Superconductivity in infinite-layer lanthanide nickelates

S. W. Zeng1,*, C. J. Li2,3,*, L. E. Chow1, Y. Cao4, Z. T. Zhang1, C. S. Tang5,6, X. M. Yin7, Z. S. Lim1, J. X. Hu1, P. Yang2,5, A. Ariando1,*

1Department of Physics, Faculty of Science, National University of Singapore, Singapore 117551, Singapore
2Department of Materials Science and Engineering, National University of Singapore, Singapore 117575, Singapore
3Department of Materials Science and Engineering, Southern University of Science and Technology, Shenzhen 518055, China
4Department of Electrical and Computer Engineering, National University of Singapore, 4 Engineering Drive 3, Singapore 117583, Singapore
5Singapore Synchrotron Light Source (SSLS), National University of Singapore, Singapore 117603, Singapore
6Institute of Materials Research and Engineering, A*STAR (Agency for Science, Technology and Research), 2 Fusionopolis Way, Singapore 138634, Singapore
7Shanghai Key Laboratory of High Temperature Superconductors, Physics Department, Shanghai University, Shanghai 200444, China

*The authors contributed equally to this work.
*To whom correspondence should be addressed.

E-mail: phyzen@nus.edu.sg, ariando@nus.edu.sg
The origin of high-$T_c$ superconductivity remains an enigma even though tremendous research effort and progress have been made on cuprate and iron pnictide superconductors. Aiming to mimic the cuprate-like electronic configuration of transition metal, superconductivity has been recently found in nickelates\cite{1}. This discovery hallmarks a new era in the search and understanding of the high-$T_c$ superconductivity. However, unlike the cuprate and iron pnictide, in which the superconductivity was initially found in a compound containing La$^{2-3}$, the superconductivity in the nickelate has only been observed in Nd- and Pr-based compounds$^{1,4-10}$. This raises a central question of whether the $f$ electron of the rare-earth element is critical for superconductivity in the nickelates. Here, we report the observation of superconductivity in infinite-layer Ca-doped LaNiO$_2$ (La$_{1-x}$Ca$_x$NiO$_2$) thin films and construct their phase diagram. Unlike the metal-insulator transition in Nd- and Pr-based nickelates$^{1,4,5,8}$, the undoped and underdoped La$_{1-x}$Ca$_x$NiO$_2$ thin films are entirely insulating from 300 down to 2 K. A superconducting dome is observed from 0.15 $< x < 0.3$ with weakly insulating behavior at the overdoped regime. Moreover, the sign of the Hall coefficient $R_H$ changes at low temperature for samples with a higher doping level. However, distinct from the Nd- and Pr-based nickelates, the $R_H$-sign-change temperature remains around 35 K as the doping increases, suggesting a different multiband structure in the La$_{1-x}$Ca$_x$NiO$_2$. These results also emphasize the significant role of lattice correlation on the multiband structures of the infinite-layer nickelates.
The perovskite nickelates $\text{R} \text{NiO}_3$ ($\text{R} =$ rare-earth element) show a structural transition and exhibit a metal-insulator transition upon cooling when $\text{R} =$ Nd and Pr, while it remains metallic when $\text{R} =$ La. To mimic the cuprate-like $3d^9$ electronic configuration, the infinite-layer LaNiO$_2$ is required and can be realized by oxygen deintercalation of the LaNiO$_3$ precursor. Much effort has been devoted to dope carriers in this LaNiO$_2$, but it failed to obtain superconductivity. To increase the electronic bandwidth, the La was substituted by a rare earth element with a smaller ionic radius (e.g., Nd atom), resulting in the observation of superconductivity in Nd$_{0.8}$Sr$_{0.2}$NiO$_2$. This route to superconductivity contrasts the heavily studied copper- and iron-based superconductors in which superconductivity was first obtained in La-based compounds, while up to now, the superconducting nickelate has only been observed in Sr-doped compounds with $\text{R} =$ Nd or Pr (i.e., $\text{R}_{1-x}\text{Sr}_x\text{NiO}_2$). Moreover, the trilayer nickelates $\text{R}_4\text{Ni}_3\text{O}_8$ ($\text{R} =$ La and Pr) that possesses the same NiO$_2$ square plane as in the infinite-layer nickelates and an effective $1/3$ hole doping showed an insulating ground state in the case of La$_4$Ni$_3$O$_8$, in contrast to the metallic state in the Pr$_4$Ni$_3$O$_8$. Theoretical calculation attributed the absence of superconductivity to the intercalation of H atoms in energetically favorable LaNiO$_2$ to form LaNiO$_2$H during the reduction process. It has also been shown that hybridization with Nd $4f$ orbitals is a non-negligible ingredient for the superconductivity in doped NdNiO$_2$, while the $f$ orbitals are far from the Fermi level in LaNiO$_2$. This suggests the importance of the $4f$ state for the electronic structure and thus for the superconducting properties. Therefore, the realization of superconductivity in the La series is key to understanding the superconducting properties in the nickelates.
In unconventional superconductors containing the rare-earth element, the substitution of an isovalent ion with a smaller radius causes an increase in inner chemical pressure due to the shrinkage of the crystal lattice. This is considered as an important method to enhance $T_c$, as experimentally demonstrated in cuprates and pnictides\textsuperscript{18,19}. For the nickelates, the discovery of superconductivity in Nd$_{0.8}$Sr$_{0.2}$NiO$_2$ was also inspired by substituting the La with a smaller ionic radius atom Nd\textsuperscript{1}. In the Nd- and Pr-based nickelates, the $R_H$ sign-change temperature varies with Sr doping level, indicating that the Sr doping not only introduces charges but also modulates the band structures\textsuperscript{4,5,8,20-23}. Moreover, the lattice constant increases with increasing Sr doping level, and the superconducting dome occurs near the $R_H$-sign-change boundary. It is therefore anticipated to induce superconductivity in LaNiO$_2$ through doping with a smaller ionic radius. Here we present the observation of superconductivity in infinite-layer La$_{1-x}$Ca$_x$NiO$_2$ thin films through Ca doping.

