Supplementary Information for "Evidence of filamentary-like superconductivity in pressurized La$_3$Ni$_2$O$_{7-\delta}$ single crystals"

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1 Experimental method

1.1 The principle and high-pressure measurement of modulated *ac* susceptibility

The *ac* susceptibility measurement is a technique used to assess how a material responds to an alternating current (*ac*) magnetic field. It is particularly useful in diagnosing the degree of diamagnetism exhibited in a superconducting material when it is in a superconducting state. This measurement plays a crucial role in the studies on the pressure-induced superconducting transition in various compounds[1–6]. However, performing *ac* susceptibility measurements in a high-pressure environment, such as in a diamond anvil cell (DAC), has posed technically challenges and the obtained results has sometimes sparked intense debate[7–12]. This is primarily due to the weak signal obtained from the small sample or the minor superconducting phase within the sample, which makes it difficult to be captured reproducibly.

The principle of modulated *ac* susceptibility measurement involves applying a small *ac* magnetic field to a sample and measuring the resulting change in its magnetic response. This technique is commonly used to investigate the superconducting properties of materials. In this method, the *ac* magnetic field is typically applied at a

fixed frequency and amplitude. As the temperature of the sample is varied, the *ac* susceptibility (the sample's magnetic response to the applied field) is recorded.

When a superconducting transition occurs in the sample, there is a sudden change in its magnetic properties. This is reflected by a distinct peak in signal of the modulated *ac* susceptibility data because the data is collected by using a two-stage phase-locked amplifier. While, in the traditional *ac* susceptibility measurement, the response of superconducting diamagnetic signal is collected by using a single phase-locked amplifier, therefore, it shows a step-like function (Fig.S1). Among the fashions of *ac* susceptibility measurements, the modulated *ac* susceptibility is the most sensitive approach - the superconducting diamagnetic transition can be clarified among other signals, such as the signal from diamond anvils and metallic gaskets with weakly field-sensitive characteristics. As a results, this method enhances the signal-to-noise ratio by dozens of times[1,5]. By analyzing the temperature dependence of the modulated *ac* susceptibility, important information about the superconducting properties, such as the critical temperature (T_c) and the superconducting volume fraction, can be obtained.

In this study, we applied these two kinds of methods in our high-pressure studies. High pressure magnetic susceptibility measurements were carried out in a diamond anvil cell fabricated from Cu-Be alloy, which is equipped with the gas membrane system. To minimize the temperature-dependent background, the nonmagnetic gasket made from the Ni-Cr alloy was adopted in these experiments. The sample is surrounded by a secondary coil (pickup coil) and a field-generating primary coil which is wound on the top of the secondary coil. The alternating flux through the pickup coil produces an *ac* voltage which is the measured signal. When the sample is cooled below T_c, the field is expelled from the sample due to the superconducting shielding effect, forcing some of the flux lines out of the pickup coil and leading to a reduction in the induced voltage in the pickup coil [3,13,14]. For the primary coil, the alternating magnetic field was stimulated at 13 KHz, and the signal was collected at the same frequency. The superconducting transition can be captured by a step-like diamagnetic signal in this *ac* susceptibility measurement. The modulated magnetic field is provided by the secondary coil that is stimulated at 13 Hz. Here, the modulated susceptibility can be expressed by

$\Delta\chi'= \chi'$ (*H≠0*) - χ'(*H=0*). Consequently, the result of $\chi'(B)$ produces a peak-like function in the secondary locked-in amplifier.
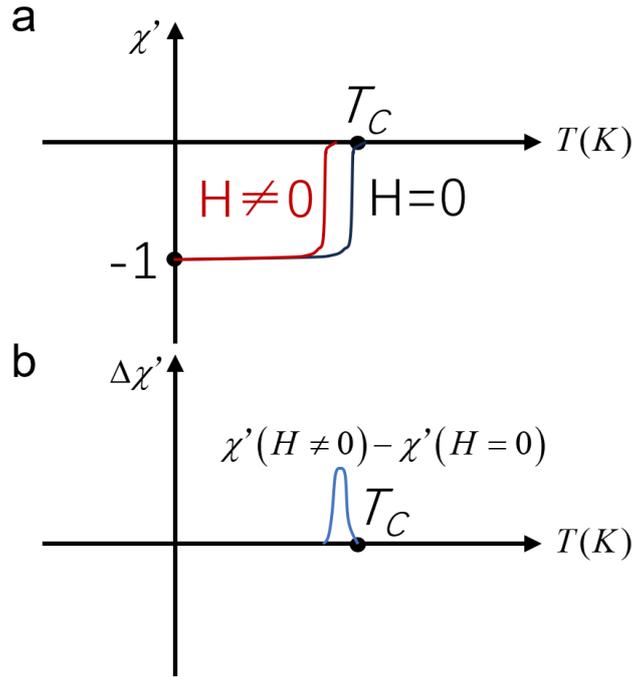

