

Bulk superconductivity up to 96 K in pressurized nickelate single crystals

Corresponding Author: Professor Junjie Zhang

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This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Version 0:

Reviewer comments:

Referee #1

(Remarks to the Author)

The manuscript reports on the ambient pressure flux growth of bilayer nickelate single crystals, $\text{La}_{3-x}\text{R}_x\text{Ni}_2\text{O}_7$ -d ($\text{R} = \text{Pr-Er}$; $x \leq 2.7$), with superconductivity observed up to 91 K under high pressure. The authors highlight two key aspects of their work: (1) their flux-growth method as an alternative to the floating zone technique, which they claim produces cleaner crystals, and (2) an enhanced superconducting transition temperature (T_c), which they attribute to increased Sm substitution at the La site. While the topic is of interest, the manuscript lacks self-consistency, and its significance does not meet the high standards required for publication in Nature.

A major concern arises from the inconsistency in the resistance data presented for two different $\text{La}_2\text{SmNi}_2\text{O}_7$ -d crystals (labeled as Crystal 1 and Crystal 2). Crystal 2 exhibits a sharp superconducting transition around 80–90 K under pressure, while Crystal 1 shows at least two transitions, one near 80–90 K and another around 50 K, with no complete zero-resistance state. This discrepancy raises concerns about sample homogeneity and reproducibility. The authors claim that flux growth yields purer single crystals compared to the floating zone method, which has been criticized for producing inhomogeneous products with varied superconducting properties. However, the significant variation between their two flux-grown samples contradicts this claim and weakens the argument for the superiority of their growth method.

Additionally, the manuscript lacks clarity regarding the proposed approach to achieving higher T_c . The authors suggest that increasing Sm content at the La site leads to an enhanced superconducting transition, yet they do not provide a clear rationale or sufficient evidence to support this claim. A more detailed discussion is necessary to establish a compelling correlation between Sm substitution and T_c enhancement.

In summary, while this work presents an alternative synthesis method for bilayer nickelates, it does not offer a sufficiently novel or well-substantiated breakthrough to warrant publication in Nature. Strengthening the scientific justification, addressing inconsistencies in sample behavior, and providing a clearer mechanism for T_c enhancement would be necessary for broader impact.

Referee #2

(Remarks to the Author)

Li et al. report the growth of bilayer La-nickelate single crystals with various rare-earth substitutions using a straightforward ambient pressure flux method. They provide comprehensive characterization of the crystals by powder and single-crystal X-ray diffraction, nuclear quadrupole resonance (NQR), energy-dispersive spectroscopy (EDS), and scanning transmission electron microscopy (STEM). Among the investigated compositions, Sm-substituted crystals exhibit the highest phase purity, and in high-pressure transport measurements, a superconducting transition onset temperature of 91 K at 22.1 GPa is observed.

From a technical standpoint, the execution of both crystal growth and characterization by Li et al. is sound. Furthermore, interest in the topic of superconducting nickelates has recently surged within condensed matter physics, materials synthesis, and solid-state chemistry, particularly since the discovery of superconductivity in $\text{La}_3\text{Ni}_2\text{O}_7$ with a T_c of 80 K above pressures of 14 GPa [1]. Nonetheless, critical challenges persist in the field, particularly: (1) How can the synthesis process be optimized to enhance sample quality? and (2) To what extent can the T_c be pushed higher?

To some extent, the study by Li et al. addresses both of these questions. Specifically, theoretical predictions have suggested that rare-earth substitution with different ionic radii could either increase or decrease T_c [5,6]. In the present manuscript, the authors report that Sm, which has a smaller ionic radius than La, yields a T_c of 91 K. However, given that the previous record T_c in $\text{La}_3\text{Ni}_2\text{O}_7$ powder was 86 K [31], this enhancement appears rather modest. Moreover, while they have synthesized a comprehensive series of rare-earth substitutions, they present high-pressure transport data only for the Sm case. A rigorous understanding of how T_c evolves with decreasing ionic radii would require a systematic study of multiple compositions under high pressure.

Similarly, the study falls short of providing systematic insights into how sample quality can be improved. It was already known that Pr substitution enhances phase purity [33], and among the considered rare-earths, Sm appears to have grown serendipitously well under their applied conditions, while other compositions exhibit significant impurity phases. However, the authors do not offer a deeper explanation for why specifically Sm yields high-quality crystals, nor do they outline clear strategies for further improvements and T_c enhancements.

In summary, this study represents an important contribution for researchers working in the field of nickelate superconductors, particularly for those involved in the sample synthesis. It is also encouraging to see that T_c can be enhanced, even if the demonstrated improvement is modest. However, I do not see compelling reasons why this paper meets the stringent criteria for publication in Nature and would be of broad interest to a general audience. Instead, it would be better suited for a specialized journal focusing on materials synthesis and characterization.

In addition, I have several minor comments:

The authors mention that their as-grown crystals exhibit a different space group than previously reported bilayer nickelates and are likely oxygen-deficient, necessitating annealing. Can they comment on whether the annealing process alters the space group? Also, is the annealing step required for superconductivity to emerge under high pressure?

The authors may elaborate on why Sm appears to be the "sweet spot" for substitution, while all other rare-earth substitutions result in lower sample quality. Specifically, in Figs. 2b,c, there seems to be a change in trend in the lattice structure evolution beyond Nd and Sm when even smaller ions are introduced. How can they be sure this is a real effect rather than a consequence of worsening sample quality affecting their measurements? Similarly, Fig. 2a indicates that the realized substitution levels vary across different rare-earths, but the way the data is plotted in Figs. 2b,c suggests the samples are directly comparable. The authors should clarify whether their observed trends are due to intrinsic material properties or variations in sample composition.

The abstract claims that their results indicate "remarkable consistency with cuprates possessing bilayer copper-oxygen planes, suggesting a potential universal mechanism governing high-temperature superconductivity in these isostructural bilayer transition metal oxides." However, it is not obvious to me how this claim is supported by the findings presented in the manuscript. The authors should clarify how their findings substantiate this statement or revise the abstract to better reflect the study's conclusions.

Referee #3

(Remarks to the Author)

A. Summary of the key results

This work successfully synthesized $\text{La}_{3-x}\text{R}_x\text{Ni}_2\text{O}_{7-\delta}$ ($\text{R}=\text{Pr-Er}$, $x \leq 2.7$) single crystals using a flux growth method at ambient pressure, eliminating the need for high-pressure synthesis. Among these compounds, $\text{La}_2\text{SmNi}_2\text{O}_{7-\delta}$ demonstrated superior quality and superconducting behavior. After annealing in high oxygen pressure, $\text{La}_2\text{SmNi}_2\text{O}_{7-\delta}$ exhibited a superconducting transition onset temperature of up to 91 K at 22.1 GPa.

B. Originality and significance: if not novel, please include reference

Once a new high- T_c superconductor is discovered, it is crucial to ensure the reproducibility and improve the sample quality. In this context, the development of crystal growth techniques represents a valuable contribution to the field. However, I find the overall impact of the paper to be limited, particularly due to the lack of new insights into the physics of superconductivity or the structure of the superconducting phase.

C. Data & methodology: validity of approach, quality of data, quality of presentation

I do not find serious problems with the quality of the data. Please see E regarding the quality of the presentation.

D. Appropriate use of statistics and treatment of uncertainties

Looks appropriate.

E. Conclusions: robustness, validity, reliability

Here I list several comments and concerns:

1. In the abstract, the authors state “but also providing a direction for discovering superconducting nickelates with higher T_c .” This sentence is too abstract. What “direction” are the authors talking about?
2. In the abstract, the authors write “suggesting a potential universal mechanism governing high-temperature superconductivity in these isostructural bilayer transition metal oxides.” However, this claim lacks sufficient justification and is not supported by a firm theoretical or experimental foundation.
Broadly speaking, there are two approaches (weak coupling and strong coupling) for considering the pairing mechanism in high-temperature superconductors. In the weak coupling approach, the shape of the Fermi surface plays an important role. However, bilayer cuprates and nickelates differ in their band structures and electron filling, resulting in distinct Fermi surfaces. Thus, a universal mechanism based on weak coupling arguments cannot be justified. In the strong coupling approach, local electron correlations dominate. In cuprates, the x^2-y^2 orbital is nearly half-filled, leading to localized $S=1/2$ moments. In contrast, in nickelates, both a nearly half-filled z^2 orbital and a nearly quarter-filled x^2-y^2 orbital are involved, indicating a fundamentally different local electronic environment. Therefore, the underlying local physics is also not universal.
Why did the authors state this? Only from T_c ? Without firm experimental indication of a universal mechanism, I suggest the author delete this sentence.
3. The authors report a monoclinic $P2_1/m$ space group, which is different from the previous report. I recommend that the authors elaborate on this issue. In particular, the authors state that they annealed under oxygen pressure. Is there any information on the crystal structure after annealing?
4. Related to 3. I find it interesting that the effect of chemical pressure is highly anisotropic between the a and b axes. For example, when La is replaced by Sm , the b -axis decreases, and the a -axis increases slightly. What is the origin of the a -axis expansion?
5. Related to 3. I believe readers will be most interested in the crystal and electronic structures under high pressure. However, this crucial information is missing from the manuscript. While I understand that such measurements may be experimentally challenging, their absence diminishes the overall impact of the paper.
6. Although the authors discuss onset T_c , I believe that $T_c(\text{zero})$ is as important as $T_c(\text{onset})$. I recommend the authors properly mention this in the paper.
7. (optional) Did the authors observe superconductivity for their $La_3Ni_2O_{7-\delta}$ samples under pressure?

F. Suggested improvements: experiments, data for possible revision

All issues raised in E need to be carefully reexamined.

G. References: appropriate credit to previous work?

I do not find serious problems.

H. Clarity and context: lucidity of abstract/summary, appropriateness of abstract, introduction and conclusions

Please see E.

Version 2:

Reviewer comments:

Referee #2

(Remarks to the Author)

First, a few general remarks after going through the authors' replies to the three referee reports:

The repeated assertion by the authors that their "latest results represent a significant breakthrough, analogous to the discovery of YBCO in cuprates" is, frankly, greatly overstated. In my opinion, the impact of their work will be orders of magnitude lower for the field of high-temperature superconductivity compared to the discovery of YBCO.

The authors frequently argue that previous reports failed to demonstrate a clear Meissner effect in RP nickelates, claiming: "... there is no clear evidence of Meissner effect, in particular when a nickelate in a magnetic field is cooled below T_c , all or part of the magnetic field within the material is expelled or not remains elusive." Are they referring specifically to the absence of a kink-like anomaly in the field-cooled (FC) branch of DC susceptibility curves? Admittedly, the ZFC and FC curves for $\text{La}_2\text{SmNi}_2\text{O}_7$ in their current manuscript are exceptionally well resolved and stand out compared to earlier work. However, subtle FC anomalies also appear to be present in prior studies, including arXiv:2404.11369 and Extended Data Fig. 10 of Zhu et al., Nature 631, 531–536 (2024).

In response to concerns raised about the lack of systematic annealing or pressure-dependent measurements across the entire sample series, the authors complain that this would be too time-consuming. However, this is not a scientifically valid justification for omitting key control data! Nonetheless, the revised version shifts focus more strongly to the Sm-based compound, reducing the importance of comparisons to samples with other rare-earths. Therefore, this omission becomes less problematic for the current version.

Concerning the authors' replies specifically to my comments: I had initial concerns about the actual substitution levels realized in the rare-earth series, and whether the structural trends presented were robust. In this context, the authors undertook appreciable effort to provide additional characterization measurements, mitigating my concerns. In general, the new high-pressure DC susceptibility, high-pressure XRD, and TGA measurements are commendable and increase the significance of the paper.

However, the comparability of the rare-earth series presented in Figs. 1k and 1l remains limited due to variation in substitution levels across samples. This compromises the interpretability of the trends shown in these panels, and the way the data are presented there could be reconsidered.

On the other hand, I am positively impressed by the newly reported superconducting onset at 96 K in the $\text{La}_{1.57}\text{Sm}_{1.43}\text{Ni}_2\text{O}_7$ sample. While zero resistivity is not reached and the transition appears two-step-like, the result is nonetheless very remarkable. After all, the overall message of Fig. 1l is compelling, and the manuscript proposes a plausible and empirically grounded strategy for enhancing T_c in the RP nickelates, with the added comparison to previous nickelate work in Fig. 5b contextualizing the progress.

Taken together, and when considering the standard defined by other recent nickelate papers published in Nature, I consider this manuscript to be suitable for publication in Nature too. It presents noteworthy findings and clear progress over previous work, even if several aspects are not fully resolved.

However, the statement in the manuscript that it is "likely" to obtain superconductivity near 100 K in $\text{La}_{0.87}\text{Nd}_{2.13}\text{Ni}_2\text{O}_7$ is not acceptable for publication and needs to be toned down. This is pure speculation based on a hypothesis derived from empirical observations on other samples. In fact, the authors do not present a robust theoretical rationale for why the smallest lattice parameter and/or the largest in-plane lattice distortion $(a-b)/(a+b)$ (see Fig. 1k and 1l) necessarily leads to the highest T_c . If they insist on making such strong claims about this Nd-based sample, they should rather attempt to detect superconductivity in this sample, which is apparently available to them.

Referee #3

(Remarks to the Author)

In the revised version, the authors have significantly improved the quality of the experimental results. The results presented in this paper represent an important contribution to the field of high-temperature superconductivity.

Below, I provide several comments.

1. It is great that the authors achieved structural analysis under high pressure. However, I feel that new insights into the physics of superconductivity are still lacking. For example, the statement that "tetragonal structure may not be a prerequisite for superconductivity to appear in this bilayer nickelate" relaxes the structural constraint, but it does not narrow down the conditions for realizing superconductivity.

2. (Related to 1) The authors discuss the conditions for achieving higher superconducting transition temperatures (T_c) based on the anisotropy of the lattice constants $(a-b)/(a+b)$ at ambient pressure. While this is interesting to some extent, superconductivity actually emerges when this anisotropy becomes weaker or disappears. Therefore, I am not sure whether this anisotropy should be regarded as a reliable indicator.

3. (Related to 2) The authors state "Following this trend, it is likely to obtain superconductivity near 100 K in the bilayer nickelate $\text{La}_{0.87}\text{Nd}_{2.13}\text{Ni}_2\text{O}_{7-\delta}$ under high pressures." If this is merely speculation, I would recommend removing this statement.

4. The authors conduct various experiments using different samples. I think that the use of different samples should be more explicitly mentioned in both the main text and the abstract.

5. Figure 4h is a bit difficult to understand. In particular, the data points for sample #10 and the Tc data points overlap, making the figure unclear. I recommend improving the figure to enhance its readability.

Version 3:

Reviewer comments:

Referee #2

(Remarks to the Author)

The authors have comprehensively addressed the concerns I previously raised. They have appropriately revised the text to tone down earlier questionable assertions and have added new high-pressure transport data for the sample with the highest Tc. Notably, the two-step transition initially reported is no longer observed, whereas now a cleaner single-step transition is observed. I have no further objections to the publication of this work.

Referee #3

(Remarks to the Author)

I have no additional comments.

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Response to Referees' Comments

Below we detail our responses to referees' comments point-by-point and explain how we revised the manuscript accordingly.

Referee #1

The manuscript reports on the ambient pressure flux growth of bilayer nickelate single crystals, $\text{La}_{3-x}\text{R}_x\text{Ni}_2\text{O}_{7-\delta}$ ($\text{R} = \text{Pr-Er}$; $x \leq 2.7$), with superconductivity observed up to 91 K under high pressure. The authors highlight two key aspects of their work: (1) their flux-growth method as an alternative to the floating zone technique, which they claim produces cleaner crystals, and (2) an enhanced superconducting transition temperature (T_c), which they attribute to increased Sm substitution at the La site. While the topic is of interest, the manuscript lacks self-consistency, and its significance does not meet the high standards required for publication in *Nature*.

Response: We thank the Referee for agreeing that the topic is of interest, and for pointing out the issues of our manuscript. We have added more data and addressed the Referee's concerns point-by-point.

A major concern arises from the inconsistency in the resistance data presented for two different $\text{La}_2\text{SmNi}_2\text{O}_{7-\delta}$ crystals (labeled as Crystal 1 and Crystal 2). Crystal 2 exhibits a sharp superconducting transition around 80–90 K under pressure, while Crystal 1 shows at least two transitions, one near 80–90 K and another around 50 K, with no complete zero-resistance state. This discrepancy raises concerns about sample homogeneity and reproducibility. The authors claim that flux growth yields purer single crystals compared to the floating zone method, which has been criticized for producing inhomogeneous products with varied superconducting properties. However, the significant variation between their two flux-grown samples contradicts this claim and weakens the argument for the superiority of their growth method.

Response: We totally understand the Referee's concern about our sample homogeneity and reproducibility in the bilayer nickelate system.

For undoped $\text{La}_3\text{Ni}_2\text{O}_7$, the sample-dependent issues have been discussed in a number of papers, here we just list a few: (1) Hou *et al. Chin. Phys. Lett.* 40, 117302 (2023); (2) Zhou *et al. arXiv:* 2311.12631, later published at *Matter Radiat. Extremes.* 10, 027801(2025); (3) Zhang *et al. Nat. Phys.* 20, 1269-1273 (2024); (4) Dong *et al. Nature* 630, 847-852 (2024); (5) Wang *et al. Nature* 634, 579-584 (2024); (6) Chen *et al. J. Am. Chem. Soc.* 146, 3640-3645 (2024); (7) Puphal *et al. Phys. Rev. Lett.* 133, 146002 (2024); and (8) Wang *et al. Inorg. Chem.* 63, 5020-5026 (2024). Many discrepancies and controversies in the literature are rooted in the sample inhomogeneity of the $\text{La}_3\text{Ni}_2\text{O}_7$ crystals grown with high-pressure floating zone method. In order to understand the nature of high- T_c superconductivity in nickelates, the synthesis of high-quality and reproducible single crystals thus become one of the core tasks of the research on this system [Wang *et al. Chin. Phys. Lett.* 41, 077402 (2024)].

Given the difficulties in obtaining pure-phase single crystals via high pressure floating zone techniques, we thus developed a new ambient-pressure flux method, which can be used to prepare high quality single crystals of bilayer nickelates with well-controlled chemical homogeneity. This enables us to perform comprehensive examinations on its composition, average and local crystal structure, as shown in **Fig. R1** (revised **Fig. 2**). We also performed magnetic susceptibility measurements (**Fig. R2**) and Rietveld refinements on X-ray powder diffraction data (**Fig. R3**) on samples from different batches, and they show excellent reproducibility.

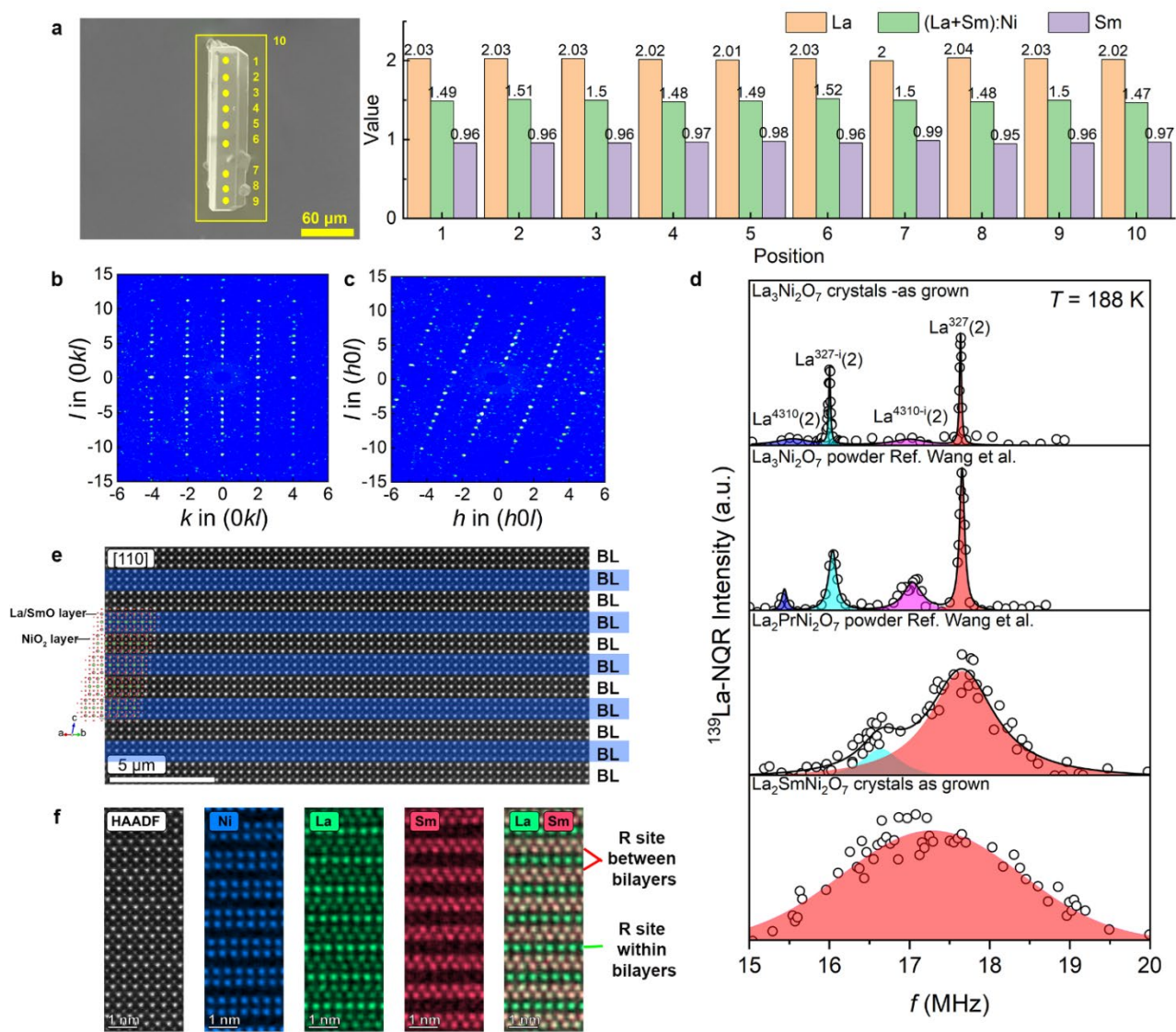


Fig. R1 (revised **Fig. 2**) Crystal quality of as-grown $\text{La}_2\text{SmNi}_2\text{O}_{7-\delta}$ single crystals.

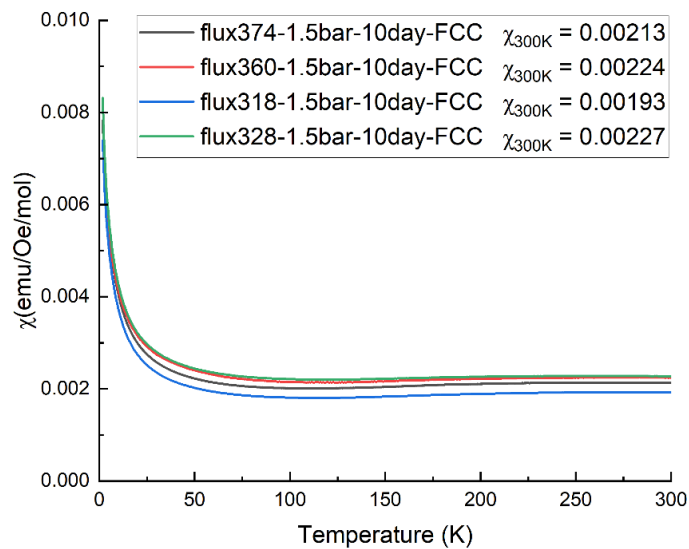


Fig. R2 Magnetic susceptibility data of pulverized $\text{La}_2\text{SmNi}_2\text{O}_{7-\delta}$ single crystals from different batches. Note FCC indicates field cooling and data collection on cooling.

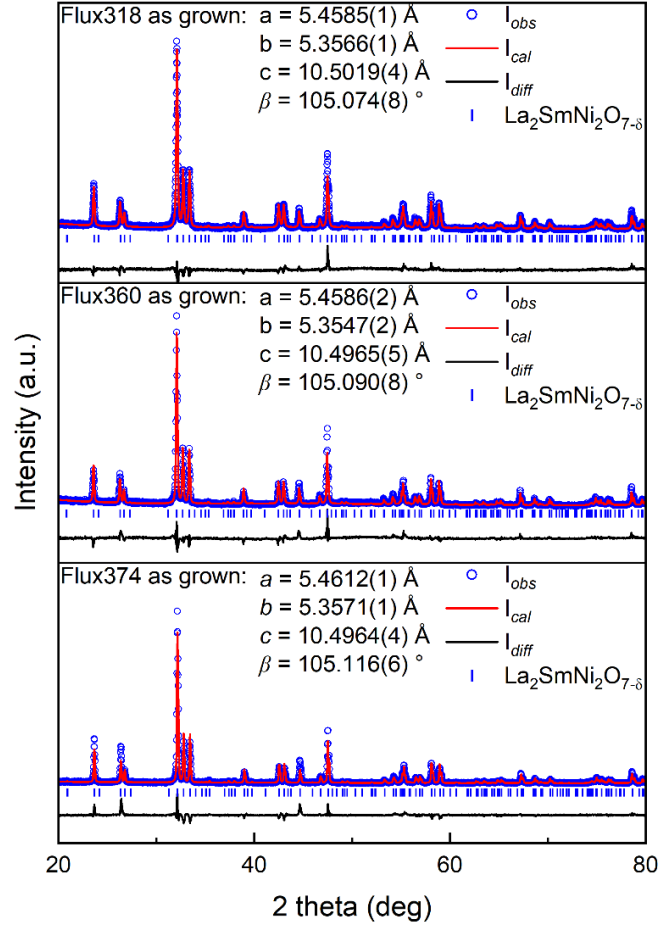


Fig. R3 Rietveld refinements on powder diffraction data of pulverized $\text{La}_2\text{SmNi}_2\text{O}_{7-\delta}$ single crystals from different batches of growth.

Our available transport measurements of $\text{La}_2\text{SmNi}_2\text{O}_{7-\delta}$ single crystals under high pressure also showed excellent reproducibility. So far, we have measured seven different single crystal samples from different batches (see [Table R1](#) for the samples' information and [Fig. R4-5](#) for the high-pressure resistivity data). These data were collected at HPSTAR from Dec. 2024 to Mar. 2025 by using the DAC up to 31.5 GPa. We first measured the as-grown single crystals, a sharp transition occurs at 87 K but no zero resistivity was obtained (Crystal #1) probably due to oxygen defects. We then optimized post-annealing conditions. Among them, Crystal #3 was measured using paraffin as the pressure transmitting medium (PTM) ([Fig. R4c](#)). An apparent drop in resistance starting at 91 K was observed, indicating a superconducting transition. At 10 K, the residual resistance is only 5.5% of that prior to the transition. Notably, the observation of similar behaviors in the electrical resistance measured along two orthogonal directions separated by approximately 90° demonstrates excellent homogeneity in the single crystal, and suggests that filamentary superconductivity is unlikely. The broad feature at ~ 50 K ([Fig. R4d](#)) is not intrinsic but due to PTM's inhomogeneity of the pressure environment. Indeed, the effects of PTM has been discussed previously in the literature [Hou *et al.* *Chin. Phys. Lett.* 40, 117302 (2023); Wen *et al.* arXiv: 2410.10275 (2024); Shi *et al.* arXiv: 2502.01018 (2025)]. All other measurements were performed using He as PTM. The use of helium, the best PTM for hydrostatic pressure, in conjunction with the four-probe method for high-pressure electrical transport measurements on single-crystal samples, ensured the high reliability of the experimental results. These data from different batches highlight the excellent reproducibility of our results.

Table R1. Information of La₂SmNi₂O_{7-δ} single crystals studied from different batches

	Growth No.	Post-annealing conditions	Measurement conditions	Results	Measurement date	Note
1	Flux318	As-grown	Nuclear quadrupole resonance (NQR)	Absence of intergrowth of R-P phases	08/23/2024	Data collected prior to the first submission (02/15/2025)
2	Flux318	As-grown	Magnetic susceptibility (MT)	$\chi_{300K}=0.00218$	09/24/2024	
3	Flux328	As-grown	MT	$\chi_{300K}=0.00214$	09/26/2024	
4	Flux318	pO ₂ = 1.5 bar, 600 °C, 10 days	Scanning transmission electron microscopy (STEM)	Clean bilayer structure without intergrowth	11/04/2024	
5	Flux360	As-grown	High-pressure resistivity (HP RT) @ HPSTAR using He as PTM	$T_c^{\text{onset}}=87$ K @ 21 GPa (Crystal #1, Fig. R4a)	12/16/2024	
6	Flux360	pO ₂ = 2.5 bar, 600 °C, 10 days	HP RT @ HPSTAR using He as PTM	$T_c^{\text{onset}}=88$ K @ 21.4 GPa (Crystal #2, Fig. R4b)	12/21/2024	
7	Flux318	pO ₂ = 1.5 bar, 600°C, 10 days	HP RT @ HPSTAR using paraffin as PTM	$T_c^{\text{onset}}=91$ K @ 22.1 GPa (Crystal #3, Fig. R4c,d,e)	12/30/2024	
8	Flux318		HP RT @ HPSTAR using He as PTM	$T_c^{\text{onset}}=91$ K @ 22.1 GPa (Crystal #4, Fig. R4f)	01/18/2025	
9	Flux374	pO ₂ = 1.5 bar, 600°C, 10 days	Thermogravimetric Analysis (TGA)	7.02(1)	02/18/2025	New data added to the revised manuscript
10	Flux360	pO ₂ = 1.5 bar, 600°C, 7 days	HP RT @ HPSTAR using He as PTM	$T_c^{\text{onset}}=91$ K @ 20.9 GPa (Crystal #5, Fig. R4g,h)	02/25/2025	
11	Flux360	pO ₂ = 1.5 bar, 600°C, 10 days	HP RT @ HPSTAR using He as PTM	$T_c^{\text{onset}}=92$ K @ 21.6 GPa (Crystal #6, Fig. R5a,b,c)	03/23/2025	
12	Flux360		High-pressure synchrotron X-ray powder diffraction (HP-XRPD)	Pulverized Crystal #8, Fig. R6	03/26/2025	
13	Flux360		HP-XRPD	Pulverized Crystal #9, Fig. R6	03/27/2025	
14	Flux360		HP RT @ HPSTAR using He as PTM	$T_c^{\text{onset}}=92$ K @ 21.2 GPa (Crystal #7, Fig. R5e)	03/29/2025	
15	Flux318		MT	$\chi_{300K}=0.0021(2)$	04/03/2025	

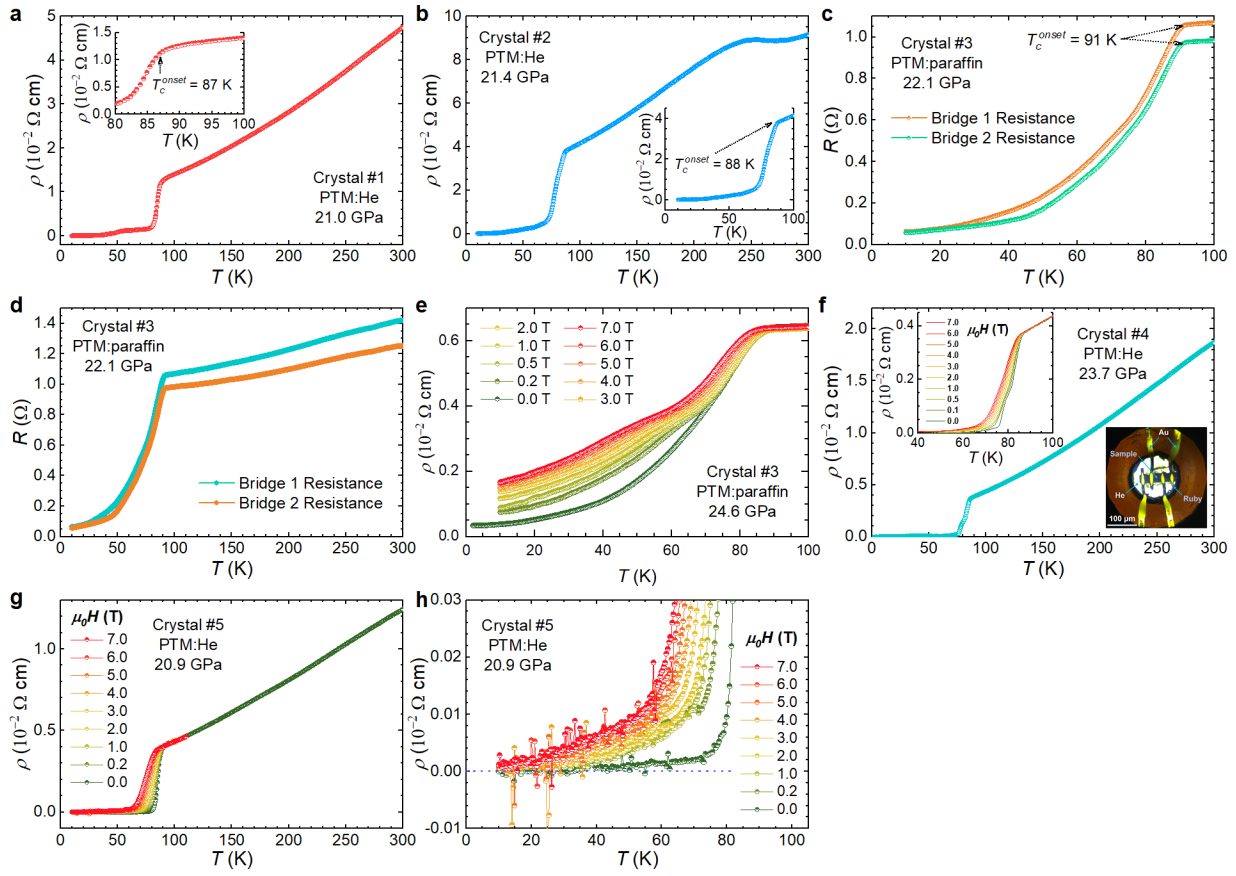


Fig. R4 (revised **Extended Data Fig. 5**) High pressure transport measurements on single crystals (Crystal #1-#5) of $\text{La}_2\text{SmNi}_2\text{O}_{7-\delta}$.

