

Effect of Pr-doping and oxygen vacancies on spin density wave in $\text{La}_3\text{Ni}_2\text{O}_{7-\delta}$: A μSR investigationKaiwen Chen^{1,*}, Xiangqi Liu^{2,*}, Ying Wang^{1,*}, Jiyuan Han¹, Ziyi Zhu³, Jiachen Jiao¹, Chengyu Jiang¹, Yanfeng Guo^{2,4}, Changlin Zheng¹ and Lei Shu^{1,5,†}¹State Key Laboratory of Surface Physics, Department of Physics, Fudan University, Shanghai 200438, China²School of Physical Science and Technology, ShanghaiTech University, Shanghai 201210, China³School of Materials, Zhengzhou University of Aeronautics, Zhengzhou 450046, China⁴ShanghaiTech Laboratory for Topological Physics, Shanghai 201210, China⁵Shanghai Research Center for Quantum Sciences, Shanghai 201315, China

(Received 24 December 2024; revised 16 April 2025; accepted 23 June 2025; published 15 July 2025)

Here we report the positive muon spin relaxation study on Pr-doped $\text{La}_{1.9}\text{Pr}_{1.1}\text{Ni}_2\text{O}_{6.97}$ and oxygen-deficient $\text{La}_3\text{Ni}_2\text{O}_{6.63}$ polycrystalline under ambient pressure. Zero-field $\mu^+\text{SR}$ experiments reveal the existence of bulk long-range magnetic order in $\text{La}_{1.9}\text{Pr}_{1.1}\text{Ni}_2\text{O}_{6.97}$ with $T_N = 161$ K, while $\text{La}_3\text{Ni}_2\text{O}_{6.63}$ exhibits a short-range magnetic ground state with $T_N = 15$ K. The microscopic magnetism of $\text{La}_{1.9}\text{Pr}_{1.1}\text{Ni}_2\text{O}_{6.97}$ is similar to the $\text{La}_3\text{Ni}_2\text{O}_7$ with ideal stoichiometry. A comparison with lightly oxygen-deficient $\text{La}_3\text{Ni}_2\text{O}_{6.92}$ reveals a crossover in magnetic dimensionality from three dimensional in $\text{La}_{1.9}\text{Pr}_{1.1}\text{Ni}_2\text{O}_{6.97}$ to two dimensional in $\text{La}_3\text{Ni}_2\text{O}_{6.92}$. Our $\mu^+\text{SR}$ experimental results reveal the destructive effect of apical-oxygen deficiencies on both intraplane and interplane magnetic correlation. On the other hand, Pr doping does not significantly alter the microscopic magnetism of $\text{La}_3\text{Ni}_2\text{O}_7$.

DOI: [10.1103/PhysRevResearch.7.L032014](https://doi.org/10.1103/PhysRevResearch.7.L032014)

Introduction. The recently discovered superconductivity with $T_c \approx 80$ K in pressurized Ruddlesden-Popper (RP) bilayer $\text{La}_3\text{Ni}_2\text{O}_7$ provides an exciting new platform for investigating the pairing mechanism of unconventional superconductivity [1]. Subsequently studies further revealed the superconductivity under pressure in trilayer RP phase $\text{La}_4\text{Ni}_3\text{O}_{10}$ and $\text{Pr}_4\text{Ni}_3\text{O}_{10-\delta}$ with $T_c \sim 30$ K [2–8], paving the way towards more potential superconducting candidates. Various experimental techniques including resonant inelastic x-ray scattering (RIXS) [9], muon spin relaxation ($\mu^+\text{SR}$) [10,11], and nuclear magnetic resonance (NMR) [12] have revealed the presence of spin density waves (SDW) below ~ 150 K in $\text{La}_3\text{Ni}_2\text{O}_{7-\delta}$ at ambient pressure. Although no long-range magnetic order was detected in early neutron scattering experiments regardless of the presence of oxygen vacancies [13,14], recent neutron scattering measurements have revealed signatures of SDW [15]. Meanwhile, a pressurized $\mu^+\text{SR}$ experiment revealed an increase in the SDW transition temperature, in contrast to the earlier transport measurements [1,16–18]. Though the nature of SDW is still controversial, most theoretical models suggest that pairing is driven by magnetic interactions [19–32].