Fig.S1 The schematic description of the magnetic susceptibility measurements by the modulated technique (a two-stage phase-locked amplifier is employed). (a) The traditional magnetic susceptibility (χ') versus temperature for a superconducting material, illustrating the step-like response of the superconducting diamagnetic transition. (b) The modulated magnetic susceptibility ($\Delta\chi' = \chi'(H \neq 0) - \chi'(H = 0)$) versus temperature for a superconducting material, showing the peak-like response of the superconducting diamagnetic transition (red, $H \neq 0$, black, $H = 0$).

1.2 The determination of the signal-to-noise ratio for our measured system of the modulated *ac* susceptibility

To estimate the superconducting volume fraction of the $La_3Ni_2O_{7-\delta}$ single crystal, we loaded the superconducting element vanadium in the same sample chamber, with the half volume of the sample, and then compared the ratio of the superconducting diamagnetic signal (peak height) between vanadium and $La_3Ni_2O_{7-\delta}$. From the ratio of

the peak height $[\Delta\chi'\,(La_3Ni_2O_{7-\delta})\,/\,\Delta\chi'(vanadium)]/2 = [11(\pm1)\,mV/\,524(\pm10)\,mV]/2$,

we obtained the signal-to-noise ratio of our measured system to be about 115:1, which

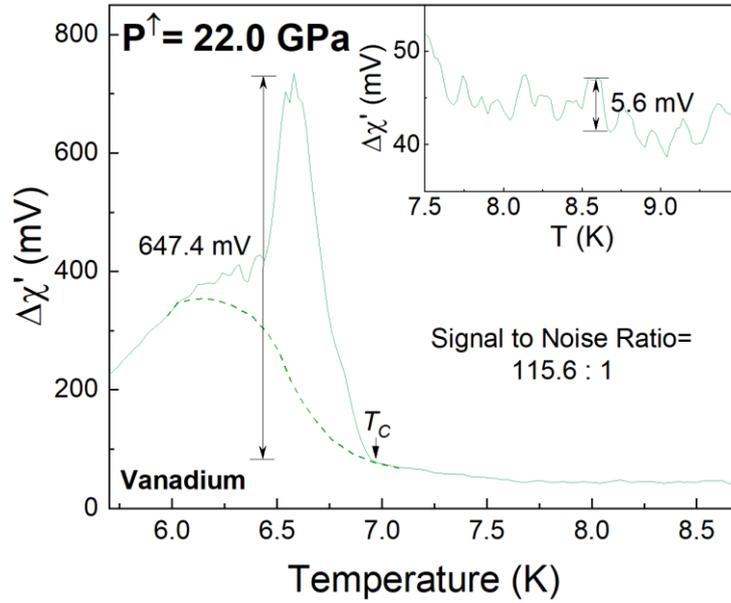allows us to capture a small superconducting volume fraction as low as 0.87% (Fig. S2).

Fig. S2 The *ac* susceptibility ($\Delta\chi'$) versus temperature measured from the superconducting vanadium at 22 GPa, showing the signal-to-noise ratio of about 115:1.

1.3 High -pressure resistance and Hall coefficient measurements

For the high-pressure resistance measurements, we used diamond anvils with 400

μm culets (the flat area of the diamond anvil) and a non-magnetic rhenium gasket with

a 200-μm-diameter hole for the measurements. The four-probe technique was used for

each run. We used a mixture of c-BN powder and epoxy as the insulating layer. To

create a hydrostatic pressure environment, we used silicon oil as the pressure

transmitting medium. The pressure was determined using the ruby fluorescence

method[15].

To measure the Hall coefficient for the $La_3Ni_2O_{7-\delta}$ sample, we used the Van der

Pauw method. The magnetic field (B) was swept from 0 T to 7 T at 90 K[5,16]. In order to

eliminate magnetoresistance contributions, we systematically reversed the polarity of the magnetic field for each pressure point. The Hall resistance (R_{xy}) was obtained using the equation $R_{xy} = V_H / I$, where V_H is the Hall voltage and I is the current. The Hall coefficient (R_H) displayed in Fig. 3 was estimated by calculating the slope of $R_{xy}(B)$.

