Large orbital polarization in a metallic square-planar nickelate

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High-temperature cuprate superconductivity remains a defining problem in condensed-matter physics. Among myriad approaches to addressing this problem has been the study of alternative transition metal oxides with similar structures and 3d electron count that are suggested as proxies for cuprate physics. None of these analogues has been superconducting, and few are even metallic. Here, we report that the low-valent, quasi-two-dimensional trilayer compound Pr4NiO8 avoids a charge-stripe-ordered phase previously reported for La3NiO6, leading to a metallic ground state. X-ray absorption spectroscopy shows that metallic Pr4NiO8 exhibits a low-spin configuration with significant orbital polarization and pronounced d_{x2-y2} character in the unoccupied states above the Fermi energy, a hallmark of the cuprate superconductors. Density functional theory calculations corroborate this finding, and reveal that the d_{x2-y2} orbital dominates the near-EF, occupied states as well. Belonging to a regime of 3d electron count found for hole-doped cuprates, Pr4NiO8 thus represents one of the closest analogues to cuprates yet reported and a singularly promising candidate for high-Tc superconductivity if electron doping could be achieved.

A collection of structural, magnetic and electronic characteristics are widely considered to be key ingredients in high-temperature cuprate superconductivity: a quasi-two-dimensional (quasi-2D) square lattice, spin-1/2, strong antiferromagnetic correlations, large orbital polarization of the unoccupied e_g states (with a single d_{x2-y2} band near the Fermi energy), strong p-d hybridization, and a plethora of broken symmetry phases (for example, charge stripes and spin density waves) proximate to the parent insulating phase. One design strategy for finding new high-T_c materials has been to build solids that possess some or all of these electronic and structural features, in hopes that superconductivity will emerge. For example, the 5d transition metal oxide Sr$_2$IrO$_4$, with a J_m = 1/2 (t_2g$^5$; valence shell) ground state, has recently been found to satisfy many of the above-mentioned criteria and predicted to show superconductivity by Angle-resolved photoemission spectroscopy measurements have shown both Fermi arcs and the opening of a d-wave gap (also seen by scanning tunnelling spectroscopy)—both hallmarks of cuprate superconductors—upon surface doping with electrons. However, no evidence for superconductivity exists, even for doped samples. Due to its proximity to copper in the periodic table, nickel-based oxides have long been considered as potential cuprate analogues, and indeed tantalizing features such as Fermi arcs have been observed in the metallic but non-superconducting nickelate Eu$_2$Sr$_2$NiO$_6$ (ref. 9). The potential for nickelate superconductivity has been the subject of much theoretical discussion. Anisimov et al. have argued that square-planar-coordinated Ni$^{4+}$ (isoelectronic with Cu$^{2+}$, d$^9$) doped with S = 0 Ni$^{2+}$ holes will host superconductivity, and Chaloupka and Khaliullin have speculated that the low-energy electronic states of LaNiO$_3$/LaMO$_3$ (M = Al, Ga, ...) heterostructures can be mapped to the single-band model as developed for cuprates. In contrast, Lee and Pickett have argued that weak p-d hybridization in LaNiO$_2$, resulting from an energy mismatch between Ni 3d and O 2p orbitals, weakens the analogy between nickelates and cuprates. Here, by combining X-ray absorption spectroscopy (XAS) and density functional theory (DFT) calculations, we demonstrate that the trilayer nickelates R$_4$NiO$_8$ (R = La, Pr, hereafter R438) express key electronic signatures of cuprates: a large orbital polarization with unoccupied Ni 3d states that are predominately d_{x2-y2} in character, a low-spin configuration for dopants (Ni$^{2+}$ holes), and a high degree of hybridization between Ni 3d and O 2p states. We further show that Pr438 avoids the charge-stripe-ordered phase found in La438 (ref. 12), leading to a metallic ground state possessing a highly orbitally polarized electronic configuration. These findings argue that the R438 family, and in particular Pr438, lies closer to superconducting cuprates than previously studied nickelates such as La$_{2-x}$Sr$_x$NiO$_4$ and LaNiO$_3$-based heterostructures.

