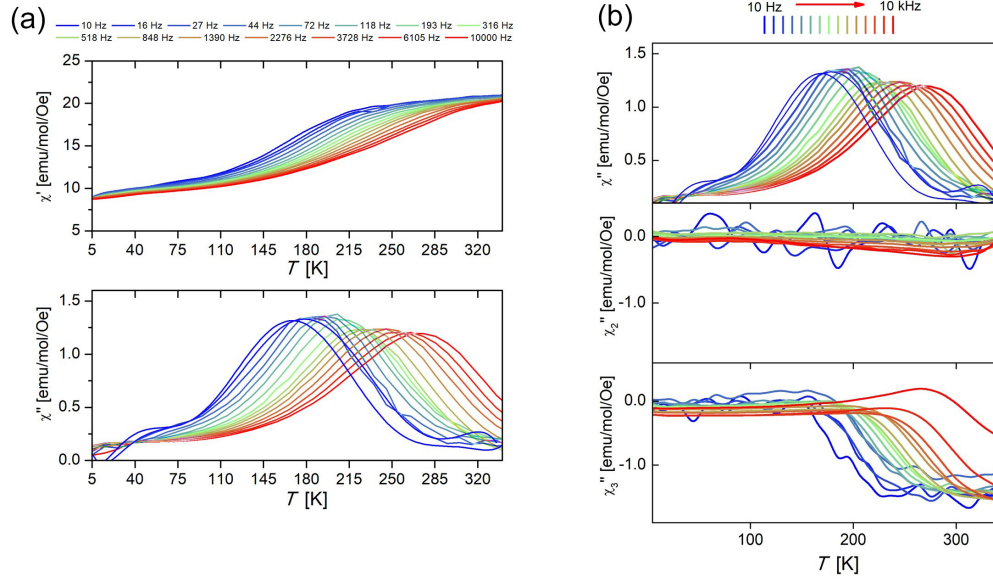


FIG. 10. Alternating current magnetic susceptibility for Li50Al50. (a) χ' and χ'' as a function of T for different frequencies between 10 Hz and 10 kHz; (b) Harmonic analysis, showing the out-of-phase component of the first (top), second (middle), and third (bottom) harmonics.

lower-magnitude process active above 25 K (SR2). There is also evidence for a third, weaker SR process suggested at very low temperatures (5–50 K), particularly at higher measurement frequencies.

The primary SR process in Li50Al50 is thermally activated and follows an Arrhenius-type behavior in the range of 100–350 K, described by $\tau(T) = \tau_0 \exp(E/k_B T)$ with the following parameters, $\tau_0 = 1.0 \pm 0.8 \cdot 10^{-10}$ s and $E/k_B = 3316 \pm 155$ K. The second SR process, which is approximately four times weaker in amplitude, occurs in the range of 25–100 K and also follows Arrhenius behavior with $\tau_0 = 7.9 \pm 2.0 \cdot 10^{-5}$ s and $E/k_B = 265 \pm 13$ K. These findings highlight the presence of multiple, thermally activated spin reorientation mechanisms, indicating a rich landscape of spin dynamics possibly linked to different magnetic sites of the non-collinear structure and the presence of domain rotations in addition to canting relaxations.

In Fig. 11(a), the resulting values for the relaxation times of the different SR processes are plotted on a semilogarithmic scale as a function of $1/T$, allowing direct comparison for both Al-LFO compounds. The observed linear trends evidence that the SR processes are thermally activated and well described by an Arrhenius-type behavior. A comparison between the two compounds reveals remarkably similar thermal dependence of the relaxation times, with slightly shorter τ values for the more diluted Al-LFO (Li50Al50). Despite these subtle differences, the activation energies and exponential prefactors remain comparable within experimental uncertainty. The shorter τ observed in the more diluted compound accounts for the onset of the main SR process in this system at lower temperatures and suggests faster dynamics, possibly due to a more distorted local environment and larger frustration effects. The LT-activated process observed in Li50Al50 [Fig. 11(b)] is not resolved in the less-diluted compound Li60Al40; however, its