2. Extended data

2.1 The selected results of modulated *ac* susceptibility versus temperature at different pressures for the other three runs
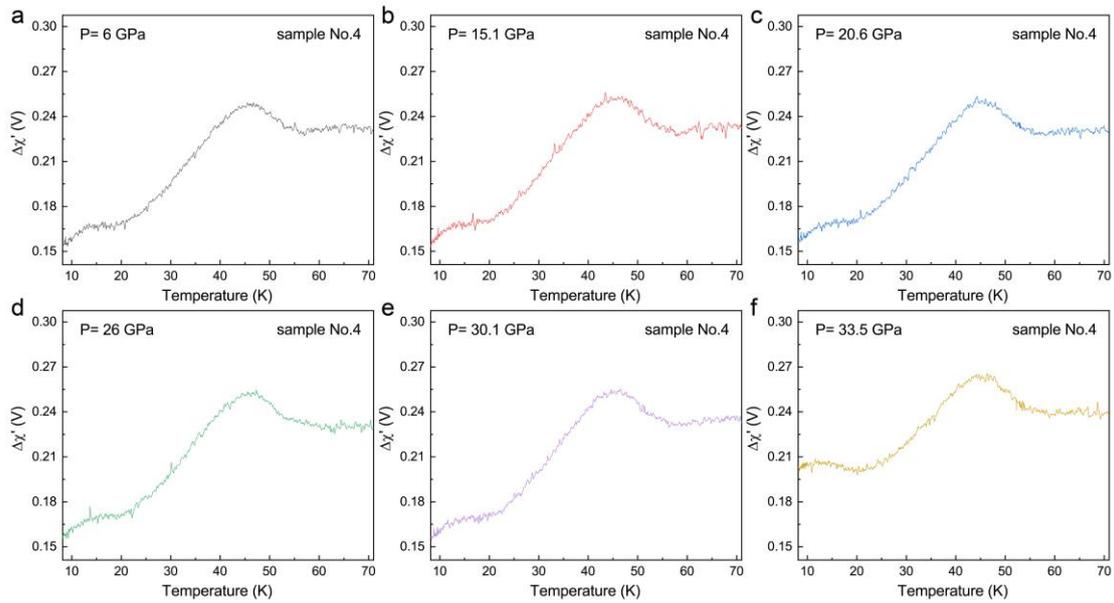
Fig. S3 The raw data of the modulated *ac* susceptibility measurements on sample No.4. In this experimental run, we utilized the same coils and the same high-pressure cell as that used for the sample described in Fig.1. No superconducting transition was observed within the pressure range up to 33.5 GPa.
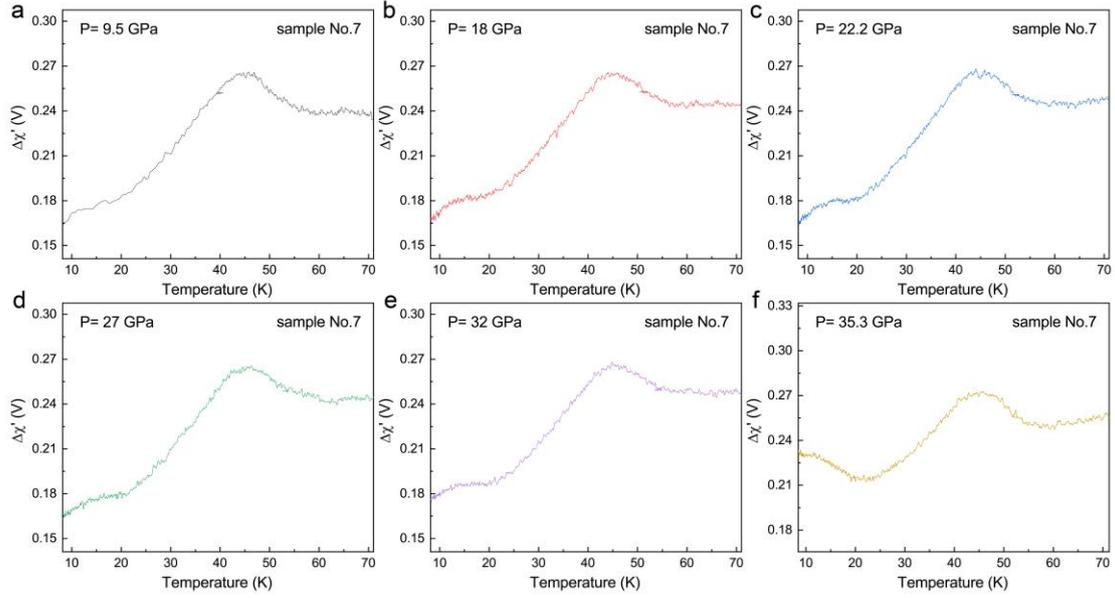
Fig. S4 The raw data of the modulated *ac* susceptibility measurements on sample No.7. In this experimental run, we also used the same coils and the same high-pressure cell as that used for the sample described in Fig.1. No superconducting transition was observed within the pressure range up to 35.3 GPa.
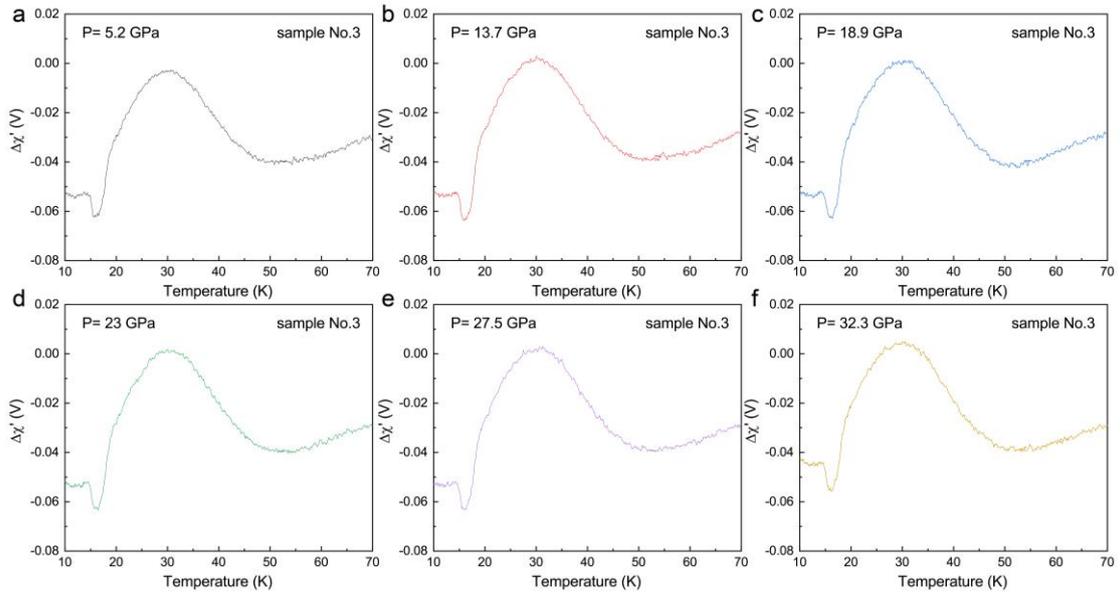