The perovskite La$_{1-x}$Ca$_x$NiO$_3$ precursor thin films were synthesized by a pulsed laser deposition technique and reduced to an infinite-layer phase using the soft-chemistry topotactic reduction method. The X-ray diffraction (XRD) $\theta-2\theta$ patterns of the as-grown La$_{1-x}$Ca$_x$NiO$_3$ thin films can be found in Supplementary Data Fig. S1. The prominent thickness oscillations in the vicinity of the (002) peak indicate the single-phase and high quality of the perovskite films. After reduction, a clear transition of the diffraction peaks is seen, confirming the transformation from the perovskite to the infinite-layer structure, as shown in Fig. 1a for a representative Ca doping level of 0.23. Figure 1b shows a high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image of the 17-nm La$_{0.77}$Ca$_{0.23}$NiO$_2$ thin film. A clear infinite-layer structure is observed with no obvious defect throughout the layer. Note
that in Nd_{1-x}Sr_{x}NiO_{2}, the pure perovskite and the resultant infinite-layer structure can only survive up to ~10 nm above which the Ruddlesden–Popper-type phase emerges\textsuperscript{4,5,24}. For the La-nickelate thin films, the pure phase is still observed for a thickness of 17 nm (Fig. 1b and Supplementary Data Fig. S1), most likely due to the lattice match between La_{1-x}Ca_{x}NiO_{3} and SrTiO_{3} substrates. Figure 1c shows the XRD \( \theta-2\theta \) patterns of infinite-layer La_{1-x}Ca_{x}NiO_{2} thin films with different Ca doping levels \( x \) from 0 to 0.35. The \( (00l) \) peak positions slightly shift towards a higher angle as Ca dopant increases, indicating a shrinking of the c-axis lattice constants \( d \) from ~3.405 Å at \( x = 0 \) to ~3.368 Å at \( x = 0.35 \) as plotted in Fig. 1d. The evolution of \( d \) is in agreement with the empirical expectation as the cation is replaced with an atom having a smaller ionic radius. The Reciprocal space mappings around the \( (-103) \) diffraction peak indicate that the films are slightly relaxed, showing the larger in-plane lattice constants compared with that of SrTiO_{3} substrate (Fig. 1d and Supplementary Data Fig. S2). The full width at half-maximum (FWHM) of the rocking curves for the \( (002) \) peaks of the infinite-layer films shows a value between 0.06° and 0.12°, supporting the high-quality thin-films after reduction (Supplementary Data Fig. S3).