In addition, the RP bilayer $\text{La}_3\text{Ni}_2\text{O}_{7-\delta}$ reported so far generally contains mixed phases and randomly distributed oxygen defects [16,33], which cause sample-dependent issues. Zero resistance is confirmed in both single crystals [17,18,34,35] and polycrystalline samples [16,36], while superconducting volume fraction varies from 1% to 48% among different samples, indicating a decisive role of crystal imperfections in pressurized superconductivity. Substituting La with Pr can effectively improve the purity of bilayer structure, resulting in higher T_c and superconducting volume fraction [16]. Similar to the early-stage studies of $\text{La}_3\text{Ni}_2\text{O}_{7-\delta}$, no evidence of magnetic ground state can be revealed from magnetization or transport measurements of $\text{La}_2\text{PrNi}_2\text{O}_7$. The microscopic magnetism of $\text{La}_2\text{PrNi}_2\text{O}_7$ is still unclear, which is crucial for understanding the bulk magnetism. On the other hand, no sign of superconductivity was observed in oxygen-deficient sample $\text{La}_3\text{Ni}_2\text{O}_{6.45}$ up to 41 GPa [37]. Meanwhile, a broad magnetic transition near 50 K was observed under ambient pressure, whose nature is still unclear. Therefore, $\text{La}_2\text{PrNi}_2\text{O}_7$ and $\text{La}_3\text{Ni}_2\text{O}_{6.45}$ provide an ideal comparison to study the evolution of magnetism with Pr doping and oxygen deficiencies in RP bilayer nickelates.

$\mu^+\text{SR}$ is a powerful technique for studying microscopic magnetism. The implanted muons act as local magnetic probes and can detect small magnetic fields in the sample [38–41]. Here we report the $\mu^+\text{SR}$ measurements on Pr-doped $\text{La}_{1.9}\text{Pr}_{1.1}\text{Ni}_2\text{O}_{6.97}$ and oxygen-deficient $\text{La}_3\text{Ni}_2\text{O}_{6.63}$ polycrystalline under ambient pressure. The ZF- $\mu^+\text{SR}$ measurements reveal the long-range magnetic order in $\text{La}_{1.9}\text{Pr}_{1.1}\text{Ni}_2\text{O}_{6.97}$ under 161 K, while a short-range magnetic order is observed in $\text{La}_3\text{Ni}_2\text{O}_{6.63}$ below 30 K. Combined with previous $\mu^+\text{SR}$ result on $\text{La}_3\text{Ni}_2\text{O}_{6.92}$ [11], we found that

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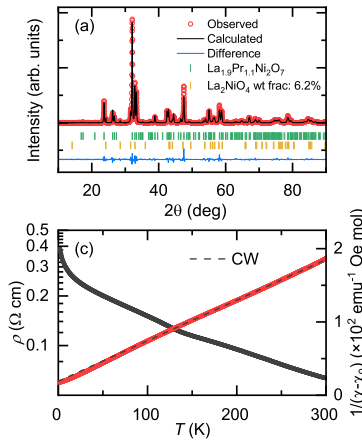


FIG. 1. (a) Rietveld refinement of powder x-ray diffraction data of $\text{La}_{1.9}\text{Pr}_{1.1}\text{Ni}_2\text{O}_{6.97}$. The refinement reveals the existence of La_2NiO_4 phase with weight fraction of 6.2(1)%. (b), (d) HAADF-STEM characterization of *c*-axis layer stacking in $\text{La}_{1.9}\text{Pr}_{1.1}\text{Ni}_2\text{O}_{6.97}$. The STEM images show little 327/214 intergrowth and 327/4310 intergrowth is nearly absent. (c) Temperature dependence of $\rho(T)$ (left axis) and $\chi(T)$ (right axis). The black dashed line shows the Curie-Weiss fitting between 100 and 300 K.

$\text{La}_{1.9}\text{Pr}_{1.1}\text{Ni}_2\text{O}_{6.97}$ exhibits higher T_N and narrower magnetic transition width. The exponent $\beta = 0.31$, being close to the value predicted by the 3D Ising model, provides evidence for a magnetic dimensional crossover driven by oxygen deficiencies. Furthermore, the long-range order is completely disrupted in the oxygen-deficient $\text{La}_3\text{Ni}_2\text{O}_{6.63}$. Our $\mu^+\text{SR}$ results reveal the destructive role of apical-oxygen deficiencies to both interplane and intraplane magnetic order. On the other hand, Pr doping enhances the Néel temperature T_N , but does not significantly alter the microscopic magnetism of the $\text{La}_3\text{Ni}_2\text{O}_7$.