Fig. S5 The raw data of the modulated *ac* susceptibility measurements on sample No.3. In this experimental run, we used the different coils and the different high-pressure cell. No superconducting transition was observed in the pressure range up to 32.3 GPa.

2.2 The results of traditional *ac* susceptibility versus temperature at different pressures for the La$_3$Ni$_2$O$_{7-\delta}$ sample

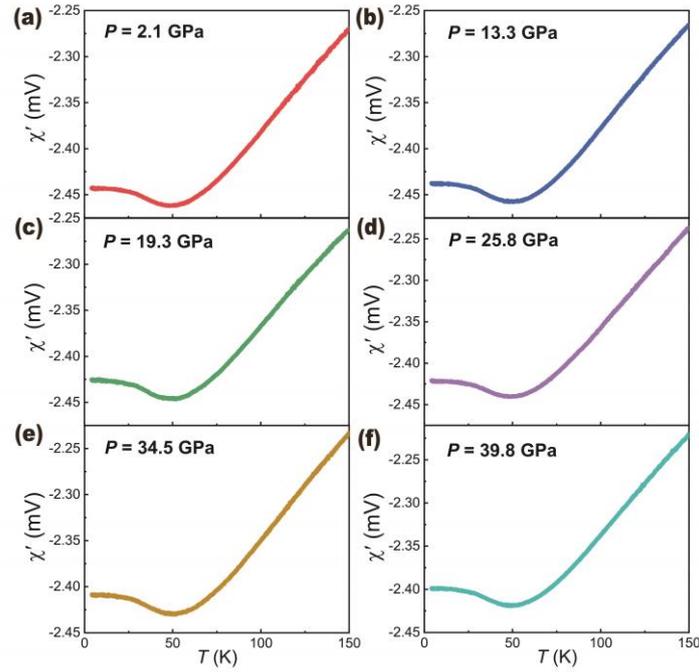Fig.S6 Temperature dependence of *ac* susceptibility measured by a single phase-locked amplifier for the La$_3$Ni$_2$O$_{7-\delta}$ sample. No superconducting diamagnetic signal is observed in the pressure range of 39.8 GPa. Instead, only background signal is detected, as evidenced by the data measured at 2.1 GPa, where the sample is in a semiconducting state (Fig.2a). Based on the signal-to-noise ratio of this measured system (5:1), we suggest that the superconducting volume fraction in this sample is below 20%.