Figure 2a shows the logarithmic-scale resistivity versus temperature \( (\rho-T) \) curves of the La_{1-x}Ca_{x}NiO_{2} thin films with Ca doping level \( x \) from 0 to 0.35. For \( x \leq 0.15 \), the samples show insulating behavior all the way below 300 K. This is different from Nd_{1-x}Sr_{x}NiO_{2} and Pr_{1-x}Sr_{x}NiO_{2} thin films, in which the undoped and underdoped samples show a metallic behavior at high temperatures with a resistivity minimum at the intermediate temperature below which a weakly insulating behavior appears\textsuperscript{1,4-6,8}. The high-temperature metallic behavior in undoped Nd- and Pr-nickelates has been thought to be due to the self-doped nature of the parent compound\textsuperscript{20,25-27}. The zoomed-
in and linear-scale $\rho$-$T$ curves of the superconducting La$_{1-x}$Ca$_x$NiO$_2$ thin films with $x$ from 0.15 to 0.27 are shown in Fig. 2b. For $x = 0.15$ and 0.18, the samples show transitions from a slightly metallic behavior to an insulating behavior and then an onset of superconducting transition with decreasing temperature. For $0.2 \leq x \leq 0.27$, the samples are superconducting with the $\rho$-$T$ curves showing metallic behavior at high temperatures. The suppression of superconductivity with increasing out-of-plane magnetic field for a representative sample with $x = 0.23$ is shown in Supplementary Data Fig. S4. The fitting of the relationship between the upper critical field and midpoint critical temperature by the Ginzburg-Landau model gives the zero-temperature in-plane coherence length of 4.59 nm, comparable to that of Nd$_{0.8}$Sr$_{0.2}$NiO$_2$ film\textsuperscript{1}. At the overdoped regime with $x \geq 0.3$, the samples show an increase in normal state resistivity compared with that of the optimally doped sample. Moreover, similar to the Nd- and Pr-nickelates, the overdoped La$_{1-x}$Ca$_x$NiO$_2$ thin films exhibit weakly insulating behavior at low temperature, suggesting a universal transport property in over-doped infinite-layer nickelates\textsuperscript{4,5,8}.

Similar to Nd- and Pr-nickelates, the room-temperature $R_H$ is negative, and its magnitude decreases with increasing $x$ and then saturates at $x = 0.2$ (Fig. 2c and 2d), suggesting the multiband structure nature for La$_{1-x}$Ca$_x$NiO$_2$ films\textsuperscript{15,16,20,21,25-28}. The $R_H$ remains negative below 300 K for samples with $x \leq 0.2$. For samples with $x \geq 0.23$ (except for $x = 0.25$), the $R_H$ undergoes a smooth transition from negative to positive sign as the temperature decreases. Figure 2d presents the $R_H$ at 20 K, clearly showing a sign change at $x = 0.2 - 0.23$ from negative to positive with increasing $x$. The doping level of $R_H$-sign-change is higher than that ($x = 0.18 - 0.2$) of Nd- and Pr-nickelates\textsuperscript{4,5,8}. However, the $R_H$-sign-change doping level for both La-nickelates and
Nd-/Pr-nickelates are at around the optimally doped regime. This suggests a generic reconstruction of the Fermi surface as the doping changes across the middle point of the superconducting dome in infinite-layer nickelates. It has been shown that in Nd\textsubscript{1-x}Sr\textsubscript{x}NiO\textsubscript{2} and Pr\textsubscript{1-x}Sr\textsubscript{x}NiO\textsubscript{2}, the \(R_{\text{H}}\)-sign-change temperature increases with increasing doping level\textsuperscript{4,5,8}. However, for La\textsubscript{1-x}Ca\textsubscript{x}NiO\textsubscript{2} films, the \(R_{\text{H}}\)-sign-change temperature does not change with Ca doping level, and it is around 35 K for \(x \geq 0.23\), suggesting a different mechanism of doping-induced electronic modulation.

