A broken translational symmetry state in an infinite-layer nickelate

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A defining signature of strongly correlated electronic systems is a rich phase diagram, which consists of multiple broken symmetries, such as magnetism, superconductivity and charge order14. In the recently discovered nickelate superconductors12–14, a large antiferromagnetic exchange energy has been reported, which implies the existence of strong electronic correlations1. However, signatures of a broken-symmetry state other than superconductivity have not yet been observed. Here we observe charge ordering in infinite-layer nickelates La1-xSr2NiO4 using resonant X-ray scattering. The parent compound orders along the Ni–O bond direction with an incommensurate wavevector, distinct from the stripe order observed in other nickelates12–14 that propagates along a direction 45° to the stripe order in other nickel oxides, such as the single-layer nickelate LaNiO2 (ref. 13) and La2NiO4 (ref. 14). In addition, no anomaly in the magnetic excitations near the Ni L2,3 absorption edge to search for signatures of broken translational symmetry states in the La-based infinite-layer nickelates. Figure 1a displays the RIXS intensity map of undoped LaNiO2 along the (h,0) direction (that is, the Ni–O bond direction). A clear enhancement of the quasi-elastic signal at an in-plane momentum transfer of QCO = (±0.344,0,0) reciprocal lattice units (r.l.u.) is seen (Fig. 1c), whereas a similar feature is absent along the (h,h) direction (that is, the Ni–Ni bond direction) as shown in Fig. 1b,d. The position of QCO is distinct from the allowed Bragg reflections of the underlying crystallographic symmetry, suggesting that the scattering of QCO is due to the presence of a CO that breaks the crystallographic translational symmetry. Indeed, as expected in a CO system, a softening of the RIXS-derived phonon dispersion is also observed (Fig. 1a and Extended Data Fig. 1). The CO in LaNiO2 has a correlation length of ξCO = 40 Å (ξCO = σ/hωCO, where h is the Planck constant and σCO is the standard deviation (s.d.) obtained from the Gaussian fit), and propagates along the (h,0) direction, distinct from the stripe order in other nickel oxides, such as the single-layer nickelates La1-xNiO4 (ref. 15) and La1-xSr2NiO4 (ref. 16) and trilayer La3NiO8 (ref. 17), which propagate along a direction 45° to the Ni–O bond (that is, along the (h,h) direction in tetragonal unit cell notation). In addition, no anomaly in the magnetic excitations near QCO can be resolved (Extended Data Fig. 2), unlike those in striped nickelates18. Thus, the short-range CO in LaNiO2 appears to bear more resemblance to the CO in hole-doped cuprates6,20,21.

To gain further insights, we examined the incident energy dependence of the CO peak across representative absorption edges of La and Ni ions using RIXS and resonant soft X-ray scattering.
The charge modulation that CO originates from the Ni $3d$ states. The peak intensity reaches a maximum at ~0.3 eV below the main resonance remains robust near the Ni $L_3$ edge. This suggests that CO probably diminishes due to increasing phase fluctuations with doping, as in the cuprate case. Interestingly, the CO wavevector decreases slightly, moving towards a common direction as a function of incident photon energy. The determination of the peak intensity is set to 1 for better comparison. Error bars in Figure 2d are smaller than the data points.

The doping evolution of the CO was further investigated using Ni $L_3$-edge RIXS, which provides higher sensitivity to the CO state in quasi-elastic scattering. Figure 2a–c presents raw RIXS intensity maps of La$_{1−x}$Sr$_x$NiO$_2$ for $x=0.04$, 0.10 and 0.15, respectively; these were used to extract CO peak profiles (Fig. 2d) from the quasi-elastic region of the RIXS spectra. As shown in Fig. 2d, the CO peak weakens and broadens monotonically with increasing doping, and becomes undetectable at $x=0.15$. Following hole doping, the CO peak height reduces (Fig. 2e). In addition, the broadening of the peak with doping (Fig. 2f) indicates a decrease of correlation length from ~40 Å in the undoped compound to ~20 Å for $x=0.10$. We note that the amplitude of the CO order parameter, which is related to the peak area (Fig. 2e, inset), seems insensitive to doping, indicating that the CO probably diminishes due to increasing phase fluctuations with doping, as in the cuprate case. Interestingly, the CO wavevector decreases slightly, moving towards a commensurate value of 1/3 r.l.u. as shown in Fig. 2f, indicating that the CO is probably arising from strong correlation effects. We argue that CO in La$_{1−x}$Sr$_x$NiO$_2$ is unlikely to arise from Fermi-surface nesting within the La Fermi-surface pockets or nesting between the La and Ni Fermi surfaces. Indeed, in these two scenarios, the CO on the La sites would be more robust than (or equally robust as) that at the Ni sites upon doping, which is inconsistent with our observations. The situation of nesting within the Ni $3d_{x^2−y^2}$ band should be analogous to the cuprate case; there, however, no apparent nesting vector...
corresponding to the CO wavevector can be unambiguously identified, nor is it compatible with the distinct doping dependence of the CO wavevector across different cuprate families.