The trilayer nickelates R438 formally have an average Ni valence of 1.33+ (d$^{8S}$)—that is, 1/3-hole-doped into the Ni$^{2+}$ background. Their quasi-2D structure can be described as three consecutive layers of corner-sharing NiO$_2$ square planes alternating with R$_2$O$_7$ fluorite-type layers, stacked along the c axis (Fig. 1a). With 8.67 d electrons per Ni on average, and no charge disproportionation, the e_g states may be energetically arranged in two different ways (assuming the t_2g states are fully occupied): the limit where the Hund’s rule coupling is larger than the crystal-field splitting between the two e_g orbitals (high-spin state, HS) or the opposite situation (low-spin state, LS), as shown in Fig. 1b. While information on Pr438 is limited only to a remark that it is a black semiconductor, La438 is well known to undergo a semiconductor–insulator transition at 105 K (refs 12,14–17). Three different mechanisms have been proposed to explain this transition: a spin density wave

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nesting instability of the Fermi surface\textsuperscript{14}, a change of the Ni spin state without charge order\textsuperscript{15,16}, and more recently the formation of charge stripes\textsuperscript{17,18}.

Single crystals of La438 and Pr438 were prepared by reducing their parent \( n = 3 \) Ruddlesden–Popper (R–P) compounds, \( \text{R}_4\text{Ni}_3\text{O}_{10} \) (\( \text{R} = \text{La, Pr} \), hereafter R4310, see Fig. 1a and Supplementary Fig. 1). To our knowledge, this is the first report of single-crystal growth of La\(_4\)Ni\(_3\)O\(_8\) (\( \text{T} = 200 \text{~K} \)).

In Fig. 1c,d we compare the polarization dependence of the XAS at the \( \text{L}_2 \) edge for R438 at 150 K and the corresponding parent compounds R4310. The Ni \( \text{L}_2 \) edge was utilized due to the strong overlap between La \( \text{M}_4 \) and Ni \( \text{L}_2 \), which obscures the spectral features\textsuperscript{19}. A large orbital polarization of the unoccupied \( e_g \) states of R438 is immediately recognized by the strong intensity difference between in-plane (polarization along \( ab \)) and out-of-plane (polarization along \( c \)) polarization near the leading part of the edge. This notable difference resembles that observed in high-\( T_c \) cuprates, for example \( \text{YBa}_2\text{Cu}_3\text{O}_7 \) (ref. 19), as shown for comparison in Fig. 1e, which are considered to exhibit empty states of predominant \( d_{x^2−y^2} \) character\textsuperscript{20}. The XAS at the leading edge can hence be attributed to orbitals oriented in the \( ab \) plane (the unoccupied Ni \( d_{x^2−y^2} \)), which is consistent with the LS state picture shown in Fig. 1b. The data indicate that the out-of-plane oriented orbitals are largely occupied, although the intensity seen in the range 868 ≤ \( E \) ≤ 876 eV implies some contribution from unoccupied \( d_{z^2} \) states. We can quantify the orbital character utilizing a sum rule analysis\textsuperscript{21}, which allows us to determine the ratio of the unoccupied orbital occupations. Specifically, the quantity \( r = \frac{\text{intensity at } d_{x^2−y^2}}{\text{intensity at } d_{z^2}} \), where \( h \) denotes holes in a particular \( e_g \) orbital, can be determined by an integration of the background-subtracted XAS data (see Supplementary Fig. 3 and Supplementary Section 3, X-ray absorption spectroscopy (XAS)). Following this approach, we find that the R438 compounds show an \( r \approx 0.5 \), which indicates an orbital polarization favouring holes with \( d_{x^2−y^2} \) character. This result agrees closely with the \( r \approx 0.4 \) derived from the theoretical density of states, and represents ∼70% of the holes in the \( d_{x^2−y^2} \) orbital. For comparison, a similar analysis of \( \text{YBa}_2\text{Cu}_3\text{O}_7 \) yields an \( r \approx 0.35 \).

