

Biaxial magnetic alignment and orthorhombic twin microstructure in layered nickelates $\text{La}_3\text{Ni}_2\text{O}_7$

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The synthesis of large bulk nickelate single crystals remains challenging. We demonstrated room-temperature biaxial magnetic alignment of polycrystalline $\text{La}_3\text{Ni}_2\text{O}_{7+\delta}$ ($\delta = 0$) using a modulated rotating field (MRF). Phase-pure powders ($\sim 5 \mu\text{m}$) were aligned under 7 T-MRF during epoxy curing, exploiting triaxial susceptibility ($\chi_a > \chi_b > \chi_c$). XRD and pole-figures confirm: $\Delta\phi = 4^\circ$ in-plane orientation degrees and orthorhombic twin domains via $(h00)/(0k0)$ peaks and fourfold symmetry. These twins, analogous to cuprates but distinct in NiO_6 origin, provide the first crystallographic evidence of domain microstructure in nickelates, enabling direction-resolved studies of anisotropy of density-order phase and superconductivity obscured by heterogeneity.

Layered nickelate superconductors, particularly $\text{La}_3\text{Ni}_2\text{O}_{7+\delta}$ (La327), are of intense interest for possible unconventional superconductivity.¹⁻⁶⁾ They adopt a Ruddlesden-Popper (RP) layered perovskite structure with conductive NiO_2 bilayers separated by rock-salt La-O blocking layers along c -axis (as shown in Fig. 1(a)), producing strong electronic anisotropy and largely in-plane superconductivity whose interlayer coupling is tuned by pressure.¹⁻⁶⁾ The resulting dimensionality and orbital selectivity bear a strong resemblance to those observed in layered cuprates superconductors, such as $\text{REBa}_2\text{Cu}_3\text{O}_7$ (RE123).⁷⁾ The bilayer NiO_2 structure in La327 introduces complexity in pairing mechanisms, with unresolved symmetries such as $s \pm$ or d -wave states.⁸⁻¹¹⁾ Although superconductivity in La327 was first observed in single crystals under high pressure (>14 GPa),¹⁾ subsequent work confirmed its presence in polycrystalline samples.²⁻³⁾ Large sample-to-sample variations, likely from oxygen nonstoichiometries, stacking faults, impurities, and inhomogeneous strains, obscure the intrinsic phase diagram. High-quality oriented polycrystals are therefore vital, and the modulated rotating magnetic field (MRF) technique¹²⁾ exploits directional magnetic susceptibility to produce single-crystal-equivalent texture composites under ambient conditions, overcoming limitations of conventional growth methods.¹³⁻¹⁴⁾

Recent advances in magnetic-alignment techniques show biaxial texturing can optimize microstructure in anisotropic nickelates. The MRF notably aligns both magnetically easy and hard axes in polycrystals at room temperature, offering a scalable, low-temperature alternative to high-temperature epitaxial growth. Unlike conventional routes, MRF has produced biaxially textured microstructures with reduced grain-boundary misorientation in analogous RE123.¹⁵⁻¹⁷⁾ The method exploits intrinsic directional susceptibility ($\chi_{ab} > \chi_c$) of layered La327, where NiO_2 planes dominate the in-plane response through correlated Ni orbital states [intermediate valence of $\text{Ni}^{2+}/\text{Ni}^{3+}$] that drive complex density-wave tendencies.¹⁸⁻²²⁾ Because La327 magnetic anisotropy is weaker than cuprates,²⁰⁾ high fields ($\mu_0 H_a \geq 7$ T) are generally required to generate sufficient torque to overcome thermal fluctuations and induce alignment.^{7,23)}

The exceptionally low superconducting volume fraction in La327 remains a fundamental obstacle to understanding its intrinsic superconducting properties. This limitation may stem from some unresolved synthesis challenges such as difficult-to-control oxygen deficiency, possible impurity of other RP phases as stacking faults, and potential coexistence of $Fmmm$ -structured impurity phases within the dominant $Amam$ matrix,²⁴⁻²⁶⁾ in addition to the inhomogeneity of the

pressure of diamond anvil cell. Crucially, large bulk single crystals with ideal stoichiometry and phase purity are not easily obtained so far. In this letter, we overcome these limitations by developing a magnetic alignment approach that enables single-crystal-equivalent studies from polycrystalline powders, providing a pathway to distinguish intrinsic superconducting properties from microstructure-driven artifacts.