The temperature dependence of CO in La$_{1-x}$Sr$_x$NiO$_2$ is summarized in Fig. 3. RIXS scans of undoped LaNiO$_2$ (Fig. 3a and Extended Data Fig. 4) reveal that the peak persists to at least 286 K (the highest achievable temperature of our experimental set-up), indicating that the onset temperature of the CO phase is notably higher than room temperature. For $x = 0.06$, the CO peak gradually weakens with temperature until the signal vanishes within the error bars at ~200 K (Fig. 3b,d). For $x = 0.10$, as the CO signal is beyond the detection limit of RIXS, we employed RIXS to reveal its temperature dependence. Figure 3e shows that the peak is already very weak and broad at low temperatures and disappears at 148 K. As summarized in Fig. 3d,e, the CO peak gradually weakens with increasing temperature, and the onset temperature lowers upon doping. The persistence of the CO correlation to high temperatures without a sharp onset appears to be consistent with the absence of a clear signature of a phase transition in transport measurements\(^6\). This is distinct from a conventional charge density wave system, but resembles the short-range CO correlation in hole-doped cuprates, which also persists to high temperatures without a sharp onset or notable signatures in transport measurements\(^6,27\).

Based on the temperature and doping dependence data of CO, we propose an updated phase diagram of La$_{1-x}$Sr$_x$NiO$_2$ as displayed in Fig. 4. Interestingly, the CO regime roughly coincides with the territory where weakly insulating behaviour is observed\(^1\), suggesting that they may be related. However, its relationship to SC appears to be puzzling. On the one hand, SC emerges at higher doping as CO diminishes, which may suggest that these two phases are competing. On the other hand, the CO is strongest in the undoped parent compound, and here SC also sets in below ~1 K (ref. \(^1\)), implying that these two may be somewhat coupled. The relationship between CO and SC remains an important open question for future investigations, much as it is under active debate for the cuprates and other materials.

It is intriguing that CO already occurs in the undoped infinite-layer nickelates, whereas CO should not exist in a half-filled Mott–Hubbard system. This indicates that a finite percentage of holes should already reside in the Ni $3d_{x^2−y^2}$ bands in the nominally $x = 0$ compounds. Although we cannot completely rule out that some of the holes are associated with possible oxygen defects in the compounds, the systematic doping evolution of the CO suggests that oxygen defects are unlikely to be a dominant factor. The holes in the Ni $3d_{x^2−y^2}$ states are probably introduced via a self-doping effect whereby charge is transferred via a coupling to the Fermi-surface pockets associated with the rare-earth $5d$ states\(^19,21\), as also inferred from transport measurements\(^24,25\). As suggested by a recent theoretical calculation for a coupled rare-earth $5d_{x^2−y^2}$ and Ni $3d_{x^2−y^2}$ two-band model, the rare-earth Ni coupling induces a self-doping effect and gives rise to a modulation in both rare-earth and Ni charge densities with similar periodicities\(^24\). When the rare-earth Fermi-surface pocket is depleted by hole doping, only the Ni charge density is modulated\(^21\). These behaviours are consistent with our experimental finding in La$_{1-x}$Sr$_x$NiO$_2$ (Fig. 1). Moreover, the fact that the parasitic CO in La states is substantially reduced...
90% of the resistivity at 20 K (resistivity data are adapted from ref. 8). The CO peak persists at the highest measured temperature of 286 K. The determination of the RSXS signal (thick lines) and background (thin lines) is explained in the Methods and Extended Data Fig. 3. Temperature dependence of RSXS scans of La1−xSrNiO2 (x = 0.06). The peak gradually decreases with increasing temperatures. Temperature evolution of the CO peak intensity for samples with doping of x = 0.06 are estimated as the largest noise fluctuation between adjacent data points of RSXS scans of b, e. Temperature dependence of the CO peak intensity for x = 0.10. The peak intensity at low temperature has been normalized to 1.