We attribute this large orbital polarization in R438 to the square-planar environment of the Ni atoms, which leads to a large crystal-field splitting of the \( e_g \) states, with \( d_{x^2−y^2} \) orbitals expected to lie higher in energy than \( d_{z^2} \). Comparing the orbital polarization of R438 with that of other nickelates that still retain the apical oxygens reveals more clearly the impact of the reduced coordination number of Ni. In sharp contrast to R438, the parent compounds R4310 give \( r \) values slightly larger than one, which indicates a small degree of orbital polarization. The single-layer R–P nickelates \( \text{La}_3\text{Sr}_2\text{NiO}_6 \) show negligible splitting at the absorption edge between in-plane and out-of-plane polarization, reflecting a small orbital polarization of the \( e_g \) states\textsuperscript{21}. By utilizing strain, charge transfer, and confinement, sizable orbital polarization at interfaces
has been engineered in LaNiO$_3$-based heterostructures, which also contain NiO$_2$ octahedra\textsuperscript{2}. We now turn to the nature of the spin state below the transition at 105 K in La$_4$NiO$_8$. As mentioned above, this transition has been attributed to a change in the Ni spin state\textsuperscript{11}, and more recently it has been ascribed to the formation of charge stripes\textsuperscript{22}. DFT calculations have found a Ni$^{1+}$/Ni$^{2+}$ charge stripe (CS) ground state with the Ni$^{2+}$ ions in a LS state (S = 0) yielding an antiferromagnetic arrangement of Ni$^{1+}$ (S = 1/2) ions (from here on denoted as the LS-CS state)\textsuperscript{22}. Figure 2a shows the polarization-dependent XAS of the Ni $L_2$ edge above and below the transition at 105 K. Notably, across the transition, there is no change in the out-of-plane-polarized XAS and only a slight change in the in-plane XAS. The $L_2$ leading edge is associated with the unoccupied Ni $d_{x^2-y^2}$ orbitals, consistent with a LS to LS-CS scenario but not with a LS–HS transition. In both LS and LS-CS states, as can be seen in Fig. 2b, the unoccupied Ni 3$d$ states are calculated to be solely $d_{x^2-y^2}$ in character. Furthermore, in agreement with the XAS data, DFT calculations show no change in the total $d_{x^2-y^2}$ occupation and only a minor change in the $d_{x^2-y^2}$ occupation across the transition due to the opening of a small gap (0.25 eV in a calculation without a Hubbard U) in the LS-CS phase (Supplementary Fig. 4).

We also measured the hybridization between Ni $d_{x^2-y^2}$ and O 2$p$ states in the vicinity of the Fermi level. Figure 3a shows the oxygen K edge XAS for La$_4$NiO$_8$ above and below the phase transition in the range 528.5–530.5 eV. Like the hole-doped single-layer nickelates and high-$T_c$ cuprates\textsuperscript{29}, a well-defined pre-peak in La$_4$NiO$_8$ is due to holes located in the O 2$p$ orbitals hybridized with the Ni $d_{x^2-y^2}$ states. This result agrees with DFT calculations, demonstrating that in both LS and LS-CS states there is significant hybridization between O 2$p$ and planar Ni $d_{x^2-y^2}$ states in the vicinity of the Fermi level (see Fig. 2b). This is a consequence of the strong interaction between Ni $d_{x^2-y^2}$ and O 2$p$ states, since the lobes of the $d$-orbitals are directed along the planar Ni–O bonds. A small but clear shift to higher energy of the pre-peak reflects the opening of a small (~0.1 eV) gap in the charge stripe phase, also consistent with our DFT calculations.

Thus far, we have shown that La$_4$NiO$_8$ shares several key features with superconducting cuprates: a large orbital polarization of the unoccupied $e_g$ orbitals, a LS state for Ni (in sharp contrast to HS in hole-doped single-layer nickelates), and a $d_{x^2-y^2}$ orbital character near the Fermi energy with strong hybridization of Ni 3$d$ and O 2$p$ states. All of these features can be traced back to the square-planar geometry of Ni, with its $D_{4h}$ crystal field and missing apical oxygen ligands. Nevertheless, as a 1/3-hole self-doped material, La$_4$NiO$_8$ forms charge stripes below the transition at 105 K to become an insulator, much like the analogous single-layer nickelates, whereas the 1/3-hole-doped cuprates examined so far are metals\textsuperscript{28}. We now demonstrate that it is possible to establish a metallic phase in the R438 system while maintaining predominantly $d_{x^2-y^2}$ orbital polarization at a carrier concentration relevant to hole-doped cuprates.