Physical properties. Details on sample growth and experimental procedures are described in the Supplemental Material [42]. Figure 1(a) shows the x-ray diffraction pattern of polycrystalline $\text{La}_{1.9}\text{Pr}_{1.1}\text{Ni}_2\text{O}_{6.97}$. The Rietveld refinement confirms an orthorhombic structure (space group $Amam$, no. 63) with $a = 5.37608(19)$ Å, $b = 5.4518(2)$ Å, and $c = 20.3847(9)$ Å. The refinement reveals the existence of La_2NiO_4 with weight fraction of 6.2(1)%. The oxygen stoichiometry of the initial phase is determined by calculating the weight loss between the phases in TGA measurement, which results in $\text{La}_{1.9}\text{Pr}_{1.1}\text{Ni}_2\text{O}_{6.97(1)}$ [42]. The resultant products La_2O_3 , Pr_2O_3 , and Ni are confirmed by powder XRD measurement. As shown in Figs. 1(b) and 1(d), the STEM images of $\text{La}_{1.9}\text{Pr}_{1.1}\text{Ni}_2\text{O}_{6.97}$ show little 327/214 intergrowth and 327/4310 intergrowth is nearly absent, which is consistent with a previous study [16]. Temperature dependence of resistivity $\rho(T)$ and dc magnetic susceptibility $\chi(T)$ of polycrystalline $\text{La}_{1.9}\text{Pr}_{1.1}\text{Ni}_2\text{O}_{6.97}$ are plotted in Fig. 1(c). No sign of transition can be observed on $\rho(T)$. The paramagnetism of $\text{La}_{1.9}\text{Pr}_{1.1}\text{Ni}_2\text{O}_{6.97}$ can be described by the Curie-Weiss law and gives $\mu_{\text{eff}} = 3.45\mu_B/\text{Pr}$, which is close to an isolate Pr^{3+} with $3.58\mu_B$. The field dependence of magnetization curve further exhibits the minimal impact of La_2NiO_4 [42].

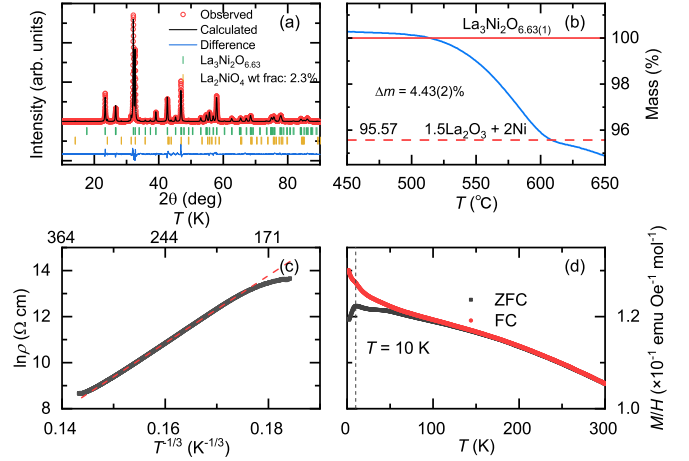


FIG. 2. (a) Rietveld refinement of powder x-ray diffraction data of $\text{La}_3\text{Ni}_2\text{O}_{6.63}$. The refinement reveals the existence of La_2NiO_4 phase with weight fraction of 2.3(1)%. (b) Thermogravimetric curves for $\text{La}_3\text{Ni}_2\text{O}_{6.63}$ in 10% H_2/Ar from 450 °C to 650 °C. (c) Temperature dependence of the resistivity $\rho(T)$. The dashed line exhibits the fitting with Eq. (1) between 185 K and 315 K. (d) Temperature dependence of magnetic susceptibility $\chi(T)$ with $\mu_0H = 0.1$ T. The magnetization curves split below 100 K between FC and ZFC setup.

