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Absence of superconductivity in bulk $\text{Nd}_{1-x}\text{Sr}_x\text{NiO}_2$

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Superconductivity at 9–15 K was recently discovered in $\text{Nd}_{0.8}\text{Sr}_{0.2}\text{NiO}_2$ films. Since the Ni^{1+} ionic state in NdNiO_2 may have the same $3d^9$ outer-shell electronic orbital as in cuprate superconductors, it is interesting to know whether superconductivity has a similar mechanism in these two systems. Here we synthesize bulk samples of $\text{Nd}_{1-x}\text{Sr}_x\text{NiO}_2$ ($x = 0, 0.2, 0.4$) with inhomogeneous Sr distribution and Ni deficiency. Resistivity measurements show insulating behavior without the presence of superconductivity, different to the previously reported films. Although applying pressure up to about 50.2 GPa significantly suppresses the insulating behavior, superconductivity remains absent. The magnetization behavior exhibits a Curie–Weiss law with a paramagnetic moment of about $2 \mu_B/\text{f.u.}$ Since the lattice constants derived from our diffraction data are very close to the previously reported superconducting $\text{Nd}_{0.8}\text{Sr}_{0.2}\text{NiO}_2$ films, we suggest that superconductivity in that system may have arisen from interface or stress-related effects, or nickel deficiency in our bulk samples that might prevent the emergence of superconductivity.

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Since the discovery of high critical temperature superconductivity (HTS) in cuprates in 1986¹, there are plenty of experimental and theoretical studies to explore the intrinsic mechanism for superconductivity^{2–5}. There is a general agreement that the parent compound of cuprates like La_2CuO_4 is a Mott insulator with a charge transfer gap and long-range antiferromagnetic (AF) order⁶. With chemical doping, the long-range AF order will be suppressed at a hole doping level ($p \approx 0.02$) and d -wave superconductivity emerges at a higher doping level ($p \geq 0.05$)^{7–9}. After the efforts more than three decades, some common features have been observed, but the intrinsic pairing mechanism of HTS remains unresolved yet. These include two-dimensional electronic structure and coexistence with an AF order or spin fluctuations, all these also occur in most iron-based¹⁰ and heavy fermion superconductors¹¹. Moreover, in cuprates, it is also important that the spin $S = 1/2$ magnetic moment from $3d^9$ electrons forms the basic structure of the AF order. One intuitive way to explore the pairing mechanism of cuprates is to find additional high- T_C superconductors with different transition metals but similar crystal and electronic structure^{12,13}. The infinite-layer materials RNiO_2 ($R = \text{La}, \text{Nd}$) are one of the ideal systems to simulate cuprates. First, the RNiO_2 compounds have the same crystal structure ($P4/mmm$) as CaCuO_2 , which is a parent compound of high- T_C cuprates and can reach a high- T_C of about 110 K by hole doping¹⁴. Second, the $\text{Ni}^{1+}(3d^9)$ oxidation state in RNiO_2 is very similar to $3d^9$ configuration of Cu^{2+} in cuprates. Thus, many theoretical and experimental efforts have been put forward to investigate the RNiO_2 as a promising candidate of cuprate-like Ni-based superconductor^{12,15–17}.

Recently, superconductivity was observed at 9–15 K in the strontium doped infinite-layer nickelate thin films of $\text{Nd}_{0.8}\text{Sr}_{0.2}\text{NiO}_2$ deposited on the SrTiO_3 substrate¹⁸. This work has stimulated enormous interests, and plenty of theoretical works have been carried out^{19–31}. Among them, Zhang et al. propose the parent compound of $\text{Nd}_{0.8}\text{Sr}_{0.2}\text{NiO}_2$ as a self-doped Mott insulator²⁶. This work suggests that the low-density $\text{Nd-}5d$ conduction electrons couple with the localized $\text{Ni-}3d$ electrons, which suppresses the long-range AF order and forms Kondo spin singlets at low temperatures. While, Botana and Norman argue that a large ratio of longer-range hopping to near-neighbor hopping is conducive for superconductivity both in cuprates and nickelates²⁰. And Ryee et al. demonstrate that magnetic two-dimensionality induced by hole doping is the key factor for superconducting $\text{Nd}_{1-x}\text{Sr}_x\text{NiO}_2$ ²⁵. Bernardini et al.³¹ propose a possible difference between cuprates and nickelates based on the computed London penetration depth, and suggest that the latter does not follow the Uemura plot which holds well in underdoped cuprates. Hirayama et al.³⁰ compare the electronic structure of cuprates and NdNiO_2 , and conclude that the Nd layer also forms Fermi pockets. And they also propose some other promising compounds analogues to high- T_C cuprates. Several other groups also studied the dominant pairing instability in the framework of t - J model^{23,27}. They proposed that superconductivity in nickelates has a d -wave symmetry, which is analogous to cuprates. However, since the report of discovering superconductivity in $\text{Nd}_{0.8}\text{Sr}_{0.2}\text{NiO}_2$ ¹⁸ thin films, no other experimental works have been reported up to now.