2.3 The selected results of resistance versus temperature at different pressures for the other three runs
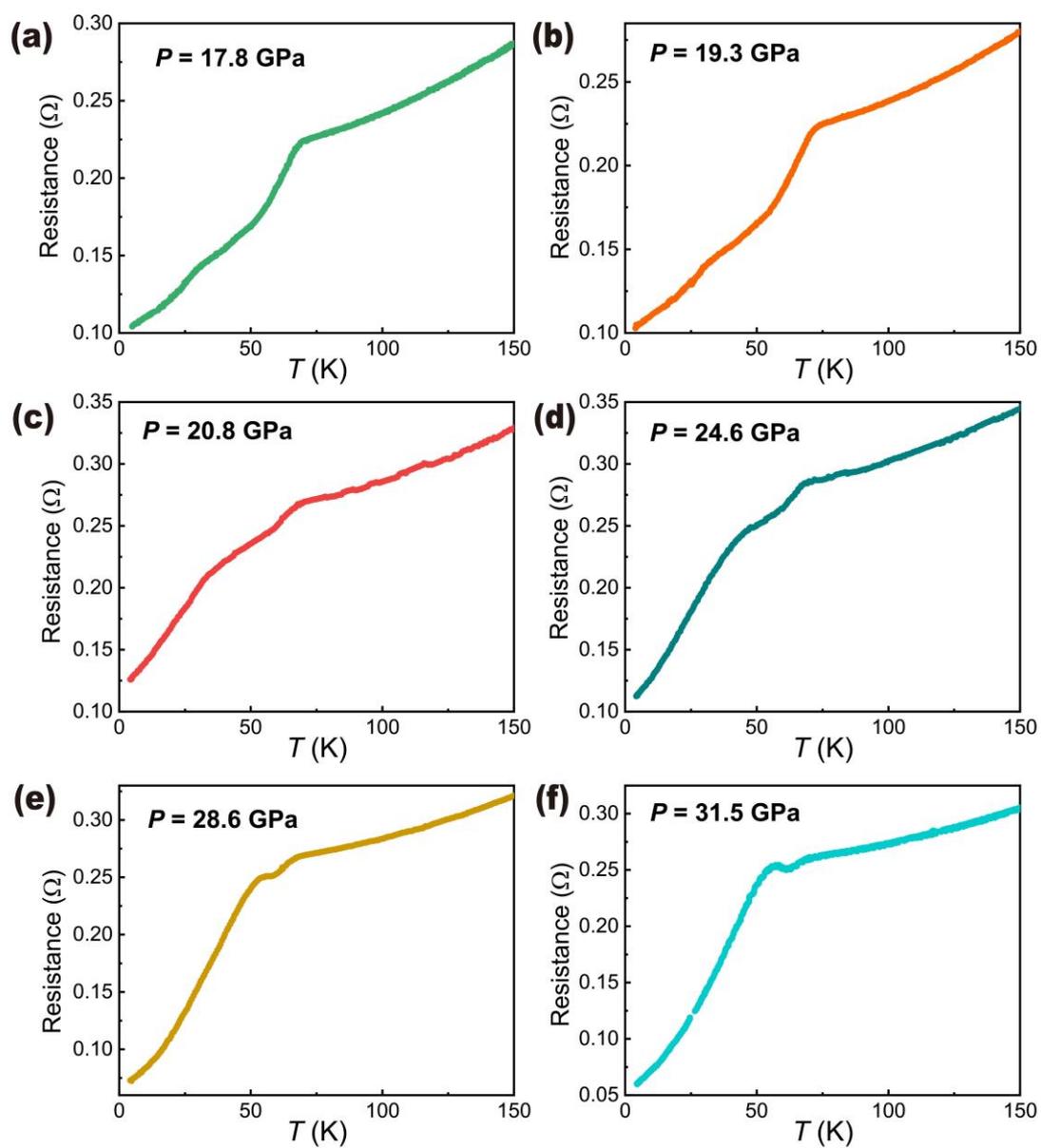
Fig. S7 Resistance versus temperature at different pressures for sample B (Fig.2) measured along different direction, showing a superconducting transition without zero resistance in the pressure range of 17.8-31.5 GPa.