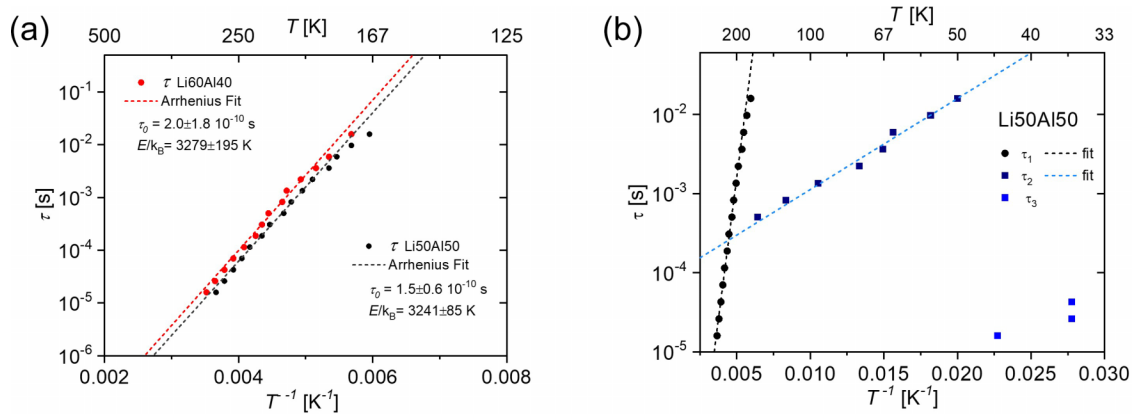


FIG. 11. (a) SR relaxation time (τ) against $1/T$ on a semilogarithmic scale for Li60Al40 (red circle) and Li50Al50 (black circle). The dashed line represents the fit to an Arrhenius law; (b) Time relaxation of different SR processes observed in Li50Al50 on a semilogarithmic scale as a function of $1/T$. Dashed black and blue lines are fits to the Arrhenius law for SR1 and SR2, respectively.

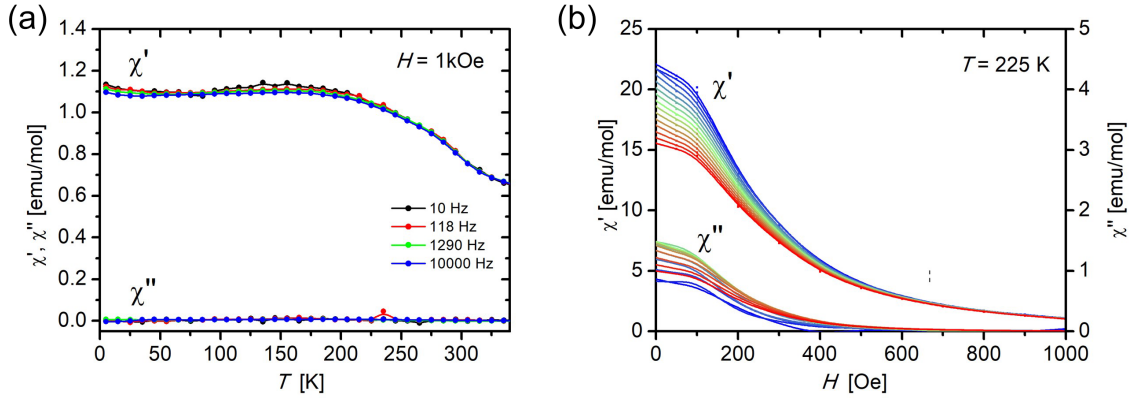


FIG. 12. (a) In-phase and out-of-phase magnetic susceptibility, $\chi'(f, T)$ and $\chi''(f, T)$, respectively, for Li50Al50 at $H = 1$ kOe as a function of temperature (T) for four different frequencies (10 Hz, 118 Hz, 1290 Hz, and 10 kHz); (b) $\chi'(f, H)$ (left scale) and $\chi''(f, H)$ (right scale) at $T = 225$ K as a function of a dc applied field H .

presence cannot be excluded, as it may be masked by the broad and extended contribution of the dominant relaxation process.

To gain deeper physical insight into the nature of the observed spin-relaxation processes, we investigated the influence of an applied polarizing magnetic field (H) on spin dynamics. These measurements were performed on the more diluted compound Li50Al50, as its dynamic behavior is both richer and more distinguishable, while differences between the two studied compositions remain subtle. Our results show that applying a magnetic field significantly suppresses the amplitude of the dynamic processes. Specifically, all SR-related features are effectively quenched at fields above 0.5 kOe. As shown in Fig. 12(a), both the in-phase (χ') and out-of-phase (χ'') components of the ac magnetic susceptibility become frequency-independent under an applied field of 1 kOe, across the entire investigated temperature range. When the temperature is fixed at 225 K, we observe that the frequency dispersion of χ_{AC} diminishes progressively with increasing field strength [Fig. 12(b)]. Ultimately, the χ'' component vanishes, and χ' is also reduced, consistent with the progressive alignment (polarization) of spins along the applied magnetic field direction.