In this paper, we report the successful synthesis and physical properties of bulk $\text{Nd}_{1-x}\text{Sr}_x\text{NiO}_2$ ($x = 0, 0.2, 0.4$) samples. By using a three-step method, we prepare bulk Sr-doped NdNiO_2 polycrystalline samples successfully with the similar doped composition of Sr as in the reported films. The structural and composition analyses reveal the formation of bulk $\text{Nd}_{1-x}\text{Sr}_x\text{NiO}_2$ phase which at this moment has low crystallinity, nickel deficiency, and inhomogeneous strontium distribution. The low crystallinity may be a common feature for the low-temperature topotactic reduction

method, which can also be seen in the bulk form NdNiO_2 samples³² and the superconducting $\text{Nd}_{0.8}\text{Sr}_{0.2}\text{NiO}_2$ ¹⁸ thin film. Magnetization measurements of the sample show a Curie–Weiss (C–W) like feature at high fields (1 and 3 T). The resistivity measurements at ambient and high pressures exhibit insulating behavior without the presence of superconductivity. We think the contradictory results compared with that of the reported films¹⁸ may be attributed to the interface or stress effect in films. Furthermore, in our samples, we find appreciable deficiency (5–9%) of Ni in the NiO_2 planes. It would be interesting to know whether this feature occurs also in the reported films, which may lead to the absence of superconductivity in our bulk samples.

Results

Sample characterization. Figure 1a shows the schematic crystal structures and the transformation from the 113 to 112 phase through the low-temperature topotactic reduction method. Here Nd/Sr, Ni and oxygen atoms are represented by the orange/purple, green and red spheres, respectively. To verify the formation of bulk $\text{Nd}_{1-x}\text{Sr}_x\text{NiO}_2$ phase, we conduct the room temperature XRD measurements with 2θ from 10° to 90° and the Rietveld refinements³³ of $\text{Nd}_{1-x}\text{Sr}_x\text{NiO}_2$ ($x = 0.2, 0.4$) bulk samples. The results are shown in Fig. 1b, c. The XRD data of undoped NdNiO_2 sample are shown in Supplementary Fig. 1. One can see that the Sr-doped samples have better crystallinity, which may be due to the fact that the valence of Ni in $\text{Nd}_{1-x}\text{Sr}_x\text{NiO}_2$ ($x = 0.2, 0.4$) is closer to 2+, and it is known that the Ni^{2+} state is much more stable than Ni^{1+} . All the samples

Fig. 1 Crystal structure and Rietveld refinement analyses. **a** The schematic structure and transformation from perovskite $\text{Nd}_{1-x}\text{Sr}_x\text{NiO}_3$ to infinite-layer $\text{Nd}_{1-x}\text{Sr}_x\text{NiO}_2$ by low-temperature reduction process with CaH_2 . **b, c** Powder X-ray diffraction patterns of $\text{Nd}_{0.8}\text{Sr}_{0.2}\text{NiO}_2$ and $\text{Nd}_{0.6}\text{Sr}_{0.4}\text{NiO}_2$ (circles) and Rietveld fitting curves (red lines) to the data. A small impurity peak around 33 degree marked with asterisk (*) in both samples may come from the unreacted $(\text{Nd,Sr})_2\text{NiO}_4$ phase. The Miller indices of $\text{Nd}_{0.6}\text{Sr}_{0.4}\text{NiO}_2$ sample are given in c.

contain mainly the infinite-layer 112 phase and some amount of extra Ni appears as disconnected segregations. Some peaks of $\text{Nd}_{1-x}\text{Sr}_x\text{NiO}_2$ seem to be broader than others or have unexpected strong intensities, which may be induced by the disorder in these reflection planes and anisotropic particle size in layered materials. And the low crystallinity is a common feature for the samples fabricated by the low-temperature topotactic reduction method³². From the indices of those peaks as shown in Fig. 1c, it is obvious that the diffraction peaks of the class $\langle h k 0 \rangle$ are sharper. And the broader peaks are from the class where l has a nonzero value. It means that the NiO_2 plane may be disordered, which is corresponding to the result of the nickel deficiency in present samples as inferred from the EDS measurement. The crystallographic data obtained from the Rietveld refinement profiles are shown in Table 1 and Supplementary Table 1. The lattice constant of c -axis increases with increasing doping contents. The lattice parameters of our bulk sample ($x = 0.2$) are $a = 3.91 \text{ \AA}$, $c = 3.33 \text{ \AA}$, which are in good agreement with the previous reports on the reported $\text{Nd}_{0.8}\text{Sr}_{0.2}\text{NiO}_2$ thin film¹⁸.

Figure 2a, b display the scanning electron microscope (SEM) images of $\text{Nd}_{1-x}\text{Sr}_x\text{NiO}_2$ ($x = 0.2, 0.4$) samples. As we can see, the grains could be clearly separated into two major morphologies, which are characterized by the argenteous crystals (dominant phase) and dark gray areas. The argenteous grains are interconnected, while the dark gray ones are well separated with each other. In order to have a deeper insight of the difference

between the two different grains, energy dispersive X-ray spectroscopy (EDS) is used to analyze the element concentration of all three samples. In each sample, we measure more than 20 spots randomly (marked by the red crosses in images of Fig. 2a, b and Supplementary Fig. 1). The results are shown in Fig. 2c–f. As there is uncertainty for the composition of carbon and oxygen, here we only study the contents of Nd, Sr, and Ni. Noting that the starting ratio of Nd/Sr/Ni in $\text{Nd}_{1-x}\text{Sr}_x\text{NiO}_2$ is stoichiometric when we fabricate the sample. The typical EDS patterns of different samples are given in Fig. 2c, d, we find that the argenteous grains have a composition of $\text{Nd}_{1-x}\text{Sr}_x\text{Ni}_y\text{O}_2$, while the dark gray grains show a composition of Ni (see Supplementary Fig. 2 and Supplementary Note 1). Two typical features can be identified for the $\text{Nd}_{1-x}\text{Sr}_x\text{Ni}_y\text{O}_2$: (1) The ratio of Ni: (Nd+Sr) is close to 1, although an appreciable deficiency of Ni can be seen from the EDS data. Figure 2e shows the mean value of Ni occupancy normalized by the summed concentration of Nd and Sr. The deficiency of Ni should be in the scale of 5–9% in all three samples ($x = 0, 0.2, 0.4$). The vacancies in nickel sites may cause the distortion of NiO_2 plane and hence result in the shrinkage of the lattice constants of a and b . And the disorder in those reflection planes may induce the peak broadening of XRD. As shown in Supplementary Table 1, the concentration of nickel metal extracted from our XRD data is about 15 wt% for $x = 0.2$ sample and 17 wt% for $x = 0.4$ sample, which is larger than the observed nickel deficiency in EDS measurement (about 5–9%).