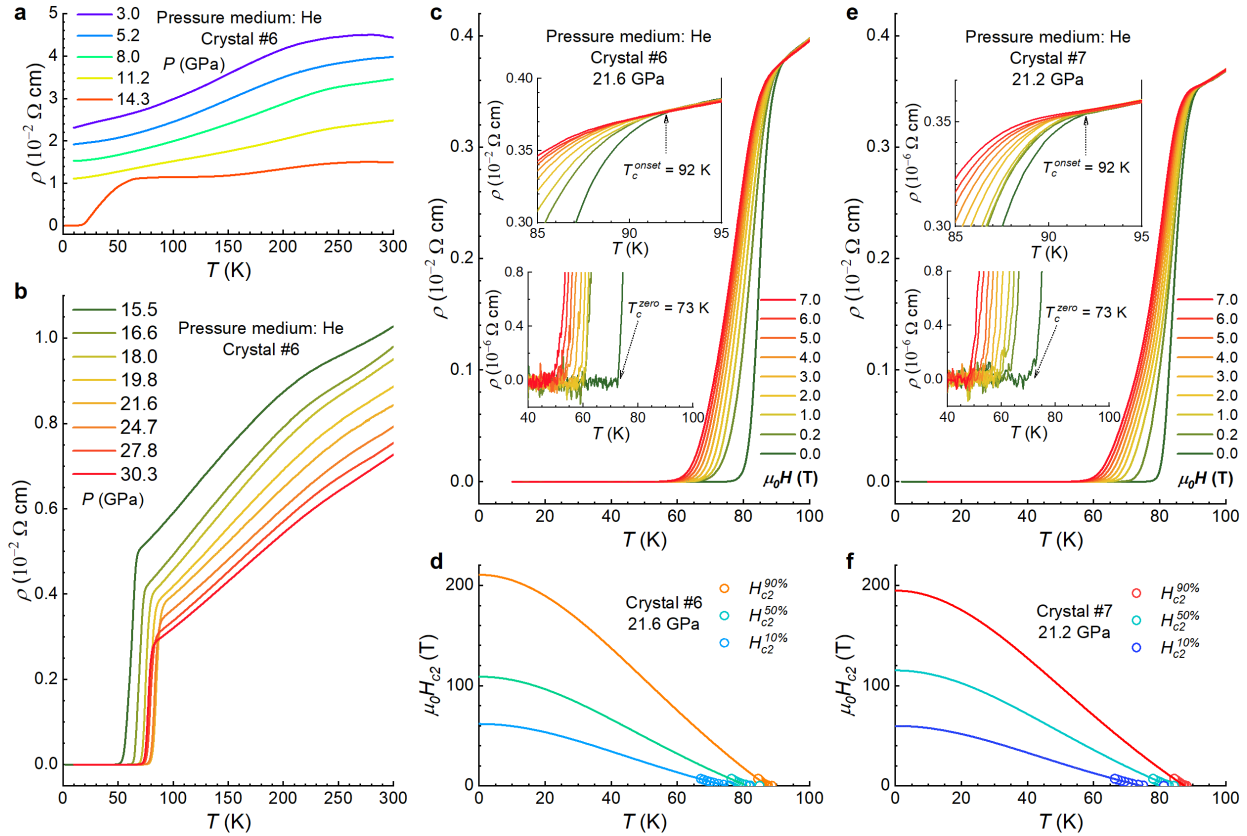


Fig. R5 (revised **Fig. 3**) High pressure transport measurements on single crystals (Crystal #6-#7) of $\text{La}_2\text{SmNi}_2\text{O}_{7-\delta}$. Complete zero resistance of $\text{La}_2\text{SmNi}_2\text{O}_7$ is observed.

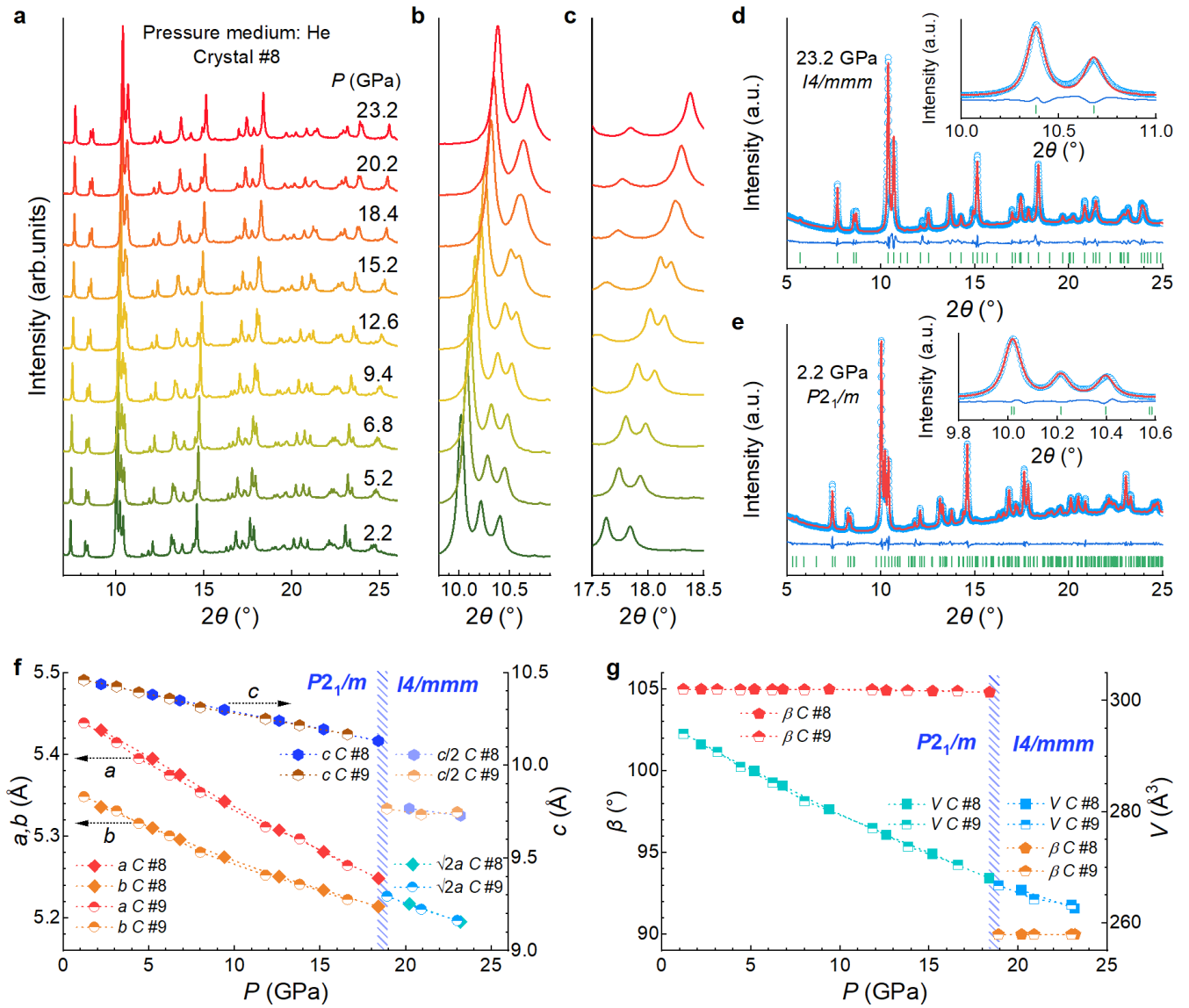


Fig. R6 (revised **Fig. 4**) Crystal structure of $\text{La}_2\text{SmNi}_2\text{O}_7$ under high pressure.

Additionally, the manuscript lacks clarity regarding the proposed approach to achieving higher T_c . The authors suggest that increasing Sm content at the La site leads to an enhanced superconducting transition, yet they do not provide a clear rationale or sufficient evidence to support this claim. A more detailed discussion is necessary to establish a compelling correlation between Sm substitution and T_c enhancement.

Response: We thank the Referee for pointing out this important issue. By analyzing the crystal structure of bilayer nickelates including $\text{La}_3\text{Ni}_2\text{O}_7$, $\text{La}_2\text{PrNi}_2\text{O}_7$ and $\text{La}_2\text{SmNi}_2\text{O}_7$ at ambient pressure, we found that with the increasing of the in-plane distortion $\Delta = (a-b)/(a+b)$, the high-pressure superconducting transition temperature, T_c^{onset} and T_c^{zero} , increases (**Fig. R7b**). Based on this correlation, we anticipate to obtain higher T_c by increasing Δ (**Fig. R7**). We are currently working on bilayer nickelates $\text{La}_{3-x}\text{R}_x\text{Ni}_2\text{O}_{7-\delta}$ ($\text{R}=\text{Eu}$, $x=0.83$; $\text{R}=\text{Sm}$, $x=1.43$; $\text{R}=\text{Nd}$, $x=1.95$ and $x=2.13$; $\text{R}=\text{Pr}$, $x=1.99$ and 2.70), which shows larger Δ (**Fig. R7**), to add more points in **Fig. R7b**. Due to time consuming of single crystal growth, post annealing, and high-pressure transport measurements using He as the PTM, this work is in progress.

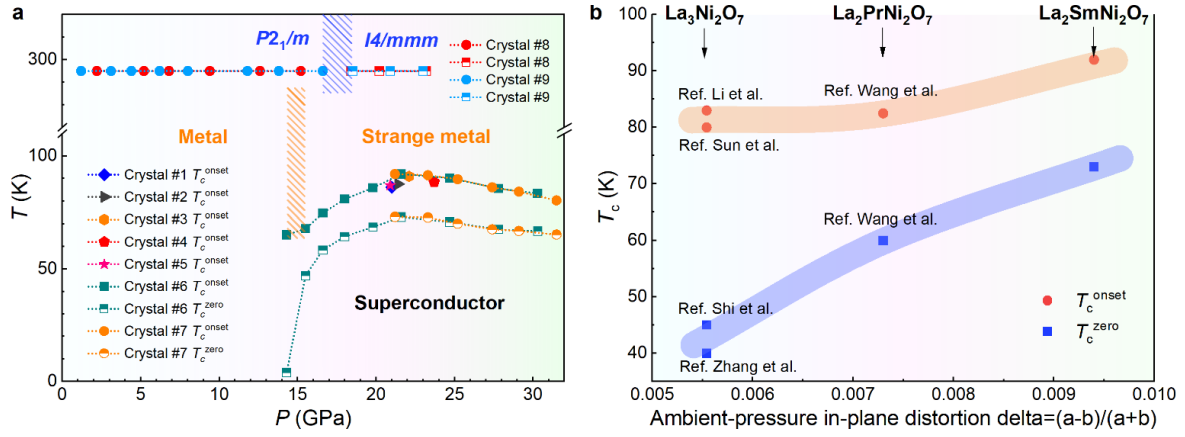


Fig. R7 (revised **Fig. 5**) Phase diagram and correlation between T_c and ambient-pressure in-plane distortion.

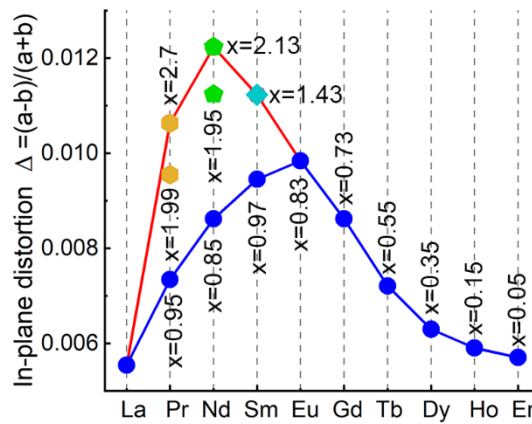


Fig. R8 (revised **Fig. 1f**) In-plane distortion for different $\text{La}_{3-x}\text{R}_x\text{Bi}_2\text{O}_{7-\delta}$ crystals obtained in our growth.

In summary, while this work presents an alternative synthesis method for bilayer nickelates, it does not offer a sufficiently novel or well-substantiated breakthrough to warrant publication in *Nature*. Strengthening the scientific justification, addressing inconsistencies in sample behavior, and providing a clearer mechanism for T_c enhancement would be necessary for broader impact.

Response: We thank the Referee for reviewing our manuscript. We have been working hard to address the Referee's criticism. We have performed further experiments. These include:

- (1) More high-pressure transport measurements to address the concern on sample inconsistencies and reproducibility (see detailed response to Comment #1);
- (2) Synchrotron X-ray powder diffraction under high pressure to address the crystal structure under high pressure. We found a structural transition from monoclinic $P2_1/m$ to tetragonal $I4/mmm$ at ~ 18 GPa (**Fig. R6**). Notably, the emergence of superconductivity occurs at ~ 14.3 GPa, prior to structural transition (**Fig. R6**). Our results indicate that tetragonal structure is not a prerequisite for emergence of superconductivity, and provide new insights into the physics of superconductivity in nickelates.

Furthermore, we conducted deeper analysis on crystal structure of bilayer nickelates. We identified a direct correlation between $T_{c,\text{max}}$ and ambient-pressure in-plane distortion $\Delta = (a-b)/(a+b)$ (**Fig. R7**), which provide a direction to further improve T_c in nickelates.

The nickelate high temperature superconductivity research is a fast-moving and highly competitive field. We have been working very hard in the past four weeks to perform additional experiments and analysis to address the Referee's concerns. Following his/her criticism and suggestions, we have significantly improve our manuscript. We hope now it reaches the high standard of publication for *Nature*.

Li et al. report the growth of bilayer La-nickelate single crystals with various rare-earth substitutions using a straightforward ambient pressure flux method. They provide comprehensive characterization of the crystals by powder and single-crystal X-ray diffraction, nuclear quadrupole resonance (NQR), energy-dispersive spectroscopy (EDS), and scanning transmission electron microscopy (STEM). Among the investigated compositions, Sm-substituted crystals exhibit the highest phase purity, and in high-pressure transport measurements, a superconducting transition onset temperature of 91 K at 22.1 GPa is observed.

From a technical standpoint, the execution of both crystal growth and characterization by Li et al. is sound. Furthermore, interest in the topic of superconducting nickelates has recently surged within condensed matter physics, materials synthesis, and solid-state chemistry, particularly since the discovery of superconductivity in $\text{La}_3\text{Ni}_2\text{O}_7$ with a T_c of 80 K above pressures of 14 GPa [1]. Nonetheless, critical challenges persist in the field, particularly: (1) How can the synthesis process be optimized to enhance sample quality? and (2) To what extent can the T_c be pushed higher?

To some extent, the study by Li et al. addresses both of these questions. Specifically, theoretical predictions have suggested that rare-earth substitution with different ionic radii could either increase or decrease T_c [5,6]. In the present manuscript, the authors report that Sm, which has a smaller ionic radius than La, yields a T_c of 91 K. However, given that the previous record T_c in $\text{La}_3\text{Ni}_2\text{O}_7$ powder was 86 K [31], this enhancement appears rather modest.

Response: We thank the Referee for his/her endorsement on our work.

Regarding the record T_c , we have plotted the resistivity data in the literature together with our data (see Fig. R9). Clearly, the so-called 86 K superconducting transition (blue curve) of $\text{La}_3\text{Ni}_2\text{O}_7$ powder is notably broad and no zero resistivity was reported (Zhang et al. *J. Mater. Sci. Technol.* 185, 147-154 (2024)). To date, the highest T_c^{onset} and T_c^{zero} for bilayer $\text{La}_3\text{Ni}_2\text{O}_7$ single crystals come from Shi *et al.* [arXiv: 2501.14202 (2025)], and they were also measured using He as the pressure transmitting medium. Thus, we can compare it (orange curve) directly with our data (red curve). We found that the enhancement of T_c is significant, in particular, T_c^{zero} (T_c^{onset} : 83→92 K; T_c^{zero} : 45→73 K).

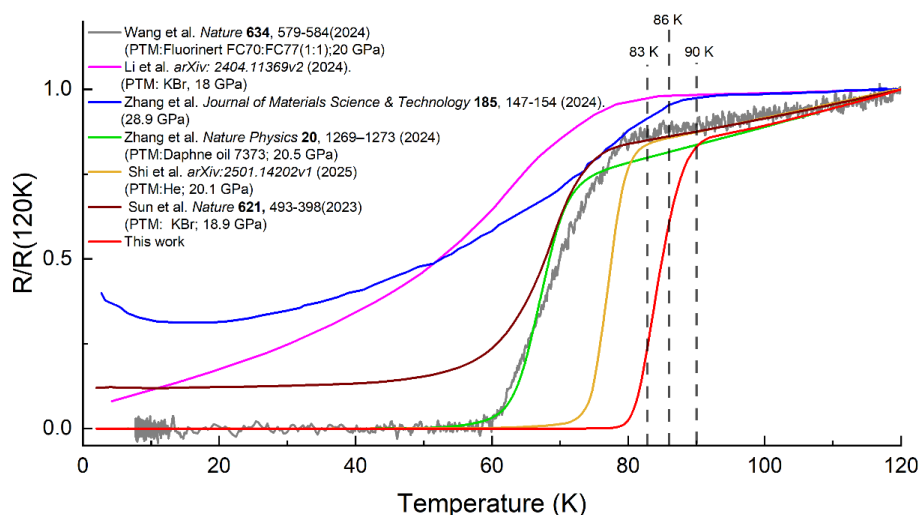


Fig. R9 Superconducting transition temperatures for bilayer nickelates.

Moreover, while they have synthesized a comprehensive series of rare-earth substitutions, they present high-pressure transport data only for the Sm case.

Response: The Referee is correct. There are two reasons:

- (1) Among the series of rare-earth substitutions, only for the case of Sm=1 we have obtained pure

phase of single crystals and the dimensions of the as-grown single crystals are the largest. While all others have secondary phases, including single-layer 2-1-4 and/or hybrid single-layer and bilayer 5-3-11. It's difficult to distinguish the 3-2-7 single crystals from the secondary phases based solely on crystal morphology.

(2) High-pressure transport measurements are very challenging, in particular measurements using He as pressure transmitting medium. In addition, the as-grown single crystals are not ideal and post-annealing is needed prior to high-pressure measurements (see more details in our response to Comment #1 of Referee #1). Both post-annealing and high-pressure transport measurements are time consuming. The optimized post-annealing process costs ten days. In order to optimize post-annealing conditions, we thus focus on the $Sm=1$ case, which has the highest purity and largest dimensions.

Optimization of single crystal growth conditions and high-pressure transport measurements on other bilayer nickelates are in progress.

A rigorous understanding of how T_c evolves with decreasing ionic radii would require a systematic study of multiple compositions under high pressure.

Response: We totally agree with the Referee that a systematic study of multiple compositions under high pressure is needed for a rigorous understanding of how T_c evolves. Considering the challenges in high-pressure transport measurements, it will take at least six months to measure all of them if we have high quality single crystals in hand for all (unfortunately not). The question is whether we need to measure all of them to find a trend. It seems not. After analyzing the crystal structure at ambient pressure and the maximum T_c under high pressure for bilayer $La_3Ni_2O_7$, $La_2PrNi_2O_7$ and $La_2SmNi_2O_7$, we found an interesting correlation between T_c and ambient-pressure in-plane distortion $\Delta=(a-b)/(a+b)$, as shown in **Fig. R7b**. Currently, there are only three compounds in this figure, we are measuring other compounds in particular those having larger Δ (**Fig. R8**).

Similarly, the study falls short of providing systematic insights into how sample quality can be improved. It was already known that Pr substitution enhances phase purity [33], and among the considered rare-earths, Sm appears to have grown serendipitously well under their applied conditions, while other compositions exhibit significant impurity phases. However, the authors do not offer a deeper explanation for why specifically Sm yields high-quality crystals, nor do they outline clear strategies for further improvements and T_c enhancements.

Response: We thank the Referee for pointing out this issue. Indeed, our characterization using X-ray single crystal diffraction, energy dispersive spectroscopy, nuclear quadrupole resonance and scanning transmission electron spectroscopy evidenced high-quality of bilayer single crystals without stacking faults within our resolution (**Fig. R1**). Our result is consistent with Wang *et al* [*Nature* 634, 579-584 (2024)] that the substitution of La using smaller rare earth elements inhibits intergrowth of Ruddlesden-Popper phases, thus protecting the bilayer structure that is responsible for high- T_c superconductivity. We have added this information in the revised manuscript.

Regarding the strategies for further improvement in T_c , we found an interesting correlation between T_c and ambient-pressure in-plane distortion $\Delta=(a-b)/(a+b)$ after analyzing the crystal structure at ambient pressure and the $T_{c,max}$ under high pressure for bilayer $La_3Ni_2O_7$, $La_2PrNi_2O_7$ and $La_2SmNi_2O_7$ (**Fig. R7**). Currently, we are measuring other rare earth substituted $La_{3-x}R_xNi_2O_7$ in particular those having larger Δ . Thus, we have offered a direction for enhancing T_c in nickelates in the revised manuscript.

In summary, this study represents an important contribution for researchers working in the field of nickelate superconductors, particularly for those involved in the sample synthesis. It is also encouraging

to see that T_c can be enhanced, even if the demonstrated improvement is modest.

Response: We thank the Referee for his/her endorsement of our work. In response to Comment #1 of this Referee, we argue that the enhancement of T_c is significant (**Fig. R9**), in particular in T_c^{zero} by 28 K (T_c^{zero} : 45 K for $\text{La}_3\text{Ni}_2\text{O}_7$ vs 73 K for $\text{La}_2\text{SmNi}_2\text{O}_7$).

However, I do not see compelling reasons why this paper meets the stringent criteria for publication in *Nature* and would be of broad interest to a general audience. Instead, it would be better suited for a specialized journal focusing on materials synthesis and characterization.

Response: We have been working hard in the past three weeks after receiving the Referees' criticism and suggestions. We have carried out more high-pressure transport measurements (see detailed information in response to **Comment #1 of Referee #1**) and synchrotron X-ray powder diffraction under high pressure. We have added the following new data/results:

(1) zero resistivity: $T_{c\text{onset}}=92$ K and $T_c^{\text{zero}}=73$ K @ 21 GPa (**Fig. R5**), which are the highest T_c up to date among the known nickelate superconductors;

(2) Correlation between T_c and ambient-pressure in-plane distortion $\Delta=(a-b)/(a+b)$ (**Fig. R7**), which provide a direction to further improve T_c in bilayer nickelates;

(3) Crystal structure under high pressure. We found a structural transition from monoclinic $P2_1/m$ to tetragonal $I4/mmm$ at ~18 GPa (**Fig. R6**). Notably, the emergence of superconductivity occurs at 14.3 GPa, prior to structural transition (**Fig. R6**). Our results indicate that tetragonal structure is not a prerequisite for emergence of superconductivity.

Considering that the nickelate high temperature superconductivity research is a fast-moving and highly competitive field, we have been working very hard in the past four weeks. Following the Referee's criticism and suggestions, we have significantly improve our manuscript. We hope now it meets the stringent criteria for publication in *Nature*.

In addition, I have several minor comments:

The authors mention that their as-grown crystals exhibit a different space group than previously reported bilayer nickelates and are likely oxygen-deficient, necessitating annealing. Can they comment on whether the annealing process alters the space group? Also, is the annealing step required for superconductivity to emerge under high pressure?

Response: We thank the Referee for asking this question. We have performed synchrotron X-ray single crystal diffraction measurements on the annealed single crystals, and we found the symmetry is still $P2_1/m$.

Post-annealing is not required for superconductivity to emerge under high pressure (**Fig. R4a**). However, we did not observe zero resistivity in the as-grown single crystals under high pressure. After optimizing annealing conditions, we obtained zero resistivity at 73 K. The best annealing conditions we obtained are: $p\text{O}_2=1.5$ bar, Temperature=600 °C, Time = 10 days. We have obtained excellent reproducibility in high-pressure transport data using this optimized annealing condition (see more details in response to **Comment #1 of Referee #1**).

The authors may elaborate on why Sm appears to be the “sweet spot” for substitution, while all other rare-earth substitutions result in lower sample quality.

Response: We thank the Referee for asking this question. Indeed, in our current growth we found Sm=1 is the best to grow and the as-grown single crystals are the largest. The ionic radius for various rare earth elements with different coordination numbers (CN) is listed in **Table R2**. As can be seen, the ionic radius monotonically decreases from La to Er. This cannot explain why Sm=1 is located at the “sweet spot” for substitution. It is possible that the chemistry of Sm_2O_3 , K_2CO_3 , and NiO favors high quality single crystal

growth for Sm substitution; however, this cannot explain why Sm=1.43 is difficult to grow. It is also possible that different rare earth substitution requires very different growth conditions, and currently, we are using similar growth conditions for all, and the current condition is close to the optimum of Sm=1. Crystal growth by flux method is a time-consuming process and a number of parameters should be optimized to obtain high quality single crystals. If we spend more time optimizing growth conditions on other compositions, we may be able to improve their crystal quality.

Table R2 Ionic radius for various rare earth elements with different coordination number (CN)

R ³⁺	La	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er
CN=9	1.216	1.179	1.163	1.132	1.12	1.107	1.095	1.083	1.072	1.062
CN=12	1.36	-	1.27	1.24	-	-	-	-	-	-

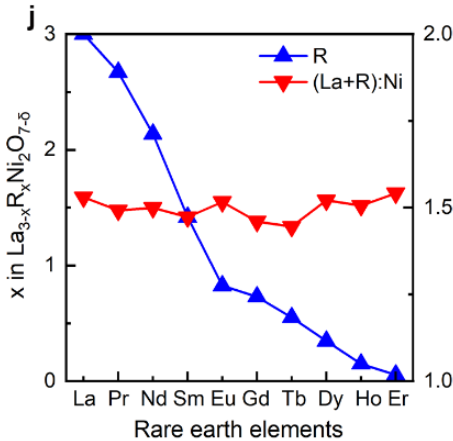


Fig. R10 (revised **Fig. 1j**) Maximum substitution of La and molar ratio of (La+R):Ni obtained from EDS for different rare earth elements in the as-grown La_{3-x}R_xNi₂O_{7-δ} (R=La-Er) single crystals.

Specifically, in Figs. 2b,c, there seems to be a change in trend in the lattice structure evolution beyond Nd and Sm when even smaller ions are introduced. How can they be sure this is a real effect rather than a consequence of worsening sample quality affecting their measurements?

Response: By combining energy dispersive spectroscopy (EDS) and lattice parameter extracted from LeBail fit on powder diffraction data, we are confident that the trend is a real effect rather than a consequence of worsening sample quality.

The first evidence is EDS. We have plotted them in **Fig. R10** (Fig. 2a in the previous manuscript). The amount of substitution decreases with the decreasing of ionic size of rare earth elements; however, the molar ratio of (La+R)/Ni maintains 3:2.

The second evidence comes from lattice parameters extracted from LeBail fit on X-ray powder diffraction data (**Fig. R11**). All compositions maintain the monoclinic *P*2₁/*m* crystal structure, indicating that substitutions of La form solid solutions. For the case of a specific rare earth element such as Pr, Nd and Sm, as shown in **Figs. R11a-f**, with the increasing of substitution, the lattice parameters change nearly monotonically. This is consistent with our EDS measurements (**Fig. R10**). For the maximum substitution of rare earth elements, the lattice parameters do not show monotonically trend, as the Referee pointed out. This is because the maximum substitution amount significantly decreases from Eu to Er (**Fig. R11g,h**).

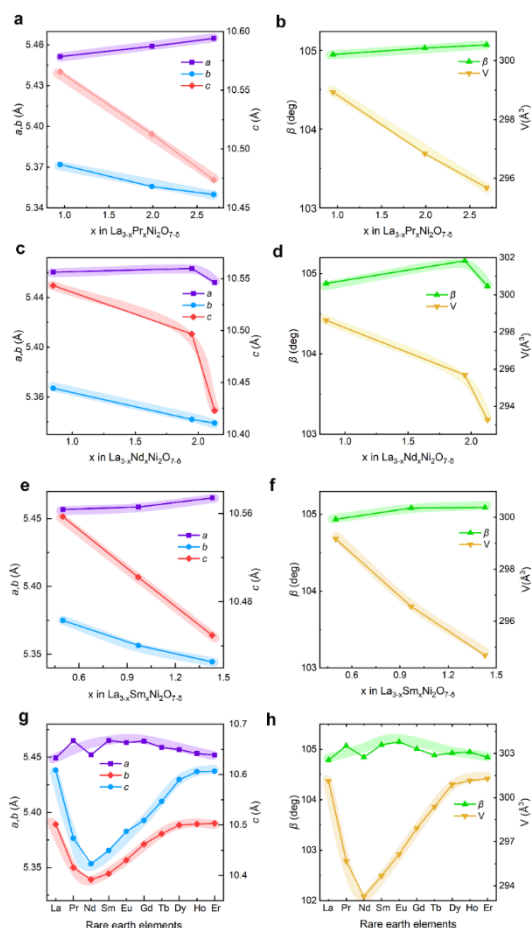


Fig. R11 (revised **Extended Data Fig. 4**) Lattice parameters extracted from Le Bail fit on powder diffraction data of pulverized $\text{La}_{3-x}\text{R}_x\text{Ni}_2\text{O}_{7-\delta}$ ($\text{R}=\text{La-Er}$) single crystals.

Similarly, Fig. 2a indicates that the realized substitution levels vary across different rare-earths, but the way the data is plotted in Figs. 2b,c suggests the samples are directly comparable. The authors should clarify whether their observed trends are due to intrinsic material properties or variations in sample composition.