Figure 3 depicts the phase diagrams of La\textsubscript{1-x}Ca\textsubscript{x}NiO\textsubscript{2} integrated with those of Nd\textsubscript{1-x}Sr\textsubscript{x}NiO\textsubscript{2} and Pr\textsubscript{1-x}Sr\textsubscript{x}NiO\textsubscript{2}\textsuperscript{4,5,8}. The onset of the critical temperature, \(T_{c,90\%R}\), is defined as the temperature at which the resistivity drops to 90\% of the normal-state value at the onset of the superconductivity. A superconducting dome between 0.15 < \(x\) < 0.3 is seen for La\textsubscript{1-x}Ca\textsubscript{x}NiO\textsubscript{2}. The doping range of the La\textsubscript{1-x}Ca\textsubscript{x}NiO\textsubscript{2} superconducting dome is comparable to that of Pr\textsubscript{1-x}Sr\textsubscript{x}NiO\textsubscript{2} and slightly wider than that of Nd\textsubscript{1-x}Sr\textsubscript{x}NiO\textsubscript{2} but is generally extended towards a higher doping level (Fig. 3b). At the two ends of the dome, the underdoped regime shows insulating behavior upon cooling, and the overdoped regime is weakly insulating at low temperature, different from the Nd- and Pr-nickelates in which both regimes show weakly insulating behavior\textsuperscript{4,5,8}. In general, the \(T_{c}\) of La\textsubscript{1-x}Ca\textsubscript{x}NiO\textsubscript{2} is lower than Nd and Pr series, possibly due to the large ionic radius of La, consistent with the experimental observation in Cu- and Fe-based superconductors that the \(T_{c}\) is enhanced as the ionic radius of the rare-earth element decreases\textsuperscript{18,19}. This observation implies that the appearance of superconductivity in infinite layer nickelates is not reliant on the 4\textit{f} electrons of the rare-earth element, and suggests that higher \(T_{c}\) in infinite-layer nickelates can be stabilized using smaller rare-earth ions.
In addition to introducing charge carriers, the chemical doping in infinite-layer nickelate can cause the change of the multiband structures due to the modification of lattice environment\textsuperscript{20-23}. Therefore, the normal-state properties and the superconducting range will depend on the lattice constant upon doping, which can be seen from the doping dependent $R_H$ and superconducting dome\textsuperscript{4,5,8}. Depending on the difference of cation and dopant radius, the extent of the lattice-constant change upon doping is different. In Nd$_{1-x}$Sr$_x$NiO$_2$\textsuperscript{4,5}, the extent of the lattice-constant change with Sr doping is $\sim$0.53 Å per one Sr atom, larger than that ($\sim$0.42 Å per one Sr atom) for Pr$_{1-x}$Sr$_x$NiO$_2$\textsuperscript{8} and that ($\sim$0.11 Å per one Ca atom) for La$_{1-x}$Ca$_x$NiO$_2$ that is observed in the current result. Interestingly, it is found that the superconducting dome of the Nd$_{1-x}$Sr$_x$NiO$_2$ is narrower than that of the Pr$_{1-x}$Sr$_x$NiO$_2$ and La$_{1-x}$Ca$_x$NiO$_2$, suggesting the intrinsic link between the superconducting range and the modulation of the lattice constant. Moreover, theoretical calculations suggested that Sr doping in Nd$_{1-x}$Sr$_x$NiO$_2$ reduces the self-doping effect, and the nickelate behaves more like a system with a pure single-band picture\textsuperscript{20,23}. This is consistent with the $R_H$-sign-change upon doping, and the sign-change temperature monotonically increases with increasing Sr doping level in Nd- and Pr-nickelates\textsuperscript{4,5,8}. However, for La$_{1-x}$Ca$_x$NiO$_2$ films, the doping-dependent $R_H$-sign-change temperature is negligible for $x \geq 0.23$. Coupled with the small change in the lattice constant, this suggests the critical role of the dopant ionic nature on the electronic modulation in the infinite-layer nickelates. For the infinite-layer bulk nickelates Nd$_{1-x}$Sr$_x$NiO$_2$ and Sm$_{1-x}$Sr$_x$NiO$_2$ in which superconductivity is absent, the $c$-lattice constant is smaller than those of superconducting thin films\textsuperscript{29-31}. Moreover, we also found that the strain effect induced electronic bandstructure modulation and the resultant change of $R_H$ in Nd$_{0.8}$Sr$_{0.2}$NiO$_2$\textsuperscript{32}. These suggest the importance of lattice environment on the superconductivity and normal state
properties in the infinite-layer nickelates. The present result also suggests a new route for new superconductors and a unique way for tailoring normal state properties through dopants in the nickelate superconductors.

Note: During the preparation of this manuscript, we became aware of a report on superconductivity in (La, Sr)NiO₂ [33].