Table 1 Lattice parameters obtained from the Rietveld refinements.				
Compound	Space group	$V \text{ (\AA}^3\text{)}$	$a, b \text{ (\AA)}$	$c \text{ (\AA)}$
NdNiO_2	$P4/mmm$	49.63 (5)	3.914 (2)	3.239 (6)
$\text{Nd}_{0.8}\text{Sr}_{0.2}\text{NiO}_2$	$P4/mmm$	51.01 (6)	3.9138 (9)	3.3303 (8)
$\text{Nd}_{0.6}\text{Sr}_{0.4}\text{NiO}_2$	$P4/mmm$	50.44 (9)	3.8850 (6)	3.3425 (1)
$\text{Nd}_{0.8}\text{Sr}_{0.2}\text{NiO}_2$ thin films ¹⁸	$P4/mmm$	51.06–51.67	3.91	3.34–3.38

Lattice parameters obtained from the Rietveld refinements of $\text{Nd}_{1-x}\text{Sr}_x\text{NiO}_2$ ($x = 0, 0.2, 0.4$) at room temperature and a comparison with superconducting $\text{Nd}_{0.8}\text{Sr}_{0.2}\text{NiO}_2$ thin film¹⁸.

Fig. 2 Scanning electron micrograph images and energy dispersive spectroscopy analyses. **a, b** SEM images of $\text{Nd}_{0.8}\text{Sr}_{0.2}\text{NiO}_2$ and $\text{Nd}_{0.6}\text{Sr}_{0.4}\text{NiO}_2$ samples. **c, d** The typical energy dispersive spectroscopy (EDS) of the spot 8 in (a) and spot 9 in (b), respectively. **e** The mean value of occupied ratio of nickel in $\text{Nd}_{1-x}\text{Sr}_x\text{NiO}_2$ ($x = 0, 0.2, 0.4$) samples. **f** The proportion distribution of Sr concentration by measuring EDS on different grains of the samples. A clear inhomogeneity of strontium content is observed. The strontium content can be addressed as 0.16 ± 0.04 for $x = 0.2$ sample and 0.39 ± 0.05 for $x = 0.4$ sample from the Gaussian fitting.

Fig. 3 Magnetic properties of $\text{Nd}_{1-x}\text{Sr}_x\text{NiO}_2$ ($x = 0, 0.2, 0.4$) samples. **a–c** Temperature dependence of magnetic moment measured at the fields of 1 and 3 T for NdNiO_2 , $\text{Nd}_{0.8}\text{Sr}_{0.2}\text{NiO}_2$ and $\text{Nd}_{0.6}\text{Sr}_{0.4}\text{NiO}_2$ samples. **d** Magnetization hysteresis loops for $\text{Nd}_{0.8}\text{Sr}_{0.2}\text{NiO}_2$ sample at different temperatures. Inset shows a linear relation between M with H at low field. **e** Temperature dependence of $(\chi_p - \chi_{p0})^{-1}$ in the low-temperature region. The red line shows a linear relation of $(\chi_p - \chi_{p0})^{-1}$ versus T .

The inconsistent content of nickel metal concentration in Rietveld refinement and the observed nickel deficiency in EDS measurement may be induced by the different crystallinity, different grain size as well as the preferred orientation between Ni cluster and grains of $\text{Nd}_{1-x}\text{Sr}_x\text{NiO}_2$, which make the compositional ratio determined by XRD imprecise. (2) The doped Sr concentrations in $\text{Nd}_{1-x}\text{Sr}_x\text{NiO}_2$ ($x = 0.2, 0.4$) samples are close to the nominal values with a clear inhomogeneity of strontium content among grains, which indicates the effective doping level of Sr in our samples. In Fig. 2f, we show the proportion distribution of Sr concentrations, more than half of the grains reach the nominal concentration of Sr. The strontium content for both samples show distributions which are fitted to Gaussian functions. Through the fitting, we find that the average strontium content can be expressed as 0.16 ± 0.04 for $x = 0.2$ sample and 0.39 ± 0.05 for $x = 0.4$ sample. Furthermore, for both $\text{Nd}_{0.8}\text{Sr}_{0.2}\text{NiO}_2$ and $\text{Nd}_{0.6}\text{Sr}_{0.4}\text{NiO}_2$ samples, the proportion of Sr and Ni in different grains all shows a clear distribution around the nominal value, but the concentrations of Sr and Ni on each measured point have no clear correlation (see Supplementary Fig. 3). As we know, the defects and inhomogeneity in transition metal oxides should play an important role in the electronic transport, which have been widely observed in cuprates. For example, by using an X-ray microdiffraction apparatus, scientists found that the superconducting transition temperature and charge-density-wave domain are highly affected by the inhomogeneous oxygen defect order^{34–36}. And also in nickelates, by using the similar apparatus on a NdNiO_3 film, the paradigm of nanoscale phase inhomogeneity has been extended to the correlated electron system with an AFM ground state³⁷. Thus, we believe the electronic transport in $\text{Nd}_{1-x}\text{Sr}_x\text{NiO}_2$ system may also be affected by the inhomogeneous distributions of Sr and Ni concentrations. Anyway, we believe our samples contain the right phase of $\text{Nd}_{1-x}\text{Sr}_x\text{NiO}_2$ ($x = 0.2, 0.4$, y ranges from 0.91 to 0.95). The sensitivity of the SQUID instrument should be sufficient to detect the superconducting signal if partial of these grains are superconductive.