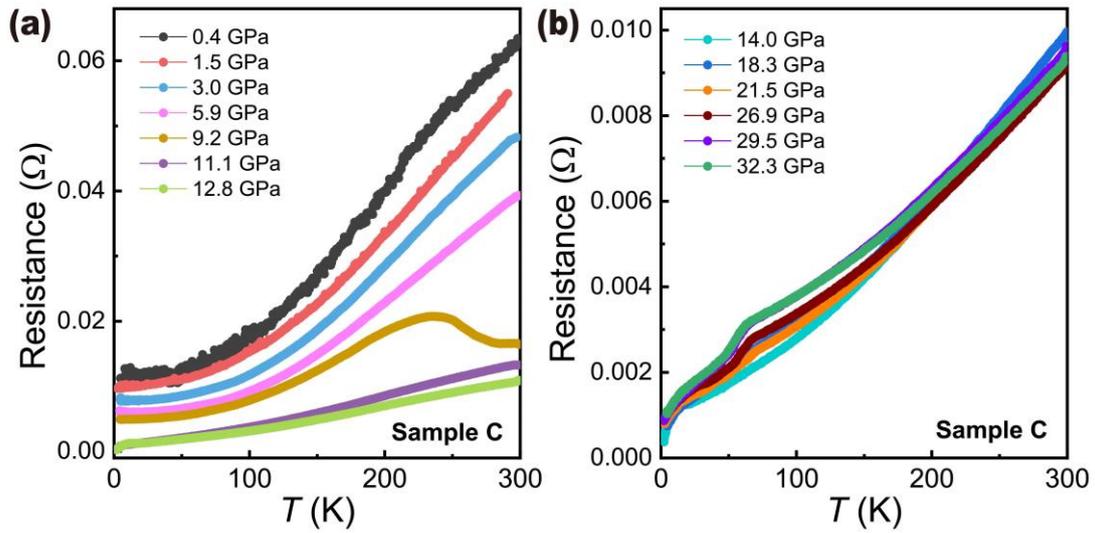
Fig. S8 Temperature dependence of resistance at different pressures for one of the La$_3$Ni$_2$O$_{7-\delta}$ samples measured in the same hydrostatic pressure environment as that of Sample A and Sample B (Fig.2), displaying a superconducting transition without zero resistance in the pressure range of 12.8- 32.3 GPa.
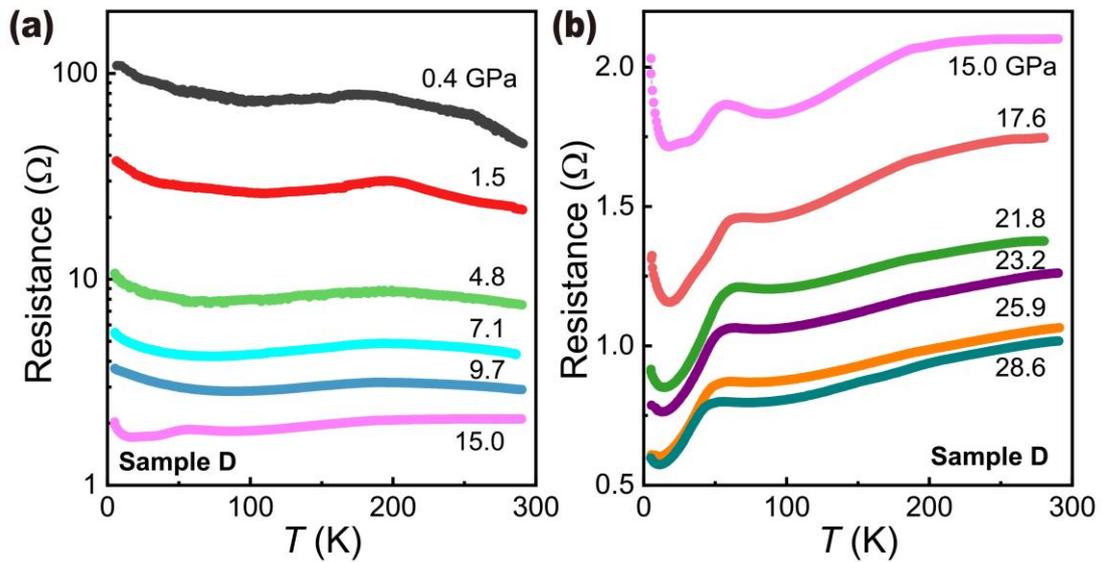