The results of $\text{La}_3\text{Ni}_2\text{O}_{6.63}$ are summarized in Fig. 2. Figure 2(a) shows the x-ray diffraction pattern of polycrystalline $\text{La}_3\text{Ni}_2\text{O}_{6.63}$. The Rietveld refinement indicates the tetragonal structure (space group $I4/mmm$, no. 139) with $a = b = 3.8881(2)$ Å and $c = 20.1163(12)$ Å. The refinement also reveals the existence of La_2NiO_4 with weight fraction of 2.3(1)%. The oxygen stoichiometry of $\text{La}_3\text{Ni}_2\text{O}_{6.63}$ is determined by the TGA measurement. Temperature dependence of resistivity $\rho(T)$ of polycrystalline $\text{La}_3\text{Ni}_2\text{O}_{6.63}$ is plotted in Fig. 2(c). Below 165 K, the resistivity exceeded the measuring range of our equipment. $\rho(T)$ between 315 K and 185 K can be fitted to Mott's law for variable range hopping (VRH) for a 2D case [43]:

$$\rho = \rho_0 \exp \left[\left(\frac{T_0}{T} \right)^{\frac{1}{3}} \right], \quad (1)$$

where $T_0 = 3.1 \times 10^6$ K is a measure of localization and $\rho_0 = 2.9 \times 10^5$ Ω cm is a resistivity factor. The fit of $\rho(T)$ to Eq. (1) could be related to the Anderson localization due to oxygen vacancy disorder in the sample. Figure 2(d) displays the temperature dependence of dc magnetic susceptibility $\chi(T)$ measured under the magnetic field of $\mu_0H = 0.1$ T. The FC and ZFC magnetization curves split below 100 K and the ZFC curve exhibits a transition at 10 K. The field dependence of magnetization curve at 300 K reveal the existence of ferromagnetism [42], which could be contributed by elemental Ni introduced during the topochemical reduction process [37].

Muon spin relaxation. Representative muon spin relaxation spectra of $\text{La}_{1.9}\text{Pr}_{1.1}\text{Ni}_2\text{O}_{6.97}$ are plotted in Fig. 3(a). The muon spin relaxation above 185 K is primarily due to the Gaussian-distributed static nuclear dipolar moments, which can be described with a single Gaussian Kubo-Toyabe (KT) function [39,41]. An exponential term emerges below 170 K without detectable oscillation signals. An oscillation term

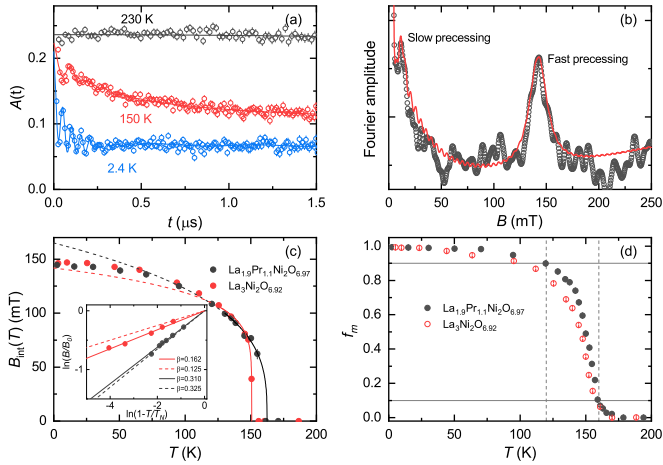


FIG. 3. (a) Temperature dependence of ZF- μ^+ SR spectra of $\text{La}_{1.9}\text{Pr}_{1.1}\text{Ni}_2\text{O}_{6.97}$ to 1.5 μs . The solid curves are the fits with Eq. (2). The 2.4 K data is fitted with two precessing components. (b) The Fourier transform diagram of ZF- μ^+ SR data measured at 2.4 K. The red line exhibits the fitting with two precessing components. (c) Temperature dependence of magnetic order parameter $B_{\text{int}}(T)$ deduced from the fitting with Eq. (2). The solid lines exhibit the fitting with the scaling function and the dashed lines indicate the extension of the fitting to low temperature region. Inset: scaling plot of $B_{\text{int}}(T)$. The dashed lines show the result of 2D Ising model ($\beta = 0.125$) and 3D Ising model ($\beta = 0.325$). (d) Magnetic volume fraction f_m extracted from wTF- μ^+ SR experiments. The black lines mark the temperature where f_m reaches 10% and 90%. The results of $\text{La}_3\text{Ni}_2\text{O}_7$ are cited from Ref. [11].