Response: The Referee understands correctly that the realized substitution levels vary across rare earths. The data plotted in **Fig. R11** (previous Figs. 2b,c) suggests that the samples are directly comparable, which remains valid. The reason is that the substitution of La using various rare earths does not change the crystal structure – all of them crystallize in the same monoclinic $P2_1/m$ space group.

Our EDS and lattice parameters extracted from Le Bail fit support that the observed trends in **Fig. R10** (previous Fig. 2a) are intrinsic material properties as a function of rare earth elements and variations in composition, and **Figs. R11a-f** demonstrate the trends of intrinsic material properties due to variations in the composition for $\text{R}=\text{Pr, Nd and Sm}$.

The abstract claims that their results indicate “remarkable consistency with cuprates possessing bilayer copper-oxygen planes, suggesting a potential universal mechanism governing high-temperature superconductivity in these isostructural bilayer transition metal oxides.” However, it is not obvious to me how this claim is supported by the findings presented in the manuscript. The authors should clarify how their findings substantiate this statement or revise the abstract to better reflect the study’s conclusions.

Response: Indeed, we wrote the statement in our previous version based on the similarity of T_c in the 90 K range. We totally agree with the referee, and we have deleted this sentence in the revised manuscript.

Referee #3

A. Summary of the key results

This work successfully synthesized $\text{La}_{3-x}\text{R}_x\text{Ni}_2\text{O}_{7-\delta}$ ($\text{R}=\text{Pr-Er}$, $x \leq 2.7$) single crystals using a flux growth method at ambient pressure, eliminating the need for high-pressure synthesis. Among these compounds, $\text{La}_2\text{SmNi}_2\text{O}_{7-\delta}$ demonstrated superior quality and superconducting behavior. After annealing in high oxygen pressure, $\text{La}_2\text{SmNi}_2\text{O}_{7-\delta}$ exhibited a superconducting transition onset temperature of up to 91 K at 22.1 GPa.

Response: We thank the Referee for reviewing our manuscript and his/her appreciation of our work.

B. Originality and significance: if not novel, please include reference

Once a new high- T_c superconductor is discovered, it is crucial to ensure the reproducibility and improve the sample quality. In this context, the development of crystal growth techniques represents a valuable contribution to the field. However, I find the overall impact of the paper to be limited, particularly due to the lack of new insights into the physics of superconductivity or the structure of the superconducting phase.

Response: We thank the Referee for his/her endorsement on our work on the development of new crystal growth technique on nickelate superconductors. Our data demonstrate excellent reproducibility (see more details in response to **Comment #1 of Referee #1**).

We thank the Referee's for pointing out our weakness in the previous version. We have performed synchrotron X-ray powder diffraction under high pressure, and we found a structural transition from monoclinic $P2_1/m$ to tetragonal $I4/mmm$ at ~ 18 GPa (**Fig. R6**). Notably, the emergence of superconductivity occurs at ~ 14.3 GPa, prior to structural transition (**Fig. R6**). Our results indicate that tetragonal structure is not a prerequisite for emergence of superconductivity, and provide new insights into the physics of superconductivity in nickelates.

We have also significantly improved our paper following the Referees' criticism and suggestions. We have added the following new data/results:

(1) zero resistivity: $T_c^{\text{onset}}=92$ K and $T_c^{\text{zero}}=73$ K @ 21 GPa (**Fig. R5**), which are the highest T_c up to date among the known nickelate superconductors;

(2) Correlation between T_c and ambient-pressure in-plane distortion $\Delta=(a-b)/(a+b)$ (**Fig. R7**), which provide a direction to further improve T_c in nickelates.

We believe that the overall impact and significance of the revised manuscript have been greatly strengthened, and hopefully it now reaches the high standards required for publication in *Nature*.

C. Data & methodology: validity of approach, quality of data, quality of presentation

I do not find serious problems with the quality of the data. Please see E regarding the quality of the presentation.

Response: We thank the Referee for his/her appreciation of our work. We have addressed all issues in E.

D. Appropriate use of statistics and treatment of uncertainties

Looks appropriate.

Response: We thank the Referee for his/her appreciation of our work.

E. Conclusions: robustness, validity, reliability

Here I list several comments and concerns:

1. In the abstract, the authors state “but also providing a direction for discovering superconducting

nickelates with higher T_c .” This sentence is too abstract. What “direction” are the authors talking about?

Response: We thank the Referee for pointing out the vague language in our previous version. We have plotted the $T_{c,max}^{onset}$ and $T_{c,max}^{zero}$ as a function of ambient-pressure in-plane distortion $\Delta=(a-b)/(a+b)$ for different $La_{3-x}R_xNi_2O_7$ ($R=La, Pr$ and $Sm, x=1$). Both $T_{c,max}^{onset}$ and $T_{c,max}^{zero}$ increase with the increasing of Δ at ambient pressure (**Fig. R7**). Our finding provides a direction for finding new nickelate superconductors with high T_c . We are currently measuring other bilayer nickelates to add more data in this figure.

2. In the abstract, the authors write “suggesting a potential universal mechanism governing high-temperature superconductivity in these isostructural bilayer transition metal oxides.” However, this claim lacks sufficient justification and is not supported by a firm theoretical or experimental foundation. Broadly speaking, there are two approaches (weak coupling and strong coupling) for considering the pairing mechanism in high-temperature superconductors. In the weak coupling approach, the shape of the Fermi surface plays an important role. However, bilayer cuprates and nickelates differ in their band structures and electron filling, resulting in distinct Fermi surfaces. Thus, a universal mechanism based on weak coupling arguments cannot be justified. In the strong coupling approach, local electron correlations dominate. In cuprates, the x^2-y^2 orbital is nearly half-filled, leading to localized $S=1/2$ moments. In contrast, in nickelates, both a nearly half-filled z^2 orbital and a nearly quarter-filled x^2-y^2 orbital are involved, indicating a fundamentally different local electronic environment. Therefore, the underlying local physics is also not universal. Why did the authors state this? Only from T_c ? Without firm experimental indication of a universal mechanism, I suggest the author delete this sentence.

Response: Indeed, we wrote the statement in our previous manuscript based on the similarity of T_c in the 90 K range. We totally agree with the referee, and we have deleted this sentence in the revised manuscript.

3. The authors report a monoclinic $P2_1/m$ space group, which is different from the previous report. I recommend that the authors elaborate on this issue. In particular, the authors state that they annealed under oxygen pressure. Is there any information on the crystal structure after annealing?

Response: We thank the Referee for pointing out this important issue. Indeed, the as-grown $La_3Ni_2O_7$ belongs to the monoclinic $P2_1/m$ space group with lattice parameters of $a=5.4370(2)$ Å, $b=5.3978(2)$ Å, $c=10.6173(4)$ Å and $\beta=104.817(1)^\circ$. The symmetry of the as-grown $La_3Ni_2O_7$ is lower than $Cmcm$. Our finding is consistent with the theoretical calculations that $P2_1/m$ has lower total energy compared with that of $Cmcm$ [Chen et al. *Phys. Rev. B* 111, 014515 (2025)]. A similar symmetry lowering from orthorhombic to monoclinic has been reported in $La_4Ni_3O_{10}$ [Zhang et al. *Phys. Rev. Mater.* 4, 083402 (2020)]. We have added this information to the revised manuscript.

We have performed synchrotron X-ray single crystal diffraction measurements on the annealed $La_2SmNi_2O_{7-\delta}$ single crystals, and we found that the symmetry maintains $P2_1/m$. We have added this information to the revised manuscript.

4. Related to 3. I find it interesting that the effect of chemical pressure is highly anisotropic between the a and b axes. For example, when La is replaced by Sm, the b -axis decreases, and the a -axis increases slightly. What is the origin of the a -axis expansion?

Response: We thank the Referee for asking this question. The substitution of smaller Sm^{3+} (1.132 Å for CN=9 and 1.24 for CN=12, and CN is short for coordination number) for La^{3+} (1.216 Å for CN=9 and 1.36 Å for CN=12) in the bilayer $La_3Ni_2O_7$ is expected to shrink the lattice and enhance local structural distortions. However, the chemical pressure is highly anisotropic. One notable feature in the crystal structure of $La_2SmNi_2O_7$ is that the substitution of rare earth elements is not randomly on all La sites.

Specifically, our X-ray single crystal diffraction and STEM measurements evidenced that the La site between bilayers is dominated by Sm while the La site within the bilayer is mostly occupied by La (**Fig. R1**). This preference of Sm substitution is likely responsible for the anisotropic chemical pressure.

5. Related to 3. I believe readers will be most interested in the crystal and electronic structures under high pressure. However, this crucial information is missing from the manuscript. While I understand that such measurements may be experimentally challenging, their absence diminishes the overall impact of the paper.

Response: We fully agree with the Referee that high-pressure crystal structure is crucial. We have performed synchrotron X-ray powder diffraction under high pressure, and we found a structural transition from monoclinic $P2_1/m$ to tetragonal $I4/mmm$ at ~ 18 GPa (**Fig. R6**). Notably, the emergence of superconductivity occurs at ~ 14.3 GPa, prior to structural transition (**Fig. R6**). Our results indicate that tetragonal structure is not a prerequisite for emergence of superconductivity, and this provides new insights into the physics of nickelate superconductivity. We believe that the overall impact of the paper is significantly strengthened.

For electronic structures, it will be very challenging to perform measurements such as Angle-resolved Photoemission Spectroscopy (ARPES) under high pressure.

6. Although the authors discuss onset T_c , I believe that T_c^{zero} is as important as T_c^{onset} . I recommend the authors properly mention this in the paper.

Response: We totally agree with the Referee. We have added $T_c^{\text{zero}}=73$ K in the revised manuscript (**Fig. R5**).

7. (optional) Did the authors observe superconductivity for their $\text{La}_3\text{Ni}_2\text{O}_{7-\delta}$ samples under pressure?

Response: We have measured the high-pressure resistance of $\text{La}_3\text{Ni}_2\text{O}_{7-\delta}$ single crystals using NaCl as the pressure transmitting medium. We observed superconductivity, but the reproducibility is not very good due to the existence of intergrowth (see **Fig. R1d**) and inhomogeneity of high-pressure environment of NaCl. We plan to measure $\text{La}_3\text{Ni}_2\text{O}_{7-\delta}$ single crystals using He as the pressure transmitting medium.

F. Suggested improvements: experiments, data for possible revision

All issues raised in E need to be carefully reexamined.

Response: We thank the Referee for his/her comments and suggestions. We have addressed almost all issues raised in E since we received the Referees' comments.

G. References: appropriate credit to previous work?

I do not find serious problems.

Response: We thank the Referee for reviewing our manuscript.

H. Clarity and context: lucidity of abstract/summary, appropriateness of abstract, introduction and conclusions

Please see E.

Response: We thank the Referee for reviewing our manuscript. We have addressed all major concerns point-by-point. Since the nickelate high temperature superconductivity research is a fast-moving and highly competitive field, we have been working very hard in the past four weeks. Following the Referee's criticism and suggestions, we have significantly improve our manuscript. We hope now it is suitable for publication for *Nature*.

Response to Referees' Comments

Below we detail our responses to referees' comments point-by-point and explain how we revised the manuscript accordingly.

Referee #1

The manuscript reports on the ambient pressure flux growth of bilayer nickelate single crystals, $\text{La}_{3-x}\text{R}_x\text{Ni}_2\text{O}_{7-\delta}$ ($\text{R} = \text{Pr-Er}$; $x \leq 2.7$), with superconductivity observed up to 91 K under high pressure. The authors highlight two key aspects of their work: (1) their flux-growth method as an alternative to the floating zone technique, which they claim produces cleaner crystals, and (2) an enhanced superconducting transition temperature (T_c), which they attribute to increased Sm substitution at the La site. While the topic is of interest, the manuscript lacks self-consistency, and its significance does not meet the high standards required for publication in *Nature*.

Response: We thank the Referee for agreeing that the topic is of interest, and for pointing out the issues of our manuscript. We have performed additional experiments and we have addressed the self-consistency issue. **The new data, including excellent reproducibility on superconductivity, zero-resistivity at 73 K, Meissner effect at 60 K, crystal structure in the superconducting state, T_c^{onset} increased to 96 K, and an effective strategy for further enhancement, have significantly enhanced the significance of our manuscript.** Hopefully the Referee will agree that the revised manuscript meets the high standards required for publication in *Nature*.

A major concern arises from the inconsistency in the resistance data presented for two different $\text{La}_2\text{SmNi}_2\text{O}_{7-\delta}$ crystals (labeled as Crystal 1 and Crystal 2). Crystal 2 exhibits a sharp superconducting transition around 80–90 K under pressure, while Crystal 1 shows at least two transitions, one near 80–90 K and another around 50 K, with no complete zero-resistance state. This discrepancy raises concerns about sample homogeneity and reproducibility. The authors claim that flux growth yields purer single crystals compared to the floating zone method, which has been criticized for producing inhomogeneous products with varied superconducting properties. However, the significant variation between their two flux-grown samples contradicts this claim and weakens the argument for the superiority of their growth method.

Response: We totally understand the Referee's concern about our sample homogeneity and reproducibility. For undoped $\text{La}_3\text{Ni}_2\text{O}_7$, the sample-dependent issues have been discussed in a number of papers, here we just list a few: (1) Hou *et al.* *Chin. Phys. Lett.* 40, 117302 (2023); (2) Zhou *et al.* arXiv: 2311.12631, later published at *Matter Radiat. Extremes.* 10, 027801(2025); (3) Zhang *et al.* *Nat. Phys.* 20, 1269-1273 (2024); (4) Dong *et al.* *Nature* 630, 847-852 (2024); (5) Wang *et al.* *Nature* 634, 579-584 (2024); (6) Chen *et al.* *J. Am. Chem. Soc.* 146, 3640-3645 (2024); (7) Puphal *et al.* *Phys. Rev. Lett.* 133, 146002 (2024); and (8) Wang *et al.* *Inorg. Chem.* 63, 5020-5026 (2024). Many discrepancies and controversies in the literature, such as bulk vs filamentary superconductivity, are rooted in the sample inhomogeneity of the $\text{La}_3\text{Ni}_2\text{O}_7$ crystals grown with high-pressure floating zone method. In order to understand the nature of high- T_c superconductivity in nickelates, the synthesis of high-quality and reproducible single crystals thus become one of the core tasks of the research on this system [Wang *et al.* *Chin. Phys. Lett.* 41, 077402 (2024)].

There are two reasons why a new method for nickelate crystal growth is demanding: (1) The lack of

reproducible high-quality bilayer nickelate single crystals hampers efforts to elucidate the underlying physics of this newly-discovered high- T_c superconductor, as various issues with the current synthesis methods including inhomogeneity, impurities, intergrowth, and oxygen vacancies have often been reported; (2) We propose to explore higher- T_c nickelate superconductors through chemical pressure via cation substitution, $\text{La}_{3-x}\text{R}_x\text{Ni}_2\text{O}_{7-\delta}$ ($\text{R}=\text{Pr-Lu}$). Single crystal growth of such smaller rare-earth substituted nickelates using the floating zone technique would require higher $p\text{O}_2$ than $\text{La}_3\text{Ni}_2\text{O}_7$ [Zhang et al. Phys. Rev. Mater. 4, 083402 (2020)]; however, increasing $p\text{O}_2$ is likely to result in impurities including $\text{La}_4\text{Ni}_3\text{O}_{10}$ [Zhang et al. Phys. Rev. Mater. 4, 083402 (2020)].

Our successful development of single crystal growth at ambient pressure represents a significant advance in materials synthesis of nickelate superconductors. This enables us to perform comprehensive examinations on its composition, average and local crystal structure, as shown in Fig. R1 (revised Fig. 2). We also performed magnetic susceptibility measurements (Fig. R2) and Rietveld refinements on X-ray powder diffraction data (Fig. R3) on samples from different batches, and they show excellent reproducibility.

Our additional transport measurements of $\text{La}_2\text{SmNi}_2\text{O}_{7-\delta}$ single crystals under high pressure also showed excellent reproducibility on superconductivity. So far, we have measured 11 different single-crystal samples from different batches (see Table R1 for the samples' information and Fig. R4-5 for the high-pressure resistivity data). These data were collected at HPSTAR from Dec. 2024 to July 2025 by using the DAC up to 31.5 GPa. We first measured the as-grown single crystals, a sharp transition occurs at 87 K but no zero resistivity was obtained (Crystal #1) probably due to oxygen defects. We then optimized post-annealing conditions. Among them, Crystal #3 was measured using paraffin as the pressure transmitting medium (PTM) (Figs. R4c,d). An apparent drop in resistance starting at 91 K was observed, indicating a superconducting transition. At 10 K, the residual resistance is only 5.5% of that prior to the transition. Notably, the observation of similar behaviors in the electrical resistance measured along two orthogonal directions separated by approximately 90° demonstrates excellent homogeneity in the single crystal. The broad feature at ~ 50 K (Fig. R4e) is not intrinsic but due to PTM's inhomogeneity of the pressure environment. Indeed, the effects of PTM has been discussed previously in the literature [Hou et al. Chin. Phys. Lett. 40, 117302 (2023); Wen et al. arXiv: 2410.10275 (2024); Shi et al. arXiv: 2502.01018 (2025)]. Therefore, all other measurements (Crystal #4 - 11) were performed using He as PTM. The use of helium, the best PTM for hydrostatic pressure, in conjunction with the four-probe method for high-pressure electrical transport measurements on single-crystal samples, ensured the high reliability of the experimental results. **Among them, Crystals #4-7 show sharp superconducting transitions, Crystal #6 and #7 exhibit excellent zero resistivity above 70 K (Fig. R4 and Fig. R5), and Crystal #11 show Meissner effect at 60 K (Fig. R5 and Fig. R6), confirming bulk high- T_c superconductivity. These data from different batches highlight the excellent reproducibility of superconductivity of our flux-grown single crystals.**

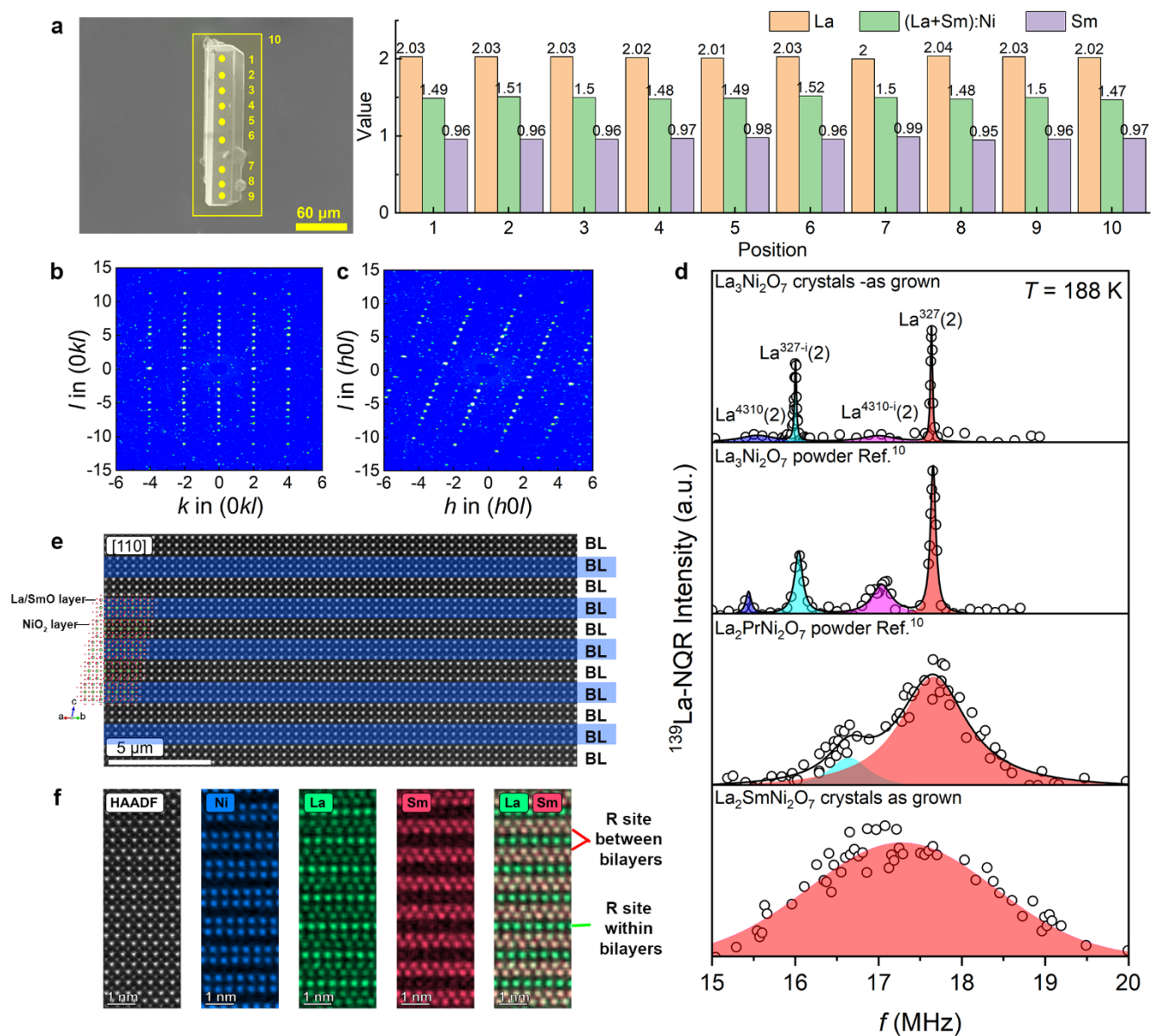


Fig. R1 (revised **Fig. 2**) Crystal quality of as-grown $\text{La}_2\text{SmNi}_2\text{O}_{7-\delta}$ single crystals. **a**, Energy dispersive spectroscopy (EDS) mapping of a typical $\text{La}_2\text{SmNi}_2\text{O}_{7-\delta}$ single crystal. **b,c**, Reconstructed $(0kl)$ and $(h0l)$ planes from in-house X-ray single crystal diffraction data of a $\text{La}_2\text{SmNi}_2\text{O}_{7-\delta}$ single crystal collected at 296(2) K. **d**, ^{139}La (2) nuclear quadrupole resonance (NQR) spectra corresponding to the $\pm 5/2 \leftrightarrow \pm 7/2$ transition in $\text{La}_3\text{Ni}_2\text{O}_{7-\delta}$ and $\text{La}_2\text{SmNi}_2\text{O}_{7-\delta}$ crystals at 188 K. The solid lines represent fits using Lorentz and Gaussian functions for $\text{La}_3\text{Ni}_2\text{O}_{7-\delta}$ ¹⁰ and $\text{La}_2\text{SmNi}_2\text{O}_{7-\delta}$, respectively. **e**, A typical atomic-scale HAADF-STEM image in the projection of $[110]$ with overlaid crystal structure model of $\text{La}_2\text{SmNi}_2\text{O}_{7-\delta}$ single crystal. Note BL is short for bilayer. **f**, EDS maps from STEM for La, Sm and Ni.

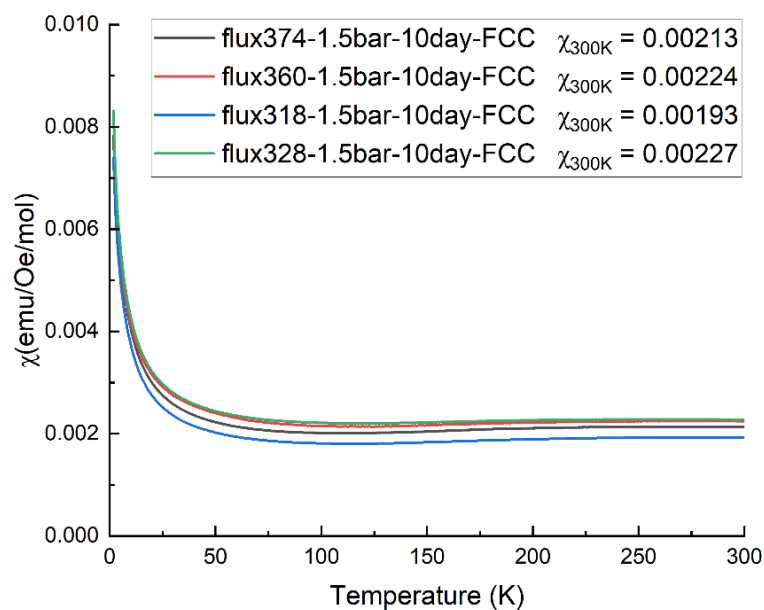


Fig. R2 Magnetic susceptibility data of pulverized $\text{La}_2\text{SmNi}_2\text{O}_{7-\delta}$ single crystals from different batches. Note FCC indicates field cooling and data collection on cooling.

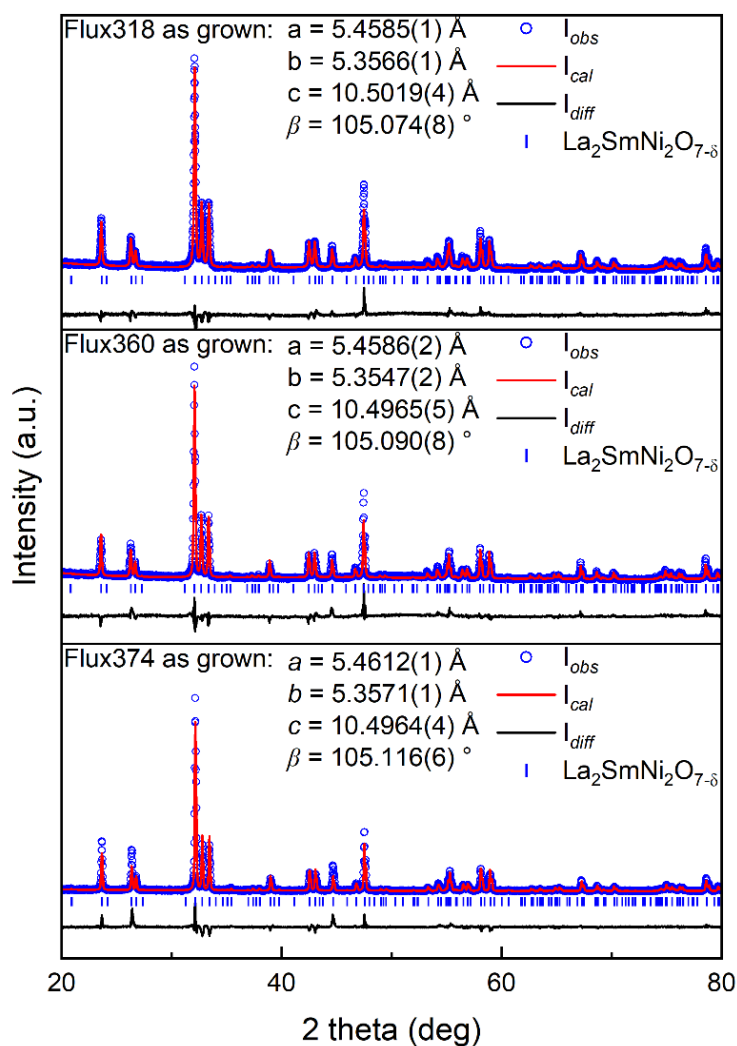


Fig. R3 Rietveld refinements on powder diffraction data of pulverized $\text{La}_2\text{SmNi}_2\text{O}_{7-\delta}$ single crystals from different batches of growth.