Figure 3b presents the resistivity of a Pr$_4$NiO$_8$ single crystal, exhibiting a metallic temperature dependence, $d\rho/dT > 0$, in the temperature range 2–300 K, a distinct contrast with both La$_4$NiO$_8$ and the hole-doped single-layer R–P nickelates\textsuperscript{22,25}, the latter of which become metallic only above a very large hole concentration $x \sim 1$ (see Fig. 4)\textsuperscript{27}. The absolute resistivity at 298 K is 67.2 $\Omega$ cm, which we attribute to poor electrical conductivity across a strain-induced network of microcracks created during the reduction process. Despite this apparently high resistivity, its temperature dependence is that of a metal. In addition, the specific heat of Pr$_4$NiO$_8$ (Fig. 3c, inset) evidences a sizable electronic contribution. Crystal structure measurements (Supplementary Fig. 5) reveal no signature of a phase transition in Pr$_4$NiO$_8$ in the temperature range studied, in sharp contrast to La$_4$NiO$_8$. Figure 3d shows the oxygen K edge XAS data for Pr$_4$NiO$_8$ at 85 and 150 K. Compared with La$_4$NiO$_8$, no shift in the pre-peak is found in Pr$_4$NiO$_8$, confirming that no gap opens from charge stripe formation in this temperature window. Finally, high-resolution single-crystal X-ray diffraction data show no superlattice peaks (Supplementary Fig. 6) for temperatures as low as 15 K. Taken together, these findings argue that Pr$_4$NiO$_8$ does not form the static charge stripe phase found in La$_4$NiO$_8$, but remains metallic down to 2 K.

One plausible explanation for metallicity in Pr$_4$NiO$_8$ is a chemical pressure effect—the ionic size of Pr$^{3+}$ is smaller than that of La$^{3+}$, leading to a negative differential volume ($V_{\text{NiLa}}/V_{\text{LaLa}} = 0.96$ at room temperature). Pardo and Pickett have predicted that even a 1% decrease in unit cell volume favours the metallic LS state in La$_4$NiO$_8$; the measured volume of Pr$_4$NiO$_8$ is indeed located in this region\textsuperscript{25}. High-pressure experiments on La$_4$NiO$_8$ by Cheng et al. confirmed the suppression of the semiconductor–insulator transition at $\sim$6 GPa (ref. 28), although a metallic phase does not emerge, possibly due to the existence of short-range charge fluctuations. We are unable to stabilize a LS-CS state in Pr$_4$NiO$_8$ via DFT calculations, a result that corroborates the stability of the metallic LS phase, with states around the Fermi level being largely $d_{x^2-y^2}$ in character (see Supplementary Fig. 7 and Supplementary Table 3). We note that a careful choice of the DFT approach is important to capture the physics of these nickelates; for instance, when the two spin states are nearly degenerate, it becomes essential, if applying the LDA+U approach, to understand the tendencies of the various choices of functional: the around mean field (AMF) scheme is known to favour the formation of charge stripes, also consistent with our DFT calculations.

Figure 2 | Temperature-dependent XAS and DFT band structure of La$_4$Ni$_2$O$_8$. a, c axis and ab plane polarized Ni $L_2$ edge XAS of La$_4$Ni$_2$O$_8$ above and below the transition at 105 K. b, Ni-$e_g$ and O-$p$ orbital resolved density of states (DOS) for the low-spin (LS), low-spin charge stripe (LS-CS) and high-spin (HS) states from DFT calculations.

$\text{O}_2p$ and planar Ni $d_{x^2-y^2}$ states in the vicinity of the Fermi level (see Fig. 2b). This is a consequence of the strong interaction between Ni $d_{x^2-y^2}$ and O 2$p$ states, since the lobes of the $d$-orbitals are directed along the planar Ni–O bonds. A small but clear shift to higher energy of the pre-peak reflects the opening of a small (~0.1 eV) gap in the charge stripe phase, also consistent with our DFT calculations.
of Pr438 vis-à-vis La438 could be a Pr valence transition as is found in other complex oxides, with a dramatic impact on electronic and magnetic properties. This possibility was tested by measuring the M edge of Pr (Supplementary Fig. 8), which shows convincingly that Pr remains trivalent in the temperature range 85–300 K.

In Fig. 4 we show a schematic electronic phase diagram of hole-doped cuprates and related quasi-2D nickelates organized by the nominal filling of the 3d levels in the range d2–d9, with the caveat that here we are not distinguishing whether the holes, which favour an in-plane character, are on copper/nickel or oxygen. Recognizing that d-count is only a proxy for the multiple degrees of freedom that impact the properties of these compounds, we use this variable as a convenient way to describe the relationships among them and to generate a roadmap for future exploration of the effects of variable electron concentration and dimensionality on these systems.