emerges below 160 K, with its volume fraction increasing upon cooling. The Fourier transform diagram of 2.4 K data shown in Fig. 3(a) is plotted in Fig. 3(b). The frequency on the x axis is divided by the muon gyromagnetic ratio ($\gamma_\mu/2\pi = 135.53 \text{ MHz/T}$) to be converted into magnetic field units. The Fourier spectrum at 2.4 K is manifested as two characteristic fields: $B_{\text{slow}} \approx 10 \text{ mT}$ and $B_{\text{fast}} \approx 140 \text{ mT}$. The ZF- μ^+ SR spectrum is therefore described with the following formula:

$$\frac{A_{\text{ZF}}(t)}{A_0} = (1 - f_m)G_{\text{KT}}(\sigma_{\text{ZF}}, t) + f_m[(1 - f_L)P_\perp(t) + f_L e^{-\lambda_L t}], \quad (2)$$

where

$$P_\perp(t) = \sum_{i=1}^2 f_i \cos(\gamma_\mu B_{\text{int},i} t) e^{-\lambda_i t}. \quad (3)$$

The first term of Eq. (2) describes the signal of the paramagnetic phase and the second term describes the signal of the magnetic phase. G_{KT} is the Gaussian Kubo-Toyabe function and f_m is the magnetic volume fraction. σ_{ZF} is found to be temperature independent in the paramagnetic state and is fixed to its average value $0.08 \mu\text{s}^{-1}$ during the fitting. Temperature dependence of λ_i and f_i are plotted in the Supplemental Material [42]. $f_L = 0.294$ is determined by the long term spectra of both ZF and wTF- μ^+ SR spectra. f_L is slightly smaller than the expected value $1/3$ in polycrystalline, which could be attributed to the spatial preferential orientation induced by the

pelletization process [44]. Fitting with Eq. (2) on the data of 2.4 K is plotted in Fig. 3(a). The volume fraction of the slow precessing term is too small to be resolved above 135 K and we cannot determine $B_{\text{slow}}(T)$ within an acceptable range of error (see the Supplemental Material [42]). The oscillation can be fitted with the summation of two cosine oscillations suggesting a commensurate magnetic order, which is consistent with the previous result on $\text{La}_3\text{Ni}_2\text{O}_{6.92}$ [11]. Temperature dependence of $B_{\text{int}}(T)$ extracted by Eq. (2) is plotted in Fig. 3(c). $B_{\text{int}}(T)$ is further fitted with the scaling function $(1 - T/T_N)^\beta$, which gives the transition temperature $T_N = 162.4(9) \text{ K}$ and the critical exponent $\beta = 0.31(2)$ [45]. The β exponent obtained from fitting is close to the value of 0.325 expected in the 3D Ising system [46]. $B_{\text{int}}(0) = 145(1) \text{ mT}$ is extracted by the power-law fitting [42]. The result of $\text{La}_3\text{Ni}_2\text{O}_{6.92}$ is also fitted by the scaling function and plotted in Fig. 3(c) for comparison. Considering the positive chemical pressure introduced by Pr substitution, a higher $T_N = 162.4 \text{ K}$ of $\text{La}_{1.9}\text{Pr}_{1.1}\text{Ni}_2\text{O}_{6.97}$ revealed by ZF- μ^+ SR is consistent with the result of pressurized μ^+ SR [10]. However, the Fourier transform diagram of $\text{La}_{1.9}\text{Pr}_{1.1}\text{Ni}_2\text{O}_{6.97}$ is different from $\text{La}_3\text{Ni}_2\text{O}_{6.92}$, which will be discussed later.

The magnetic volume fraction is extracted by the wTF- μ^+ SR experiment. In the wTF- μ^+ SR experiment, an external field perpendicular to the initial muon spin polarization direction is applied. The external field is relatively weak and will not change the internal field distribution of the magnetic phase. The muons stopping in the magnetic phase experience a broader field distribution and the muon spins depolarize rapidly. On the other hand, the muons stopping in the paramagnetic phase will precess along the external field with frequency $\omega = \gamma_\mu B_{\text{ext}}$. The wTF- μ^+ SR time spectra are shown in the Supplemental Material [42]. The spectra are fitted with

$$A(t) = A_{\text{PM}}(T) e^{-\frac{\sigma^2 t^2}{2}} \cos(\gamma_\mu B_{\text{ext}} t) + A_M(T) e^{-\lambda t}. \quad (4)$$