Methods

The ceramic targets with nominal composition La₁₋ₓCaₓNiO₃ were prepared by the conventional solid-state reaction using high-purity La₂O₃ (99.999%, Sigma-Aldrich), NiO₂ (99.99%, Sigma-Aldrich), CaCO₃ (99.995%, Sigma-Aldrich) powders as the starting materials. The mixed powders were sintered in air for 15 h at 1150, 1200 and 1250 °C, respectively, with thorough regrinding before each sintering. On the final sintering, the powder was pressed into a disk-shaped pellet. The perovskite thin films were grown on TiO₂-terminated (001) SrTiO₃ substrates using a pulsed laser deposition (PLD) technique with a 248-nm KrF excimer laser. The deposition temperature and oxygen partial pressure PO₂ for all samples were 600 °C and 150 mTorr, respectively. The laser energy density on the target surface was set to be 1.8 Jcm⁻². After deposition, the samples were annealed for 10 min at 600 °C and 150 mTorr, and then cooled down to room temperature at a rate of 8 °C/min. In order to obtain the infinite-layer structures, the as-grown films were then embedded with about 0.15 g of CaH₂ powder and wrapped in aluminium foil, and then placed into the PLD chamber for the reduction process. The wrapped sample was heated to 340 – 360 °C at a rate of 25 °C/min and kept for 80 minutes, and then cooled down to room temperature at a rate of 25 °C/min. The wire connection for the electrical transport measurement was made by Al ultrasonic wire bonding. The transport measurements
were performed using a Quantum Design Physical Property Measurement System. The X-ray diffraction (XRD) measurement was done in the X-ray Diffraction and Development (XDD) beamline at Singapore Synchrotron Light Source (SSLS) with an X-ray wavelength of $\lambda = 1.5404$ Å. The high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) imaging was carried out at 200 kV using a JEOL ARM200F microscope and the cross-sectional TEM specimens were prepared by a focused ion beam machine (FEI Versa 3D).

**Acknowledgments**

This research is supported by the Agency for Science, Technology, and Research (A*STAR) under its Advanced Manufacturing and Engineering (AME) Individual Research Grant (IRG) (A1983c0034) and the Singapore National Research Foundation (NRF) under the Competitive Research Programs (CRP Grant No. NRF-CRP15-2015-01). P. Y. is supported by Singapore Synchrotron Light Source (SSLS) via NUS Core Support C-380-003-003-001. The authors would also like to acknowledge the SSLS for providing the facility necessary for conducting the research. The Laboratory is a National Research Infrastructure under the National Research Foundation (NRF) Singapore.

**Author Contributions**

SWZ and AA conceived the project. SWZ, LEC, YC, ZTZ, ZSL, JXH prepared the thin films and conducted the electrical measurements. SWZ, PY, CST, and XMY conducted the XRD measurements. CJL conducted the STEM measurements. SWZ and AA wrote
the manuscript with contributions from all authors. All authors have discussed the results and the interpretations.

References

[1] D. Li, K. Lee, B. Y. Wang, M. Osada, S. Crossley, H. R. Lee, Y. Cui, Y. Hikita, H. Y. Hwang, Superconductivity in an infinite-layer nickelate, *Nature*, **572**, 624-627 (2019).

[2] J. G. Bednorz, K.A. Müller, Possible high-$T_c$ superconductivity in the Ba–La–Cu–O system, *Zeitschrift für Physik B Condensed Matter*, **64**, 189-193 (1986).

[3] Y. Kamihara, T. Watanabe, M. Hirano, H. Hosono, Iron-based layered superconductor La[O1-xFx]FeAs (x=0.05–0.12) with Tc= 26 K, *Journal of the American Chemical Society*, **130**, 3296-3297 (2008).

[4] D. Li, B. Y. Wang, K. Lee, S. P. Harvey, M. Osada, B. H. Goodge, L. F. Kourkoutis, H.Y. Hwang, Superconducting dome in Nd$_{1-x}$Sr$_x$NiO$_2$ infinite layer films, *Physical Review Letters*, **125**, 027001 (2020).

[5] S. Zeng, C. S. Tang, X. Yin, C. Li, M. Li, Z. Huang, J. Hu, W. Liu, G. J. Omar, H. Jani, Phase diagram and superconducting dome of infinite-layer Nd$_{1-x}$Sr$_x$NiO$_2$ thin films, *Physical Review Letters*, **125**, 147003 (2020).

[6] M. Osada, B. Y. Wang, B. H. Goodge, K. Lee, H. Yoon, K. Sakuma, D. Li, M. Miura, L. F. Kourkoutis, H. Y. Hwang, A Superconducting Praseodymium Nickelate with Infinite Layer Structure, *Nano Letters*, **20**, 5735-5740 (2020).