Table R1. Information of $\text{La}_2\text{SmNi}_2\text{O}_{7-\delta}$ single crystals studied from different batches

	Growth No.	Post-annealing conditions	Measurement conditions	Results	Measurement date	Note
1	Flux318	As-grown	Nuclear quadrupole resonance (NQR)	Significantly reduced intergrowth compared with $\text{La}_3\text{Ni}_2\text{O}_7$	08/23/2024	Data collected prior to the first submission (02/15/2025)
2	Flux318	As-grown	Magnetic susceptibility (MT)	$\chi_{300\text{K}}=0.00218$ emu/Oe/mol	09/24/2024	
3	Flux328	As-grown	MT	$\chi_{300\text{K}}=0.00214$ emu/Oe/mol	09/26/2024	
4	Flux318	$\text{pO}_2 = 1.5$ bar, 600 °C, 10 days	Scanning transmission electron microscopy (STEM)	Bilayer structure without intergrowth	11/04/2024	
5	Flux360	As-grown	High-pressure resistivity (HP RT) @ HPSTAR using He as PTM	$T_{\text{c onset}}=87$ K @ 21 GPa (Crystal #1, Fig. R4a)	12/16/2024	
6	Flux360	$\text{pO}_2 = 2.5$ bar, 600 °C, 10 days	HP RT @ HPSTAR using He as PTM	$T_{\text{c onset}}=88$ K @ 21.4 GPa (Crystal #2, Fig. R4b)	12/21/2024	
7	Flux318	$\text{pO}_2 = 1.5$ bar, 600°C, 10 days	HP RT @ HPSTAR using paraffin as PTM	$T_{\text{c onset}}=91$ K @ 22.1 GPa (Crystal #3, Fig. R4c,d,e)	12/30/2024	
8	Flux318		HP RT @ HPSTAR using He as PTM	$T_{\text{c onset}}=91$ K @ 22.1 GPa (Crystal #4, Fig. R4f)	01/18/2025	
9	Flux374	$\text{pO}_2 = 1.5$ bar, 600°C, 10 days	Thermogravimetric Analysis (TGA)	Sample #1: $\delta=7.00(2)$ Sample #2: $\delta=7.02(1)$	02/18/2025	New data added to the revised manuscript
10	Flux360	$\text{pO}_2 = 1.5$ bar, 600°C, 7 days	HP RT @ HPSTAR using He as PTM	$T_{\text{c onset}}=91$ K @ 20.9 GPa (Crystal #5, Fig. R4g,h)	02/25/2025	
11	Flux360	$\text{pO}_2 = 1.5$ bar, 600°C, 10 days	HP RT @ HPSTAR using He as PTM	$T_{\text{c onset}}=92$ K, $T_{\text{c zero}}=73$ K @ 21.6 GPa (Crystal #6, Fig. R5a,b,c)	03/23/2025	
12	Flux360		High-pressure synchrotron X-ray powder diffraction (HP-XRPD)	Pulverized Crystal #8, Fig. R7	03/26/2025	
13	Flux360		HP-XRPD	Pulverized Crystal #9, Fig. R7	03/27/2025	
14	Flux360		HP RT @ HPSTAR using He as PTM	$T_{\text{c onset}}=92$ K, $T_{\text{c zero}}=73$ K @ 21.2 GPa (Crystal #7, Fig. R4i)	03/29/2025	
15	Flux318		MT	$\chi_{300\text{K}}=0.0021(2)$ emu/Oe/mol	04/03/2025	
16	Flux360	$\text{pO}_2 = 1.5$ bar, 600°C, 10 days	In-situ high-pressure direct-current (DC) magnetic susceptibility (Meissner effect)	$T_{\text{c}}=60$ K @ 20.6 GPa (Crystal #11, Fig. R5e and Fig. R6)	06/01/2025	
17	Flux360		Low-temperature high pressure in-situ synchrotron X-ray powder diffraction	Both $P2_1/m$ and $I4/mmm$ can support superconductivity (Pulverized Crystal #10, Fig. R7 and Fig. R8)	06/21/2025	

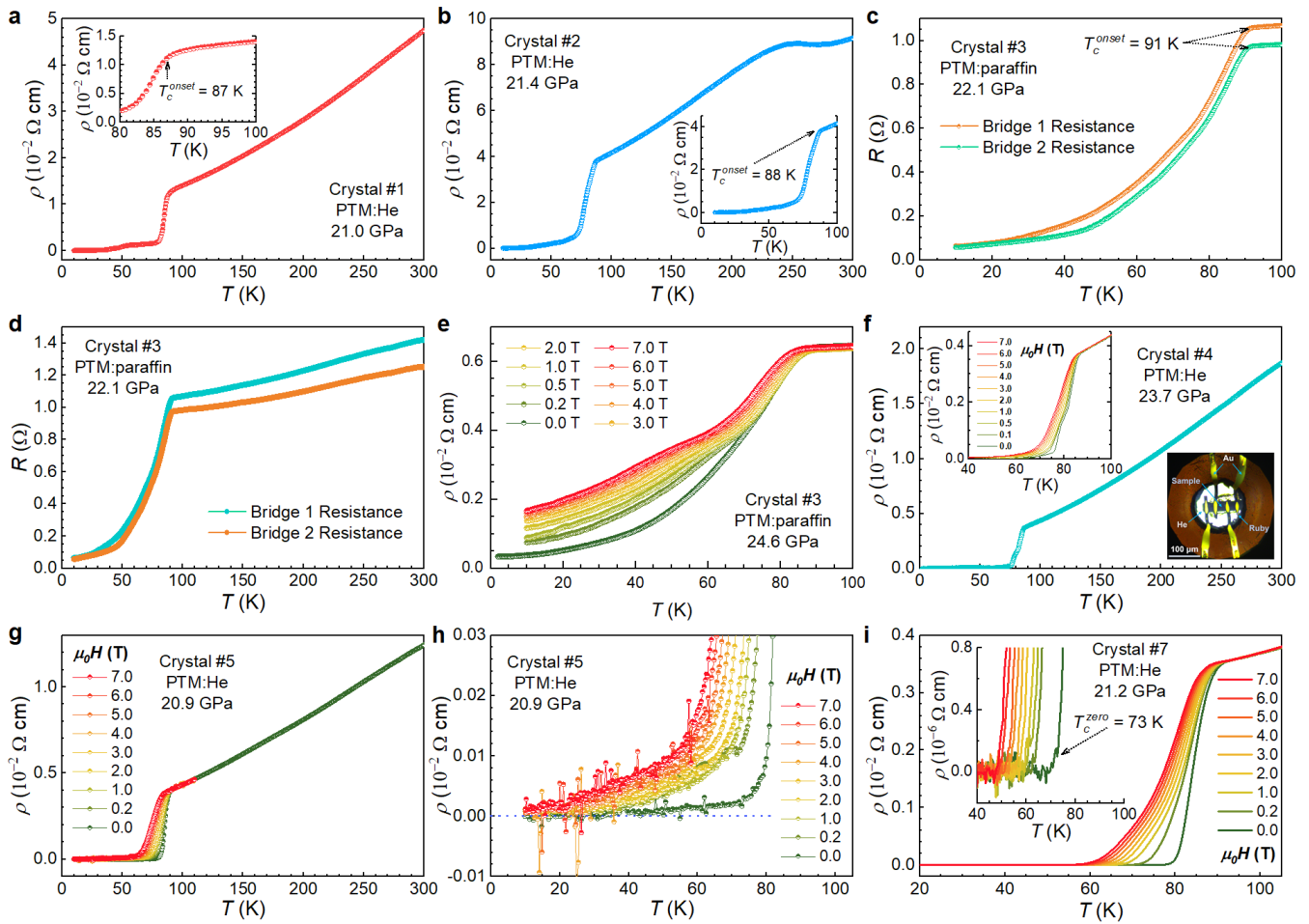


Fig. R4 (revised **Extended Data Fig. 5**) High pressure transport measurements on single crystals (Crystal #1-#7) of $\text{La}_2\text{SmNi}_2\text{O}_{7-\delta}$. **a**, Temperature-dependent resistivity of Crystal #1 (as-grown) under pressure in a helium-filled diamond anvil cell (DAC) under pressure at 21.0 GPa. The upper inset depicts the temperature-dependent resistivity around T_c^{onset} . **b**, Temperature-dependent resistivity of Crystal #2 (annealed at $p\text{O}_2=2.5$ bar for 10 days) under pressure in a helium-filled DAC under pressure at 21.4 GPa. The inset depicts the temperature-dependent resistivity in the vicinity of T_c^{onset} . **c,d**, Temperature-dependent resistance of Crystal #3 (annealed at $p\text{O}_2=1.5$ bar for 10 days) under pressure in a paraffin-filled DAC. The resistance of Bridge 1 and Bridge 2 represents the electrical resistance measured along two orthogonal directions separated by 90° . The observation of similar behaviors in the electrical resistance measured along two orthogonal directions evidences excellent homogeneity in the single crystal. **e**, Field dependence of resistivity of Crystal #3. **f**, Temperature-dependent resistivity of Crystal #4 (annealed at $p\text{O}_2=1.5$ bar for 10 days) under pressure in a helium-filled DAC under pressure at 23.7 GPa. The upper inset presents magnetic field effects on the superconducting transition in Crystal #4. The lower inset shows a photograph of the electrodes used for high-pressure resistivity measurements. Helium as the pressure transmitting medium under high pressure maintained the integrity of the single-crystal sample, and direct contact was established between the sample and the gold electrodes. **g**, Temperature-dependent resistivity of Crystal #5 (annealed at $p\text{O}_2=1.5$ bar for 7 days) under different magnetic field at 20.9 GPa, with helium as the pressure transmitting medium. **h**, Temperature-dependent resistivity for Crystal #5 at 20.9 GPa near T_c^{zero} . **i**, Resistivity of Crystal #7 (annealed at $p\text{O}_2=1.5$ bar for 10 days) under pressure in a helium-filled DAC at 21.2 GPa. The inset shows zero resistivity at 73 K.

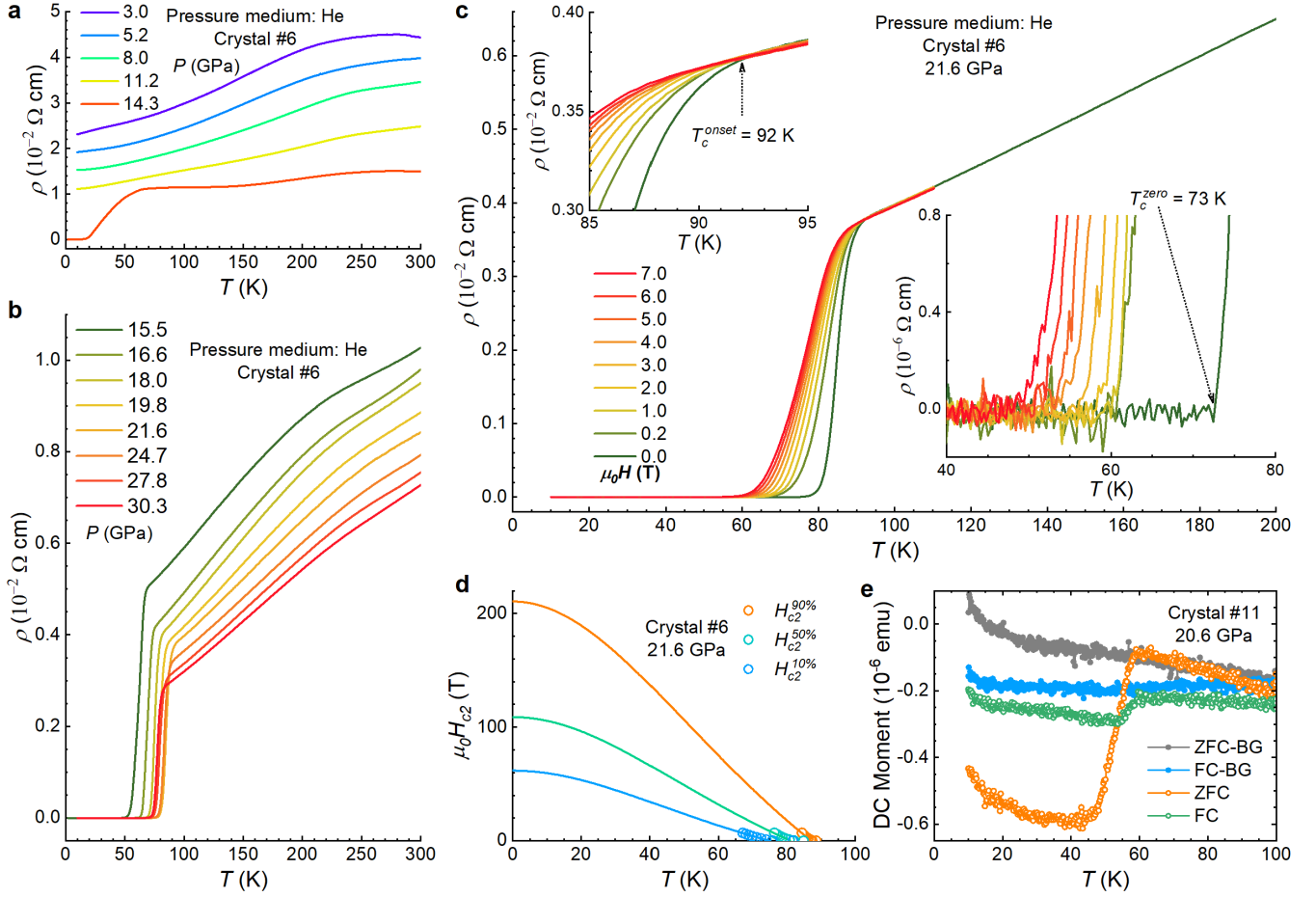


Fig. R5 (revised **Fig. 3**) **Bulk high- T_c superconductivity in $\text{La}_2\text{SmNi}_2\text{O}_7$ under high pressures.** **a**, Temperature-dependent resistivity of Crystal #6 (annealed at $p\text{O}_2=1.5$ bar for 10 days) under pressure in a helium-filled diamond anvil cell (DAC) under pressures below 14.3 GPa. **b**, Temperature-dependent resistivity of Crystal #6 under pressures from 15.5 GPa to 30.3 GPa. **c**, Field effects on the resistivity of Crystal #6 at 21.6 GPa. The upper-left and lower-right insets illustrate the temperature-dependent resistivity behavior in the vicinity of T_c^{onset} and T_c^{zero} , respectively. **d**, Upper critical fields extracted using the normal-state resistance values at 90%, 50%, and 10% of the resistivity at T_c^{onset} . Note open circles represent data and solid lines show the fit with a Ginzburg–Landau model. **e**, Direct-current (DC) magnetic susceptibility of single-crystal $\text{La}_2\text{SmNi}_2\text{O}_7$ (Crystal #11, annealed at $p\text{O}_2=1.5$ bar for 10 days) measured at 20.6 GPa under an applied magnetic field of 10 Oe using both zero-field-cooled (ZFC) and field-cooled (FC) modes. Note that BG is short for background.

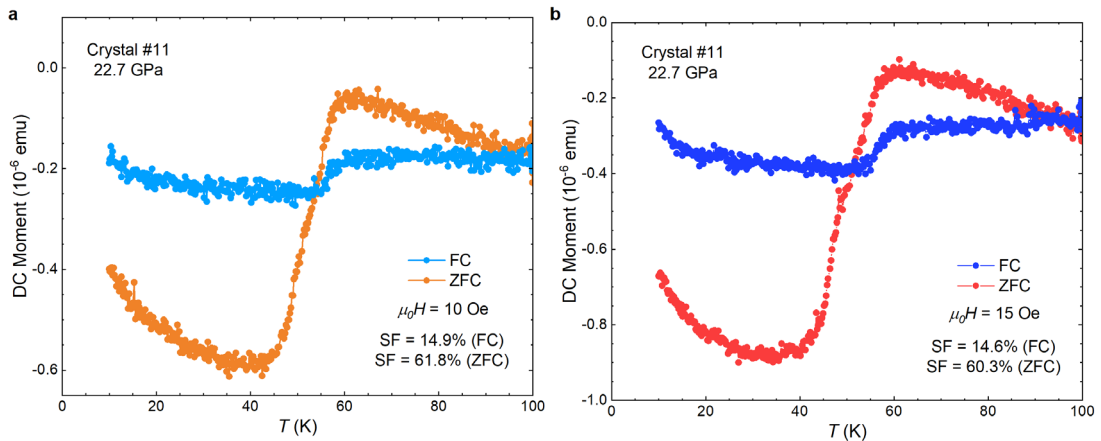


Fig. R6 (revised Extended Data Fig. 8) **Temperature-dependent magnetic susceptibility of $\text{La}_2\text{SmNi}_2\text{O}_7$ under high pressure.** **a**, Direct-current (DC) magnetic susceptibility of single-crystal $\text{La}_2\text{SmNi}_2\text{O}_7$ samples measured at 22.7 GPa under an applied magnetic field of 10 Oe using both zero-field-cooled (ZFC) and field-cooled (FC) modes. **b**, Direct-current (DC) magnetic susceptibility measured under an applied magnetic field of 15 Oe. Note SF is short for superconducting volume fraction.

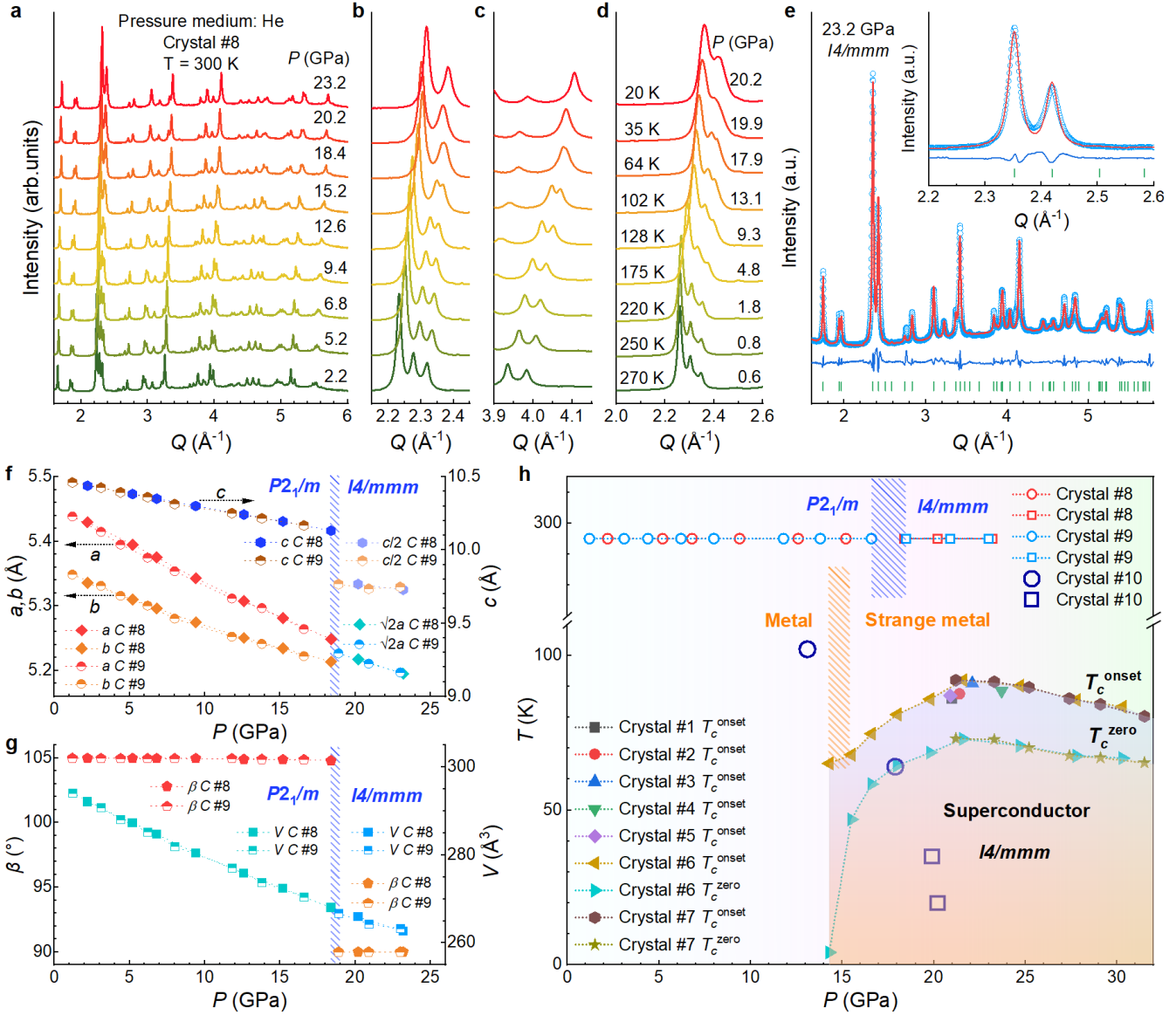


Fig. R7 (revised Fig. 4) **Structure and T - P phase diagram of $\text{La}_2\text{SmNi}_2\text{O}_{7-\delta}$.** **a**, Room-temperature synchrotron X-ray powder diffraction (XRD) patterns of annealed $\text{La}_2\text{SmNi}_2\text{O}_{7-\delta}$ (pulverized Crystal #8, annealed at $p\text{O}_2=1.5$ bar for 10 days) in the Q range of 1.6–6 $\text{\AA}^{-1}$ ($\lambda = 0.4834$ $\text{\AA}$) under different pressures with helium as the pressure transmitting medium. **b**, An enlarged view of **a** in the Q range of 2.15–2.45 $\text{\AA}^{-1}$. **c**, An enlarged view of **a** in the Q range of 3.9–4.15 $\text{\AA}^{-1}$, highlighting the gradual merging of the diffraction peaks on compression. **d**, An enlarged view of the powder diffraction patterns collected for annealed $\text{La}_2\text{SmNi}_2\text{O}_{7-\delta}$ in the Q range of 2.2–2.6 $\text{\AA}^{-1}$ ($\lambda = 0.4133$ $\text{\AA}$) at various temperatures and pressures using helium as the pressure transmitting medium. **e**, Rietveld refinement using $I4/mmm$ on the powder XRD pattern of $\text{La}_2\text{SmNi}_2\text{O}_7$ under 23.2 GPa. The inset illustrates the enlarged view of the refinement data in the Q range of 2.2–2.6 $\text{\AA}^{-1}$. Note the blue circles represent the observed diffraction intensities, the red lines denote the calculated intensities, the blue lines indicate the difference between the observed and

calculated intensities, the green bars mark the diffraction peak positions. **f,g**, Extracted lattice parameters of $\text{La}_2\text{SmNi}_2\text{O}_7$ from Rietveld refinements as a function of pressure. Crystal #8 (C #8) and Crystal #9 (C #9, annealed at $p\text{O}_2=1.5$ bar for 10 days) represent two independent experiments. **h**, T - P phase diagram of $\text{La}_2\text{SmNi}_2\text{O}_{7-\delta}$. The black solid squares, red solid circles, blue solid triangles, green solid triangles, violet solid diamonds, khaki solid triangles, and wine solid hexagons represent the T_c^{onset} of single crystals #1 to #7 under pressure, respectively. The cyan solid triangles and light-green solid stars represent the T_c^{zero} of single crystal #6 and #7 under pressure, respectively. The red hollow circles and red hollow squares represent the $P_{21/m}$ and $I4/mmm$ of pulverized single crystals C #8, respectively. The cyan hollow circles and cyan hollow squares represent the $P_{21/m}$ and $I4/mmm$ of pulverized single crystals C #9, respectively. The blue hollow circles and blue hollow squares represent the $P_{21/m}$ and $I4/mmm$ of pulverized single crystals Crystal #10, respectively.

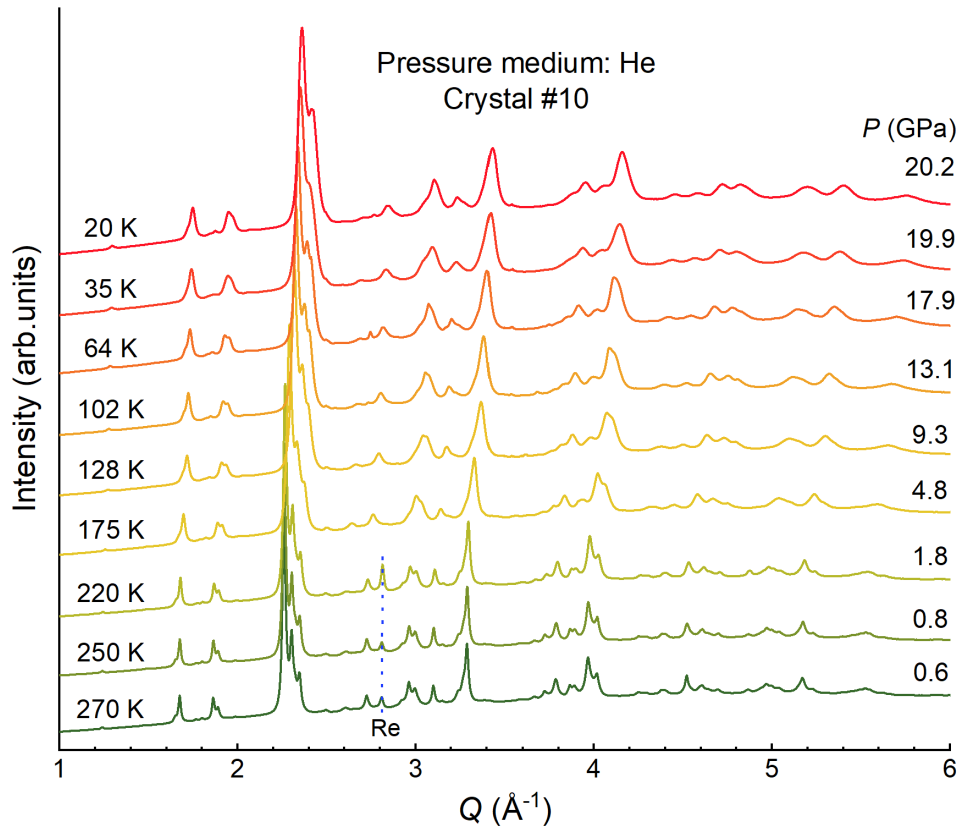


Fig. R8 (revised Extended Data Fig. 11) Synchrotron X-ray powder diffraction patterns of $\text{La}_2\text{SmNi}_2\text{O}_7$ (pulverized Crystal #10, annealed at $p\text{O}_2 = 1.5$ bar for 10 days) under high pressure at low temperatures. Data were collected in the Q range of 1-6 $\text{\AA}^{-1}$ ($\lambda = 0.4133$ $\text{\AA}$) at various temperatures (20-270 K) and pressures (0.6-20.2 GPa) using helium as the pressure transmitting medium. Note that blue dot line indicates diffraction peaks from Re.

Additionally, the manuscript lacks clarity regarding the proposed approach to achieving higher T_c . The authors suggest that increasing Sm content at the La site leads to an enhanced superconducting transition, yet they do not provide a clear rationale or sufficient evidence to support this claim. A more detailed discussion is necessary to establish a compelling correlation between Sm substitution and T_c enhancement.

Response: We thank the Referee for pointing out this important issue. By analyzing the crystal structure of bilayer nickelates including $\text{La}_3\text{Ni}_2\text{O}_7$, $\text{La}_2\text{PrNi}_2\text{O}_7$ and $\text{La}_2\text{SmNi}_2\text{O}_7$ at ambient pressure, we found that with the increasing of the in-plane distortion $\Delta=(a-b)/(a+b)$, the high-pressure superconducting transition

temperature, T_c^{onset} and T_c^{zero} , increases (**Fig. R9a**). Guided by this insight, we measured the resistivity of $\text{La}_{1.57}\text{Sm}_{1.43}\text{Ni}_2\text{O}_{7-\delta}$ at high pressures and found a $T_{c, \text{max}}^{\text{onset}}$ of 96 K at 26.8 GPa using paraffin as PTM (**Fig. R10**), which is the highest T_c among all nickelate superconductors (**Fig. R9b**). This result validates our strategy for T_c enhancement. Following this trend, it is likely to obtain superconductivity near 100 K in the bilayer nickelate $\text{La}_{0.87}\text{Nd}_{2.13}\text{Ni}_2\text{O}_{7-\delta}$ under high pressures (**Fig. R11**). We have included this in the revised manuscript.

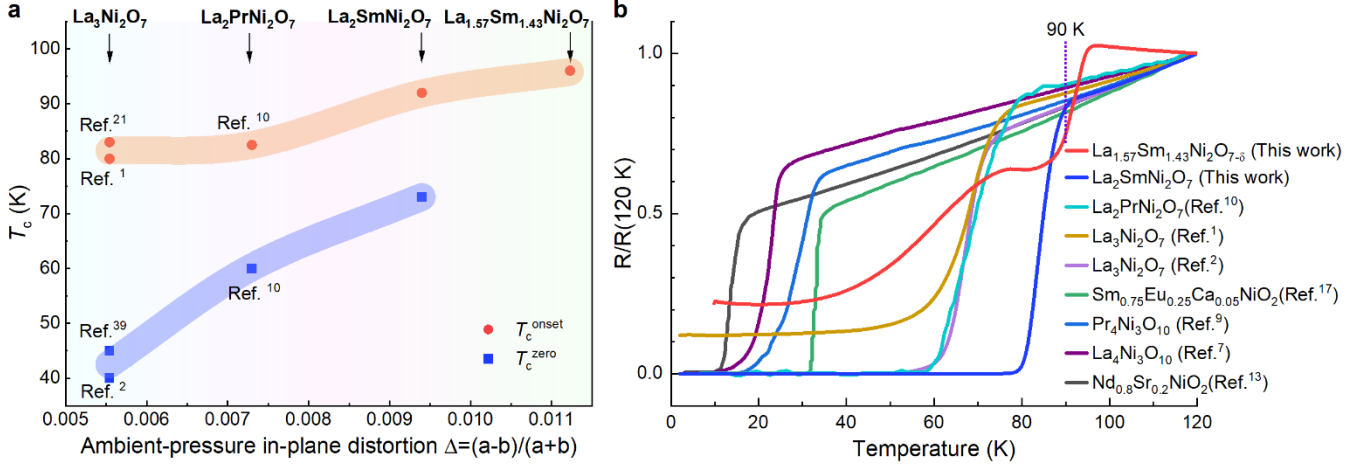


Fig. R9 (revised **Fig. 5**) **A strategy for T_c enhancement and record-high T_c .** **a**, Maximum T_c of bilayer nickelates as a function of ambient-pressure in-plane lattice distortion $\Delta=(a-b)/(a+b)$. T_c^{onset} and T_c^{zero} of $\text{La}_3\text{Ni}_2\text{O}_7$ and $\text{La}_2\text{PrNi}_2\text{O}_7$ are from resistivity measurements. The blue and yellow lines are only for guiding eyes. **b**, Maximum T_c for various nickelates. Note the plateau at around 80 K in $\text{La}_{1.57}\text{Sm}_{1.43}\text{Ni}_2\text{O}_{7-\delta}$ is an artifact due to inhomogeneity of the pressure transmitting medium (see more details in Extended Data Fig. 13).

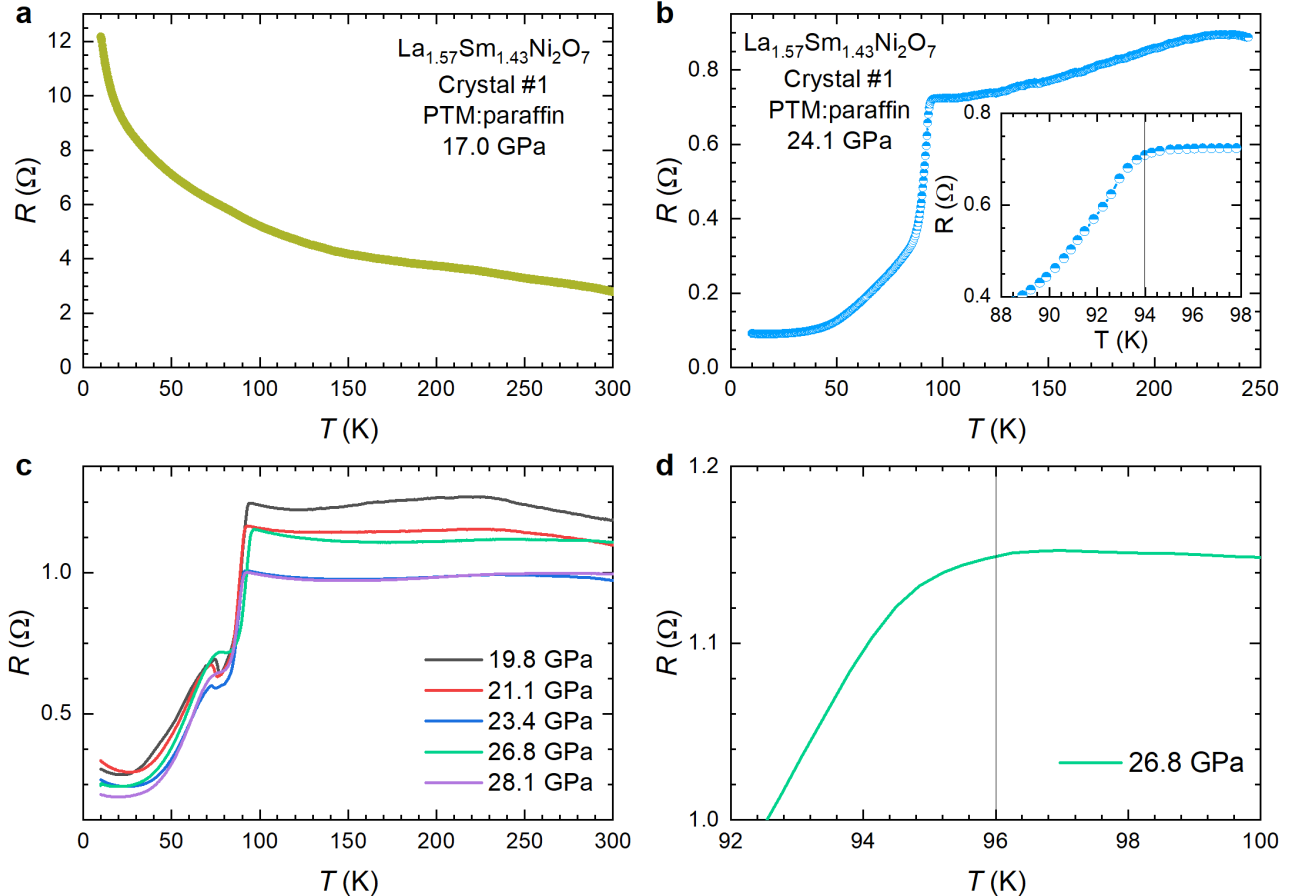


Fig. R10 (revised **Extended Data Fig. 13**) Superconductivity at 96 K in $\text{La}_{1.57}\text{Sm}_{1.43}\text{Ni}_2\text{O}_{7-\delta}$ single crystals at high pressures using paraffin as the pressure transmitting medium. **a**, Temperature-dependent resistance at 17 GPa. **b**, Temperature-dependent resistance at 24.1 GPa. The Inset shows the zoom-in region around T_c^{onset} . **c**, Temperature-dependent resistance in the range of 19.8–28.1 GPa. The pressure was lowered from 24.1 GPa in **b** to 19.8 GPa, and then increased to 28.1 GPa. Note the feature at around 80 K is absent in **b**, and it's an artifact due to inhomogeneity of pressure environment of paraffin during changing pressure. **d**, A zoom-in region around T_c^{onset} at 26.8 GPa.

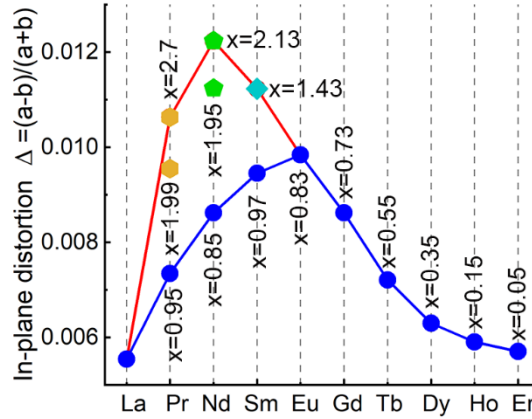


Fig. R11 (revised **Fig. 1f**) In-plane distortion for different $\text{La}_{3-x}\text{R}_x\text{Ni}_2\text{O}_{7-\delta}$ crystals obtained in our growth.