On the top-right (d2–d8) lies the known single-layer R3−xSr2NiO4 (R = rare earth) nickelates, where charge/spin stripe order (d2–d8) is observed. The inset shows the low temperature data. Pr remains trivalent in the temperature range 85–300 K.

Figure 3 | Oxygen K edge XAS and physical properties of La2Ni3O8 and Pr2Ni3O8. a, The pre-peak in the oxygen K edge XAS for La2Ni3O8 above and below 105 K. b, Resistivity in the ab plane. c, Heat capacity. The inset shows the low temperature data. d, The pre-peak in the oxygen K edge XAS for Pr438 at 85 K and 200 K.

cuprate-like phases. Conversely, hole doping towards d8 offers the opportunity to reveal potential emergent phases in the ‘ overdoped regime’ beyond those currently unavailable in the cuprates. The potential role of dimensionality in the square-planar nickelates can be explored both in the ‘ overdoped regime’ (d8–d6) or the optimally doped regime (d7–d5) by hole doping trilayer R438 and electron doping bilayer La4Ni3O8, or electron doping trilayer R438 and hole doping infinite-layer LaNiO3, respectively. The opportunity space exposed by comparisons of these phase diagrams, matched with new capability for producing single crystals of these materials under high-pO2 conditions, justifies a vigorous effort to do so.

Finally, the R–P trilayer La4310 exhibits a metallic ground state, sharply contrasting with the insulating behaviour observed in single-layer R–P phases La4310Sr2NiO4, despite the same 3d electron count. A similar situation is found for metallic bilayer La4Ni3O8 versus insulating La4310Sr2NiO4 (ref. 34), Seo et al. have predicted charge density wave formation in La3Ni2O7 and La4310 based on the extended Hückel tight binding method; whether they exhibit any form of charge/spin order remains an open question. Recent work has also shown that La3Ni2O7 and R4310 phases can be prepared in thin-film form, which offers a starting point to explore these phases, their electron/hole-doped congeners, as well as pure and doped R438 and La4Ni3O8 phases under the influence of strain, interfacial charge transfer, and confinement.

In summary, we have shown that bulk Pr438 crystals possess a combination of traits that are widely considered as important ingredients for high-Tc superconductivity in cuprates. In particular, they exhibit a low-spin state for Ni, in which a large orbital polarization of the unoccupied c5 states yields predominantly d5 states at the Fermi energy, and significant hybridization with O 2p states. Looking ahead, we note that current understanding of the cuprate phase diagram has relied on chemically doping holes or electrons into a d4 parent compound, introducing quenched disorder along with carriers. Lying formally in the heavily overdoped regime of the cuprate phase diagram, the R438 system, and in particular metallic Pr438, offers a 1/3-doped parent phase that is a priori unperturbed by quenched disorder. These unique layered...
compounds thus provide a novel, complementary starting point for interrogating this correlated electron phase space and a promising set of candidates for unconventional superconductivity.

Methods

Methods, including statements of data availability and any associated accession codes and references, are available in the online version of this paper.

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Author contributions

J.E.M. and J.Z. directed the project. J.Z. and H.Z. grew single crystals. J.Z. and D.P. performed the transport measurements. J.Z. performed the powder and single-crystal synchrotron X-ray diffraction experiments. J.W.F. and J.Z. performed the XAS experiments. J.W.F., J.Z. and M.R.N. analysed data. A.S.B. and V.P. performed DFT calculations. J.Z., A.S.B., J.W.F. and J.F.M. wrote the manuscript, with contributions from all coauthors.

Additional information

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Competing financial interests

The authors declare no competing financial interests.
Methods

High-pressure single-crystal growth. Single-crystal growth of R$_4$Ni$_3$O$_8$ (R = La, Pr) was performed in an optical-image floating zone furnace (HKZ-1, Scimed Products GmbH) with 20 bar O$_2$ for La$_4$Ni$_3$O$_8$ and 140 bar for Pr$_4$Ni$_3$O$_8$. A flow rate of 0.11 min$^{-1}$ of oxygen was maintained during growth. Feed and seed rods were counter-rotated at 30 r.p.m. and 27 r.p.m., respectively, to improve zone homogeneity. The travelling speed of the seed was 4 mm h$^{-1}$. After ∼30 h of growth, the zone and boule were quenched by shutting down the lamp. La$_4$Ni$_3$O$_8$ and Pr$_4$Ni$_3$O$_8$ single crystals (1–2 mm$^2$ × 0.5 mm) were obtained by reducing specimens cleaved from boules of La$_4$Ni$_3$O$_8$ and Pr$_4$Ni$_3$O$_8$, respectively (flowing 4% H$_2$/Ar gas, 350 °C, five days).