[7] Q. Gu, Y. Li, S. Wan, H. Li, W. Guo, H. Yang, Q. Li, X. Zhu, X. Pan, Y. Nie, H.-H. Wen, Single particle tunneling spectrum of superconducting Nd$_{1-x}$Sr$_x$NiO$_2$ thin films, *Nature Communications*, **11**, 6027 (2020).

[8] M. Osada, B.Y. Wang, K. Lee, D. Li, H.Y. Hwang, Phase diagram of infinite layer praseodymium nickelate Pr$_{1-x}$Sr$_x$NiO$_2$ thin films, *Physical Review Materials*, **4**, 121801 (2020).
[9] Q. Gao, Y. Zhao, X. Zhou, Z. Zhu, Preparation of superconducting thin film of infinite-layer nickelate Nd$_{0.8}$Sr$_{0.2}$NiO$_2$, https://arxiv.org/abs/2102.10292, (2021).

[10] X. Zhou, Z. Feng, P. Qin, H. Yan, X. Wang, P. Nie, H. Wu, X. Zhang, H. Chen, Z. Meng, Z. Zhu, Z. Liu, Negligible oxygen vacancies, low critical current density, electric-field modulation, in-plane anisotropic and high-field transport of a superconducting Nd$_{0.8}$Sr$_{0.2}$NiO$_2$/SrTiO$_3$ heterostructure, https://arxiv.org/abs/2104.07316, (2021).

[11] S. Catalano, M. Gibert, J. Fowlie, J. Iniguez, J.-M. Triscone, J. Kreisel, Rare-earth nickelates RNiO$_3$: thin films and heterostructures, Reports on Progress in Physics, 81, 046501 (2018).

[12] M. A. G. M. A. Hayward, M. J. Rosseinsky, and J. Sloan, Sodium Hydride as a Powerful Reducing Agent for Topotactic Oxide Deintercalation-Synthesis and Characterization of the Nickel(I) Oxide LaNiO$_2$, Journal of the American Chemical Society, 121, 8843 (1999).

[13] J. Zhang, A. Botana, J. Freeland, D. Phelan, H. Zheng, V. Pardo, M. Norman, J. Mitchell, Large orbital polarization in a metallic square-planar nickelate, Nature Physics, 13, 864-869 (2017).

[14] L. Si, W. Xiao, J. Kaufmann, J.M. Tomczak, Y. Lu, Z. Zhong, K. Held, Topotactic Hydrogen in Nickelate Superconductors and Akin Infinite-Layer Oxides ABO$_3$, Physical Review Letters, 124, 166402 (2020).

[15] P. Jiang, L. Si, Z. Liao, Z. Zhong, Electronic structure of rare-earth infinite-layer R Ni O 2 (R= La, Nd), Physical Review B, 100, 201106(R) (2019).

[16] M.-Y. Choi, K.-W. Lee, W. E. Pickett, Role of 4f states in infinite-layer NdNiO$_3$, Physical Review B, 101, 020503(R) (2020).

[17] S. Bandyopadhyay, P. Adhikary, T. Das, I. Dasgupta, T. Saha-Dasgupta, Superconductivity in infinite-layer nickelates: Role of f orbitals, Physical Review B, 102, 220502 (2020).

[18] H. Hosono, K. Kuroki, Iron-based superconductors: Current status of materials and pairing mechanism, Physica C: Superconductivity and its Applications, 514, 399-422 (2015).
[19] N. P. Armitage, P. Fournier, R. L. Greene, Progress and perspectives on electron-doped cuprates, *Reviews of Modern Physics*, **82**, 2421-2487 (2010).

[20] A. S. Botana, M. R. Norman, Similarities and Differences between LaNiO2 and CaCuO2 and Implications for Superconductivity, *Physical Review X*, **10**, 011024 (2020).

[21] J. Gao, Z. Wang, C. Fang, H. Weng, Electronic structures and topological properties in nickelates Ln_{n+1}Ni_{n+2},[120x695]https://doi.org/10.1093/nsr/nwaa218.

[22] F. Lechermann, Doping-dependent character and possible magnetic ordering of NdNiO2, *Physical Review Materials*, **5**, 044803 (2021).