In summary, while this work presents an alternative synthesis method for bilayer nickelates, it does not offer a sufficiently novel or well-substantiated breakthrough to warrant publication in *Nature*. Strengthening the scientific justification, addressing inconsistencies in sample behavior, and providing a clearer mechanism for T_c enhancement would be necessary for broader impact.

Response: We thank the Referee for agreeing with us that this work presents an alternative synthesis method for bilayer nickelates. We also want to add the point that the current synthesis method for single crystals is unlikely to work for smaller rare earth substituted $\text{La}_{3-x}\text{R}_x\text{Ni}_2\text{O}_{7-\delta}$ ($\text{R}=\text{Pr-Lu}$), which we propose to explore higher- T_c nickelate superconductors. According to the phase diagram [Zhang et al. Phys. Rev. Mater. 4, 083402 (2020)], single crystal growth of such smaller rare-earth substituted nickelates using the floating zone technique would require higher $p\text{O}_2$ than $\text{La}_3\text{Ni}_2\text{O}_7$; however, increasing $p\text{O}_2$ is likely to result in impurities including $\text{La}_4\text{Ni}_3\text{O}_{10}$. Thus, our flux method not only provides an alternative synthesis method for $\text{La}_3\text{Ni}_2\text{O}_7$ but also make it possible to grow other bilayer nickelates that cannot be done previously.

Regarding the lack of sufficiently novel or well-substantiated breakthrough, we have performed additional experiments and we have added the following data in the revised manuscript:

(1) zero resistivity. We have obtained $T_c^{\text{zero}}=73\text{ K @ }21\text{ GPa}$ (Fig. R5 and Fig. R4), which is the highest up to date among the known nickelate superconductors (Fig. R9).

(2) Enhancing T_c to 96 K in nickelate superconductors (Fig. R9 and Fig. R10). Increasing the superconducting transition temperature (T_c) is a grand challenge for high- T_c superconductivity research and potential application. The T_c in nickelates has been maintained to be $\sim 80\text{ K}$ since the discovery of superconductivity in $\text{La}_3\text{Ni}_2\text{O}_7$ (Sun et al. *Nature*). We are the first team to successfully enhance T_c to the 90 K range (arXiv: 2501.14584). After the first submission, we have further enhanced the $T_{c, \text{max}}^{\text{onset}}$ to 96 K, which is 5 K higher than our previously reported value ($T_{c, \text{max}}^{\text{onset}}=91\text{ K}$). The T_c enhancement was

guided by the in-plane distortion mechanism proposed in our revised manuscript (Figs.5 and 1f). This new $T_{c, \max}^{\text{onset}}$ value of 96 K significantly surpasses previous records in the literature. **Our results clearly demonstrate the effectiveness of our proposed in-plane distortion strategy for further increasing T_c . We are confident that these findings will stimulate extensive exploration, higher and higher T_c values can be further achieved by the research community once our results get formally published. We believe these latest results represent a significant breakthrough, analogous to the discovery of “YBCO” in cuprates, and hold significant importance for the field of high-temperature superconductivity.**

(3) Determining crystal structure in the superconducting state (Fig. R7). The structure in the superconducting state in nickelate superconductors remains elusive. After our first submission, we have carried out additional low temperature high pressure synchrotron x-ray diffraction experiments. We found that both monoclinic $P2_1/m$ and $I4/mmm$ can support superconductivity. Specifically, we found $\text{La}_2\text{SmNi}_2\text{O}_7$ crystalize in the monoclinic $P2_1/m$ symmetry at 50 K under 18 GPa, and tetragonal $I4/mmm$ at 20 K under 22 GPa. **These results show that a tetragonal structure is not a prerequisite for the emergence of superconductivity in nickelates. This result lays the ground for theoretical calculations in the crystallographic aspect.**

(4) Meissner effect in nickelate superconductors (Fig. R5). Zero resistance and Meissner effect are two basic characteristics for superconductivity. In the literature, zero resistance has been reported for nickelate superconductors including $\text{La}_3\text{Ni}_2\text{O}_7$, $\text{La}_2\text{PrNi}_2\text{O}_7$, and $\text{La}_4\text{Ni}_3\text{O}_{10}$; however, there is no clear evidence of Meissner effect, in particular *when a nickelate in a magnetic field is cooled below T_c , all or part of the magnetic field within the material is expelled or not remains elusive*. **Our direct-current magnetic susceptibility measurements clearly show diamagnetic signal in both zero-field-cooling (ZFC) and field-cooling curve (FC) in $\text{La}_2\text{SmNi}_2\text{O}_7$, evidencing Meissner effect in bilayer nickelates. The superconducting volume fraction is estimated to be $> 60\%$ at 20.6 GPa at 40 K, demonstrating bulk superconductivity.**

Regarding the inconsistencies in sample behavior and reproducibility of superconductivity, we have carried out more high-pressure transport measurements, please see detailed response to Comment #1.

In sum, our additional experimental data significantly enhance the novelty and breakthrough of our manuscript, and comprehensively address the Referee's concerns. Following the Referee's criticism and suggestions, we have significantly improve our manuscript. We sincerely hope it now meets the standards for publication in *Nature*.

Referee #2

Li et al. report the growth of bilayer La-nickelate single crystals with various rare-earth substitutions using a straightforward ambient pressure flux method. They provide comprehensive characterization of the crystals by powder and single-crystal X-ray diffraction, nuclear quadrupole resonance (NQR), energy-dispersive spectroscopy (EDS), and scanning transmission electron microscopy (STEM). Among the investigated compositions, Sm-substituted crystals exhibit the highest phase purity, and in high-pressure transport measurements, a superconducting transition onset temperature of 91 K at 22.1 GPa is observed.

From a technical standpoint, the execution of both crystal growth and characterization by Li et al. is sound. Furthermore, interest in the topic of superconducting nickelates has recently surged within condensed matter physics, materials synthesis, and solid-state chemistry, particularly since the discovery

of superconductivity in $\text{La}_3\text{Ni}_2\text{O}_7$ with a T_c of 80 K above pressures of 14 GPa [1]. Nonetheless, critical challenges persist in the field, particularly: (1) How can the synthesis process be optimized to enhance sample quality? and (2) To what extent can the T_c be pushed higher?

To some extent, the study by Li et al. addresses both of these questions. Specifically, theoretical predictions have suggested that rare-earth substitution with different ionic radii could either increase or decrease T_c [5,6]. In the present manuscript, the authors report that Sm, which has a smaller ionic radius than La, yields a T_c of 91 K. However, given that the previous record T_c in $\text{La}_3\text{Ni}_2\text{O}_7$ powder was 86 K [31], this enhancement appears rather modest.

Response: We thank the Referee for his/her endorsement on our work.

We argue that the 86 K superconducting transition of $\text{La}_3\text{Ni}_2\text{O}_7$ powder reported by Zhang et al is notably broad (**Fig. R12**), so it is difficult to tell the precise T_c^{onset} . In addition, zero resistivity was not achieved [Zhang et al. *J. Mater. Sci. Technol.* 185, 147-154 (2024)].

So far, the highest T_c^{onset} and T_c^{zero} for bilayer $\text{La}_3\text{Ni}_2\text{O}_7$ single crystals come from Li et al. [T_c^{onset} = 83 K, J. Li et al., *Natl. Sci. Rev.*, nwaf220 (2025)] and Zhang et al. [T_c^{zero} = 40 K, Zhang et al., *Nat. Phys.* 20, 1269-1273 (2024)]. Recently, we have enhanced T_c^{onset} to 96 K (**Fig. R10**, revised **Extended Data Fig. 13**) and T_c^{zero} to 73 K (**Fig. R5**, revised **Fig. 3**). Although we haven't obtained zero resistivity for the sample with T_c^{onset} of 96 K, the superconducting transition is sharp.

Our additional data demonstrate significant enhancement in both T_c^{onset} and T_c^{zero} (T_c^{onset} : 83 $\rightarrow$ 96 K; T_c^{zero} : 40 $\rightarrow$ 73 K). **Fig. R12 presents the high-pressure resistivity of our flux-grown bilayer crystals as well as the data in the literature [$\text{La}_3\text{Ni}_2\text{O}_7$: Sun et al., *Nature* 621, 493-498 (2023), and Zhang et al., *Nat. Phys.* 20, 1269-1273 (2024); $\text{La}_2\text{PrNi}_2\text{O}_7$: Wang et al., *Nature* 634, 579-584 (2024); $\text{Sm}_{0.75}\text{Eu}_{0.25}\text{Ca}_{0.05}\text{NiO}_2$: Chow et al., *Nature* 642, 58-63 (2025); $\text{Pr}_4\text{Ni}_3\text{O}_{10}$: Zhang et al., *Phys. Rev. X* 15, 021008 (2025); $\text{La}_4\text{Ni}_3\text{O}_{10}$: Zhu et al., *Nature* 631, 531-536 (2024); $\text{Nd}_{0.8}\text{Sr}_{0.2}\text{NiO}_2$: Li et al., *Nature* 572, 624-627 (2019)]. We also have included this information in **Fig. R9** (revised Fig. 5)**

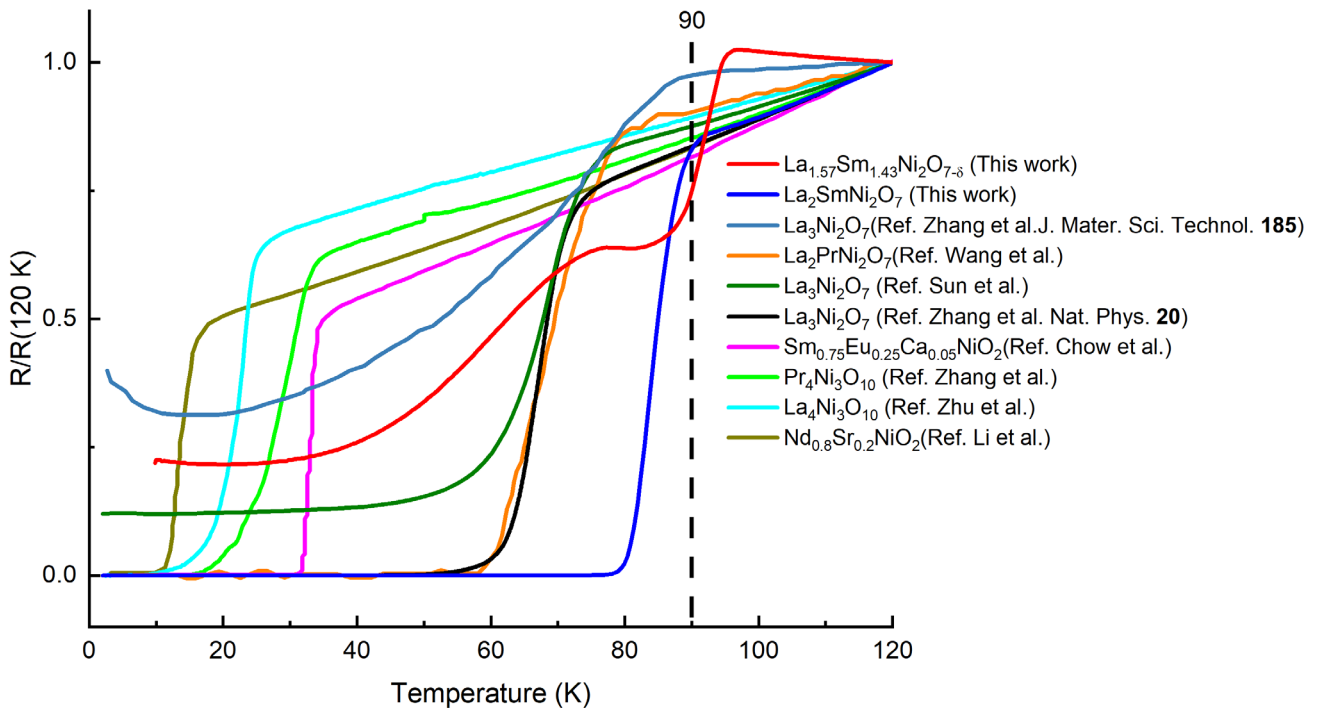


Fig. R12 Comparison of maximum T_c for various nickelates. $\text{La}_3\text{Ni}_2\text{O}_7$: Sun et al., *Nature* 621, 493-498 (2023), Zhang et al., *Nat. Phys.* 20, 1269-1273 (2024), and Zhang et al. *J. Mater. Sci. Technol.* 185, 147-154 (2024); $\text{La}_2\text{PrNi}_2\text{O}_7$: Wang et al., *Nature* 634, 579-584 (2024); $\text{Sm}_{0.75}\text{Eu}_{0.25}\text{Ca}_{0.05}\text{NiO}_2$: Chow et

al., *Nature* 642, 58-63 (2025); $\text{Pr}_4\text{Ni}_3\text{O}_{10}$: Zhang *et al.*, *Phys. Rev. X* 15, 021008 (2025); $\text{La}_4\text{Ni}_3\text{O}_{10}$: Zhu *et al.*, *Nature* 631, 531-536 (2024); $\text{Nd}_{0.8}\text{Sr}_{0.2}\text{NiO}_2$: Li *et al.*, *Nature* 572, 624-627 (2019).

Moreover, while they have synthesized a comprehensive series of rare-earth substitutions, they present high-pressure transport data only for the Sm case.

Response: The Referee is correct. There are two reasons:

(1) Among the series of rare-earth substitutions, for the case of Sm we have obtained the largest single crystals while the others are much smaller. Large single crystals are suitable for high-pressure transport measurements. In addition, others have impurity phases, including single-layer 2-1-4 and/or hybrid single-layer and bilayer 5-3-11. It's difficult to distinguish the 3-2-7 single crystals from the secondary phases based on crystal morphology.

(2) High-pressure transport measurements are very challenging and time-consuming, in particular measurements using He as pressure transmitting medium. In addition, the as-grown single crystals are not ideal due to oxygen defects, thus post-annealing is needed prior to high-pressure measurements (see more details in our response to Comment #1 of Referee #1). Both post-annealing and high-pressure transport measurements are time consuming. The optimized post-annealing process costs ten days. In order to optimize post-annealing conditions, we thus focus on the Sm case, which has the highest purity and largest dimensions.

Despite the above challenges, we have succeeded measuring the high-pressure transport measurement on another Sm variant, $\text{La}_{1.57}\text{Sm}_{1.43}\text{Ni}_2\text{O}_7$, guided by our strategy for T_c enhancement. Indeed, we successfully increased T_c to 96 K, which is the highest so far among all nickelate superconductors (**Fig. R12**).

A rigorous understanding of how T_c evolves with decreasing ionic radii would require a systematic study of multiple compositions under high pressure.

Response: We totally agree with the Referee that a systematic study of multiple compositions under high pressure is needed for a rigorous understanding of how T_c evolves. Indeed, we can take the advantage of the literature data on $\text{La}_3\text{Ni}_2\text{O}_7$ and $\text{La}_2\text{PrNi}_2\text{O}_7$. By analyzing the crystal structure at ambient pressure and the maximum T_c under high pressure for bilayer $\text{La}_3\text{Ni}_2\text{O}_7$, $\text{La}_2\text{PrNi}_2\text{O}_7$ and our $\text{La}_2\text{SmNi}_2\text{O}_7$, we found an interesting correlation between max T_c under high pressure and ambient-pressure in-plane distortion $\Delta=(a-b)/(a+b)$, as shown in **Fig. R9** (revised **Fig. 5**). Guided by this insight, we extracted the lattice parameters of all $\text{La}_{3-x}\text{R}_x\text{Ni}_2\text{O}_{7-\delta}$ ($\text{R}=\text{La}-\text{Er}$) and calculated their Δ (**Fig. R11**, **Fig. 11**). Notably, Δ shows a dome shape as a function of rare earth elements with the largest value from $\text{La}_{0.87}\text{Nd}_{2.13}\text{Ni}_2\text{O}_{7-\delta}$ and the second largest from $\text{La}_{1.57}\text{Sm}_{1.43}\text{Ni}_2\text{O}_{7-\delta}$. We measured the resistivity of $\text{La}_{1.57}\text{Sm}_{1.43}\text{Ni}_2\text{O}_{7-\delta}$ at high pressures and found a $T_{c, \text{max}}^{\text{onset}}$ of 96 K at 26.8 GPa using paraffin as PTM, which is the highest T_c among all nickelate superconductors (**Fig. R10** and **Fig. R12**). This result validates our strategy for T_c enhancement. Following this trend, it is likely to obtain superconductivity near 100 K in the bilayer nickelate $\text{La}_{0.87}\text{Nd}_{2.13}\text{Ni}_2\text{O}_{7-\delta}$ under high pressures.

Similarly, the study falls short of providing systematic insights into how sample quality can be improved. It was already known that Pr substitution enhances phase purity [33], and among the considered rare-earths, Sm appears to have grown serendipitously well under their applied conditions, while other compositions exhibit significant impurity phases. However, the authors do not offer a deeper explanation for why specifically Sm yields high-quality crystals, nor do they outline clear strategies for further improvements and T_c enhancements.

Response: We thank the Referee for pointing out this issue. Indeed, our characterization using energy dispersive spectroscopy, X-ray single crystal diffraction, nuclear quadrupole resonance and scanning transmission electron spectroscopy evidenced high-quality of bilayer single crystals without stacking faults (**Fig. R1, revised Fig. 2**). Our result is consistent with Wang *et al* [*Nature* 634, 579-584 (2024)] that the substitution of La using smaller rare earth elements inhibits intergrowth of Ruddlesden-Popper phases, thus protecting the bilayer structure that is responsible for high- T_c superconductivity. We have added this information in the revised manuscript.

Regarding the strategies for further improvement on T_c , we found an interesting correlation between T_c and ambient-pressure in-plane distortion $\Delta=(a-b)/(a+b)$ after analyzing the crystal structure at ambient pressure and the $T_{c,max}$ under high pressure for bilayer $\text{La}_3\text{Ni}_2\text{O}_7$, $\text{La}_2\text{PrNi}_2\text{O}_7$ and $\text{La}_2\text{SmNi}_2\text{O}_7$ (**Fig. R9**). Guided by this insight, we extracted the lattice parameters of all $\text{La}_{3-x}\text{R}_x\text{Ni}_2\text{O}_{7-\delta}$ ($\text{R}=\text{La-Er}$) we obtained and calculated their Δ (**Fig. R11, Fig. 11**). Notably, Δ shows a dome shape as a function of rare earth elements with the largest value from $\text{La}_{0.87}\text{Nd}_{2.13}\text{Ni}_2\text{O}_{7-\delta}$ and the second largest from $\text{La}_{1.57}\text{Sm}_{1.43}\text{Ni}_2\text{O}_{7-\delta}$. We measured the resistivity of $\text{La}_{1.57}\text{Sm}_{1.43}\text{Ni}_2\text{O}_{7-\delta}$ at high pressures and found a $T_{c,max}^{\text{onset}}$ of 96 K at 26.8 GPa using paraffin as PTM, which is the highest T_c among all nickelate superconductors (**Fig. R10 and Fig. R12**). This result validates our strategy for T_c enhancement. Following this trend, it is likely to obtain superconductivity near 100 K in the bilayer nickelate $\text{La}_{0.87}\text{Nd}_{2.13}\text{Ni}_2\text{O}_{7-\delta}$ under high pressures.

In summary, this study represents an important contribution for researchers working in the field of nickelate superconductors, particularly for those involved in the sample synthesis. It is also encouraging to see that T_c can be enhanced, even if the demonstrated improvement is modest.

Response: We thank the Referee for his/her endorsement of our work. Our additional data show that the enhancement of T_c^{onset} is significant (T_c^{onset} : from 83 K in $\text{La}_3\text{Ni}_2\text{O}_7$ to 96 K in $\text{La}_{1.57}\text{Sm}_{1.43}\text{Ni}_2\text{O}_7$; T_c^{zero} : from 40 K in $\text{La}_3\text{Ni}_2\text{O}_7$ to 73 K in $\text{La}_2\text{SmNi}_2\text{O}_7$). Please see **Fig. R5, Fig. R9 and Fig. R10**.

However, I do not see compelling reasons why this paper meets the stringent criteria for publication in *Nature* and would be of broad interest to a general audience. Instead, it would be better suited for a specialized journal focusing on materials synthesis and characterization.

Response: Regarding the lack of likely wider impact and significance of the findings, we have performed additional experiments and we have added our latest results in the revised manuscript:

(1) zero resistivity. We have obtained $T_c^{\text{zero}}=73$ K @ 21 GPa (**Fig. R9, revised Fig. 5**), which is the highest to date among the known nickelate superconductors.

(2) Enhancing T_c to 96 K in nickelate superconductors (Fig. R9 and Fig. R10). Increasing the superconducting transition temperature (T_c) is a grand challenge for high- T_c superconductivity research and potential application. The T_c in nickelates has been maintained to be ~ 80 K since the discovery of superconductivity in $\text{La}_3\text{Ni}_2\text{O}_7$ (Sun *et al. Nature*). We are the first team to successfully enhance T_c to the 90 K range (arXiv: 2501.14584). After the first submission, we have further enhanced the $T_{c,max}^{\text{onset}}$ to 96 K, which is 5 K higher than our previously reported value ($T_{c,max}^{\text{onset}}=91$ K). The T_c enhancement was guided by the in-plane distortion mechanism proposed in our revised manuscript (Figs.5 and 11). This new $T_{c,max}^{\text{onset}}$ value of 96 K significantly surpasses previous records in the literature. **Our results clearly demonstrate the effectiveness of our proposed in-plane distortion strategy for further increasing T_c . We are confident that these findings will stimulate extensive exploration, higher and higher T_c values can be further achieved by the research community once our results get formally published. We believe these latest results represent a significant breakthrough, analogous to the discovery of “YBCO” in cuprates, and hold significant importance for the field of high-temperature**

superconductivity.

(3) Determining crystal structure in the superconducting state (Fig. R7). The structure in the superconducting state in nickelate superconductors remains elusive. After our first submission, we have carried out additional low temperature high pressure synchrotron x-ray diffraction experiments. We found that both $P2_1/m$ and $I4/mmm$ can support superconductivity. Specifically, we found $\text{La}_2\text{SmNi}_2\text{O}_7$ crystalize in the monoclinic $P2_1/m$ symmetry at 50 K under 18 GPa, and tetragonal $I4/mmm$ at 20 K under 22 GPa. **These results indicate that a tetragonal structure is not a prerequisite for the emergence of superconductivity in nickelates. This result lays the ground for theoretical calculations in the crystallographic aspect.**

(4) Meissner effect in nickelate superconductors (Fig. R5). Zero resistance and Meissner effect are two basic characteristics for superconductivity. In the literature, zero resistance has been reported for nickelate superconductors including $\text{La}_3\text{Ni}_2\text{O}_7$, $\text{La}_2\text{PrNi}_2\text{O}_7$, and $\text{La}_4\text{Ni}_3\text{O}_{10}$; however, there is no clear evidence of Meissner effect, in particular *when a nickelate in a magnetic field is cooled below T_c , all or part of the magnetic field within the material is expelled or not remains elusive*. **Our direct-current magnetic susceptibility measurements clearly show diamagnetic signal in both zero-field-cooling (ZFC) and field-cooling curve (FC) in $\text{La}_2\text{SmNi}_2\text{O}_7$, evidencing Meissner effect in bilayer nickelates. The superconducting volume fraction is estimated to be $> 60\%$ at 20.6 GPa at 40 K, demonstrating bulk superconductivity.**

In sum, our additional experimental data significantly enhance the impact and significance of our manuscript, and comprehensively address the Referee's concerns. Following the Referee's criticism and suggestions, we have significantly improve our manuscript. We sincerely hope it now meets the standards for publication in *Nature*.

In addition, I have several minor comments:

The authors mention that their as-grown crystals exhibit a different space group than previously reported bilayer nickelates and are likely oxygen-deficient, necessitating annealing. Can they comment on whether the annealing process alters the space group? Also, is the annealing step required for superconductivity to emerge under high pressure?

Response: We thank the Referee for asking this question. We have performed synchrotron X-ray single crystal diffraction measurements on the annealed single crystals, and we found the symmetry maintains $P2_1/m$ (Fig. R13, revised Extended Data Fig. 6).

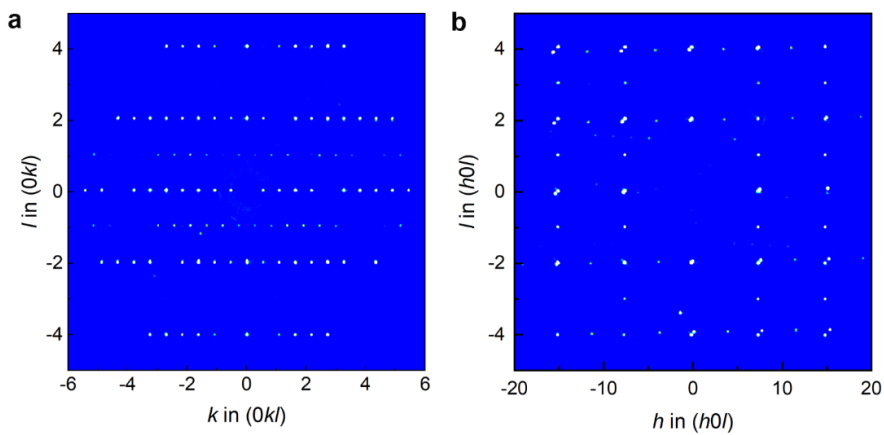


Fig. R13 (revised Extended Data Fig. 6) Reconstructed $(0kl)$ and $(h0l)$ planes of $\text{La}_2\text{SmNi}_2\text{O}_7$ (annealed at $p\text{O}_2=1.5$ bar for 10 days) from single crystal X-ray diffraction using $Cmcm$ with $a \sim 20.3 \text{ \AA}$, $b \sim 5.46 \text{ \AA}$ and $c \sim 5.36 \text{ \AA}$ at 296(2) K. Violations are clearly seen in the $(0kl)$ plane with $k=\text{odd}$

and in the (*h*0*l*) plane with *l*=odd. We find the crystal symmetry maintains *P*2₁/*m*.

Post-annealing is not required for superconductivity to emerge under high pressure (Table R1 and Fig. R4a). However, we did not observe zero resistivity in the as-grown single crystals under high pressure. After optimizing annealing conditions, we obtained zero resistivity at 73 K (Fig. R4i and Fig. R5c). The best annealing conditions we obtained are: pO₂=1.5 bar, Temperature=600 °C, Time = 10 days. We have obtained excellent reproducibility in high-pressure transport data using this optimized annealing condition (Please see more details in response to Comment #1 of Referee #1).

The authors may elaborate on why Sm appears to be the “sweet spot” for substitution, while all other rare-earth substitutions result in lower sample quality.

Response: We thank the Referee for asking this question. Indeed, in our current growth we found Sm=1 is the best to grow and the as-grown single crystals are the largest (Extended Data Table 2). The ionic radius for various rare earth elements with different coordination numbers (CN) is listed in Table R2. As can be seen, the ionic radius monotonically decreases from La to Er. However, this cannot explain why Sm=1 is located at the “sweet spot” for substitution. It is possible that the chemistry of Sm₂O₃, K₂CO₃, and NiO favors high quality single crystal growth for Sm substitution. It is also possible that different rare earth substitution requires substantial different growth conditions, and currently, we are using similar growth conditions for all, and the current condition is close to the optimum of Sm=1. Crystal growth by flux method is a time-consuming process and a number of parameters should be optimized to obtain high quality single crystals. If more time is spent in optimizing growth conditions on other compositions, we believe we will be able to improve their crystal quality.

Table R2 Ionic radius for various rare earth elements with different coordination number (CN)

R ³⁺	La	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er
CN=9	1.216	1.179	1.163	1.132	1.12	1.107	1.095	1.083	1.072	1.062
CN=12	1.36	-	1.27	1.24	-	-	-	-	-	-

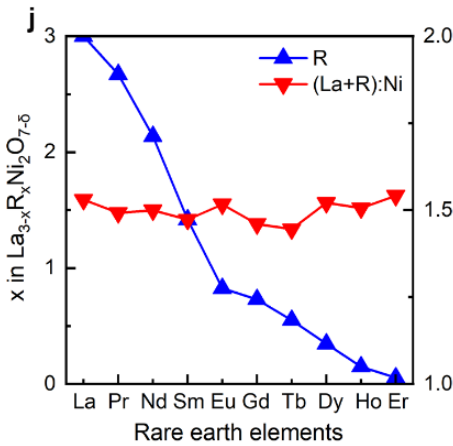


Fig. R14 (revised Fig. 1j) Maximum substitution of La and molar ratio of (La+R):Ni obtained from EDS for different rare earth elements in the as-grown La_{3-x}R_xNi₂O_{7-δ} (R=La-Er) single crystals.

Specifically, in Figs. 2b,c, there seems to be a change in trend in the lattice structure evolution beyond Nd and Sm when even smaller ions are introduced. How can they be sure this is a real effect rather than a consequence of worsening sample quality affecting their measurements?

Response: By combining energy dispersive spectroscopy (EDS) and lattice parameter extracted from LeBail fit on powder diffraction data, we are confident that the trend is a real effect rather than a

consequence of worsening sample quality.

The first evidence is EDS. We have plotted them in **Fig. R14** (revised Fig. 11). The amount of substitution decreases with the decreasing of ionic size of rare earth elements; however, the molar ratio of (La+R)/Ni maintains 3:2.

The second evidence comes from lattice parameters extracted from LeBail fit on X-ray powder diffraction data (**Fig. R15**). Our structural study revealed that all compositions maintain the monoclinic $P2_1/m$ crystal structure (**Fig. R16 and Fig. R1e**), indicating that substitutions of La form solid solutions. For the case of a specific rare earth element such as Pr, Nd and Sm, as shown in **Figs. R15a-f**, with the increasing of substitution, the lattice parameters change nearly monotonically. This is consistent with our EDS measurements (**Fig. R17**). For the maximum substitution of rare earth elements, the lattice parameters do not show monotonically trend, as the Referee pointed out. This is because the maximum substitution significantly decreases from Eu to Er (**Fig. R15g,h**).

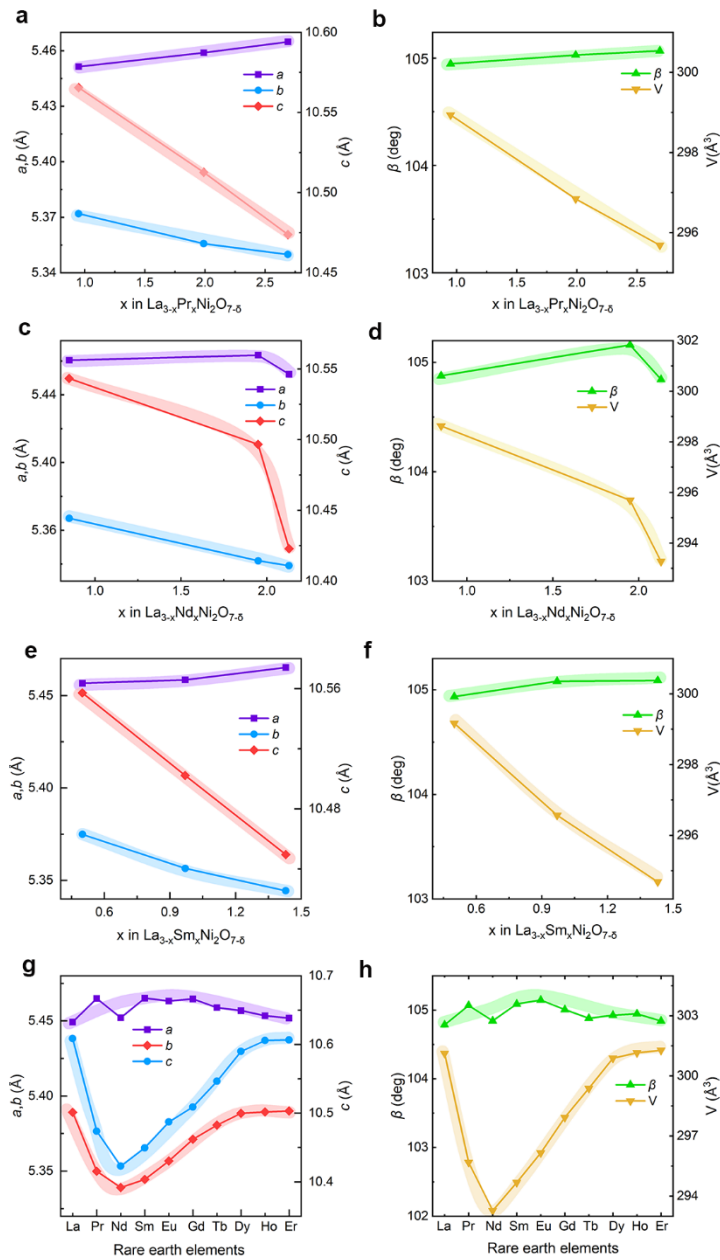


Fig. R15 (revised **Extended Data Fig. 4**) Lattice parameters extracted from LeBail fit on powder diffraction data of pulverized $\text{La}_{3-x}\text{R}_x\text{Ni}_2\text{O}_{7-\delta}$ ($\text{R}=\text{La-Er}$) single crystals.