Powder X-ray diffraction. To confirm the phase purity, powder X-ray diffraction data of R$_4$Ni$_3$O$_8$ and R$_4$Ni$_3$O$_4$ (R = La, Pr) were collected on a PANalytical X’Pert powder diffractometer with Cu K$_\alpha$ radiation ($\lambda$ = 1.5418 Å) in the 2θ range 20°–60° at room temperature.

Single-crystal X-ray diffraction. Single-crystal X-ray diffraction data of Pr$_4$Ni$_3$O$_8$ were collected using a Bruker SMART APEX2 charge-coupled device (CCD) area detector on a D8 goniometer operated with graphite-monochromated Mo K$_\alpha$ radiation ($\lambda$ = 0.71073 Å). A single crystal with dimensions of ∼0.061 × 0.041 × 0.039 mm$^3$ was used to determine the structure at room temperature. To check for superlattice peaks at low temperature in Pr$_4$Ni$_3$O$_8$, single-crystal X-ray diffraction data were collected with an APEX2 area detector using synchrotron radiation ($\lambda$ = 0.41328 Å) at Beamline 15-ID-B at the Advanced Photon Source, Argonne National Laboratory. Single crystals with dimensions approximately 10 μm on edge and exposure times of 1.0 s/0.2° scans were used. Data were collected at 15 K by flowing helium gas. Φ-scans were used.

Variable-temperature high-resolution powder X-ray diffraction. High-resolution powder X-ray diffraction data were collected on pulverized Pr$_4$Ni$_3$O$_8$ crystals at beamline 11-1M (APS) in the range 1° ≤ 2θ ≤ 28°, with a step size of 0.001° and counting time of 0.1 s.

Transport measurements. Electrical resistivity of Pr$_4$Ni$_3$O$_8$ single crystals was measured using the conventional four-probe method using silver paint contacts on a Quantum Design PPMS in the temperature range 2–300 K. The current was applied in the ab plane.

Heat capacity. Heat capacity was measured in a Quantum Design Physical Properties Measurement System (PPMS) using the relaxation method under a magnetic field of 0 T.

X-ray absorption spectroscopy (XAS). To study the electronic structure of R$_4$Ni$_3$O$_8$ and R$_4$Ni$_3$O$_4$ (R = La, Pr), XAS was performed at beamline 4-ID-C at the Advanced Photon Source (APS), Argonne National Laboratory. We carried out polarization-dependent soft X-ray absorption spectroscopy at the L edge of Ni using the bulk sensitive total fluorescence yield (TFY) mode with the beam at grazing (15°) incidence. By controlling the polarization of the X-rays at the undulator source, we measured the orbital character projected in the ab plane and along the c-axis without changing the beam path within the sample.

Density functional theory (DFT) calculations. Electronic structure calculations were performed within DFT using the all-electron, full potential code WIEN2k based on an augmented plane wave plus local orbital (APW+lo) basis set. For La$_4$Ni$_3$O$_8$, the LDA+U scheme that incorporates the on-site Coulomb repulsion U and Hund’s rule coupling J$_H$ for the Ni 3d states has been applied since it is needed to converge the HS state. The values for U and J$_H$ are 4.75 and 0.68 eV, respectively, as used in earlier work. For the structural relaxations in the low-spin charge stripe (LS-CS) state of La$_4$Ni$_3$O$_8$, we have used the Perdew–Burke–Ernzerhof version of the generalized gradient approximation (GGA) for Pr$_4$Ni$_3$O$_8$, a full study on the energetics of the LS and HS states’ dependence on U has been performed within LDA + U using different schemes: the around mean field (AMF) and the fully localized limit (FLL). For Pr$_4$Ni$_3$O$_8$, a full study on the energetics of the LS and HS states’ dependence on U has been performed within LDA + U using different schemes: the around mean field (AMF) and the fully localized limit (FLL).

Data availability. The data that support the plots within this paper and other findings of this study are available from the corresponding author upon request.

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