Magnetic and Electrical transport properties. Figure 3a–c shows the temperature dependence of magnetic moment (M – T) curves at different external magnetic fields for $\text{Nd}_{1-x}\text{Sr}_x\text{NiO}_2$ ($x = 0, 0.2, 0.4$) samples. The magnetic moment of all samples at high fields ($\mu_0 H = 1$ T and 3 T) increases with decreasing temperature in the whole temperature range, exhibiting approximately linear behavior at high temperature and a C–W like enhancement at low temperature. It should be noted that the low field ($\mu_0 H = 1$ mT) magnetization of all three samples shows a drop of magnetization at about 5 K, together with an obvious irreversibility between the ZFC and FC curves (see Supplementary Fig. 4). Such abnormal behavior at low field magnetization curve may indicate the presence of spin glassy state, probably due to magnetic impurities in compounds. To obtain a deeper understanding of magnetization behavior, we measure the magnetization hysteresis (M – H) curves of the $\text{Nd}_{0.8}\text{Sr}_{0.2}\text{NiO}_2$ sample at different temperatures and show the data in Fig. 3d. We can safely exclude the possibility that the anomalous drop of magnetization at about 5 K is caused by superconductivity, because no superconducting like M – H curve is observed at 3 K (inset of Fig. 3d). The M – H curves show the presence of paramagnetic background with a ferromagnetic component, and the paramagnetic component decreases as the temperature increases. We think the ferromagnetic component is originated from the segregated phase of Ni. And the paramagnetic behavior is attributed to the $\text{Nd}_{1-x}\text{Sr}_x\text{NiO}_2$ phase. We have tried to fit the high field M – T curves in low-temperature region by the C–W law $\chi = \chi_0 + \frac{C}{T + T_\theta}$. The fitting results are given in Fig. 3e, as shown by the red solid line, indicating a good quality of C–W fitting. Through the C–W fitting, we derive the effective magnetic moments μ_{eff} of $\text{Nd}_{0.8}\text{Sr}_{0.2}\text{NiO}_2$ and $\text{Nd}_{0.6}\text{Sr}_{0.4}\text{NiO}_2$, which are about $2.32 \mu_B/\text{f.u.}$ and $2.03 \mu_B/\text{f.u.}$, respectively. It should be noted that, before doing the C–W fitting, we need to remove the ferromagnetic background of nickel from the M – T curves by subtracting the curves of 1 T from those of 3 T. This is valid since the magnetization of Ni gets already saturated at the magnetic fields of 1 T and 3 T, as shown in Supplementary Fig. 5. The subtracted paramagnetic magnetic

Fig. 4 Temperature dependent resistivity and magnetoresistance at ambient pressure. **a** Temperature dependence of resistivity for $\text{Nd}_{1-x}\text{Sr}_x\text{NiO}_2$ ($x = 0, 0.2, 0.4$) samples. **b** Temperature dependence of resistivity in $\ln \rho$ versus $T^{-1/4}$ for $\text{Nd}_{0.8}\text{Sr}_{0.2}\text{NiO}_2$. The top inset shows the curve of ρ versus $\log(1/T)$ and the bottom inset shows the curve of $\ln \rho$ versus $1/T$ (band gap model) for $\text{Nd}_{0.8}\text{Sr}_{0.2}\text{NiO}_2$. **c, d** Field dependence of magnetoresistance $\Delta\rho/\rho_0$ at different temperatures for $\text{Nd}_{0.8}\text{Sr}_{0.2}\text{NiO}_2$ and $\text{Nd}_{0.6}\text{Sr}_{0.4}\text{NiO}_2$ samples. Both samples exhibit a reversal from negative magnetoresistance to positive magnetoresistance above 20 K.

values $\chi_p = (M_{3T} - M_{1T})/\Delta H$ is thus taken as the pure signal from the paramagnetic term. More details are given in Supplementary Note 2.

Electrical transport measurements are carried out at ambient pressure in the temperature range from 2 to 300 K. Figure 4a shows the comparison of the temperature dependence of resistivity for $\text{Nd}_{1-x}\text{Sr}_x\text{NiO}_2$ ($x = 0, 0.2, 0.4$) samples. It can be clearly seen that the resistivity of the three samples all show insulating behaviors. The inhomogeneous distributions of Sr and Ni concentrations we discussed above may play an important role in electrical transport behavior, but it cannot affect the conclusion that superconductivity is absent in our samples. Assuming partial grains or some fraction of the grains show superconductivity below a certain temperature, the resistivity and magnetization should present a drop. To understand the underlying physics of the electrical transport behavior in present materials, in Fig. 4b we present the $\rho(T)$ curve within the frame of variable range hopping (VRH) model³⁸ described as $\rho = \rho_0 \exp(T_0/T)^{-1/4}$, we can see that in a short period of temperature, it gives a linear relationship as highlighted by the red line, while the global fitting is not good. Also the band-gap model ($\ln \rho \propto 1/T$, shown in the bottom-right inset) and resistivity versus $\log 1/T$ (shown in the top-left inset) are plotted, but all failed to fit the data at ambient pressure, suggesting that the insulating is not originated from the band gap and should possess by itself some exotic scattering reasons. Figure 4c, d shows the magnetic field dependent resistivity measured at different temperatures ($T = 2, 5, 10, 20, 50$ K). A sizable negative magnetoresistance (MR) $\Delta\rho/\rho_0 = (\rho_H - \rho_0)/\rho_0$ (about -10% at 5 T) is observed at 2 K. The negative MR at low temperature decreases with the increase of temperature, then the MR shows the crossover from a negative to a small positive MR behavior above 20 K. The negative MR in correlated oxides may be attributed to various mechanisms such as hopping conduction, magnetic scattering, or de-localization