Fig. S9 Resistance as a function of temperature at different pressures for the La$_3$Ni$_2$O$_{7-\delta}$ sample surrounded by NaCl pressure medium, showing a superconducting transition without zero resistance in the pressure range of 15-28.6 GPa.

2.3 The results of high-pressure Hall coefficient measurements

High-pressure Hall coefficient measurements were performed by sweeping the magnetic field (B) at 90 K. As shown in Fig.S10, the Hall resistance R_{xy} remains positive under pressure up to 28.8 GPa, indicating the dominance of hole carriers in this compound. Since $R_{xy}(B)$ exhibits a linear behavior, we employed a single-carrier model to estimate R_H by fitting the slope of $R_{xy}(B)$.
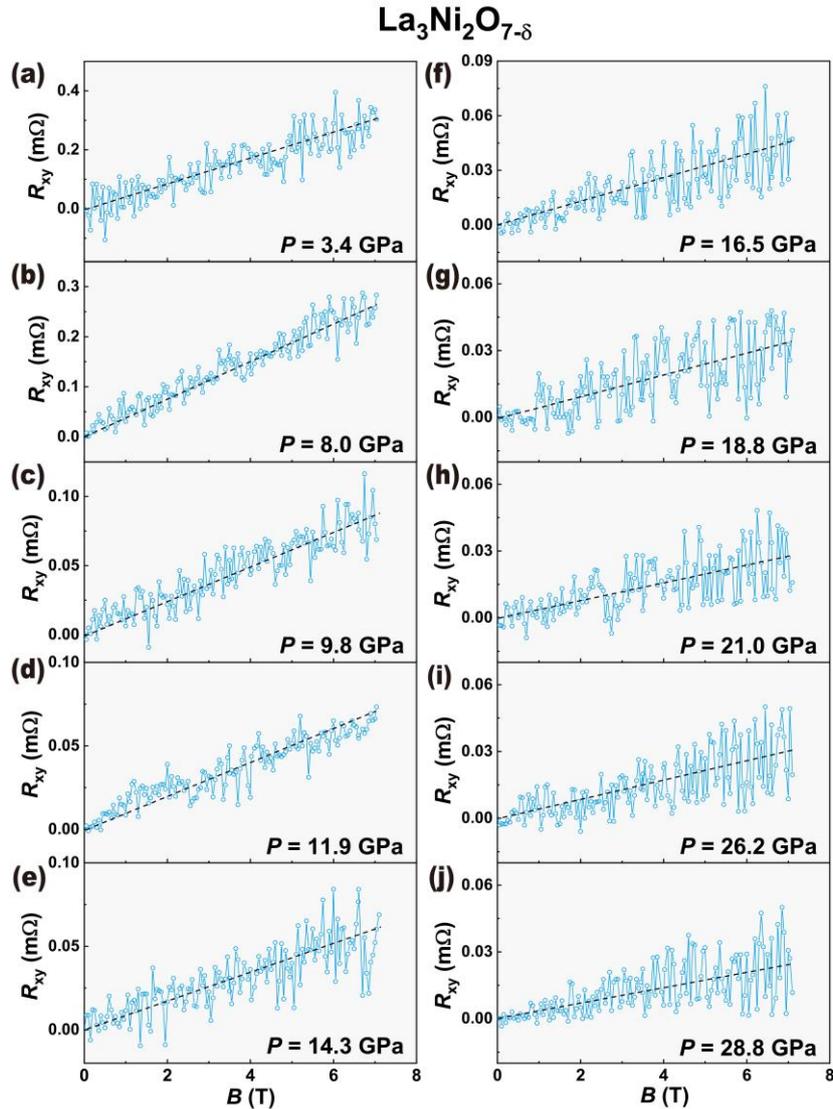

Fig. S10 Hall resistance (R_{xy}) as a function of magnetic-field (B) for the La$_3$Ni$_2$O$_{7-\delta}$ single crystal at different pressures. The dashed lines represent the linear fittings applied for the raw data, highlighting the pressure-induced changes in slope.