[23] M. Kitatani, L. Si, O. Janson, R. Arita, Z. Zhong, K. Held, Nickelate superconductors—a renaissance of the one-band Hubbard model, *npj Quantum Materials*, **5**, 59 (2020).

[24] K. Lee, B.H. Goodge, D. Li, M. Osada, B. Y. Wang, Y. Cui, L. F. Kourkoutis, H. Y. Hwang, Aspects of the synthesis of thin film superconducting infinite-layer nickelates, *APL Materials*, **8**, 041107 (2020).

[25] G.-M. Zhang, Y.-f. Yang, F.-C. Zhang, Self-doped Mott insulator for parent compounds of nickelate superconductors, *Physical Review B*, **101**, 020501(R) (2020).

[26] A. S. Botana, F. Bernardini, A. Cano, Nickelate superconductors: an ongoing dialog between theory and experiments, [https://arxiv.org/abs/2012.02764](https://arxiv.org/abs/2012.02764), (2020).

[27] M. Hepting, D. Li, C. J. Jia, H. Lu, E. Paris, Y. Tseng, X. Feng, M. Osada, E. Been, Y. Hikita, Y. D. Chuang, Z. Hussain, K. J. Zhou, A. Nag, M. Garcia-Fernandez, M. Rossi, H. Y. Huang, D. J. Huang, Z. X. Shen, T. Schmitt, H. Y. Hwang, B. Moritz, J. Zaanen, T. P. Devereaux, W. S. Lee, Electronic structure of the parent compound of superconducting infinite-layer nickelates, *Nature Materials*, **19**, 381-385 (2020).

[28] K.-W. Lee, W. Pickett, Infinite-layer LaNiO2: Ni^{1+} is not Cu^{2+}, *Physical Review B*, **70**, 165109 (2004).

[29] Q. Li, C. He, J. Si, X. Zhu, Y. Zhang, H.-H. Wen, Absence of superconductivity in bulk Nd_{1-x}Sr_{x}NiO_{2}, *Communications Materials*, **1**, 16 (2020).
[30] B.-X. Wang, H. Zheng, E. Krivyakina, O. Chmaissem, P. P. Lopes, J. W. Lynn, L. C. Gallington, Y. Ren, S. Rosenkranz, J. Mitchell, Synthesis and characterization of bulk \( \text{Nd}_{1-x}\text{Sr}_x\text{NiO}_2 \) and \( \text{Nd}_{1-x}\text{Sr}_x\text{NiO}_3 \), *Physical Review Materials*, 4, 084409 (2020).

[31] C. He, X. Ming, Q. Li, X. Zhu, J. Si, H. H. Wen, Synthesis and physical properties of perovskite \( \text{Sm}_{1-x}\text{Sr}_x\text{NiO}_3 \) (\( x = 0, 0.2 \)) and infinite-layer \( \text{Sm}_{0.8}\text{Sr}_{0.2}\text{NiO}_2 \) nickelates, *J Physics: Condens Matter*, DOI 10.1088/1361-648X/abfb90 (2021).

[32] S. Zeng, X. Yin, C. Li, C. Tang, K. Han, Z. Huang, Y. Cao, L. Chow, D. Wan, Z. Zhang, Z. Lim, C. Diao, P. Yang, A. Wee, S. Pennycook, A. Ariando, Observation of perfect diamagnetism and interfacial effect on the electronic structures in \( \text{Nd}_{0.8}\text{Sr}_{0.2}\text{NiO}_2 \) superconducting infinite layers, https://arxiv.org/abs/2104.14195 (2021).

[33] M. Osada, B. Y. Wang, B. H. Goodge, S. P. Harvey, K. Lee, D. F. Li, L. F. Kourkoutis, H. Y. Hwang, Nickelate superconductivity without rare-earth magnetism: \( \text{K}_x\text{La}_{1-x}\text{Sr}_2\text{NiO}_4 \), *Unpublished*. 
Figures and Captions