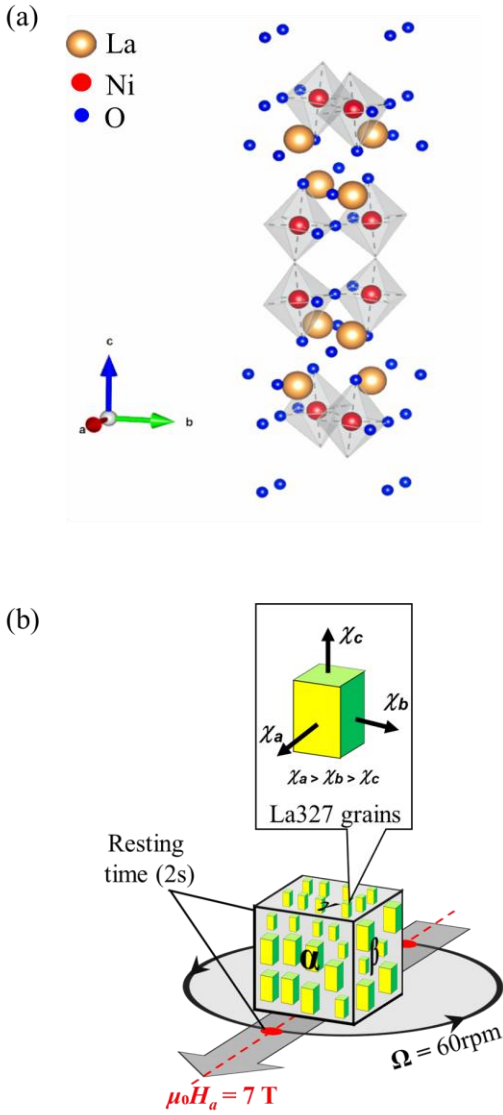


Fig. 1. Crystal structure and magnetic anisotropy axes of $\text{La}_3\text{Ni}_2\text{O}_7$ (La327). (a) Schematic of the Ruddlesden-Popper structure, featuring bilayer NiO_2 planes separated by rock-salt La-O blocking layers along the c -axis. (b) Illustration of the triaxial magnetic susceptibility hierarchy $\chi_a > \chi_b > \chi_c$, which facilitates biaxial grain alignment under a modulated rotating magnetic field ($\mu_0 H_a = 7$ T).

Polycrystalline samples of $\text{La}_3\text{Ni}_2\text{O}_{7+\delta}$ (La327, $\delta = 0$) were synthesized via a solid-state reaction method following the procedure detailed in previous studies.²⁷⁾ The phase purity and orthorhombic crystal structure were confirmed by X-ray diffraction (XRD), with refined lattice parameters ($a = 5.3920 \text{ \AA}$, $b = 5.4510 \text{ \AA}$, $c = 20.533 \text{ \AA}$).²⁷⁾ Oxygen stoichiometry ($\delta = 0$) was verified by thermogravimetric analysis (TGA), and the absence of a $\text{La}_4\text{Ni}_3\text{O}_{10}$ impurity phase was confirmed by ^{139}La -NQR spectroscopy.²¹⁾ Microstructural analysis via scanning electron microscopy (SEM) revealed faceted grains suitable for magnetic alignment.

For magnetic alignment, phase-pure La327 ($\delta = 0$) powder was mixed with Araldite Standard epoxy resin (Huntsman Corp.) at a 1:5 weight ratio. The epoxy with an initial viscosity of $40 \text{ Pa}\cdot\text{s}$ allowed uniform dispersion of the powder while minimizing sedimentation during alignment. The mixture was poured into a $10 \text{ mm} \times 10 \text{ mm} \times 15 \text{ mm}$ mold and subjected to a modulated rotating magnetic field (MRF) of $\mu_0 H_a = 7 \text{ T}$ for over 12 h at room temperature. The magnetic field was generated by a superconducting magnet (JASTEC Co. Ltd.).

The biaxial magnetic-alignment procedure (as shown in Fig. 1(b)) was adapted from prior RE123 studies.¹⁵⁾ The specimens were rotated horizontally in a transverse static field $\mu_0 H_a = 7 \text{ T}$ using a two-step sequence illustrated in Fig. 1(b). The original angle of the specimen is defined as when a direction normal to the α -plane of the specimen is parallel to the horizontal $\mu_0 H_a$ direction. At 0° and 180° the specimen was held for 2 s; elsewhere it was rotated at $\Omega = 60 \text{ rpm}$. In principle, materials with triaxial magnetic anisotropy (upper side of Fig. 1(b)) experience differential torque under MRF, allowing the first-easy, second-easy, and hard magnetization axes to align with the α -, β -, and γ -planes, respectively. Cured composites exhibited pseudo-single-crystal behavior from strong biaxial texture. Aligned blocks ($10 \text{ mm} \times 10 \text{ mm} \times 15 \text{ mm}$) were used for XRD on the α -, β -, and γ -planes and for (206) pole-figure measurements on the γ plane. These planes are defined as: the γ -planes is normal to the c -axis (hard magnetization axis, while α - and β -planes are normal to the a -axis (first easy axis) and b -axis (second easy axis), respectively.