The first term describes the muons stopping in the paramagnetic phase. The second term describes the long time “1/3” component of the magnetic phase. The fitting is limited to the data after 0.5 μs to avoid the impact of the fast relaxation component of the magnetic phase. The magnetic volume fraction can be obtained by

$$f_m(T) = 1 - A_{\text{PM}}(T)/A_{\text{PM}}(300 \text{ K}). \quad (5)$$

The obtained magnetic volume fraction is plotted in Fig. 3(d), together with the result of $\text{La}_3\text{Ni}_2\text{O}_{6.92}$. The magnetic transition width of $\text{La}_{1.9}\text{Pr}_{1.1}\text{Ni}_2\text{O}_{6.97}$ is narrower, indicating a purer phase.

The μ^+ SR experiment results of $\text{La}_3\text{Ni}_2\text{O}_{6.63}$ are summarized in Fig. 4. wTF- μ^+ SR spectra are shown in the Supplemental Material [42]. There is no detectable oscillating component in the ZF- μ^+ SR spectrum. Instead, an initial asymmetry loss is observed below 300 K. Meanwhile, ZF and wTF- μ^+ SR spectra at 300 K split before and after applying the field, indicating the presence of ferromagnetism at 300 K, which is also confirmed by magnetization measurement [42]. The magnetic volume fraction obtained by Eqs. (4) and (5) is plotted in Fig. 4(b). $f_m(T)$ exhibits a two-step transition: the first one gradually reaches 50% of total amplitude from

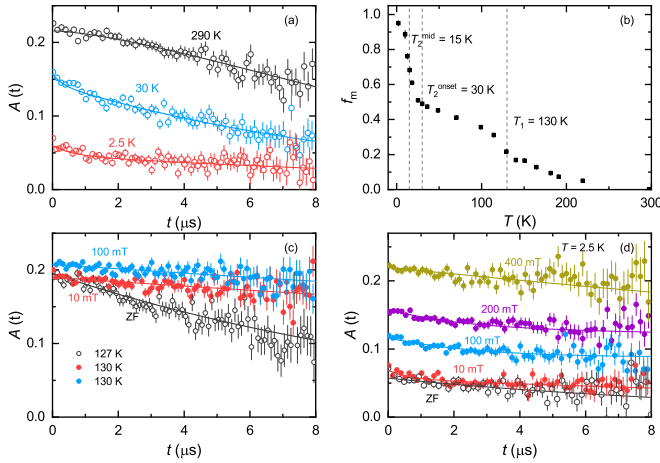


FIG. 4. (a) Temperature dependence of ZF- μ^+ SR spectra of $\text{La}_3\text{Ni}_2\text{O}_{6.63}$ to 1.5 μs . The solid curves are the fits with Eq. (6). (b) Temperature dependence of magnetic volume fraction $f_m(T)$ obtained by Eq. (5). (c), (d) LF- μ^+ SR spectrum measured at 130 K and 2.5 K. The solid lines are guides for eyes.

300 K to 30 K and a second sharper transition below 30 K finally reaches the value of 95%. The midpoint of the transition $T_2^{\text{mid}} = 15$ K is close to the antiferromagnetic transition temperature $T = 10$ K revealed by magnetic susceptibility [42]. To clarify the dynamic characteristic and magnitude of magnetism, longitudinal fields were applied at 130 K and 2.5 K. A longitudinal field ten times larger than the static internal magnetic field can fully decouple the muon spins from the internal field, which is manifested as the suppression of muon spin relaxation in the spectrum. On the other hand, a dynamic internal field is much more robust to the longitudinal field [41]. The LF- μ^+ SR spectra at 130 K and 2.5 K are shown in Figs. 4(c) and 4(d), respectively. At 130 K, the muon spins are totally decoupled from the local field under a 10 mT longitudinal field, indicating a static internal field of 1 mT order or even smaller. At 2.5 K, a 10 mT longitudinal field has almost no effect on the muon spin relaxation behavior. The loss of initial asymmetry is gradually suppressed by the longitudinal field on the order of 100 mT, indicating a static internal field of the same order of magnitude.