by introducing a small hole doping implies a small Fermi-surface pocket of the La states. Thus, although both Ni 3d_{3−y}z and La 5d_{3−y}z bands cross the Fermi energy in the undoped parent compounds, the La Fermi-surface pocket rapidly shrinks and should eventually disappear with increasing doping; consequently, the Ni 3d_{3−y}z Fermi-surface pocket dominates the electronic properties. This evolution lends support to the conjecture that the infinite-layer nickelates become increasingly like a single-band 3d_{3−y}z system with doping[21,29,30]. Although, in cuprates, the CO emerges from the 3d^9L configuration (L denotes a hole in the O ligand states) with a strong O 2p character, the CO in the infinite-layer nickelates is hosted on a dominant 3d^9 character strongly associated with the doped holes[17,39], with less wavefunction weight from O 2p states due to the relatively large charge-transfer energy. Thus, although the O sites should exhibit charge modulation because of the finite Ni–O hybridization, the O involvement in CO is expected to be less than that in cuprates. We also remark that a CO modulation along the (h, 0) direction would disfavour the formation of long-range AFM order along the (h, h) direction. In other words, the competition between the CO and the AFM correlation might be another reason why long-range AFM

![Fig. 4 | Phase diagram of La_{1-x}SrNiO_2](image)

The red domain represents the region of the phase diagram where CO is present and bounded by red circles, indicating the CO onset temperature T_{CO}. Error bars are estimated from the temperature interval used in the measurements. The light blue domain represents the region where the sample is superconducting (SC). Blue squares indicate the onset temperature of SC (T), which is defined as 90% of the resistivity at 20 K (resistivity data are adapted from ref. 1).
order has not been observed\cite{3,4}, despite a sizable spin-exchange interaction\cite{5}. Finally, an important question remains regarding whether the CO is ubiquitous in other infinite-layer nickelates. We note that the emergence of CO in the infinite-layer nickelates might be very sensitive to the local environment, such as epitaxial strain, chemical pressure induced by different rare-earth elements, or disorder. Nonetheless, our result establishes the infinite-layer nickelate as a new type of strongly correlated electron system.

**Note added in proof:** During the review process, we became aware of the observation of CO in Nd-based infinite-layer nickelates without a SrTiO\textsubscript{3} capping layer\cite{5,25,26}.

**Online content**

Any methods, additional references, Nature Research reporting summaries, source data, extended data, supplementary information, acknowledgements, peer review information; details of author contributions and competing interests; and statements of data and code availability are available at https://doi.org/10.1038/s41567-022-01660-6.

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Methods

Materials and sample characterization. Thin films of the precursor phase La$_{1-x}$Sr$_x$NiO$_3$ with thickness of ~9 nm were grown by pulsed laser deposition on a single-crystalline SrTiO$_3$ (001) substrate. A capping layer of SrTiO$_3$ with thickness of five unit cells was grown on top of the film to preserve the crystal structure. The infinite-layer phase La$_{1-x}$Sr$_x$NiO$_3$ was obtained by means of a topotactic reduction process using CaH$_2$ powder. Details on the thin-film growth and characterization are reported in ref. ^1.

Ultrahigh-resolution Ni L$_3$-edge RIXS measurements. Ni L$_3$-edge RIXS measurements were performed at beamline I21 of the Diamond Light Source (United Kingdom). The incident energy was tuned 0.1 eV below the maximum of the Ni L$_3$ absorption spectrum, and the incident photon polarization was orthogonal to the scattering plane ($\pi$ polarization), unless otherwise indicated. The combined energy resolution was 36 meV for RIXS spectra measured with $\pi$ polarization. The scattering angle was fixed to 154°. RIXS data are plotted as a function of $q$, the in-plane momentum transfer, and the incident photon polarization and 41 meV for RIXS spectra measured with $\sigma$ polarization, respectively. The in-plane momentum transfer is denoted in r.l.u., that is, in units of $(2\pi/a, 2\pi/b)$ with $a = b = 3.91$ Å. In our convention, positive $q_x$ corresponds to grazing emission geometry, and negative $q_x$ corresponds to grazing incidence geometry.

La M$_5$-edge RIXS measurements. La M$_5$-edge RIXS measurements were performed at qRIXS endstation at beamline 8.0.1 of the Advanced Light Source (United States). The incident photon polarization was parallel to the scattering plane ($\pi$ polarization). The scattering angle was fixed to 150°. The combined energy resolution was ~0.6 eV.

RSXS measurements. RSXS measurements were carried out at beamline 13-3 of the Stanford Synchrotron Radiation Lightsource (United States). The incident photon polarization was orthogonal to the scattering plane ($\sigma$ polarization). The scattering angle was fixed to 150°. Rocking scans of the CO peak were obtained by rotating the sample around the $b$ axis ($\theta$ scan). For each $\theta$, an image of 256 × 1024 pixels was collected using a two-dimensional charge-coupled detector (CCD). The signal from each row of 256 pixels was then integrated to obtain the final two-dimensional image, whose horizontal axis corresponds to $\theta$ and the vertical axis to the detector vertical pixel (Extended Data Fig. 3a). The vertically wide CCD covers the signal of interest from the $(h, 0)$ plane near the centre of the detector as well as signals from the $(h, \pm k)$ planes that are dominated by a fluorescence background. This allows us to simultaneously record the CO peak profile by integrating the signal over a window of 550 pixels near the centre of the detector as well as the fluorescence background by integrating the signal over a window of 124 pixels far away from the detector centre (Extended Data Fig. 3a,b).