**Figure 1** | Structural characterization of infinite-layer La$_{1-x}$Ca$_x$NiO$_2$ thin films.  
**a,** The XRD $\theta$–$2\theta$ scan patterns of the perovskite La$_{0.77}$Ca$_{0.23}$NiO$_3$ and infinite-layer La$_{0.77}$Ca$_{0.23}$NiO$_2$ thin films. The arrow denotes the transition of diffraction peaks related to the transformation from a perovskite to an infinite-layer structure.  
**b,** The HAADF-STEM image of the 17-nm La$_{0.77}$Ca$_{0.23}$NiO$_2$ on SrTiO$_3$ substrate.  
**c,** The XRD $\theta$–$2\theta$ scan patterns of the La$_{1-x}$Ca$_x$NiO$_2$ thin films with different Ca doping levels $x$. The intensity is vertically displaced for clarity.  
**d,** The room-temperature $c$-axis lattice constants, $d$, and in-plane lattice constant, $a$, as a function of $x$. 
**Figure 2** | **Electrical transport properties of infinite-layer La$_{1-x}$Ca$_x$NiO$_2$ thin films.**

**a**, The logarithmic-scale resistivity versus temperature ($\rho$-$T$) curves of the La$_{1-x}$Ca$_x$NiO$_2$ thin films with Ca doping level $x$ from 0 to 0.35, measured from 300 to 2 K.

**b**, The zoomed-in and linear-scale $\rho$-$T$ curves of the La$_{1-x}$Ca$_x$NiO$_2$ thin films with $x$ from 0.15 to 0.27. For clarity, the resistivity of samples with $x = 0.15, 0.18$ and 0.27 is diminished to 0.3 of the initial value.

**c**, The temperature dependence of the normal-state Hall coefficients $R_H$.

**d**, The $R_H$ at $T = 300$ and 20 K as a function of $x$. The dash lines are guides to the eye.
Figure 3| Phase diagram of infinite-layer La$_{1-x}$Ca$_x$NiO$_2$ thin films and the comparison to Nd$_{1-x}$Sr$_x$NiO$_2$ and Pr$_{1-x}$Sr$_x$NiO$_2$ thin films. a, The critical temperature as a function of doping level $x$ for La$_{1-x}$Ca$_x$NiO$_2$ in the present results. The $T_{c,90\%R}$ is defined as the temperature at which the resistivity drops to 90% of the value at 10 K (the onset of the superconductivity). b, The combined phase diagram of La$_{1-x}$Ca$_x$NiO$_2$, Nd$_{1-x}$Sr$_x$NiO$_2$ and Pr$_{1-x}$Sr$_x$NiO$_2$. The data of Nd$_{1-x}$Sr$_x$NiO$_2$ is adapted from references [4, 5], and the data of Pr$_{1-x}$Sr$_x$NiO$_2$ is adapted from reference [8].
Supplementary Data - Figure S1 | a, The XRD $\theta - 2\theta$ scan patterns of the as-grown perovskite La$_{1-x}$Ca$_x$NiO$_3$ thin films with different Ca doping levels $x$ from 0 to 0.35. The intensity is vertically displaced for clarity. Only the (00$l$) perovskite peaks are observed, where $l$ is an integer, confirming the $c$-axis oriented epitaxial growth. b, The zoomed-in XRD $\theta - 2\theta$ scan patterns at angles from 40 to 55 degrees. The clear thickness oscillations in the vicinity of the (002) peak indicate the single-phase and high quality of the perovskite films. The thickness of around 17 nm is obtained by calculating the period of thickness oscillations in the vicinity of the (002) peak. The (002) peak positions shift towards a higher angle as the Ca doping level increase, indicating a shrinking of the $c$-axis lattice, in agreement with the empirical expectation when replacing the cation with an atom having a smaller ionic radius.
**Supplementary Data - Figure S2** | Reciprocal space mappings around (-103) diffraction peak for La$_{1-x}$Ca$_x$NiO$_2$ thin films with Ca doping level $x$ from 0.1 to 0.35.
**Supplementary Data – Figure S3** | **a**, The rocking curves for the (002) peaks of the infinite-layer La$_{1-x}$Ca$_x$NiO$_2$ thin films with different Ca doping level $x$. **b**, The full width at half-maximum (FWHM) of the (002) rocking curves as a function of $x$. The value of FWHM is between $0.06^\circ$ and $0.12^\circ$. 
Supplementary Data – Figure S4 | The resistance-temperature (R-T) curves for a sample with Ca doping level of 0.23 under various magnetic fields applied perpendicularly to the $a$-$b$ plane. The inset shows the relationship between the upper critical field $\mu_0 H_{c,\perp}$ and $T_C$ (extracted by the midpoint of the resistive transition) with a linear Ginzburg-Landau fitting. The red line is the fitting curve. The fitting gives a zero-temperature in-plane Ginzburg-Landau coherence length of 4.59 nm.