Figure 2(a) shows a representative SEM image of ground La327 ($\delta = 0$) polycrystalline powders, revealing a squarish grain morphology suitable for magnetic alignment. The particle size analysis revealed that most grains fell within the $1\text{-}10 \text{ }\mu\text{m}$ range, with the largest particles being smaller than $25 \text{ }\mu\text{m}$. The average size was estimated to be $\sim 5 \text{ }\mu\text{m}$. This size distribution balances two critical requirements for effective alignment: (i) sufficient magnetic volume for torque

dominance over thermal fluctuations ($V > 1 \mu\text{m}^3$), and (ii) minimized sedimentation/agglomeration during epoxy curing.

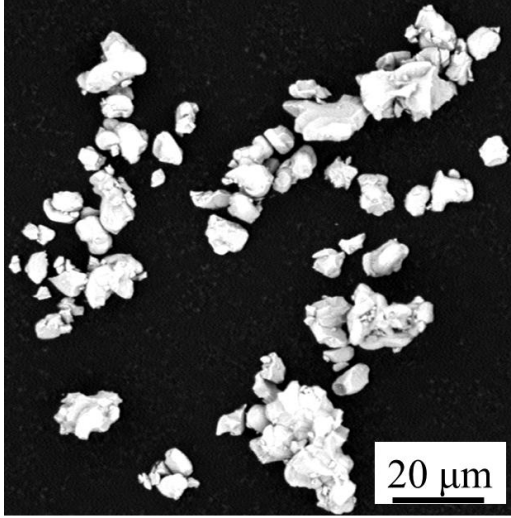


Fig.2. Scanning electron microscopy (SEM) image of ground $\text{La}_3\text{Ni}_2\text{O}_{7+\delta}$ (La327, $\delta = 0$) polycrystalline powders, showing squarish grain morphology suitable for magnetic alignment. The average particle size is $\sim 5 \mu\text{m}$.

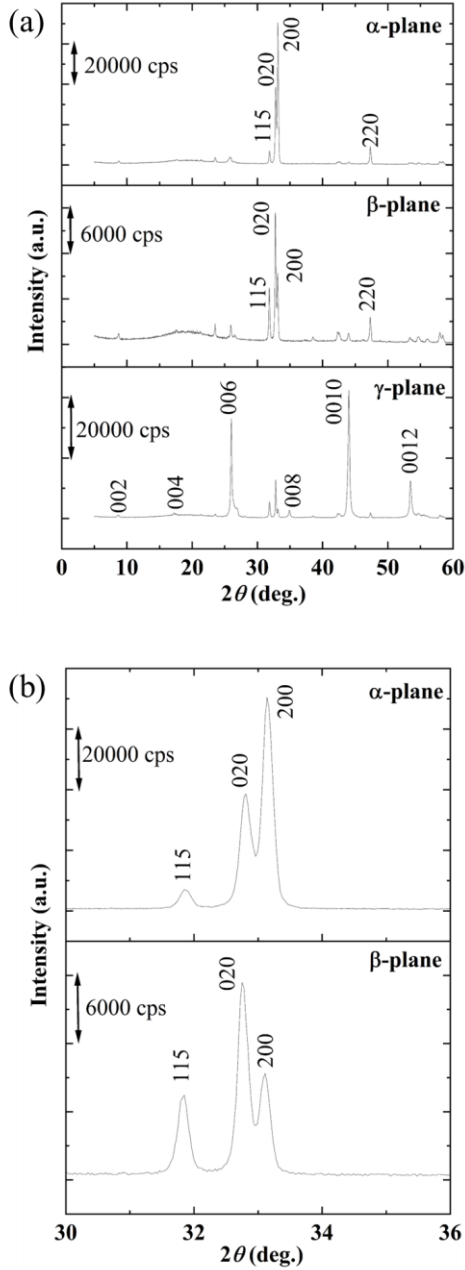


Fig. 3. (a) X-ray diffraction (XRD) patterns of the magnetically aligned polycrystalline powders of $\text{La}_3\text{Ni}_2\text{O}_{7+\delta}$ (La327 , $\delta = 0$) at the α -, β -, and γ -planes. (b) Magnified view of the 2θ range (30° - 36°), highlighting the (115), (020), and (200) peaks and their variation across different planes.