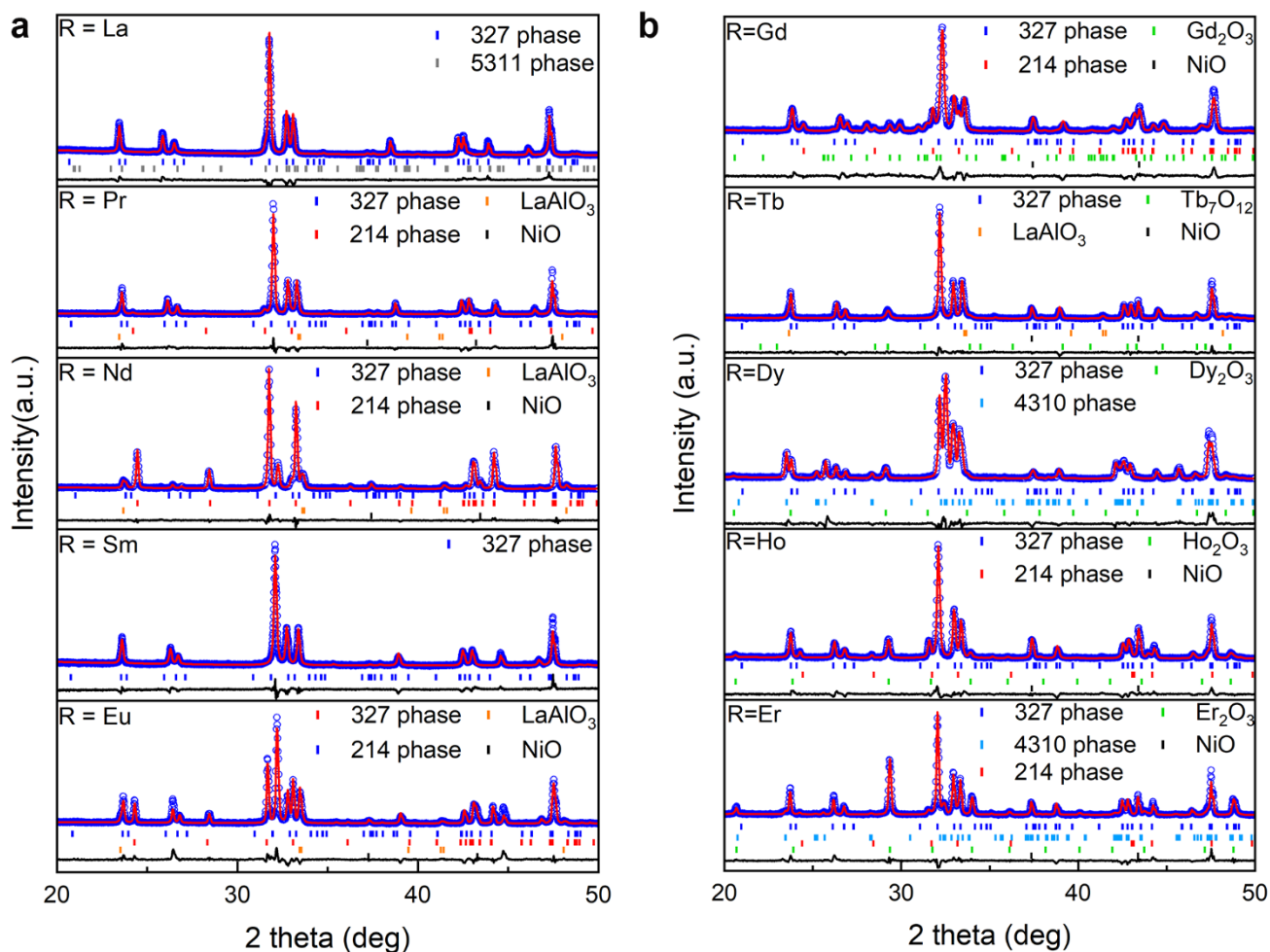
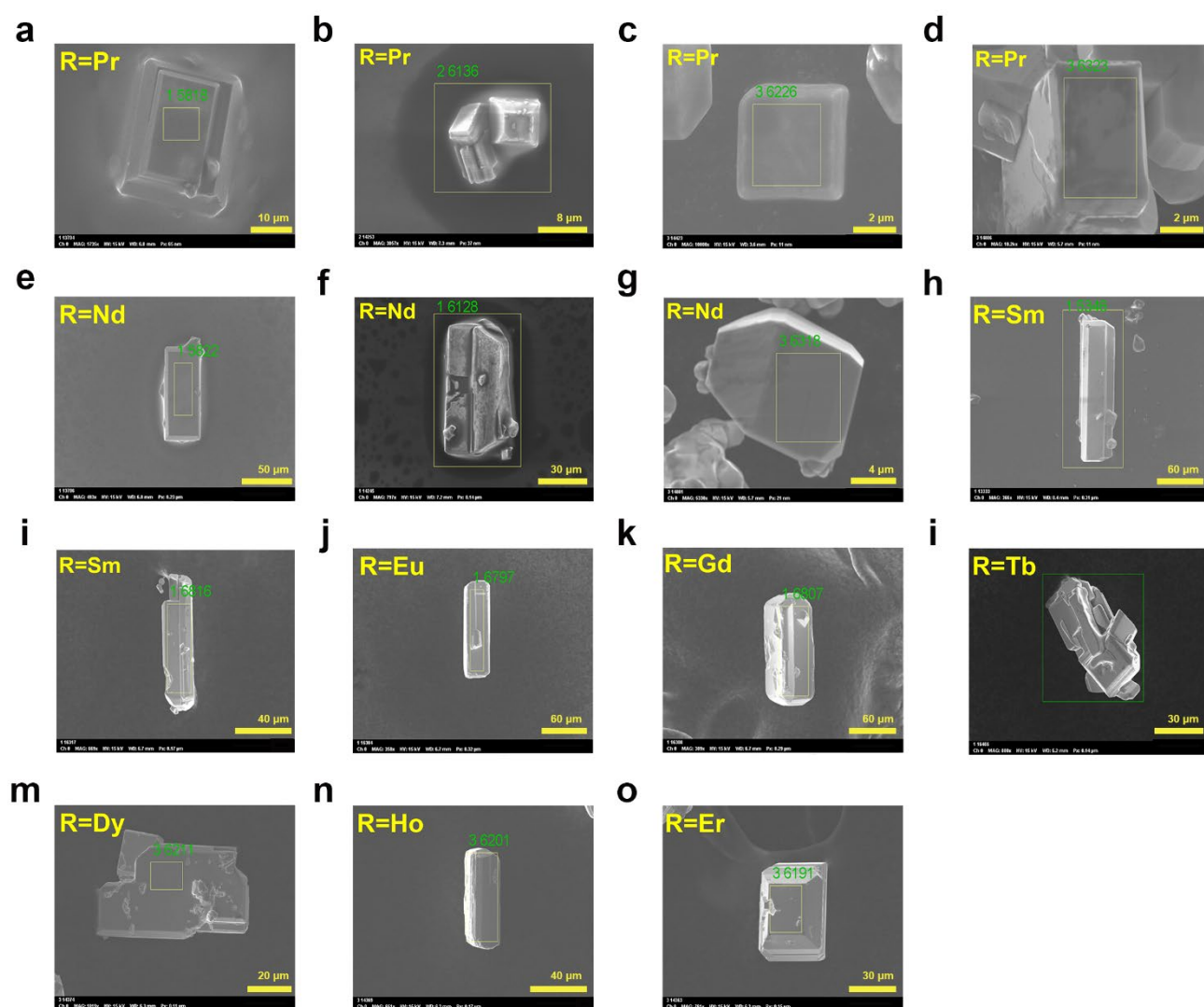


Fig. R16 (revised Extended Data Fig. 3) LeBail fit on powder diffraction data collected at room temperature of pulverized $\text{La}_{3-x}\text{R}_x\text{Ni}_2\text{O}_{7-\delta}$ ($\text{R}=\text{La-Eu}$) single crystals grown from $\text{La}:\text{R}=2:1$ (feeding) in the flux. **a.** $\text{R}=\text{La-Eu}$. **b.** $\text{R}=\text{Gd-Er}$. The circle represents I_{obs} , the red line represents I_{cal} , and the black line represents I_{diff} , and 327 phase indicates $\text{La}_{3-x}\text{R}_x\text{Ni}_2\text{O}_{7-\delta}$ (Space group: $P2_1/m$), 5311 indicates $\text{La}_2\text{NiO}_4 \cdot \text{La}_3\text{Ni}_2\text{O}_7$ (Space group: $Immm$), 214 phase indicates $\text{La}_{2-x}\text{R}_x\text{NiO}_4$ (Space group: $I4/mmm$) and 4310 phase indicates $\text{La}_{4-x}\text{R}_x\text{Ni}_3\text{O}_{10-\delta}$ (Space group: $P2_1/a$).



No.	R	La:R in flux (molar ratio)	La:R in as-grown crystals via EDS Measurement			No.	R	La:R in flux (molar ratio)	La:R in as-grown crystals via EDS Measurement		
			La	R	(La+R): Ni				La	R	(La+R): Ni
a	Pr	2:1	2.05	0.95	1.58	i	Sm	1:2	1.57	1.43	1.43
b		1:2	1.01	1.99	1.49	j	Eu	2:1	2.17	0.83	1.52
c		1:5	0.45	2.55	1.47	k	Gd		2.27	0.73	1.46
d		1:9	0.3	2.7	1.52	l	Tb		2.45	0.55	1.45
e	Nd	2:1	2.15	0.85	1.47	m	Dy		2.65	0.35	1.52
f		1:2	1.05	1.95	1.46	n	Ho		2.85	0.15	1.51
g		7:23	0.87	2.13	1.48	o	Er		2.95	0.05	1.54
h	Sm	2:1	2.03	0.97	1.49						

Fig. R17 (revised Extended Data Fig. 2) SEM images and EDS measurements of $\text{La}_{3-x}\text{R}_x\text{Ni}_2\text{O}_{7-\delta}$ ($\text{R}=\text{Pr}-\text{Er}$) single crystals.

Similarly, Fig. 2a indicates that the realized substitution levels vary across different rare-earths, but the way the data is plotted in Figs. 2b,c suggests the samples are directly comparable. The authors should clarify whether their observed trends are due to intrinsic material properties or variations in sample composition.

Response: The Referee understands correctly that the realized substitution levels vary across rare earths. The data plotted in **Figs. R15g,h** (previous **Figs. 2b,c**) suggest that the samples are directly comparable, which remains valid. **The reason is that the substitution of La using various rare earths does not change the crystal structure – all of them crystallize in the same monoclinic $P2_1/m$ space group.**

Our EDS and lattice parameters extracted from LeBail fit support that the observed trends in **Fig. R14** (previous Fig. 2a) are intrinsic material properties as a function of rare earth elements and variations in composition, and **Figs. R15a-f** demonstrate the trends of intrinsic material properties due to variations in the composition for R=Pr, Nd and Sm.

The abstract claims that their results indicate “remarkable consistency with cuprates possessing bilayer copper-oxygen planes, suggesting a potential universal mechanism governing high-temperature superconductivity in these isostructural bilayer transition metal oxides.” However, it is not obvious to me how this claim is supported by the findings presented in the manuscript. The authors should clarify how their findings substantiate this statement or revise the abstract to better reflect the study’s conclusions.

Response: We thank the Referee for pointing out this issue. Indeed, we wrote the statement in our previous version based on the similarity of T_c in the 90 K range. We totally agree with the referee, and we have removed this sentence.

Referee #3

A. Summary of the key results

This work successfully synthesized $\text{La}_{3-x}\text{R}_x\text{Ni}_2\text{O}_{7-\delta}$ (R=Pr-Er, $x \leq 2.7$) single crystals using a flux growth method at ambient pressure, eliminating the need for high-pressure synthesis. Among these compounds, $\text{La}_2\text{SmNi}_2\text{O}_{7-\delta}$ demonstrated superior quality and superconducting behavior. After annealing in high oxygen pressure, $\text{La}_2\text{SmNi}_2\text{O}_{7-\delta}$ exhibited a superconducting transition onset temperature of up to 91 K at 22.1 GPa.

Response: We thank the Referee for reviewing our manuscript and his/her endorsement of our work.

B. Originality and significance: if not novel, please include reference

Once a new high- T_c superconductor is discovered, it is crucial to ensure the reproducibility and improve the sample quality. In this context, the development of crystal growth techniques represents a valuable contribution to the field. However, I find the overall impact of the paper to be limited, particularly due to the lack of new insights into the physics of superconductivity or the structure of the superconducting phase.

Response: We thank the Referee for his/her endorsement on our work on the development of new crystal growth technique on nickelate superconductors. Our additional data demonstrate excellent reproducibility of superconductivity (Please see details in response to **Comment #1 of Referee #1**).

We thank the Referee’s for pointing out our weakness in the previous version. Regarding the lack of new insights into the physics of superconductivity or the structure of the superconducting phase, we have performed additional experiments and we have added our latest results in the revised manuscript:

(1) zero resistivity. We have obtained $T_c^{\text{zero}}=73 \text{ K @ } 21 \text{ GPa}$ (**Fig. R5** and **Fig. R4**), which is the highest up to date among the known nickelate superconductors (**Fig. R9**).

(2) Meissner effect (Fig. R5). Zero resistance and Meissner effect are two basic characteristics for

superconductivity. In the literature, zero resistance has been reported for nickelate superconductors including $\text{La}_3\text{Ni}_2\text{O}_7$, $\text{La}_2\text{PrNi}_2\text{O}_7$, and $\text{La}_4\text{Ni}_3\text{O}_{10}$; however, there is no clear evidence of Meissner effect, in particular *when a nickelate in a magnetic field is cooled below T_c , all or part of the magnetic field within the material is expelled or not remains elusive*. **Our direct-current magnetic susceptibility measurements clearly show diamagnetic signal in both zero-field-cooling (ZFC) and field-cooling curve (FC) in $\text{La}_2\text{SmNi}_2\text{O}_7$, evidencing Meissner effect in bilayer nickelates. The superconducting volume fraction is estimated to be $> 60\%$ at 20.6 GPa at 40 K, demonstrating bulk superconductivity.**

(3) Determining crystal structure in the superconducting phase (Fig. R7). The structure in the superconducting state in nickelate superconductors remains elusive. After our first submission, we have carried out additional low temperature high pressure synchrotron x-ray diffraction experiments. We found that both $P2_1/m$ and $I4/mmm$ can support superconductivity. Specifically, we found $\text{La}_2\text{SmNi}_2\text{O}_7$ crystalize in the monoclinic $P2_1/m$ symmetry at 50 K under 18 GPa, and tetragonal $I4/mmm$ at 20 K under 22 GPa. **These results suggest that a tetragonal structure is not a prerequisite for the emergence of superconductivity in nickelates. This result lays the ground for theoretical calculations in the crystallographic aspect.**

(4) Enhancing T_c to 96 K in nickelate superconductors (Fig. R9 and Fig. R10). Increasing the superconducting transition temperature (T_c) is a grand challenge for high- T_c superconductivity research and potential application. The T_c in nickelates has been maintained to be ~ 80 K since the discovery of superconductivity in $\text{La}_3\text{Ni}_2\text{O}_7$ (Sun et al. *Nature*). We are the first team to successfully enhance T_c to the 90 K range (arXiv: 2501.14584). After the first submission, we have further enhanced the $T_{c, \text{max}}^{\text{onset}}$ to 96 K, which is 5 K higher than our previously reported value ($T_{c, \text{max}}^{\text{onset}}=91$ K). The T_c enhancement was guided by the in-plane distortion mechanism proposed in our revised manuscript (Figs.5 and 1l). This new $T_{c, \text{max}}^{\text{onset}}$ value of 96 K significantly surpasses previous records in the literature. **Our results clearly demonstrate the effectiveness of our proposed in-plane distortion strategy for further increasing T_c . We are confident that these findings will stimulate extensive exploration, higher and higher T_c values can be further achieved by the research community once our results get formally published. We believe these latest results represent a significant breakthrough, analogous to the discovery of “YBCO” in cuprates, and hold significant importance for the field of high-temperature superconductivity.**

In sum, following the Referee’s criticism and suggestions, we have performed additional experiments and these data significantly enhance the overall impact of our manuscript. In particular, we provide new insights into the physics of superconductivity and resolve the structure of the superconducting phase.

C. Data & methodology: validity of approach, quality of data, quality of presentation

I do not find serious problems with the quality of the data. Please see E regarding the quality of the presentation.

Response: We thank the Referee for reviewing our manuscript. We have addressed all issues in E.

D. Appropriate use of statistics and treatment of uncertainties

Looks appropriate.

Response: We thank the Referee for reviewing our manuscript.

E. Conclusions: robustness, validity, reliability

Here I list several comments and concerns:

1. In the abstract, the authors state “but also providing a direction for discovering superconducting nickelates with higher T_c .” This sentence is too abstract. What “direction” are the authors talking about?

Response: We thank the Referee for pointing out the vague language in our previous version. We found an interesting correlation between T_c and ambient-pressure in-plane distortion $\Delta=(a-b)/(a+b)$ after analyzing the crystal structure at ambient pressure and the $T_{c,max}$ under high pressure for bilayer $\text{La}_3\text{Ni}_2\text{O}_7$, $\text{La}_2\text{PrNi}_2\text{O}_7$ and $\text{La}_2\text{SmNi}_2\text{O}_7$ (**Fig. R9**). Guided by this insight, we extracted the lattice parameters of all $\text{La}_{3-x}\text{R}_x\text{Ni}_2\text{O}_{7-\delta}$ ($\text{R}=\text{La-Er}$) and calculated their Δ (**Fig. R11**). Notably, Δ shows a dome shape as a function of rare earth elements with the largest value from $\text{La}_{0.87}\text{Nd}_{2.13}\text{Ni}_2\text{O}_{7-\delta}$ and the second largest from $\text{La}_{1.57}\text{Sm}_{1.43}\text{Ni}_2\text{O}_{7-\delta}$. We measured the resistivity of $\text{La}_{1.57}\text{Sm}_{1.43}\text{Ni}_2\text{O}_{7-\delta}$ at high pressures and found a $T_{c,max}^{\text{onset}}$ of 96 K at 26.8 GPa using paraffin as PTM, which is the highest T_c among all nickelate superconductors (**Fig. R10**). This result validates our strategy for T_c enhancement. Following this trend, it is likely to obtain superconductivity near 100 K in the bilayer nickelate $\text{La}_{0.87}\text{Nd}_{2.13}\text{Ni}_2\text{O}_{7-\delta}$ under high pressures. We have included this information in the revised manuscript.

2. In the abstract, the authors write “suggesting a potential universal mechanism governing high-temperature superconductivity in these isostructural bilayer transition metal oxides.” However, this claim lacks sufficient justification and is not supported by a firm theoretical or experimental foundation. Broadly speaking, there are two approaches (weak coupling and strong coupling) for considering the pairing mechanism in high-temperature superconductors. In the weak coupling approach, the shape of the Fermi surface plays an important role. However, bilayer cuprates and nickelates differ in their band structures and electron filling, resulting in distinct Fermi surfaces. Thus, a universal mechanism based on weak coupling arguments cannot be justified. In the strong coupling approach, local electron correlations dominate. In cuprates, the x^2-y^2 orbital is nearly half-filled, leading to localized $S=1/2$ moments. In contrast, in nickelates, both a nearly half-filled z^2 orbital and a nearly quarter-filled x^2-y^2 orbital are involved, indicating a fundamentally different local electronic environment. Therefore, the underlying local physics is also not universal. Why did the authors state this? Only from T_c ? Without firm experimental indication of a universal mechanism, I suggest the author delete this sentence.

Response: We thank the Referee for pointing out this issue. Indeed, we wrote the statement in our previous manuscript based on the similarity of T_c in the 90 K range. We totally agree with the referee, and we have deleted this sentence.

3. The authors report a monoclinic $P2_1/m$ space group, which is different from the previous report. I recommend that the authors elaborate on this issue. In particular, the authors state that they annealed under oxygen pressure. Is there any information on the crystal structure after annealing?

Response: We thank the Referee for pointing out this issue. Indeed, the as-grown $\text{La}_3\text{Ni}_2\text{O}_7$ belongs to the monoclinic $P2_1/m$ space group with lattice parameters of $a=5.4370(2)$ Å, $b=5.3978(2)$ Å, $c=10.6173(4)$ Å and $\beta=104.817(1)^\circ$. The symmetry of the as-grown $\text{La}_3\text{Ni}_2\text{O}_7$ is lower than $Cmcm$. Our finding is consistent with the theoretical calculations that $P2_1/m$ has lower total energy compared with that of $Cmcm$ [Chen et al. *Phys. Rev. B* 111, 014515 (2025)]. A similar symmetry lowering from orthorhombic to monoclinic has been reported in $\text{La}_4\text{Ni}_3\text{O}_{10}$ [Zhang et al. *Phys. Rev. Mater.* 4, 083402 (2020)]. We have added the above information to the revised manuscript.

We have performed synchrotron X-ray single crystal diffraction measurements on the annealed $\text{La}_2\text{SmNi}_2\text{O}_{7-\delta}$ single crystals, and we found that the symmetry maintains $P2_1/m$ (**Fig. R13**). We have included this information in the revised manuscript.

4. Related to 3. I find it interesting that the effect of chemical pressure is highly anisotropic between the a and b axes. For example, when La is replaced by Sm, the b -axis decreases, and the a -axis increases slightly. What is the origin of the a -axis expansion?

Response: We thank the Referee for asking this question. The substitution of smaller Sm^{3+} (1.132 Å for CN=9 and 1.24 for CN=12, and CN is short for coordination number) for La^{3+} (1.216 Å for CN=9 and 1.36 Å for CN=12) in the bilayer $\text{La}_3\text{Ni}_2\text{O}_7$ is expected to shrink the lattice and enhance local structural distortions. However, the chemical pressure is highly anisotropic. One notable feature in the crystal structure of $\text{La}_2\text{SmNi}_2\text{O}_7$ is that the substitution of rare earth elements is not randomly on all La sites. Specifically, our X-ray single crystal diffraction and STEM (**Fig. R1f**) measurements evidenced that the La site between bilayers is dominated by Sm while the La site within the bilayer is mostly occupied by La (**Figs. R18f,g**). This preference on Sm substitution is likely responsible for the anisotropic chemical pressure.

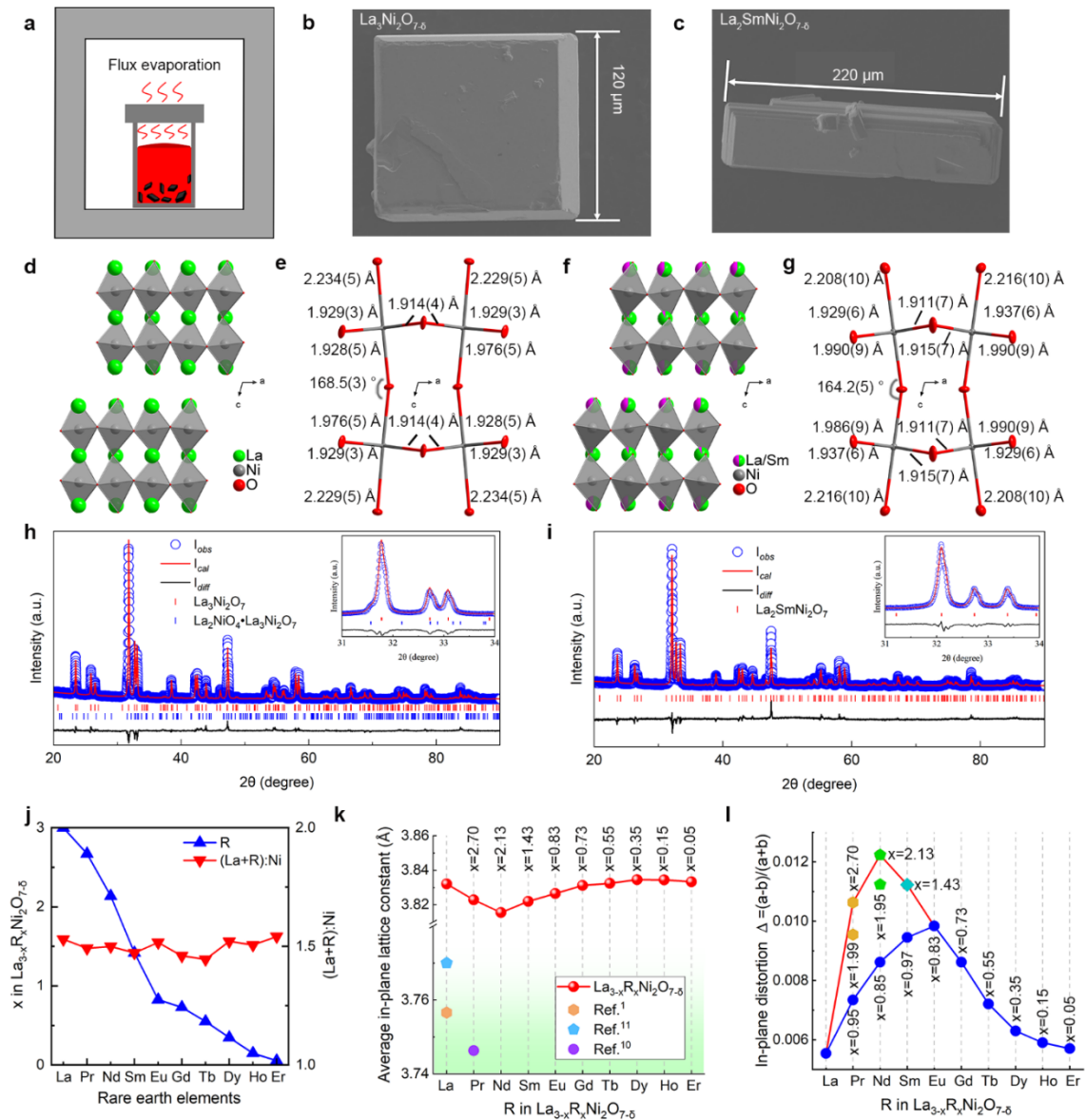


Fig. R18 (revised **Fig. 1**) **Ambient-pressure flux growth and characterization.** **a**, Scheme of crystal growth at ambient pressure. **b,c**, Typical scanning electron microscopy (SEM) images of $\text{La}_3\text{Ni}_2\text{O}_{7-\delta}$ and $\text{La}_2\text{SmNi}_2\text{O}_{7-\delta}$ single crystals. **d**, Crystal structure of $\text{La}_3\text{Ni}_2\text{O}_{7-\delta}$. **e**, Ellipsoid drawings of the NiO_6 octahedra of $\text{La}_3\text{Ni}_2\text{O}_{7-\delta}$ with bond distances and bond angles labeled. **f**, Crystal structure of $\text{La}_2\text{SmNi}_2\text{O}_{7-\delta}$.

δ . **g**, Ellipsoid drawings of the NiO_6 octahedra of $\text{La}_2\text{SmNi}_2\text{O}_{7-\delta}$ with bond distances and bond angles labeled. **h,i**, Rietveld refinements on X-ray powder diffraction data of pulverized single crystals of $\text{La}_3\text{Ni}_2\text{O}_{7-\delta}$ and $\text{La}_2\text{SmNi}_2\text{O}_{7-\delta}$, respectively. **j**, Maximum substitution of La and molar ratio of $(\text{La}+\text{R}):\text{Ni}$ for different rare earth elements in as-grown $\text{La}_{3-x}\text{R}_x\text{Ni}_2\text{O}_{7-\delta}$ ($\text{R}=\text{La}-\text{Er}$) single crystals. **k**, The average in-plane lattice constants of $\text{La}_{3-x}\text{R}_x\text{Ni}_2\text{O}_{7-\delta}$ ($\text{R}=\text{La}-\text{Er}$) calculated by $a_{\text{average}}=(a^2+b^2)^{1/2}/2$ compared with those in superconducting states^{1,10,11}. **l**, Ambient-pressure in-plane lattice distortion $\Delta = (a-b)/(a+b)$ of bilayer nickelates $\text{La}_{3-x}\text{R}_x\text{Ni}_2\text{O}_{7-\delta}$ ($\text{R}=\text{La}-\text{Er}$).

5. Related to 3. I believe readers will be most interested in the crystal and electronic structures under high pressure. However, this crucial information is missing from the manuscript. While I understand that such measurements may be experimentally challenging, their absence diminishes the overall impact of the paper.

Response: We fully agree with the Referee that high-pressure crystal structure is crucial. We have performed synchrotron X-ray powder diffraction under high pressure at low temperatures, and we found that both monoclinic $P2_1/m$ and tetragonal $I4/mmm$ can support superconductivity (**Fig. R7**). Our results demonstrate that tetragonal structure is not a prerequisite for emergence of superconductivity, and this provides new insights into the physics of nickelate superconductivity.

For electronic structures under high pressure, it is very challenging to perform such measurements including angle-resolved photoemission spectroscopy (ARPES) and Scanning Tunneling Microscope (STM). To the best of our knowledge, few groups, if any, can do such measurements.