Based on the above information, the ZF- μ^+ SR spectra above 30 K are fitted with

$$A(t) = A_0(T)G_{\text{KT}}(\sigma, t)e^{-\lambda t}. \quad (6)$$

The KT term describes the muon spin relaxation due to the nuclear dipolar moments and the exponential decay term describes the additional depolarization rate due to the randomly distributed magnetic moment discussed later. $\sigma = 0.07 \mu\text{s}^{-1}$ is fixed during the fitting. The ZF- μ^+ SR spectra below 30 K are fitted by

$$A(t) = A_{\text{fast}}(T)e^{-\lambda_{\text{fast}}t} + A_{\text{tail}}(T)e^{-\lambda_{\text{tail}}t}. \quad (7)$$

The first term describes the early time fast relaxation and the second term describes the “1/3” tail of the magnetic signal. The fitting is shown in Fig. 4(a). The obtained ZF- μ^+ SR fitting parameters are summarized in the Supplemental Material

TABLE I. Exponents (α and β) and magnetic transition temperature (T_N) from ZF- μ^+ SR experiments.

Sample	α	β	T_N (K)	Ref.
$\text{La}_3\text{Ni}_2\text{O}_7$	1.73(7)	0.31(2)	156.5(1.1)	[15]
$\text{La}_{1.9}\text{Pr}_{1.1}\text{Ni}_2\text{O}_{6.97}$	1	0.31(2)	162.4(9)	This work
	1.9(2)	0.33(2)	161.4(5)	
$\text{La}_2\text{PrNi}_2\text{O}_{6.96}$	2.02(15)	0.35(2)	160.9(5)	[47]
$\text{La}_3\text{Ni}_2\text{O}_{6.92}$	1	0.16(2)	150.7(2)	[11]
	1.7(2)	0.26(2)	154.0(1.0)	

[42]. The loss of initial asymmetry A_0 indicates a short-range magnetism in $\text{La}_3\text{Ni}_2\text{O}_{6.63}$.

Discussion. The microscopic magnetization of $\text{La}_{1.9}\text{Pr}_{1.1}\text{Ni}_2\text{O}_{6.97}$ revealed by ZF- μ^+ SR is different from lightly oxygen-deficient $\text{La}_3\text{Ni}_2\text{O}_{6.92}$. First, the broadened high-field precession signal observed in $\text{La}_3\text{Ni}_2\text{O}_{6.92}$ is absent in $\text{La}_{1.9}\text{Pr}_{1.1}\text{Ni}_2\text{O}_{6.97}$. This can be explained by a better phase purity and a more uniform oxygen distribution. Second, the β exponent changes from 0.16 to 0.31. Though substitution of Pr for La introduces positive chemical pressure, similar changes were not observed in the μ^+ SR experiment under pressure [10]. Therefore, such a difference cannot be simply attributed to the reduction of interlayer distance. The μ^+ SR results for 327 samples are summarized in Table I. β exponent is sensitive to oxygen content, while T_N is sensitive to the substitution of Pr. As oxygen vacancies are known to preferentially occupy apical sites [33], the resulting disruption of interlayer antiferromagnetic exchange pathways between the adjacent NiO planes leads to a reduced magnetic dimensionality. On the other hand, Pr doping introduces a positive chemical pressure that enhances T_N , which is also supported by μ^+ SR measurements under external pressure [10,47].

We next turn to the magnetism of $\text{La}_3\text{Ni}_2\text{O}_{6.63}$ observed above 30 K. An extrinsic origin of the magnetism detected by μ^+ SR can be ruled out based on the following experimental evidence. (1) The magnetic volume fraction exhibit temperature dependence, reaching 20% at 130 K and 50% at 30 K. A signal originating from magnetic impurities would not exhibit such a pronounced temperature dependence and a volume fraction as high as 20% is unlikely to be missed by PXRD. (2) As shown in Fig. 4(c), the LF- μ^+ SR spectrum has already been quenched by a field of 10 mT. This indicates that the magnetic field sensed by most muons at high temperature (130 K) does not exceed 1 mT. This rules out the magnetism originating from RP-type nickelates, whose internal fields sensed by muons are on the order of 100 mT [11,48–50]. (3) The La_2NiO_4 content determined by PXRD is about 2.3%, which is insufficient to account for the magnetic volume fraction on the order of several tens of percent. Therefore, the weak high-temperature magnetism appears to be an intrinsic property of $\text{La}_3\text{Ni}_2\text{O}_{6.63}$. Such magnetism can be related to the magnetic moment localized near the oxygen vacancies proposed by real-space random-phase-approximation calculation [19]. These moments can further form short-range spatial correlations, leading to the loss of initial asymmetry in μ^+ SR spectra. The fact that the resistivity follows a two-dimensional VRH behavior further supports the presence of

localized electronic states in this temperature regime, which may originate from oxygen vacancies and lead to the formation of localized magnetic moments.