Figure 3 presents the XRD patterns of La327 ($\delta = 0$) powders magnetically aligned under a MRF of $\mu_0 H_a = 7$ T at room temperature, measured on the α , β , and γ planes. Figure 3(a) presents a wide range 2θ scan (0° - 60°), while Fig. 3(b) provides an enlarged view in the 30° - 36° range to closely examine the diffraction behavior of the (115), (020), and (200) peaks. By increasing the

applied magnetic field to 7 T we achieved nearly biaxial alignment: the α - and β -planes exhibit strong in-planes ($h00$) and ($0k0$) peaks, while the γ -plane is dominated by ($00l$) peaks. In particular, (200), (020) and (220) are clearly observed in the α - and β -planes, whereas (002), (004), (006) and higher-order ($00l$) peaks dominate the γ -plane. From the relative intensities of these peaks, we assign the magnetization easy-axis hierarchy as a -axis (first easy) $>$ b -axis (second easy), with the c -axis behaving as the hard magnetization axis, an assignment that is consistent with the pole-figure results discussed in the later part. The concurrent ($h00$) and ($0k0$) peaks in α and β indicate ab -plane crystallographic variants, a hallmark of orthorhombic twin domains.²⁸⁾ Close inspection of Fig. 3(b) reveals residual (115) intensity in all three planes and weak ($h00$) and ($0k0$) peaks in the γ -plane indicating a small fraction of misoriented or slightly tilted grains arising from incomplete torque, agglomerates/multigrain particles, powder-epoxy inhomogeneity, or edge effects during curing.

Next, we focus on the in-plane orientation degrees of the suspected twin microstructure. To test whether ($h00$) and ($0k0$) coexistence originates from orthorhombic twins, we performed (206) pole-figure analysis on γ -plane La327 ($\delta = 0$) powders aligned at 7 T by MRF. Figure 4(a) presents the resulting (206) pole-figure, revealing four sharp, symmetric intensity maxima spaced 90° apart. This four-fold symmetry unambiguously confirms biaxial alignment in La327 grains. This configuration fundamentally differs from uniaxial alignment scenarios, which would exhibit either continuous rings (random in-plane orientation degrees) or twofold symmetry expected for ideal orthogonal structure of La327 crystal in pole-figures. This pattern specifically requires two orthogonal domain orientation degrees: (i) For one twin domain, the a -axis (first easy axis) is parallel to the $\mu_0 H_a$, which results in the c -axis (hard axis) being perpendicular to the $\mu_0 H_a$ and thus parallel to the normal of the γ -plane. Consequently, the b -axis is perpendicular to the α -plane. (ii) For the other twin domain, the b -axis (second easy axis) is parallel to the $\mu_0 H_a$, which also results in the c -axis being perpendicular to the $\mu_0 H_a$ and parallel to the normal of the γ -plane. This configuration makes the a -axis perpendicular to the β -plane. As shown in Fig. 4(a), the (206) pole-figure at γ -plane exhibits four-fold symmetric spots at tilt angle $\Psi \approx 42^\circ$. For a quantitative measure of the in-plane orientation degrees, Fig. 4(b) shows azimuthal ($\Delta\phi$) scans at $\Psi = 42^\circ$ of the (206) pole-figure, showing sharp peaks with a full width at half maximum (FWHM) of $\approx 4^\circ$. Compared to standard texturing techniques for RE123 superconductors,²⁹⁻³¹⁾ MRF achieves superior alignment ($\Delta\phi = 4^\circ$) in La327 despite its twin microstructure.