effect. As for the positive MR, researchers have proposed that the exchange correlation in different hopping sites (VRH type conduction) could give rise to positive MR^{39,40}. Owing to the nickel segregations in our samples, the origin of negative and positive MR observed in the present compounds is not clear and more works deserve to be done.

Resistivity under high pressure. As shown above, an obvious conclusion drawn from the $\rho(T)$ curves at ambient pressure is the insulating behavior. One can see that not only the magnitude of resistivity, but also the insulating features are strongly suppressed by doping more Sr. In order to induce a metallic or even a superconducting state, we also conduct high pressure electrical resistance measurement. The temperature dependence of resistivity at various pressures in $\text{Nd}_{0.8}\text{Sr}_{0.2}\text{NiO}_2$ and $\text{Nd}_{0.6}\text{Sr}_{0.4}\text{NiO}_2$ samples are shown in Fig. 5a and Supplementary Fig. 6. As discussed above, $\rho(T)$ curves of $\text{Nd}_{1-x}\text{Sr}_x\text{NiO}_2$ exhibit an insulating behavior at ambient pressure. With application of pressure, the overall magnitude of the resistivity is continuously reduced. The insulating behavior is significantly weakened. The ratio ρ_{2K}/ρ_{300K} of $\text{Nd}_{0.8}\text{Sr}_{0.2}\text{NiO}_2$ sample is about 350 with the external pressure of 3.2 GPa. With increasing pressure, the magnitude of ρ_{2K}/ρ_{300K} decreases progressively as shown in Fig. 5b. The improvement of conductivity under high pressures may be related to the redistribution of the Sr concentrations and modification of the nickel deficiency within grains. However, to prove this, one may need some microscopic analysis tools, such as synchrotron hard X-ray nanoimaging or small-angle scattering under high pressures, which have been used to reveal a novel micron-scaled ribbon phase in optimally doped $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ ⁴¹. At the highest pressure of 50.2 GPa, the value of ρ_{2K}/ρ_{300K} has dropped to 6; however the $\rho(T)$ curve still exhibits a semiconducting-like feature in whole temperature region. Then we try to fit the electrical transport behavior of $\text{Nd}_{0.8}\text{Sr}_{0.2}\text{NiO}_2$ sample at the highest

Fig. 5 Temperature dependent resistivity of $\text{Nd}_{0.8}\text{Sr}_{0.2}\text{NiO}_2$ under pressures. **a** Temperature dependence of resistivity for $\text{Nd}_{0.8}\text{Sr}_{0.2}\text{NiO}_2$ at various pressures. **b** The applied pressure dependence of $\rho_{2\text{K}}/\rho_{300\text{K}}$ for $\text{Nd}_{0.8}\text{Sr}_{0.2}\text{NiO}_2$ sample derived from the $\rho - T$ curve at different pressures. **c** The ρ versus $\ln(1/T)$ curve for $\text{Nd}_{0.8}\text{Sr}_{0.2}\text{NiO}_2$ in the temperature range from 3.5 to 23 K at the pressure of 50.2 GPa together with the corresponding linear fit (red line). The top inset shows the curve of $\ln \rho$ versus $1/T$, corresponding to band gap model. The bottom inset shows the curve of $\ln \rho$ versus $T^{-1/4}$, corresponding to the VRH model.

pressure and show the fitting in Fig. 5c. The fitting curves of band gap model (the top-left inset) and VRH model (the bottom-right inset) are given. The results show that both the band gap model and the VRH model fail to fit the data. Surprisingly, the ρ versus $\log(1/T)$ curve at the highest pressure ($P = 50.2$ GPa) becomes roughly linear, as highlighted by the red linear line in a temperature range between 3.5 and 23 K. This strange $\rho \propto \log(1/T)$ behavior has been reported in some correlated oxides such as underdoped and overdoped cuprates or vanadium oxide $\text{V}_2\text{Se}_2\text{O}$, which may result from the electron correlation effect in correlated oxides with 3d transition metals^{42–44}. Meanwhile, the high pressure may change the distribution of Sr element and Ni deficiency within the grains, but due to the high diffusing barrier between different grains, we would not believe the high pressure will change the composition distribution of Sr and Ni among different grains. Thus the improvement of conductivity under pressure may be attributed to two factors. (1) The pressure can improve the electric conduction through optimizing the grain boundaries among different grains; (2) The pressure can modify the electronic band structure by making the redistribution of Sr and Ni deficiency within each grain, as well as the bandwidth through compressing the atomic lattice. These possibilities can be better resolved in future work.