The second transition below 30 K may originate from the intrinsic magnetism of the 327 phase. First, as shown in Fig. 4(d), the internal magnetic field sensed by muons is on the order of 100 mT. Second, the magnetic volume fraction reaches 95% at 2.5 K. The absence of an oscillating signal and a further loss of initial asymmetry indicate that the long-range order breaks into the short-range order, which could be due to the spinless nickel site induced by oxygen vacancies, as suggested by DFT calculations [51].

The μ^+ SR experiments on three $\text{La}_{3-x}\text{Pr}_x\text{Ni}_2\text{O}_{7-\delta}$ samples reveal the destructive role of apical-oxygen deficiencies to both intraplane and interplane magnetic correlation. The ZF- μ^+ SR spectra of $\text{La}_{1.9}\text{Pr}_{1.1}\text{Ni}_2\text{O}_{6.97}$ can be described with the summation of two single cosine functions and indicating a commensurate 3D magnetic structure. For $\text{La}_3\text{Ni}_2\text{O}_{6.92}$, the internal magnetic field distribution is broadened due to oxygen deficiencies, indicating a less-ordered long-range magnetic structure. When the oxygen deficiencies are further increased, the long-range magnetic order breaks down into short-range order and the magnetic transition temperature is greatly reduced to $T_2^{\text{mid}} = 15$ K in $\text{La}_3\text{Ni}_2\text{O}_{6.63}$. Since muons detect magnetism on a shorter length scale compared to neutrons, the μ^+ SR result of $\text{La}_3\text{Ni}_2\text{O}_{6.63}$ can help to explain the absence of long-range magnetic order in early NPD measurements.

Conclusion. In conclusion, the microscopic magnetism of $\text{La}_{1.9}\text{Pr}_{1.1}\text{Ni}_2\text{O}_{6.97}$ and $\text{La}_3\text{Ni}_2\text{O}_{6.63}$ has been investigated using the μ^+ SR technique. Bulk commensurate long-range magnetic order below 162.4 K is confirmed in

$\text{La}_{1.9}\text{Pr}_{1.1}\text{Ni}_2\text{O}_{6.97}$. The extracted β exponent is close to the 3D Ising model, indicating an enhanced interlayer coupling compared to lightly oxygen-deficient $\text{La}_3\text{Ni}_2\text{O}_{6.92}$. On the other hand, two types of magnetism are observed in $\text{La}_3\text{Ni}_2\text{O}_{6.63}$. The magnetism over 30 K might be related to the magnetic moments localized near the oxygen vacancies and the order below 30 K reflects the intrinsic magnetic order of the $\text{La}_3\text{Ni}_2\text{O}_{7-\delta}$ phase. The long-range order is completely disrupted by the oxygen vacancies, resulting in the experimental observation of short-range magnetic correlations. Our μ^+ SR experiments reveal the destructive effect of apical-oxygen deficiencies on both intraplane and interplane magnetic correlation. On the other hand, Pr doping does not significantly alter the magnetism of $\text{La}_3\text{Ni}_2\text{O}_7$. These results offer a comprehensive perspective on how oxygen vacancies and Pr doping influence the microscopic magnetism in the Ruddlesden-Popper nickelates.

Acknowledgments. We are grateful to B. Hitt and D. Arsenau of the TRIUMF CMMS for assistance during the experiments. This research was funded by the National Key Research and Development Program of China, Grant No. 2022YFA1402203, the National Natural Science Foundations of China, Grants No. 12174065 and No. 62171136, Innovation Program for Quantum Science and Technology (Grant No. 2024ZD0300104), and the Shanghai Municipal Science and Technology Major Project (Grant No. 2019SHZDZX01). Y.G. acknowledges the National Key R&D Program of China (Grant No. 2023YFA1406100) and the Double First-Class Initiative Fund of ShanghaiTech University.

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

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