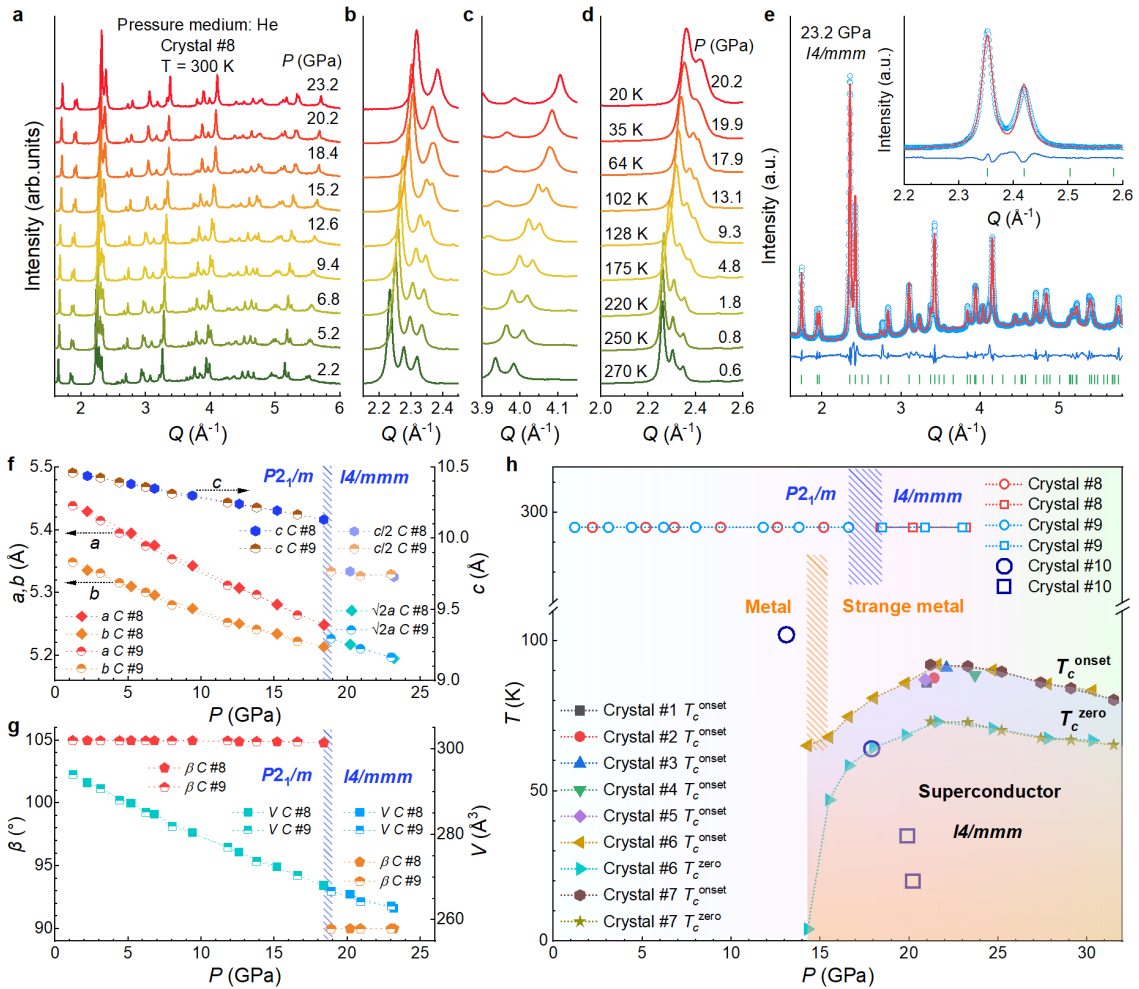


Fig. R7 (revised **Fig. 4**) Structure and T - P phase diagram of $\text{La}_2\text{SmNi}_2\text{O}_{7-\delta}$. **a**, Room-temperature

synchrotron X-ray powder diffraction (XRD) patterns of annealed $\text{La}_2\text{SmNi}_2\text{O}_{7-\delta}$ (pulverized Crystal #8, annealed at $p\text{O}_2=1.5$ bar for 10 days) in the Q range of $1.6\text{--}6\text{ \AA}^{-1}$ ($\lambda = 0.4834\text{ \AA}$) under different pressures with helium as the pressure transmitting medium. **b**, An enlarged view of **a** in the Q range of $2.15\text{--}2.45\text{ \AA}^{-1}$. **c**, An enlarged view of **a** in the Q range of $3.9\text{--}4.15\text{ \AA}^{-1}$, highlighting the gradual merging of the diffraction peaks on compression. **d**, An enlarged view of the powder diffraction patterns collected for annealed $\text{La}_2\text{SmNi}_2\text{O}_{7-\delta}$ in the Q range of $2.2\text{--}2.6\text{ \AA}^{-1}$ ($\lambda = 0.4133\text{ \AA}$) at various temperatures and pressures using helium as the pressure transmitting medium. **e**, Rietveld refinement using $I4/mmm$ on the powder XRD pattern of $\text{La}_2\text{SmNi}_2\text{O}_7$ under 23.2 GPa. The inset illustrates the enlarged view of the refinement data in the Q range of $2.2\text{--}2.6\text{ \AA}^{-1}$. Note the blue circles represent the observed diffraction intensities, the red lines denote the calculated intensities, the blue lines indicate the difference between the observed and calculated intensities, the green bars mark the diffraction peak positions. **f,g**, Extracted lattice parameters of $\text{La}_2\text{SmNi}_2\text{O}_7$ from Rietveld refinements as a function of pressure. Crystal #8 (C #8) and Crystal #9 (C #9, annealed at $p\text{O}_2=1.5$ bar for 10 days) represent two independent experiments. **h**, T - P phase diagram of $\text{La}_2\text{SmNi}_2\text{O}_{7-\delta}$. The black solid squares, red solid circles, blue solid triangles, green solid triangles, violet solid diamonds, khaki solid triangles, and wine solid hexagons represent the T_c^{onset} of single crystals #1 to #7 under pressure, respectively. The cyan solid triangles and light-green solid stars represent the T_c^{zero} of single crystal #6 and #7 under pressure, respectively. The red hollow circles and red hollow squares represent the $P2_1/m$ and $I4/mmm$ of pulverized single crystals C #8, respectively. The cyan hollow circles and cyan hollow squares represent the $P2_1/m$ and $I4/mmm$ of pulverized single crystals C #9, respectively. The blue hollow circles and blue hollow squares represent the $P2_1/m$ and $I4/mmm$ of pulverized single crystals Crystal #10, respectively.

6. Although the authors discuss onset T_c , I believe that T_c^{zero} is as important as T_c^{onset} . I recommend the authors properly mention this in the paper.

Response: We totally agree with the Referee. We have added $T_c^{\text{zero}}=73\text{ K}$ in the revised manuscript (**Fig. R4 and Fig. R5**).

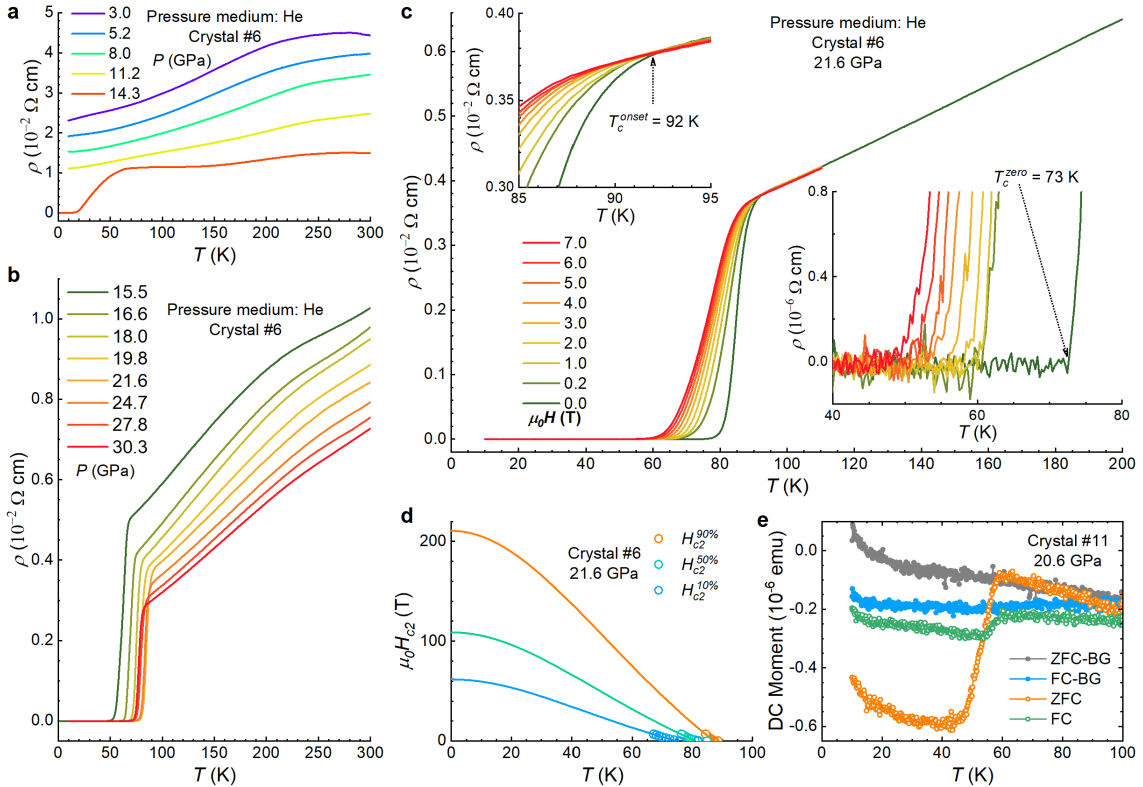


Fig. R5 (revised **Fig. 3**) **Bulk high- T_c superconductivity in $\text{La}_2\text{SmNi}_2\text{O}_7$ under high pressures.** **a**, Temperature-dependent resistivity of Crystal #6 (annealed at $p\text{O}_2=1.5$ bar for 10 days) under pressure in a helium-filled diamond anvil cell (DAC) under pressures below 14.3 GPa. **b**, Temperature-dependent resistivity of Crystal #6 under pressures from 15.5 GPa to 30.3 GPa. **c**, Field effects on the resistivity of Crystal #6 at 21.6 GPa. The upper-left and lower-right insets illustrate the temperature-dependent resistivity behavior in the vicinity of T_c^{onset} and T_c^{zero} , respectively. **d**, Upper critical fields extracted using the normal-state resistance values at 90%, 50%, and 10% of the resistivity at T_c^{onset} . Note open circles represent data and solid lines show the fit with a Ginzburg–Landau model. **e**, Direct-current (DC) magnetic susceptibility of single-crystal $\text{La}_2\text{SmNi}_2\text{O}_7$ (Crystal #11, annealed at $p\text{O}_2=1.5$ bar for 10 days) measured at 20.6 GPa under an applied magnetic field of 10 Oe using both zero-field-cooled (ZFC) and field-cooled (FC) modes. Note that BG is short for background.

7. (optional) Did the authors observe superconductivity for their $\text{La}_3\text{Ni}_2\text{O}_{7-\delta}$ samples under pressure?

Response: We have measured the high-pressure resistance of $\text{La}_3\text{Ni}_2\text{O}_{7-\delta}$ single crystals using NaCl as the pressure transmitting medium. We observed superconductivity with $T_c^{\text{onset}} \sim 80$ K and $T_c^{\text{zero}} = 56$ K, but the reproducibility is not very good due to the existence of intrinsic intergrowth and inhomogeneity of high-pressure environment of NaCl.

F. Suggested improvements: experiments, data for possible revision

All issues raised in E need to be carefully reexamined.

Response: We thank the Referee for his/her comments and suggestions. We have addressed all issues raised in E.

G. References: appropriate credit to previous work?

I do not find serious problems.

Response: We thank the Referee for reviewing our manuscript.

H. Clarity and context: lucidity of abstract/summary, appropriateness of abstract, introduction and conclusions

Please see E.

Response: We thank the Referee for reviewing our manuscript. We have addressed all concerns in E point-by-point. We hope now it is suitable for publication for *Nature*.

Other major changes we have made to improve the manuscript

1. Title.

We have changed the title from “Ambient pressure growth of bilayer nickelate single crystals with superconductivity over 90 K under high pressure” to “**Bulk superconductivity up to 96 K in pressurized nickelate single crystals grown at ambient pressure**” to better reflect our work.

2. Authors

We have added Zhenfang Xing, Tieyan Chang, Yu-Sheng Chen, Yuzhu Wang, Yuxin Liu, Tao Luo, Naohisa Hirao, Takahiro Matsuoka, Hirokazu Kadobayashi, and Zhidan Zeng in the author list to reflect their contribution.

3. Abstract

We have rewritten the abstract to include the new results.

4. Introduction.

We have rewritten the Introduction part. In the revised manuscript, we present the background and motivation more succinctly, focusing on the T_c enhancement and single crystal growth technique issue addressed in this study.

5. Main text

We have rewritten the transport results by including zero resistance and Meissner effect. We have added three parts: crystal structure in the superconducting state, T-P phase diagram, and T_c increased to 96 K. We have also rewritten the Conclusion part.

6. Meissner effect.

We have performed direct-current magnetic susceptibility measurements at high pressures ([Fig. R5e](#) and [Fig. R6](#)). Diamagnetic signal in both ZFC and FC is clearly seen, demonstrating Meissner effect. The superconducting volume fraction is estimated to be $> 60\%$, evidencing bulk superconductivity. We have added the above information in the revised manuscript.

RESPONSE TO EDITORIAL SUGGESTIONS

From a stylistic point of view, the paper is in reasonably good shape, although there are a few issues that require attention. Below I will run through our full formatting guidelines. The main points to note are:

1. Title. With 100 characters, this is too long - our length limit is 75 characters (including spaces). We suggest that you simply truncate the present title by omitting “grown at ambient pressure”. But do feel free to suggest alternatives.

Response: We have removed “grown at ambient pressure” from the title. The revised title is “Bulk superconductivity up to 96 K in pressurized nickelate single crystals”.

2. Length. With 5 display items (most of them large), the main paper is already pushing at our length limits. You should please ensure that the main paper gets no longer in revision (making greater use of the Methods section if necessary).

Response: We have revised the manuscript according to the Editor’s suggestions and the Referees’ comments/advice. The length of the revised manuscript has not increased compared to the previous version.

3. Extended data. Our normal limit for the number of extended data items (tables plus figures) is 10 - the present version of the paper has 15 items. We can be a bit flexible, but must nevertheless ask you to reduce the total number to 12 (perhaps by combining some of the existing extended data items into single multi-panel displays).

Response: We have reduced the number of extended data items to 12. Specifically, we have moved the previous Extended Data Figs. 3 and 4 to the Supplementary Materials (current Supplementary Figs. 1 and 2), and merged previous Extended Data Figs. 10 and 11 into a single figure (current Extended Data Fig. 8).

4. Data/code availability. We *strongly* discourage the formulation “available on reasonable request”, as this is ambiguous, open to interpretation and implies some level of undeclared access restrictions. Ideally you should make arrangement for all of the relevant data should be made fully and freely available at the point of publication (e.g. via a recognized data repository). But if such materials can only be made available directly from you on request, any restrictions to potential access need to be clearly and precisely specified in the availability statement.

Response: We have changed “available on reasonable request” to “available on request”. The revised Data availability statement reads:

“The data supporting the findings of this study are available from the corresponding authors upon request or at Zenodo (<https://doi.org/10.5281/zenodo.17310348>)⁵⁵. The detailed crystal structure data from this study have been deposited in the Cambridge Crystallographic Data Centre (CCDC) website with the deposition numbers 2315725 and 2418256. Source data are provided with this paper”.

Now for our general guidelines.

Please note that the presentation of a *Nature* paper has undergone significant changes in recent years to improve its readability and navigability online. Specifically, in most instances any supplementary text and data figures/tables can now be integrated into the main paper rather than presented in a separate

Supplementary Information file. An overview of the key features and differences may be found in the Composition of a *Nature* Paper (http://s3-service-broker-live-19ea8b98-4d41-4cb4-be4c-d68f4963b7dd.s3.amazonaws.com/uploads/ckeditor/attachments/7824/3g_Paper_composition.pdf).

Response: Due to the limit of Extended Data figures/tables, we have included three figures in the Supplementary Information file.

This journal strongly supports public availability of data and custom code. Please place the data and code used in your paper into a public data repository, or alternatively, present the data as Supplementary Information. If data and code can only be shared on request, please explain why in your Data Availability Statement, and also in the correspondence with your editor. Please note that for some data types, deposition in a public repository is mandatory.

If you need help with our data sharing policies or finding a suitable data repository, you should consider:

- Contacting Springer *Nature*'s Research Data [Helpdesk](#) for advice. The helpdesk provides free advice on research data policies of funders, institutions and journals and on finding research data repositories.
- Finding a suitable [data repository](#) for your data from our recommended repository list. Where they are available, community specific repositories are preferred. Unstructured repositories are suitable alternatives if no structured public repositories exist.

Response: We have uploaded all the data supporting this study into the public data repository Zenodo (<https://doi.org/10.5281/zenodo.17310348>).

LENGTH: We estimate the current length of your paper (main text, excluding abstract and Methods) to be ~2,500 words. With 5 display items (most of them large) as at present, this is a bit longer than we would normally allow. We can live with this, but please ensure that the main paper gets no longer in revision. Keep in mind that important technical details that are not central to the main message of the paper can be moved into the Methods section or, if necessary, a Supplementary Information section (see below).

Response: The revision has not increased the length of the manuscript.

TITLES: Titles cannot exceed 75 characters (including spaces); they must not contain punctuation. We suggest "Bulk superconductivity up to 96 K in pressurized nickelate single crystals".

Response: We have adopted the suggested title.

SUMMARY PARAGRAPH: This is fine as it stands - I give you the guidelines for your information. All *Nature* papers begin with a fully referenced paragraph, typically no longer than 200 words, aimed at readers in other disciplines. This paragraph starts with a 2- to 3-sentence, basic introduction to the field; continues with a 1-sentence statement of the main findings starting 'Here we show' or an equivalent phrase; and finally, concludes with 2 to 3 sentences putting the main findings into general context so it is clear how the results described in the paper have moved the field forward. A downloadable, annotated example is available at <https://www.nature.com/nature/for-authors/formatting-guide>. In some cases it may be necessary to exceed this limit in order to explain complex material for readers in other fields - in such cases, summary paragraphs can be up to 230 words in length. The extra length, however, is for introduction and context, and not for additional technical information.

Response: We thank the Editor for the guidelines for the Summary Paragraph. In response to Comment #1, Referee #3, we have changed the sentence “Our low-temperature high-pressure structural study indicates that the tetragonal structure may not be a prerequisite for superconductivity to appear in this bilayer nickelate.” to “Our low-temperature high-pressure structural study indicates that both monoclinic and tetragonal structures can support superconductivity in this bilayer nickelate.”

MAIN TEXT: Further introductory material in the main text of the paper should not be necessary. Any discussion at the end of the paper should also be brief, and not repeat what is already written in the initial summary paragraph. Subheadings of up to 40 characters (including spaces) may be used to separate sections of the paper if this aids navigation.

Response: We have revised the subheadings to stay within the 40-character limit. Specifically, we have changed “Single crystal growth at ambient pressure” to “Single crystal growth at 1 atm”, and changed “Crystal structure in the superconducting state” to “Structure in the superconducting state”.

STATISTICS: Authors should ensure that any statistical analysis used is sound and that it conforms to the journal's guidelines (see <https://www.nature.com/nature/for-authors/formatting-guide> for guidance).

Response: We have checked and confirmed that all statistics analyses comply with *Nature*'s guidelines.

METHODS: At the end of the main text document (after the main figure legends), there should be a section entitled "Methods", which provides a more detailed discussion of the additional methodological information that would allow other researchers to replicate the results (we define “Methods” quite broadly, so this is not limited to details of experimental protocols – supplementary discussion and analysis can also be included). The Methods section will not appear in the print version but will be fully copy-edited and appear online in the full-text HTML and PDF versions. The Methods section should be written as concisely as possible but should contain all elements necessary to allow interpretation and reproduction of the results. If there are additional references in the Methods section, their numbering should continue from the last reference in the main paper, and the list should follow the Methods section. If the methods require chemical structures, figures or tables, these should be supplied as Extended Data (see below). For supplemental material that cannot be accommodated in Methods/Extended Data, the excess should instead be supplied as a separate Supplementary Information file. (But please do prioritise Methods/Extended Data over Supplementary Information, as the former will be fully integrated into the main paper.)

Response: We have checked our Methods and ensured it is in line with these guidelines.

REFERENCES: As a guideline, most papers should need no more than 50 references in the main text; additional references can be cited in (and listed after) the Methods section, as detailed above.

Response: We thank the Editor's guidelines. We have 48 references in the main text, and 7 in the Methods section.

MAIN TEXT STATEMENTS: We require authors to provide a detailed Author Contribution statement immediately after the acknowledgements; the specific contributions of each author must be listed. It is also a condition of publication that authors include an Author Information statement indicating how to access information regarding reprints and permissions, stating whether or not there is a financial or non-financial competing interest, and naming the author to whom correspondence and requests for materials

should be addressed. Please ensure that this section is included in the manuscript file after the Methods (but before the Extended Data legends) - it will not appear in the print version but will appear online in the full-text HTML and PDF versions. For details of "end note" style and an example see <https://www.nature.com/nature/for-authors/formatting-guide>.

Response: We thank the Editor's guidelines. We have provided a detailed Author Contribution statement immediately after the acknowledgements. We have included an Author Information statement between Methods and Extended Data legends, indicating how to access information regarding reprints and permissions, stating there is no competing interests, and to whom correspondence and requests for materials should be addressed.

DATA AVAILABILITY STATEMENT: All published manuscripts reporting original research in *Nature* Portfolio journals must include a data availability statement. The data availability statement must make the conditions of access to the "minimum dataset" that are necessary to interpret, verify and extend the research in the article, transparent to readers. This minimum dataset may be provided through deposition in public community/discipline-specific repositories, custom proprietary repositories for certain types of datasets, or general repositories like Figshare, Zenodo and Dryad. Providing large datasets in supplementary information is strongly discouraged and the preferred approach is to make data available in repositories. More information on Nature Portfolio's reporting standards and preparing your Data Availability Statement can be found here: <https://www.nature.com/nature-portfolio/editorial-policies/reporting-standards#reporting-requirements>

Response: We have provided the following Data availability Statement in the revised manuscript:

"The data supporting the findings of this study are available from the corresponding authors upon request or at Zenodo (<https://doi.org/10.5281/zenodo.17310348>)⁵⁵. The detailed crystal structure data from this study have been deposited in the Cambridge Crystallographic Data Centre (CCDC) website with the deposition numbers 2315725 and 2418256. Source data are provided with this paper".

For all studies using custom code or mathematical algorithm that is deemed central to the conclusions, a statement must be included under the heading "Code availability", indicating whether and how the code or algorithm can be accessed, including any restrictions to access. Code availability statements should be provided as a separate section after the data availability statement but before the References. Code should be deposited in a DOI-minting repository such as Zenodo, Gigantum or Code Ocean and cited in the reference list. Authors are encouraged to manage subsequent code versions and to use a license approved by the open source initiative. Additional details can be found here: <https://www.nature.com/nature-research/editorial-policies/reporting-standards#availability-of-computer-code>.

Response: We have no custom code or mathematical algorithm that is central to the conclusions.

FIGURE LEGENDS: These should be listed sequentially after the references in the main text and not in the figures files. Each legend should begin with a brief title for the whole figure and continue with a short description of each panel and the symbols used. Any error bars in the figures must be defined (for example, s.d., s.e.m.) and the value of n indicated; see <https://www.nature.com/nature/for-authors/formatting-guide> for further explanation.

Response: We have listed Figure legends sequentially after the references in the main text, as required.

DISPLAY ITEMS: We ask that you take stock of all the data that have been generated throughout the review process and ensure that only the data most central to the conclusions are presented in the main

figures. Figures should be comprehensible to readers in other or related disciplines, and assist their understanding of the paper. We encourage authors who are describing complex processes to include a schematic of the main finding as part of the Extended Data to aid readers unfamiliar with the immediate discipline. Figures should be as small and simple as is compatible with clarity. All panels of a figure should be logically connected; each panel of a multipart figure should be sized so that the whole figure can be reduced by the same amount and reproduced on the printed page at the smallest size at which essential details are visible. For guidance, *Nature's* standard figure sizes are 89 mm (one column), 120 mm (one and a half columns), or exceptionally 183 mm (two columns) wide; the full depth of a Nature page is 247 mm. All panels of figures should be presented on a single page and assembled into a rectangular shape for publication; please indicate any essential alignments (parts horizontal, vertical, spacings of stereo pairs, etc.). Tables should be prepared using the Table menu in Microsoft Word.

Response: We thank the Editor for the guidelines for Display items. We have checked our display items according to these guidelines.

FIGURE FORMATTING: Lettering in all figures (labelling of axes and so on) should be in uniform, sans-serif font, in lower-case type, and large enough to permit substantial reduction for publication (minimum font size 5 pt). Separate parts of a figure are labelled a, b, etc. Units have a single space between the number and the unit, and follow SI nomenclature or the nomenclature common to a particular field. Thousands are separated by commas (1,000). Unusual units or abbreviations are defined in the legend. Scale bars rather than magnification factors should be used.

Response: We thank the Editor for the guidelines for Figure Formatting. We have checked our figures according to these guidelines.

IMAGE PRESENTATION: Authors should be aware that any image provided for publication, either in print or online (as Extended Data or Supplemental Information), may be subject to a quality control process to check for image integrity and manipulation. For a full discussion of our standards regarding how images should be prepared and presented, see www.nature.com/authors/editorial_policies/image.html.

Response: We are aware that any image may be subject to a quality control process to check for image integrity and manipulation.

EXTENDED DATA: *Nature* is now integrating the supplemental figures and tables into the final version of most papers. Extended Data do not appear in the printed version of the paper but are included online within the full-text HTML and at the end of the online PDF. Extended Data are an integral part of the paper and only data that directly contribute to the main message should be presented. All Extended Data must be referred to in the main text, figure legends and/or Methods section, and their figure legends should be listed sequentially at the end of the main text, not in the Extended Data files. Authors should assemble the Extended Data into a maximum of ten, A4 size, multi-panelled display items, submitted as individual JPEG, TIFF or EPS files (we can stretch this to 12 in the present case). They must be provided at the same quality as figures for print, but there are important differences in their formatting. More specific instructions are provided in the Extended Data Formatting Guide ([http://s3-service-broker-live-19ea8b98-4d41-4cb4-be4c-](http://s3-service-broker-live-19ea8b98-4d41-4cb4-be4c-d68f4963b7dd.s3.amazonaws.com/uploads/ckeditor/attachments/7823/3h_Extended_data.pdf)

[d68f4963b7dd.s3.amazonaws.com/uploads/ckeditor/attachments/7823/3h_Extended_data.pdf](http://s3-service-broker-live-19ea8b98-4d41-4cb4-be4c-d68f4963b7dd.s3.amazonaws.com/uploads/ckeditor/attachments/7823/3h_Extended_data.pdf)).

Response: We thank the Editor for the guidelines for Extended Data. We have checked our Extended Data according to these guidelines. We have uploaded the Extended Data in the format of TIFF.

SUPPLEMENTARY INFORMATION: Supplementary Information is online-only material published with the manuscript (<https://www.nature.com/nature/for-authors/supp-info>). For most papers, there should be no need for Supplementary Information beyond that already provided as Methods and Extended Data, the aim being to avoid unnecessary fragmentation of the paper online. Exceptions to this rule include large datasets that cannot be accommodated within Extended Data; video material; and more complex “Supplemental Methods” (and any associated references) that do not readily fit within the constraints of the Methods/Extended Data formats.

Please note that after the paper has been formally accepted you can only provide amended Supplementary Information files for critical changes to the scientific content, not for style. You should clearly explain what changes have been made if you do resupply any such files.

Response: We thank the Editor for the guidelines for Supplementary Information. We have included three Supplementary figures in the Supplementary Materials due to the limit on Extended Data figures/tables.

SOURCE DATA: To further increase transparency, we encourage authors to provide, in spreadsheet form, the data underlying the graphical representations used in the figures. This is in addition to our well-established data-deposition policy for specific types of experiments and large datasets. Readers of the online manuscript will be able to access the Source Data directly from the figure legend. Spreadsheets can only be submitted in .xls, .xlsx or .csv formats. One file per figure is permitted; thus, if there is a multi-panelled figure the Source Data for each panel should be clearly labeled in the csv/Excel file; alternatively, the data for a figure can be included in multiple, clearly labeled sheets within an Excel file. File sizes of up to 30 MB are permitted; however, it is expected that the vast majority of Source Data files will be considerably smaller than this. When submitting these files with your manuscript, please select the file type “Source Data” and use the title field in the file description tab to indicate the figure to which the Source Data pertain.

Response: Source data in the format of .xlsx have been provided with the revised manuscript.

Nature is committed to improving transparency in authorship. As part of our efforts in this direction, we are now requesting that all authors identified as ‘corresponding author’ create and link their Open Researcher and Contributor Identifier (ORCID) with their account on the Manuscript Tracking System prior to acceptance. ORCID helps the scientific community achieve unambiguous attribution of all scholarly contributions. You can create and link your ORCID from the home page of the Manuscript Tracking System by clicking on ‘Modify my Springer Nature account’ and following the instructions in the link below. If you experience problems in linking your ORCID, please contact the [Platform Support Helpdesk](#).

Response: All authors identified as ‘corresponding author’ – Di Peng, Qiaoshi Zeng, Xutang Tao and Junjie Zhang - have linked their ORCID with their account on the Manuscript Tracking System.

RESPONSE TO REFEREES' COMMENTS

Below, we detail our responses to referees' comments point-by-point and explain how we revised the manuscript accordingly.

Referee #2

First, a few general remarks after going through the authors' replies to the three referee reports:

The repeated assertion by the authors that their "latest results represent a significant breakthrough, analogous to the discovery of YBCO in cuprates" is, frankly, greatly overstated. In my opinion, the impact of their work will be orders of magnitude lower for the field of high-temperature superconductivity compared to the discovery of YBCO.

Response: We thank the Referee for this perspective and we agree that the YBCO discovery set a uniquely high bar for impact. We have tempered our language accordingly and now emphasize the specific advances of this work (record high T_c for nickelates, a reproducible growth route, and a practical strategy for further T_c enhancement) without invoking direct analogies to YBCO.

The authors frequently argue that previous reports failed to demonstrate a clear Meissner effect in RP nickelates, claiming: "... there is no clear evidence of Meissner effect, in particular when a nickelate in a magnetic field is cooled below T_c , all or part of the magnetic field within the material is expelled or not remains elusive." Are they referring specifically to the absence of a kink-like anomaly in the field-cooled (FC) branch of DC susceptibility curves? Admittedly, the ZFC and FC curves for $\text{La}_2\text{SmNi}_2\text{O}_7$ in their current manuscript are exceptionally well resolved and stand out compared to earlier work. However, subtle FC anomalies also appear to be present in prior studies, including arXiv: 2404.11369 and Extended Data Fig. 10 of Zhu et al., *Nature* 631, 531-536 (2024).

Response: We appreciate this clarification. We are pleased that the Referee endorses that "the ZFC and FC curves for $\text{La}_2\text{SmNi}_2\text{O}_7$ in their current manuscript are exceptionally well resolved and stand out compared to earlier work". Yes, our prior statement specifically referred to the absence of a clear kink-like anomaly in the field-cooled (FC) DC magnetic susceptibility curves. We agree with the Referee and acknowledge that subtle FC anomalies appear in arXiv: 2404.11369v3 (2024) and Extended Data Fig. 10 of Zhu et al. *Nature* 631, 531-536 (2024).

In response to concerns raised about the lack of systematic annealing or pressure-dependent measurements across the entire sample series, the authors complain that this would be too time-consuming. However, this is not a scientifically valid justification for omitting key control data! Nonetheless, the revised version shifts focus more strongly to the Sm-based compound, reducing the importance of comparisons to samples with other rare-earths. Therefore, this omission becomes less problematic for the current version.

Response: We agree that full series-wide annealing/pressure measurements would be ideal. However, as the Referee notes, our revised focus on the Sm-based crystals reduces the need for exhaustive cross-series comparisons. We have clarified this scope in the text and framed our contribution as establishing a practical, and empirically grounded strategy for enhancing T_c in the RP nickelates, with the added comparison to previous nickelate work in **Fig. 5b** contextualizing the progress.

Concerning the authors' replies specifically to my comments: I had initial concerns about the actual substitution levels realized in the rare-earth series, and whether the structural trends presented were robust. In this context, the authors undertook appreciable effort to provide additional characterization measurements, mitigating my concerns. In general, the new high-pressure DC susceptibility, high-pressure XRD, and TGA measurements are commendable and increase the significance of the paper.

Response: We thank the Reviewer for reviewing our manuscript. We are pleased that the Referee is satisfied with our previous revision.

However, the comparability of the rare-earth series presented in Figs. 1k and 1l remains limited due to variation in substitution levels across samples. This compromises the interpretability of the trends shown in these panels, and the way the data are presented there could be reconsidered.

Response: The Referee asked a helpful clarifying question.