Discussions

After a systematic analysis of the data, a main experimental finding in bulk infinite-layer nickelates $\text{Nd}_{1-x}\text{Sr}_x\text{NiO}_2$ ($x = 0, 0.2, 0.4$) is the insulating behavior, which is in contrast to the metallic state and the superconductivity below 9–15 K in $\text{Nd}_{0.8}\text{Sr}_{0.2}\text{NiO}_2$ thin film¹⁸. It is certainly very important to know whether the insulating behavior in the bulk $\text{Nd}_{1-x}\text{Sr}_x\text{NiO}_2$ is intrinsic. Based on the nice fitting to the XRD data and composition analysis on the grains of the samples, we can safely conclude that the main phase in the samples is definitely the $\text{Nd}_{1-x}\text{Sr}_x\text{NiO}_2$ ($x = 0.2, 0.4$) with only some disconnected segregation clusters of Ni. From previous literatures, we find that nickel is a metal with the resistivity of about 7.2 mΩ cm at room temperature⁴⁵, so it would

be a metallic behavior if the segregated grains of nickel form a conductive network. However, from our SEM image, the segregated nickel grains are well separated with each other. The behavior of resistance both in ambient and high pressure indicates that the insulating behavior is robust in our samples. Thus, the existence of disconnected nickel regions in samples may only affect the absolute value of resistivity, but not gives rise to the intrinsic insulating behavior. In principle, high pressure can compress the cell volume and reduce the lattice parameters of compound, resulting in insulator–metal transitions and even superconductivity^{46,47}. The clear suppression of insulating behavior in our high-pressure study may be induced by the improving of the grain boundaries, modification of the bands, or the weakening of the correlation effect, which leads to an enhanced effective density of states at the Fermi energy.

Since we do not find superconductivity in our bulk samples with the same structure and close lattice constants as the reported films¹⁸, we would like to suggest several reasons to interpret this discrepancy. Firstly, the superconductivity in $\text{Nd}_{0.8}\text{Sr}_{0.2}\text{NiO}_2$ films may arise from the interface or the stress effect given by the substrates. In the interface region, both the electron band and the doping level would be strongly modified, which could lead to superconductivity. The second reason may be the appreciable Ni deficiency (5–9%) in grains of $\text{Nd}_{1-x}\text{Sr}_x\text{NiO}_2$ of our samples, which may cause stronger buckling of the NiO_2 planes and lead to a strong localization or scattering of charges. If this is the case, we need to make samples without Ni deficiency. It would be interesting to know whether the reported films also have Ni deficiency.

To summarize, we have successfully synthesized bulk $\text{Nd}_{1-x}\text{Sr}_x\text{NiO}_2$ ($x = 0, 0.2, 0.4$) samples and performed comprehensive studies of the physical properties. From structure and composition analyses by XRD and EDS, the tetragonal $\text{Nd}_{1-x}\text{Sr}_x\text{NiO}_2$ ($x = 0, 0.2, 0.4$) phase is established and the strontium content is inhomogeneous and sufficient in most grains, but the Ni is deficient. The electrical transport and magnetization measurements reveal an insulating behavior and a C–W like feature with a ferromagnetic background caused by nickel segregations.

Electrical transport measurements under high pressure show that the insulating behavior can be effectively suppressed but superconductivity is still not observed.

Methods

Sample growth. To synthesize polycrystalline samples of $\text{Nd}_{1-x}\text{Sr}_x\text{NiO}_2$ ($x = 0, 0.2, 0.4$), we first prepare polycrystalline $\text{Nd}_{2-2x}\text{Sr}_{2x}\text{NiO}_4$ ($x = 0, 0.2, 0.4$) samples by the solid-state reaction of Nd_2O_3 , NiO , and SrO at 1200°C for 24 h. And then we use precursor $\text{Nd}_{2-2x}\text{Sr}_{2x}\text{NiO}_4$, NiO , and KClO_4 to synthesize the $\text{Nd}_{1-x}\text{Sr}_x\text{NiO}_3$ ($x = 0, 0.2, 0.4$) with high pressure and high temperature. Here KClO_4 is used as an excess oxygen source. Then the mixture is pressed into a pellet and sealed in a gold capsule. This procedure is done in a glove box with oxygen and water concentrations less than 0.1 ppm. The gold capsule is placed in a BN capsule and heated up to 1000°C and stayed for 2 h at this temperature under a pressure of 2 GPa. The resultant compound is the perovskite $\text{Nd}_{1-x}\text{Sr}_x\text{NiO}_3$ phase which is verified by powder X-ray diffraction at room temperature (see Supplementary Fig. 7 and Supplementary Note 3). Next, the samples of $\text{Nd}_{1-x}\text{Sr}_x\text{NiO}_2$ are obtained by reacting $\text{Nd}_{1-x}\text{Sr}_x\text{NiO}_3$ ($x = 0, 0.2, 0.4$) with CaH_2 , which is similar to the previous report^{48,49}. The obtained $\text{Nd}_{1-x}\text{Sr}_x\text{NiO}_3$ samples are washed by distilled water and then dried, ground with the CaH_2 in a ratio of 1:3 and then pressed into pellets. The pellets are sealed in a quartz tube, followed by heating treatment at 280°C for 20 h. Then the resultant pellets are crushed and washed with saturated NH_4Cl in anhydrous ethanol to remove the residual CaH_2 and the reacted byproduct CaO , and then dried in an evacuated oven. The target sample of the 112 phase in powder form is obtained. For measuring resistivity, the powders are pressed into a pellet again, and sealed with untouched CaH_2 powders in a quartz tube, followed by another heating treatment at 180°C for 10 h.