Importantly, no direct correlation could be established between these dynamical effects and the heat capacity data. Since specific heat is a static measurement, it is not sensitive to the timescales of the SR processes and thus cannot capture their dynamical signatures. The observed low-temperature differences in heat capacity under magnetic fields are likely due to a Zeeman shift of the magnetic entropy contribution to higher temperatures, rather than being a direct consequence of SR dynamics. Overall, while the applied magnetic field quenches SR processes, it does not eliminate geometric frustration in these materials. The underlying frustrated spin network remains intact, suggesting that frustration and dynamic spin reorientation are decoupled phenomena in this class of compounds.

IV. CONCLUSION

A noncollinear magnetic order could be elucidated in an Al-doped lithium ferrite, $(\text{Li}_{0.5}\text{Al}_{0.5})(\text{Fe}_{0.75}\text{Li}_{0.25})_2\text{Fe}_3\text{O}_8$

(Li50Al50) at 3 and 50 K in a tetragonal MSG, $P4_32'_12'$ using neutron powder diffraction techniques. The largest spin-canting angle at Fe1a with respect to the c axis, determined by the structural analysis using 3K-HRNPd is comparable with the Yafet-Kittel value 21° from the M_s data extrapolated to 0 K. This spin-noncollinearity is contributed by spin reorientations of Fe^{3+} of FeO_6 in the geometrically frustrated hyperkagome lattice (B-sublattice). The electric polarization induced by geometrical distortion is pronounced within the nonmagnetic $(\text{Li}, \text{Al})\text{O}_6$ polyhedra at high temperatures. In contrast, SR-enhanced electric polarization is dominant in FeO_6 at low temperatures, adumbrating a high correlation between magnetic and electric moments in Al-doped LFO-type compounds. The tetragonal lattice distortion could be a sign of weakening of the magnetic interaction J_{AB} due to SRs of Fe^{3+} in the B-sublattice. The collinear spin arrangement in the diamond lattice of FeO_4 (A-sublattice) is intact below T_c down to 3 K. The entire noncollinear spin-canting textures are thermally averaged to yield collinear spin alignment along [001] at 300 K in the absence of external fields.

The principal SR processes in differently diluted Li50Al50 and Li60Al40 are thermally activated above 100 K and exhibit Arrhenius behavior, without altering the spontaneous magnetic polarization below their T_c points. In addition, a secondary, weaker SR process is activated at 25 K in Li50Al50, while all SR dynamics are frozen at 5 K. These thermally driven SRs affect a major fraction of the title system's magnetic susceptibility response. In the more diluted Li50Al50, the temperature-induced SR is attributed to a reduction of approximately 57% in the real part of the ac magnetic susceptibility from 350 to 5 K.

In this study, we could show that several thermally activated spin reorientations involve energy barriers. The obtained prefactors are typical of collective spin dynamics, and the activation energy range is similar to that observed for domain wall dynamics in ferromagnets [29]. Therefore, we can associate these spin dynamical processes with collective spin reorientation phenomena of the canted spin structure of Al-LFOs.

On the other hand, all SR-related features in both Al-LFOs are effectively quenched by applied polarizing magnetic fields above 0.5 kOe, independent of frequency or temperature. Overall, magnetic frustration and dynamic spin reorientation appear to be decoupled phenomena in these LFO-type multiferroic compounds.

In summary, Al-doped lithium ferrite stabilizes a non-collinear magnetic state, giving rise to multiple dynamic processes associated with the canted spin structure and lattice-distortion-induced electric polarization. We anticipate that this work will be of fundamental relevance for the design of multiferroic materials with enhanced magnetoelectric coupling, as well as for their potential implementation in emerging technologies such as photovoltaics and spintronic devices.

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The corresponding authors, S.H.P. and A.A., disclose any potential competing or nonfinancial interests on behalf of all authors of this manuscript.

DATA AVAILABILITY

The data that support the findings of this article are not publicly available. The data are available from the authors upon reasonable request.

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- [15] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/rqyh-8cdf> for Table S1 interatomic distances of Li_5OAl_5 at 3 K and 50 K; Table S2 average polyhedral distortion degrees [%] in Li_5OAl_5 at room temperature; Fig. S1 the spin-canting arrangements in Li_5OAl_5 at 3 and 300 K; and Fig. S2 saturation magnetization of the compounds Li_5OAl_5 , which includes Ref. [5].
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