References

1. Struzhkin, V. V., Hemley, R. J., Mao, H. & Timofeev, Y. A. Superconductivity at 10–17 K in compressed sulphur. *Nature* **390,** 382–384 (1997).

2. Chen, X.-J., Struzhkin, V. V., Yu, Y., Goncharov, A. F., Lin, C.-T., Mao, H. & Hemley, R. J. Enhancement of superconductivity by pressure-driven competition in electronic order. *Nature* **466,** 950–953 (2010).

3. Sun, L., Chen, X.-J., Guo, J., Gao, P., Huang, Q.-Z., Wang, H., Fang, M., Chen, X., Chen, G., Wu, Q., Zhang, C., Gu, D., Dong, X., Wang, L., Yang, K., Li, A., Dai, X., Mao, H. & Zhao, Z. Re-emerging superconductivity at 48 kelvin in iron chalcogenides. *Nature* **483,** 67–69 (2012).

4. Deng, L., Zheng, Y., Wu, Z., Huyan, S., Wu, H.-C., Nie, Y., Cho, K. & Chu, C.-W. Higher superconducting transition temperature by breaking the universal pressure relation. *Proceedings of the National Academy of Sciences of the United States of America* **116,** 2004–2008 (2019).

5. Zhou, Y., Guo, J., Cai, S., Zhao, J., Gu, G., Lin, C., Yan, H., Huang, C., Yang, C., Long, S., Gong, Y., Li, Y., Li, X., Wu, Q., Hu, J., Zhou, X., Xiang, T. & Sun, L. Quantum phase transition from superconducting to insulating-like state in a pressurized cuprate superconductor. *Nat. Phys.* **18,** 406–410 (2022).

6. Cai, S., Guo, J., Shu, H., Yang, L., Wang, P., Zhou, Y., Zhao, J., Han, J., Wu, Q., Yang, W., Xiang, T., Mao, H. & Sun, L. No evidence of superconductivity in a compressed sample prepared from lutetium foil and H_2/N_2 gas mixture. *Matter*

and Radiation at Extremes **8,** 48001 (2023).

7. van der Marel, D. & Hirsch, J. E. Room-temperature superconductivity — or not? Comment on Nature 586, 373 (2020) by E. Snider et al. *Int. J. Mod. Phys. B* **37,** 2375001 (2023).

8. Hirsch, J. E. & Marsiglio, F. Clear evidence against superconductivity in hydrides under high pressure. *Matter and Radiation at Extremes* **7,** 58401 (2022).

9. Hirsch, J. E. & van der Marel, D. Incompatibility of published ac magnetic susceptibility of a room temperature superconductor with measured raw data. *Matter and Radiation at Extremes* **7,** 48401 (2022).

10. van der Marel, D. & Hirsch, J. E. Extended Comment on Nature 586, 373 (2020) by E. Snider et al. *arXiv.2201.07686* (2022).

11. Hirsch, J. E. & Marsiglio, F. Unusual width of the superconducting transition in a hydride. *Nature* **596,** E9-E10 (2021).

12. Snider, E., Dasenbrock-Gammon, N., McBride, R., Debessai, M., Vindana, H., Vencatasamy, K., Lawler, K. V., Salamat, A. & Dias, R. P. Room-temperature superconductivity in a carbonaceous sulfur hydride. *Nature* **586,** 373–377 (2020).

13. Timofeev, Y. A., Struzhkin, V. V., Hemley, R. J., Mao, H. & Gregoryanz, E. A. Improved techniques for measurement of superconductivity in diamond anvil cells by magnetic susceptibility. *Review of Scientific Instruments* **73,** 371–377 (2002).

14. Hamlin, J. J., Tissen, V. G. & Schilling, J. S. Superconductivity at 17K in yttrium metal under nearly hydrostatic pressures up to 89GPa. *Phys. Rev. B* **73,** 94522

(2006).

15. Mao, H. K., Xu, J. & Bell, P. M. Calibration of the ruby pressure gauge to 800 kbar under quasi‑hydrostatic conditions. *J. Geophys. Res.* **91,** 4673–4676 (1986).

16. van der PAUW, L. J. A METHOD OF MEASURING SPECIFIC RESISTIVITY AND HALL EFFECT OF DISCS OF ARBITRARY SHAPE. *Semiconductor Devices: Pioneering Papers. March,* 174–182 (1991).