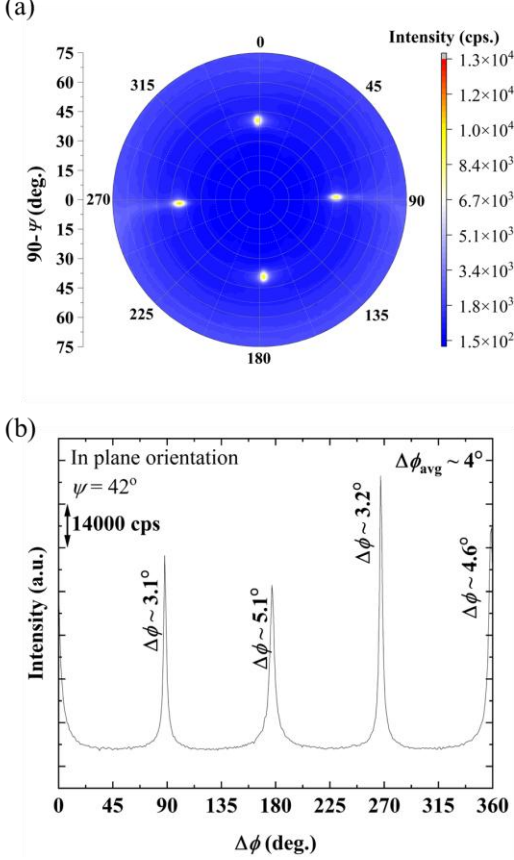


Fig. 4. (a) Pole-figure of the (206) plane on the γ -planes for $\text{La}_3\text{Ni}_2\text{O}_{7+\delta}$ ($\delta = 0$) powder aligned under a 7 T-MRF at room temperature, showing sharp four-fold symmetric spots indicative of biaxial grain orientation. (b) Azimuthal intensity profile ($\Delta\phi$) of the (206) plane, showing a narrow average full width at half maximum (FWHM) of $\approx 4^\circ$, confirming high in-plane orientation degrees.

The combined evidence, (i) concurrent ($h00$) and ($0k0$) peaks in the α - and β -plane XRD (Fig. 3(a)) and (ii) the fourfold-symmetric (206) pole-figure on the γ plane (Fig. 4(a)), provides the first direct crystallographic confirmation of orthorhombic twin domains in bulk La327. These twin microstructures likely originate from NiO_6 octahedral distortions.³²⁾ Prior work on cuprates indicates that twin microstructure degrades in-plane anisotropy and impedes full tri-axial alignment, supporting our assignment.²⁸⁾ While TEM studies confirm twin microstructures in magnetically aligned Dy123,³³⁾ La327 evidence remained indirect prior to this work. Though similar magnetic domains were postulated in thin films,¹⁸⁾ the presence of structural domain was not confirmed. Our biaxial XRD and (206) pole-figures now provide direct crystallographic evidence of twin domains. We note that the boundaries derived from domains with a - b -axes and

b - a axes can be found in the report of scanning near-field optical microscopy.²⁶⁾ Further high-resolution TEM remains essential to resolve twin boundary morphology and their impact on physical properties.

The biaxial alignment achieved under 7 T-MRF, quantified by sharp pole-figure spots $\Delta\phi = 4^\circ$ and unambiguous crystallographic signatures produces pseudo-single-crystal textures from polycrystalline La327 ($\delta = 0$) powders will directly address central challenge: resolving the sample-to-sample variations that relate with the complicated spin/charge order at ambient pressure and low superconducting volume fractions at high pressure. These textured samples enable two critical advances beyond powder-averaged studies: (i) Domain-selective spectroscopy to distinguish oxygen disorder effects from phase coexistence artifacts. (ii) Atomic-resolution TEM to quantify twin boundary widths and their impact on emergent orders. Specifically, directional NMR can now probe anisotropy of spin dynamics along individual crystallographic axes, complementary to previous NQR observations.²¹⁾ This approach provides one possible viewpoint to disentangle the intrinsic electronic phase diagram of the superconductivity in layered nickelates.

In summary, we demonstrate that room-temperature biaxial magnetic alignment under a 7 T modulated rotating field yields pseudo-single-crystal textures ($\Delta\phi = 4^\circ$) in polycrystalline $\text{La}_3\text{Ni}_2\text{O}_7$ ($\delta = 0$). Two independent signatures, (i) concurrent ($h00$) and ($0k0$) peaks in α - and β -plane XRD patterns and (ii) sharp fourfold symmetry in (206) pole-figures, constitute direct crystallographic evidence for orthorhombic twin domains. This twin microstructure offers one of the possible factors for interpreting the strong sample dependence of normal-state and superconducting properties in La327. Key next steps are: (i) atomic-resolution TEM to image and quantify twin boundaries, and (ii) domain-selective spectroscopies (e.g., NMR) to separate oxygen-disorder effects from twin-boundary effects. The MRF method thus provides an ambient, scalable route to single-crystal-equivalent samples for resolving intrinsic anisotropic behavior in nickelates.

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