Physical properties measurements. The crystal structures of the prepared samples are determined by powder X-ray diffraction (XRD) (Bruker D8 Advance) using $\text{Cu-K}\alpha$ radiation at room temperature with a scanning step of 0.01° and 2θ from 10° to 90° . The Rietveld refinements are done based on the TOPAS4.2 software^{32,50}. The SEM photograph of the polycrystalline and the energy dispersive X-ray microanalysis spectrum are done by Phenom ProX (Phenom). The measurements are performed at an accelerating voltage of 15 kV. The DC magnetization is measured with a SQUID based on the vibrating sample technique (SQUID-VSM 7T, Quantum Design). The electrical resistances at ambient pressure are measured by the standard four-probe method using the physical property measurement system (PPMS 16T, Quantum Design). The high pressure resistivity measurements are performed by using the diamond anvil cell (cryoDACPPMS, Almax easyLab)⁵¹.

Data availability

The data supporting the findings of this study are available from the corresponding author upon reasonable request.

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References

- Bednorz, J. G. & Müller, K. A. Possible high T_c superconductivity in the Ba-La-Cu-O system. *Z. Phys. B: Condens. Matter* **64**, 189–193 (1986).
- Anderson, P. W. The resonating valence bond state in La_2CuO_4 and superconductivity. *Science* **235**, 1196–1198 (1987).
- Tsuei, C. C. & Kirtley, J. R. Pairing symmetry in cuprate superconductors. *Rev. Mod. Phys.* **72**, 969–1016 (2000).
- Lee, P. A., Nagaosa, N. & Wen, X.-G. Doping a Mott insulator: physics of high-temperature superconductivity. *Rev. Mod. Phys.* **78**, 17–85 (2006).
- Keimer, B. et al. From quantum matter to high-temperature superconductivity in copper oxides. *Nature* **518**, 179–186 (2015).
- Vaknin, D. et al. Antiferromagnetism in $\text{La}_2\text{CuO}_{4-y}$. *Phys. Rev. Lett.* **58**, 2802–2805 (1987).
- Shen, Z.-X. et al. Anomalous Large Gap Anisotropy in the a - b Plane of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$. *Phys. Rev. Lett.* **70**, 1553–1556 (1993).
- Wollman, D. A. et al. Experimental determination of the superconducting pairing state in YBCO from the phase coherence of YBCO-Pb dc SQUIDs. *Phys. Rev. Lett.* **71**, 2134–2137 (1993).
- Tsuei, C. C. et al. Pairing symmetry and flux quantization in a tricrystal superconducting ring of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. *Phys. Rev. Lett.* **73**, 593–596 (1994).
- Kamihara, Y. et al. Iron-based layered superconductor $\text{La}[\text{O}_{1-x}\text{F}_x]\text{FeAs}$ ($x = 0.05$ – 0.12) with $T_c = 26$ K. *J. Am. Chem. Soc.* **130**, 3296–3297 (2008).
- Si, Q. & Steglich, F. Heavy fermions and quantum phase transitions. *Science* **329**, 1161–1166 (2010).
- Chaloupka, J. & Khaliullin, G. Orbital order and possible superconductivity in $\text{LaNiO}_3/\text{LaMO}_3$ superlattices. *Phys. Rev. Lett.* **100**, 016404 (2008).
- Zhang, J. et al. Large orbital polarization in a metallic square-planar nickelate. *Nature Phys.* **13**, 864–869 (2017).
- Azuma, M. et al. Superconductivity at 110 K in the infinite-layer compound $(\text{Sr}_{1-x}\text{Ca}_x)_{1-y}\text{CuO}_2$. *Nature* **356**, 775–776 (1992).
- Anisimov, V. I., Bukhvalov, D. & Rice, T. M. Electronic structure of possible nickelate analogs to the cuprates. *Phys. Rev. B* **59**, 7901–7906 (1999).
- Boris, A. V. et al. Dimensionality control of electronic phase transitions in nickel-oxide superlattices. *Science* **332**, 937–940 (2011).
- Middey, S. et al. Physics of ultrathin films and heterostructures of rare-earth nickelates. *Annu. Rev. Mater. Res.* **46**, 305–334 (2016).
- Li, D. et al. Superconductivity in an infinite-layer nickelate. *Nature* **572**, 624–627 (2019).
- Hirsch, J. E. & Marsiglio, F. Hole superconductivity in infinite-layer nickelates. *Physica C: Supercond. Appl.* **566**, 1353534 (2019).
- Botana, A. S. & Norman, M. R. Similarities and differences between infinite-layer nickelates and cuprates and implications for superconductivity. *Phys. Rev. X* **10**, 011024 (2020).
- Sakakibara, H. et al. Model construction and a possibility of cuprate-like pairing in a new d^9 nickelate superconductor $(\text{Nd,Sr})\text{NiO}_2$. Preprint at <https://arxiv.org/abs/1909.00060> (2019).
- Hepting, M. et al. Electronic structure of the parent compound of superconducting infinite-layer nickelates. *Nat. Mater.* (2020). <https://doi.org/10.1038/s41563-019-0585-z>.
- Wu, X. et al. Robust $d_{x^2-y^2}$ -wave superconductivity of infinite-layer nickelates. *Phys. Rev. B* **101**, 060504 (2020).
- Nomura, Y. et al. Formation of 2D single-component correlated electron system and band engineering in the nickelate superconductor NdNiO_2 . *Phys. Rev. B* **100**, 205138 (2019).