The intent of Fig. 1k is to show that it's impossible to achieve ambient-pressure superconductivity in these bulk bilayer nickelates because their average in-plane lattice constant is too large compared with those in the superconducting states. Thus, high pressure is still needed to induce superconductivity. Although we synthesized more compositions as presented in **Extended Data Table 2**, we only show the maximum substitution for each rare earth element because the smaller substitution has a larger average in-plane lattice constant (see **Fig. R1**). To be concise and clear, we only plot the average in-plane lattice constant of maximum substitution as a function of rare earth elements in **Fig. 1k**. We have included **Figure R1** in the revised Supplementary Materials, as **Supplementary Fig. 3**.

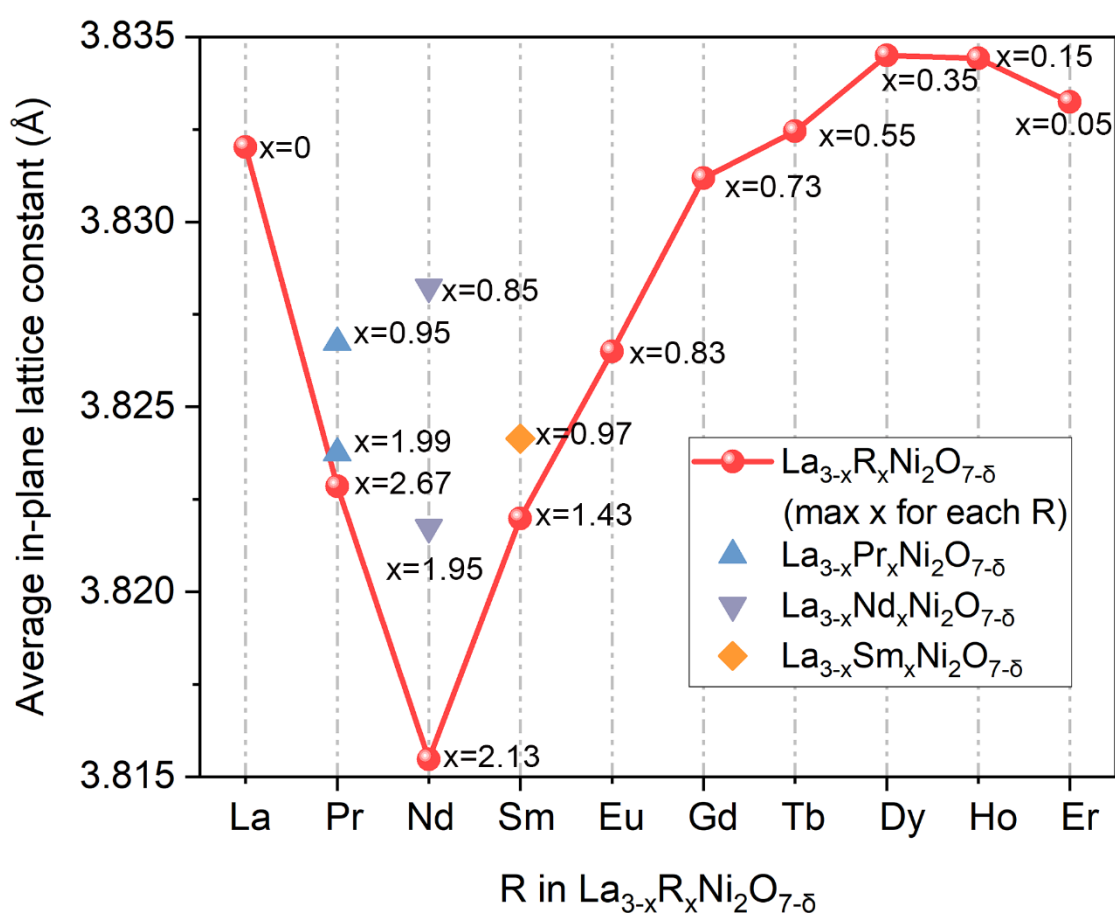


Fig. R1 (revised Supplementary Fig. 3) The average in-plane lattice constants of $\text{La}_{3-x}\text{R}_x\text{Ni}_2\text{O}_{7-\delta}$ ($\text{R}=\text{La}-\text{Er}$) calculated by $a_{\text{average}}=(a^2+b^2)^{1/2}/2$.

The purpose of Fig. 11 is to establish a correlation between the ambient-pressure in-plane distortion $\Delta=(a-b)/(a+b)$ and rare earth elements. To be clear, we first demonstrate that Δ show a maximum value for Eu when La:R=2:1 was used in the starting materials in our growth. Notably, Δ can be increased for R=Pr, Nd and Sm because their substitution is not saturated. We then maximized the substitution levels for R=Pr, Nd and Sm, and found that the largest Δ is from La_{0.87}Nd_{2.13}Ni₂O₇ among the compounds we grown at ambient pressure. Considering the strong correlation between Δ and $T_{c,max}$ (**Fig. 5a**), we then proposed to carry out high-pressure transport measurements on La_{1.57}Sm_{1.43}Ni₂O₇, which shows the second largest Δ . The observation of 96 K superconductivity in La_{1.57}Sm_{1.43}Ni₂O_{7- δ} supporting Δ as a useful empirical guide to higher T_c .

We believe the message conveyed in Fig. 1k and Fig. 11 is clear.

On the other hand, I am positively impressed by the newly reported superconducting onset at 96 K in the La_{1.57}Sm_{1.43}Ni₂O₇ sample. While zero resistivity is not reached and the transition appears two-step-like, the result is nonetheless very remarkable. After all, the overall message of Fig. 11 is compelling, and the manuscript proposes a plausible and empirically grounded strategy for enhancing T_c in the RP nickelates, with the added comparison to previous nickelate work in Fig. 5b contextualizing the progress.

Response: We thank the Referee for his/her endorsement on our discovery of $T_c^{onset}=96$ K in La_{1.57}Sm_{1.43}Ni₂O_{7- δ} and our strategy for enhancing T_c in the RP nickelates.

Regarding the absence of zero resistivity and the two-step-like transition, we have performed additional high-pressure transport measurements on La_{1.57}Sm_{1.43}Ni₂O_{7- δ} single crystals. First, we measured Crystal #2 (as grown) using paraffin as the pressure-transmitting medium. As shown in **Figs. R2e,f**, we reproduced the superconducting transition onset temperature of 96 K. Notably, there is no step-like feature at ~80 K, confirming that the step-like feature at ~80 K is not intrinsic, as we explained in our previous version. Then, we measured Crystal #3 (annealed at pO₂=1.5 bar for 10 days) using helium as the pressure-transmitting medium. **Fig. R2g** shows temperature-dependent resistivity of Crystal #3 at 21.6, 24.3 and 26.5 GPa. The superconducting transition onset temperature of 96 K at 21.6 GPa is also observed (**Fig. R2h**). **Fig. R2i** presents field dependence of resistivity of Crystal #3 at 21.6 GPa. A pronounced suppression of superconductivity by applied magnetic fields is observed. We have included transport data of Crystal #2 and #3 in the revised **Extended Data Fig. 10**. We have also updated **Fig. 5b** (**Fig. R3b**) for La_{1.57}Sm_{1.43}Ni₂O_{7- δ} .

We acknowledge that zero resistivity has not yet been achieved for La_{1.57}Sm_{1.43}Ni₂O_{7- δ} probably due to oxygen defects (Similar phenomena have been observed in La₂SmNi₂O_{7- δ} , as shown in **Extended Data Fig. 3**). We outline ongoing steps aiming at attaining zero resistivity: (1) optimizing annealing conditions to reduce oxygen defects and tune oxygen content, and (2) performing high pressure transport measurements using helium as the pressure-transmitting medium.

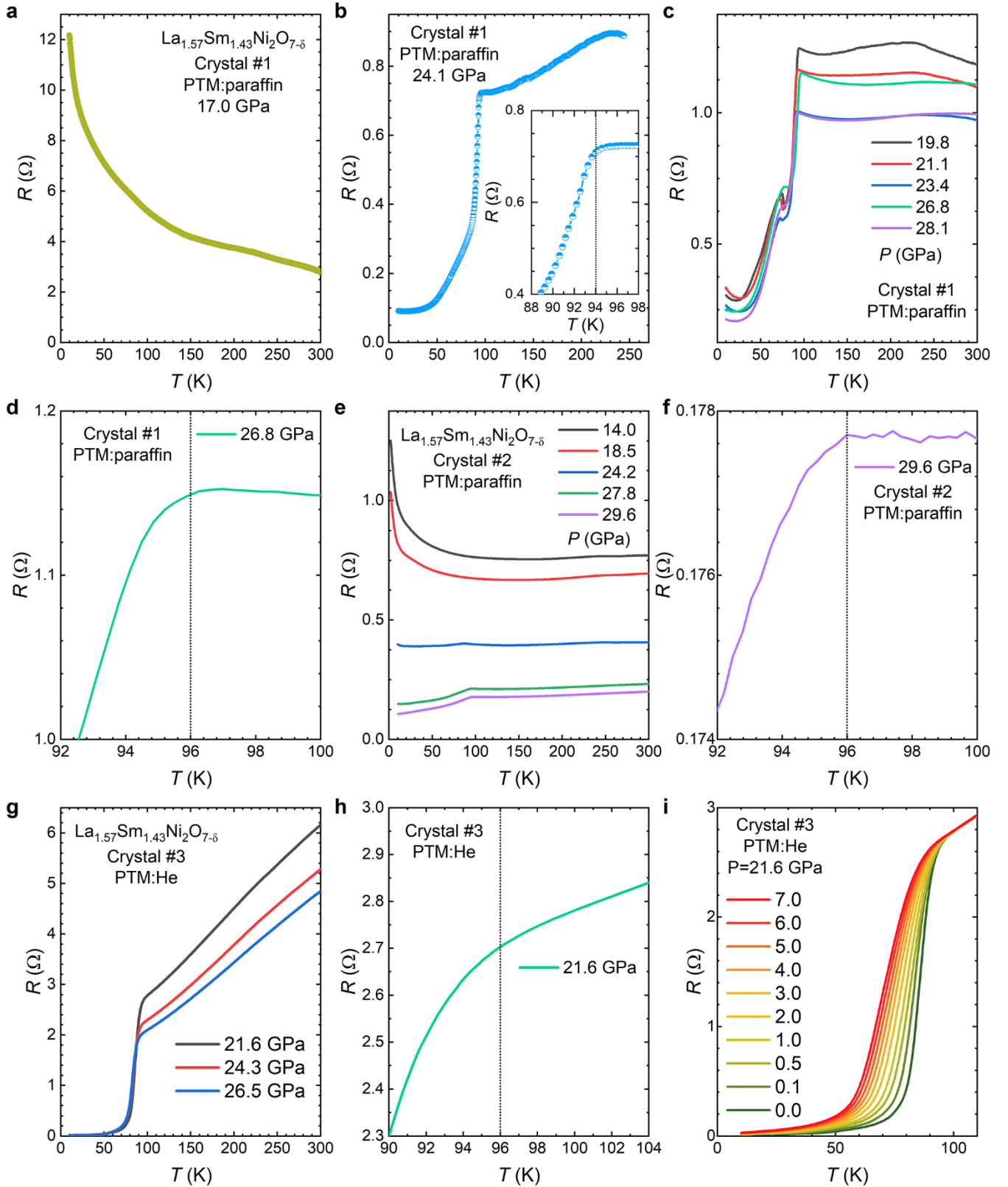


Fig. R2 (revised Extended Data Fig. 10) | Superconductivity at 96 K in $\text{La}_{1.57}\text{Sm}_{1.43}\text{Ni}_2\text{O}_{7-\delta}$ single crystals under high pressures. **a**, Temperature-dependent resistance of Crystal #1 at 17 GPa. **b**, Temperature-dependent resistance of Crystal #1 (annealed at $p_{\text{O}_2}=1.5$ bar for 10 days) at 24.1 GPa. The Inset shows the zoom-in region around $T_{c^{\text{onset}}}$. **c**, Temperature-dependent resistance of Crystal #1 in the range of 19.8-28.1 GPa. The pressure was lowered from 24.1 GPa in **b** to 19.8 GPa, and then increased to 28.1 GPa. Note the step-like feature at around 80 K is absent in **b**, thus it's an artifact due to

inhomogeneity of pressure environment of paraffin. **d**, A zoom-in region around $T_c^{\text{onset}} = 96$ K at 26.8 GPa for Crystal #1. **e**, Temperature-dependent resistance of Crystal #2 in the pressure range of 14.0-29.6 GPa. **f**, Temperature-dependent resistance of Crystal #2 (as grown) at 29.6 GPa. The Inset shows the zoom-in region around $T_c^{\text{onset}} = 96$ K. **g**, Temperature-dependent resistivity of Crystal #3 (annealed at $pO_2 = 1.5$ bar for 10 days) at 21.6, 24.3 and 26.5 GPa. **h**, The zoom-in region around $T_c^{\text{onset}} = 96$ K at 21.6 GPa. **i**, Field dependence of resistivity of Crystal #3 at 21.6 GPa. Note that zero resistivity has not yet been achieved for $\text{La}_{1.57}\text{Sm}_{1.43}\text{Ni}_2\text{O}_{7-\delta}$ probably due to oxygen defects.

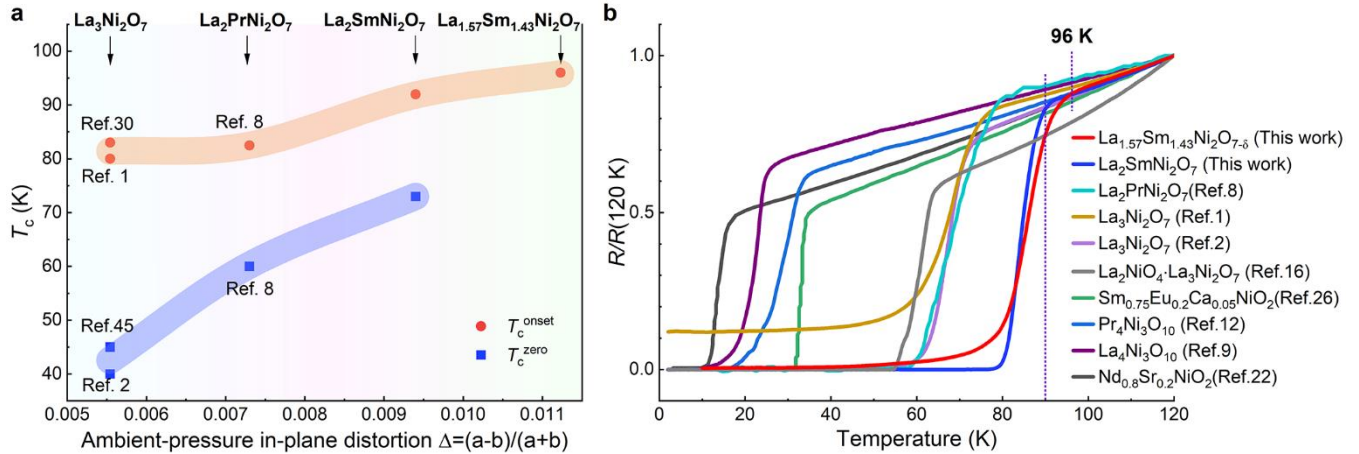


Fig. R3 (revised Fig. 5) | A strategy for T_c enhancement and record-high T_c . **a**, Maximum T_c of bilayer nickelates as a function of ambient-pressure in-plane lattice distortion $\Delta = (a-b)/(a+b)$. $T_{c,\text{max}}^{\text{onset}}$ and $T_{c,\text{max}}^{\text{zero}}$ of $\text{La}_3\text{Ni}_2\text{O}_7$ ^{1,2,30,45} and $\text{La}_2\text{PrNi}_2\text{O}_7$ ⁸ are from resistivity measurements. The blue and yellow lines are only for guiding eyes. **b**, Maximum T_c for various nickelates^{1,2,8,9,12,16,22,26}.

Taken together, and when considering the standard defined by other recent nickelate papers published in *Nature*, I consider this manuscript to be suitable for publication in *Nature* too. It presents noteworthy findings and clear progress over previous work, even if several aspects are not fully resolved.

Response: We thank the Referee for this assessment and for his/her recommendation for publication in *Nature*.

However, the statement in the manuscript that it is “likely” to obtain superconductivity near 100 K in $\text{La}_{0.87}\text{Nd}_{2.13}\text{Ni}_2\text{O}_7$ is not acceptable for publication and needs to be toned down. This is pure speculation based on a hypothesis derived from empirical observations on other samples. In fact, the authors do not present a robust theoretical rationale for why the smallest lattice parameter and/or the largest in-plane lattice distortion $(a-b)/(a+b)$ (see Fig. 1k and 1l) necessarily leads to the highest T_c . If they insist on making such strong claims about this Nd-based sample, they should rather attempt to detect superconductivity in this sample, which is apparently available to them.

Response: We agree with the Referee and we have removed the sentence suggesting ~ 100 K superconductivity in $\text{La}_{0.87}\text{Nd}_{2.13}\text{Ni}_2\text{O}_7$. Currently the single crystals of $\text{La}_{0.87}\text{Nd}_{2.13}\text{Ni}_2\text{O}_7$ samples are too small to perform high pressure transport measurements, and we will pursue this as crystal size improves in the future.

Referee #3

In the revised version, the authors have significantly improved the quality of the experimental results. The results presented in this paper represent an important contribution to the field of high-temperature superconductivity.

Response: We thank the Referee for reviewing our manuscript and for his/her endorsement on our work.

Below, I provide several comments.

1. It is great that the authors achieved structural analysis under high pressure. However, I feel that new insights into the physics of superconductivity are still lacking. For example, the statement that “tetragonal structure may not be a prerequisite for superconductivity to appear in this bilayer nickelate” relaxes the structural constraint, but it does not narrow down the conditions for realizing superconductivity.

Response: We have revised the statement in Summary Paragraph to be precise and constructive: “both monoclinic and tetragonal structures can support superconductivity in this bilayer nickelate”. This provides a concrete crystallographic boundary condition for future theoretical modeling.

2. (Related to 1) The authors discuss the conditions for achieving higher superconducting transition temperatures (T_c) based on the anisotropy of the lattice constants $(a-b)/(a+b)$ at ambient pressure. While this is interesting to some extent, superconductivity actually emerges when this anisotropy becomes weaker or disappears. Therefore, I am not sure whether this anisotropy should be regarded as a reliable indicator.

Response: We agree with the Referee that superconductivity emerges when $\Delta=(a-b)/(a+b)$ becomes weaker or disappears under high pressure. One key question is: prior to high pressure experiments, is it possible to assess how high the T_c of a nickelate superconductor could be under high pressure? Unfortunately, the origin of high- T_c superconductivity in the Ruddlesden-Popper nickelates under high pressure remains an open question, and no reliable prediction can be made by theory. Motivated by these, we found a strong correlation between ambient-pressure lattice distortion Δ and the highest $T_{c,max}$ under high pressure for bilayer $\text{La}_3\text{Ni}_2\text{O}_7$, $\text{La}_2\text{PrNi}_2\text{O}_7$ and $\text{La}_2\text{SmNi}_2\text{O}_7$, i.e., the larger Δ , the higher $T_{c,max}$. Notably, this guide indeed led to our discovery of the 96 K superconductivity in $\text{La}_{1.57}\text{Sm}_{1.43}\text{Ni}_2\text{O}_{7-\delta}$. We have clarified this framing in the text and emphasized that Δ is a heuristic, not a definitive predictor.

3. (Related to 2) The authors state “Following this trend, it is likely to obtain superconductivity near 100 K in the bilayer nickelate $\text{La}_{0.87}\text{Nd}_{2.13}\text{Ni}_2\text{O}_{7-\delta}$ under high pressures.” If this is merely speculation, I would recommend removing this statement.

Response: We thank the Referee for his/her recommendation. We have removed the sentence “Following this trend, it is likely to obtain superconductivity near 100 K in the bilayer nickelate $\text{La}_{0.87}\text{Nd}_{2.13}\text{Ni}_2\text{O}_{7-\delta}$ under high pressures.”

4. The authors conduct various experiments using different samples. I think that the use of different samples should be more explicitly mentioned in both the main text and the abstract.

Response: We thank the Referee for his/her constructive suggestion. We have explicitly mentioned the samples in the main text:

(1). In “Bulk superconductivity at 92 K” section (Page 5, Line 154), we have added “Crystal #1-5,7”

(2). In “Structure in the superconducting state” section, we have added “pulverized Crystal #8” (Page 5, Line 184-185), “pulverized Crystal #9” (Page 5, Line 187-188), and “on pulverized Crystal #10” (Page 6, Line 195).

5. Figure 4h is a bit difficult to understand. In particular, the data points for sample #10 and the T_c data points overlap, making the figure unclear. I recommend improving the figure to enhance its readability.

Response: We thank the Referee for pointing out this issue. To enhance its readability, we have modified Figure 4h in the following three aspects (see **Fig. R4**):

- (1) The symbol size of Crystal #10 is enlarged, so that it does not block the T_c data of Crystal #6;
- (2) We have added $P2_1/m$ to the blue circle to clearly indicate the structural symmetry;
- (3) We have changed the legends in the up-right corner to clearly show the crystal symmetries;
- (4) We have unified the legend style in **Figs. 4f,g,h** to make them consistent.

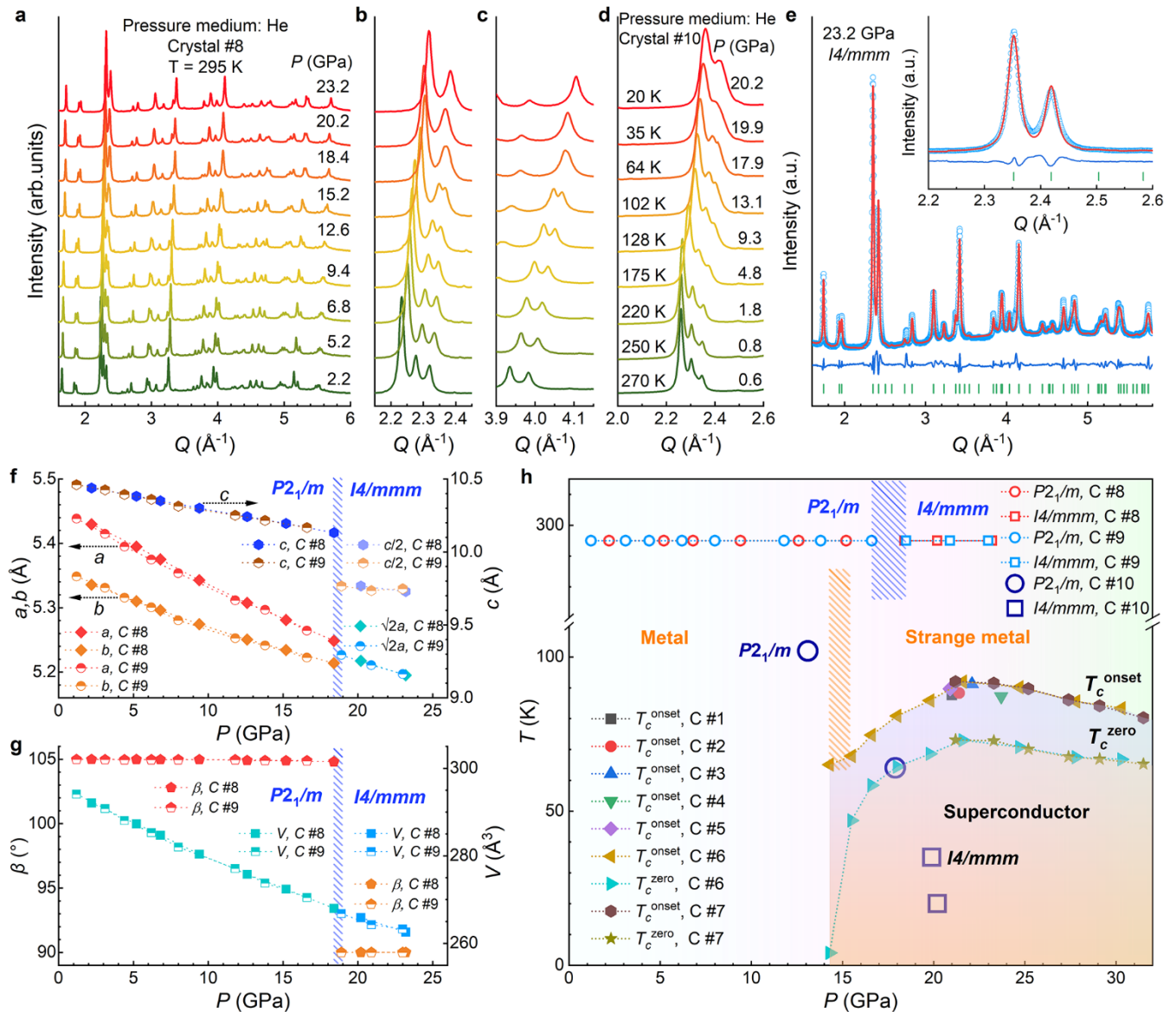


Fig.R4 (revised Fig. 4) | Structure and T - P phase diagram of $\text{La}_2\text{SmNi}_2\text{O}_{7-\delta}$. **a**, Room-temperature synchrotron X-ray powder diffraction (XRD) patterns of $\text{La}_2\text{SmNi}_2\text{O}_7$ (pulverized Crystal #8, annealed at $p\text{O}_2=1.5$ bar for 10 days) in the Q range of $1.6\text{--}6\text{ \AA}^{-1}$ ($\lambda = 0.4834\text{ \AA}$) under different pressures with helium as the pressure transmitting medium. **b**, An enlarged view of **a** in the Q range of $2.15\text{--}2.45\text{ \AA}^{-1}$. **c**,

An enlarged view of **a** in the Q range of 3.9-4.15 $\text{\AA}^{-1}$, highlighting the gradual merging of the diffraction peaks on compression. **d**, An enlarged view of the powder diffraction patterns collected for $\text{La}_2\text{SmNi}_2\text{O}_7$ (pulverized Crystal #10, annealed at $p\text{O}_2=1.5$ bar for 10 days) in the Q range of 2.2-2.6 $\text{\AA}^{-1}$ ($\lambda = 0.4133$ $\text{\AA}$) at various temperatures and pressures using helium as the pressure transmitting medium. **e**, Rietveld refinement using $I4/mmm$ on the powder XRD pattern of $\text{La}_2\text{SmNi}_2\text{O}_7$ under 23.2 GPa at 295 K. The inset illustrates the enlarged view of the refinement data in the Q range of 2.2-2.6 $\text{\AA}^{-1}$. Note the blue circles represent the observed diffraction intensities, the red lines denote the calculated intensities, the blue lines indicate the difference between the observed and calculated intensities, the green bars mark the diffraction peak positions. **f,g**, Extracted lattice parameters of $\text{La}_2\text{SmNi}_2\text{O}_7$ from Rietveld refinements as a function of pressure at 295 K. Crystal #8 (C #8) and Crystal #9 (C #9, annealed at $p\text{O}_2=1.5$ bar for 10 days) represent two independent experiments. **h**, T - P phase diagram of $\text{La}_2\text{SmNi}_2\text{O}_{7-\delta}$. The black solid squares, red solid circles, blue solid triangles, green solid triangles, violet solid diamonds, khaki solid triangles, and wine solid hexagons represent the T_c^{onset} of Crystal #1 to #7 under pressure, respectively. The cyan solid triangles and light-green solid stars represent the T_c^{zero} of Crystal #6 and #7 under pressure, respectively. The red hollow circles and red hollow squares represent the $P_{21/m}$ and $I4/mmm$ of pulverized Crystal #8 (C #8), respectively. The cyan hollow circles and cyan hollow squares represent the $P_{21/m}$ and $I4/mmm$ of pulverized Crystal #9 (C #9), respectively. The blue hollow circles and blue hollow squares represent the $P_{21/m}$ and $I4/mmm$ of pulverized Crystal #10 (C #10, annealed at $p\text{O}_2=1.5$ bar for 10 days), respectively.

Other major changes we have made to improve the manuscript

No.	Position	Original	Revised
1	For all powder diffraction patterns in the revision: Figs. 1h,i Extended Data Figs. 5b,c,e,f Supplementary Fig.1	2θ ($^\circ$)	Q ($\text{\AA}^{-1}$)
2	Fig. 5b	-	We have added the recently published resistivity data of $\text{La}_2\text{NiO}_4 \cdot \text{La}_3\text{Ni}_2\text{O}_7$ ¹⁶ for comparison.
3	“Single crystal growth at 1 atm” section (Page 4, Line 114-115 in revision)	With the increasing of x , a increases while b , c and V decreases (Extend Data Fig. 4a-f)	Anisotropic change in lattice parameters is observed with the increase of x (Supplementary Fig. 2a-f)
4	“Single crystal growth at 1 atm” section (Page 4, Line 119-122 in revision)	Fig. 1k shows the average in-plane lattice constants for the maximum substitution in $\text{La}_{3-x}\text{R}_x\text{Ni}_2\text{O}_{7-\delta}$ ($\text{R}=\text{La-Er}$) calculated by $a_{\text{average}}=(a^2+b^2)^{1/2}/2$ along with the lattice constants in the superconducting states ^{1,10,11}	Fig. 1k shows the average in-plane lattice constants for the maximum substitution (Supplementary Fig. 3) in $\text{La}_{3-x}\text{R}_x\text{Ni}_2\text{O}_{7-\delta}$ ($\text{R}=\text{La-Er}$) calculated by $a_{\text{average}}=(a^2+b^2)^{1/2}/2$ along with the lattice constants in the superconducting states ^{1,8,17}

5	“Bulk superconductivity at 92 K” section (Page 5, Line 177 in revision)	As can be seen, clear diamagnetic signals below 60 K with substantial superconducting shielding volume fractions (>60%) was detected (Extend Data Fig. 8)	As can be seen, clear diamagnetic signals below 60 K with substantial superconducting shielding volume fractions (>60%) was detected (Extended Data Fig. 6 and Calculation of superconducting volume fraction in Methods)
6	“Structure in the superconducting state” section (Page 6, Line 192 in revision)	A similar high symmetry phase characterized by $I4/mmm$ was previously reported in $\text{La}_3\text{Ni}_2\text{O}_7$ ³⁶ , $\text{La}_2\text{PrNi}_2\text{O}_7$ ¹⁰ , and $\text{La}_4\text{Ni}_3\text{O}_{10}$ ⁷ under high pressure	Such a high symmetry has been previously reported in $\text{La}_3\text{Ni}_2\text{O}_7$ ⁴⁴ , $\text{La}_2\text{PrNi}_2\text{O}_7$ ⁸ , and $\text{La}_4\text{Ni}_3\text{O}_{10}$ ⁹ under high pressure
7	“T-P phase diagram” section (Page 6, Line 209-211 in revision)	Both monoclinic and tetragonal structure can support superconductivity. This result is in contrast to nickelates such as $\text{La}_3\text{Ni}_2\text{O}_7$, ³⁶ $\text{La}_2\text{PrNi}_2\text{O}_7$, ¹⁰ $\text{La}_5\text{Ni}_3\text{O}_{11}$, ³⁷ and $\text{La}_4\text{Ni}_3\text{O}_{10}$, ⁷ where tetragonal structure was reported as a prerequisite condition for emergence of superconductivity	Both monoclinic and tetragonal structures can support superconductivity, indicating that tetragonal structure is not a prerequisite for emergence of superconductivity. Our result is consistent with Shi et al ⁴⁵ , who reported that orthorhombic $\text{La}_3\text{Ni}_2\text{O}_7$ superconduct under high pressure

RESPONSE TO REFEREES' COMMENTS

Referee #2

The authors have comprehensively addressed the concerns I previously raised. They have appropriately revised the text to tone down earlier questionable assertions and have added new high-pressure transport data for the sample with the highest T_c . Notably, the two-step transition initially reported is no longer observed, whereas now a cleaner single-step transition is observed. I have no further objections to the publication of this work.

Response: We thank the Referee for reviewing our manuscript. We are pleased that the Referee is satisfied with our revision.

Referee #3

I have no additional comments.

Response: We thank the Referee for reviewing our manuscript. We are glad that the Referee has no further questions.