Data availability

All data presented in this work are available online at Harvard Dataverse^3.

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Author contributions

M.R. and W.-S.L. conceived the research project and designed the experiments. M.R., H.L., D.J., Y.L., J.C., S.A., A.N., K.-J.Z. and W.-S.L. performed RIXS experiments at DLS and discussed the results. M.R., D.J., Y.L., H.L., C.-T.K., S.-J.L., J.-S.L. and W.-S.L. performed RSXS experiments at SSRL and discussed the results. M.R., H.L., Y.-D.C. and W.-S.L. performed RIXS experiments at ALS and discussed the results. M.O., B.Y.W., K.L. and H.Y.H. synthesized and characterized the samples. M.R. and W.-S.L. analysed the data. M.R., Z.-X.S., B.M., T.P.D., H.Y.H. and W.-S.L. interpreted the results. M.R. and W.-S.L. wrote the manuscript with input from all authors.

Competing interests

The authors declare no competing interests.

Additional information

Extended data is available for this paper at https://doi.org/10.1038/s41567-022-01660-6. Correspondence and requests for materials should be addressed to Wei-Sheng Lee.

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Extended Data Fig. 1 | RIXS phonon softening in LaNiO$_2$ at 20 K and fit of the spectra. a. Representative RIXS spectrum of LaNiO$_2$ (black circles) at $q_x = (0.4, 0)$ r.l.u. and corresponding fit (red solid line). The fit function includes a Gaussian for the elastic line (orange), anti-symmetrized Lorentzian for phonon (blue) and magnon (green) and a constant background (thin black line). The fit function is convolved with a Gaussian with FWHM = 36 meV.

b. Phonon dispersion clearly showing the softening of the RIXS phonon. The phonon dispersion is also shown in Fig. 1a of the main text. c. Raw RIXS spectra of LaNiO$_2$ (black circles) with fit superimposed (red lines). The data shown here were taken using $\sigma$ incident photon polarization to optimize the RIXS phonon signal.
Extended Data Fig. 2 | See next page for caption.
Extended Data Fig. 2 | Magnetic excitations in LaNiO$_2$ at 20 K and fit of the spectra. a, RIXS intensity map of LaNiO$_2$ measured with $\pi$ incident photon polarization, which optimize the cross-section of the magnetic excitations. White circles correspond to the undamped mode energies of the magnetic excitation as determined from the damped harmonic oscillator function used for fitting the data. b, Intensity of the RIXS quasi-elastic line of LaNiO$_2$ determined from a Gaussian fit. c, Representative RIXS spectrum of LaNiO$_2$ (black circles) at $\mathbf{q}_\parallel = (0.4, 0)$ r.l.u. and corresponding fit (red solid line). The fit function includes a Gaussian for the elastic line (orange), anti-symmetrized Lorentzian for phonon (blue) and high-energy background (dashed line) and damped harmonic oscillator function for the magnon (green). The fit function is convolved with a Gaussian with FWHM = 40 meV. d, Raw RIXS spectra of LaNiO$_2$ (black circles) measured with $\pi$ polarization with fit superimposed (red lines).
Extended Data Fig. 3 | Extraction of RSXS data from two-dimensional images. a, Ni L₃-edge RSXS scan of LaNiO₂ at 33 K obtained by rotating the sample around the b axis (θ-scan), which is orthogonal to the scattering plane. Every column is obtained by integrating the rows of the two-dimensional CCD detector collected at a specific θ angle. The CO peak profile is obtained by integrating the columns near the centre of the detector (solid red window), while the background is estimated from the fluorescence signal collected at the top of the detector (dashed red window). The region of interest corresponds to k ~ ±0.015 r.l.u., while the top window corresponds to k ~ 0.02-0.03 r.l.u., which is well separated from the CO signal. b, The corresponding CO peak profile (thick solid line) and the fluorescence background (thin dashed line). In the main text, the theta angle is converted to in-plane momentum transfer.
Extended Data Fig. 4 | CO peak profile of LaNiO$_2$, measured at the La $M_4$ and $M_5$ absorption edges. 

**a**. Waterfall plot showing RSXS scans of LaNiO$_2$ as a function of temperature measured with incident photon energy tuned at the La $M_4$ edge (~850.58 eV).

**b**. CO peak profile obtained by fitting the RIXS quasielastic line measured at the La $M_5$ edge (~834.1 eV). The CO signal is clearly visible at both absorption edges up to the highest measured temperature.