- Ryee, S. et al. Induced magnetic two-dimensionality by hole doping in superconducting $\text{Nd}_{1-x}\text{Sr}_x\text{NiO}_2$. *Phys. Rev. B* **101**, 064513 (2020).
- Zhang, G.-M., Yang, Y.-F. & Zhang, F.-C. Self-doped Mott insulator for parent compounds of nickelate superconductors. *Phys. Rev. B* **101**, 020501 (2020).
- Zhang, Y.-H. & Vishwanath, A. Type II $t - J$ model in superconducting nickelate $\text{Nd}_{1-x}\text{Sr}_x\text{NiO}_2$. Preprint at <https://arxiv.org/abs/1909.12865> (2019).
- Gu, Y. et al. Hybridization and correlation effects in the electronic structure of infinite-layer nickelates. Preprint at <https://arxiv.org/abs/1911.00814> (2019).
- Hu, L.-H. & Wu, C. Two-band model for magnetism and superconductivity in nickelates. *Phys. Rev. Research* **1**, 032046 (2019).
- Hirayama, M. et al. Materials design of dynamically stable d^9 layered nickelates. *Phys. Rev. B* **101**, 075107 (2020).
- Bernardini, F., Olevano, V. & Cano, A. Magnetic penetration depth and T_C in superconducting nickelates. *Phys. Rev. Research* **2**, 013219 (2020).
- Hayward, M. A. et al. Sodium hydride as a powerful reducing agent for topotactic oxide deintercalation: synthesis and characterization of the nickel(I) oxide LaNiO_2 . *J. Am. Chem. Soc.* **121**, 8843–8854 (1999).
- Rietveld, H. M. A profile refinement method for nuclear and magnetic structures. *J. Appl. Cryst.* **2**, 65–71 (1969).
- Fratini, M. et al. Scale-free structural organization of oxygen interstitials in $\text{La}_2\text{CuO}_{4+y}$. *Nature* **466**, 841–844 (2010).
- Poccia, N. et al. Optimum inhomogeneity of local lattice distortions in $\text{La}_2\text{CuO}_{4+y}$. *Proc. Natl Acad. Sci.* **109**, 15685–15690 (2012).
- Campi, G. et al. Inhomogeneity of charge-density-wave order and quenched disorder in a high- T_c superconductor. *Nature* **525**, 359–362 (2015).
- Li, J. et al. Scale-invariant magnetic textures in the strongly correlated oxide NdNiO_3 . *Nat. Commun.* **10**, 1–7 (2019).
- Mott, N. F. & Davis, E. A. *Electronic Processes in Non-Crystalline Materials* (Clarendon, Oxford, 1979).
- Frydman, A. & Ovadyahu, Z. Spin and quantum interference effects in hopping conductivity. *Solid State Commun.* **94**, 745–749 (1995).
- Vaknin, A. et al. High-field magnetoresistance in Anderson insulators. *Phys. Rev. B* **54**, 13604–13610 (1996).
- Zhang, J. et al. Evolution of a novel ribbon phase in optimally doped $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ at high pressure and its implication to high- T_C superconductivity. *J. Phys. Chem. Lett.* **9**, 4182–4188 (2018).
- Ando, Y. et al. Logarithmic divergence of both in-plane and out-of-plane normal-state resistivities of superconducting $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ in the zero-temperature limit. *Phys. Rev. Lett.* **75**, 4662–4665 (1995).
- Ono, S. et al. Metal-to-insulator crossover in the low-temperature normal state of $\text{Bi}_2\text{Sr}_{2-x}\text{La}_x\text{CuO}_{6+\delta}$. *Phys. Rev. Lett.* **85**, 638–641 (2000).
- Lin, H. et al. Structure and physical properties of $\text{CsV}_2\text{Se}_{2-x}\text{O}$ and $\text{V}_2\text{Se}_2\text{O}$. *Phys. Rev. B* **98**, 075132 (2018).
- Jordan, L. & Swanger, W. H. The properties of pure nickel. *Bur. Stand. J. Res.* **5**, 1291–1307 (1930).
- Wang, Y. et al. Emergent superconductivity in an iron-based honeycomb lattice initiated by pressure-driven spin-crossover. *Nat. Commun.* **9**, 1914 (2018).
- Coak, M. J. et al. Isostructural Mott transition in 2D honeycomb antiferromagnet $\text{V}_{0.9}\text{PS}_3$. *npj Quantum Mater.* **38**, (2019).

48. Takamatsu, T. et al. Low-temperature synthesis of the infinite-layer compound LaNiO_2 by soft-chemical techniques. *Jpn. J. Appl. Phys.* **49**, 093101 (2010).
49. Hayward, M. A. & Rosseinsky, M. J. Synthesis of the infinite layer $\text{Ni}(\text{I})$ phase NdNiO_{2+x} by low temperature reduction of NdNiO_3 with sodium hydride. *Solid State Sci.* **5**, 839–850 (2003).
50. Cheary, R. W. & Coelho, A. A fundamental parameters approach to x-ray line-profile fitting. *J. Appl. Cryst.* **25**, 109–121 (1992).
51. Wang, E. et al. Pressure induced superconductivity in the compound ScZrCo . *New J. Phys.* **20**, 073036 (2018).

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Author contributions

The samples were grown by Q.L., C.P.H., Y.Z., and X.Y.Z. The physical properties measurements were conducted by Q.L. and J.S. The structure and composition analyses were done by Q.L., C.P.H. and X.Y.Z. H.-H.W., X.Y.Z., and Q.L. wrote the manuscript with the supplementary by others. All authors have discussed the results and the interpretations.

Competing interests

The authors declare no competing interests.

Additional information

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