## **Supplementary Information**

## Stability of the local electronic properties of La<sub>3</sub>Ni<sub>2</sub>O<sub>7</sub> under pressure

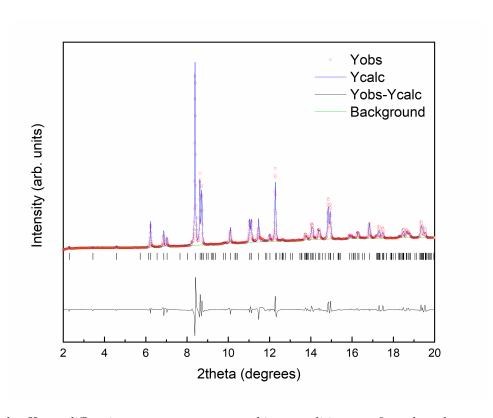


Figure S1: Powder X-ray diffraction measurements at ambient conditions confirm that the sample is phase-pure La<sub>3</sub>Ni<sub>2</sub>O<sub>7</sub>. The diffraction pattern was fitted using the ambient pressure orthorhombic structure with the Cmmm space group. The refined lattice parameters (a = 5.38902 Å, b = 5.44791 Å, c = 20.50644 Å) are in good agreement with previously reported literature values. Diffraction pattern was collected at ID15b beamline of ESRF with x-ray photon energy at 30 keV ( $\lambda \sim 0.41$  Å).

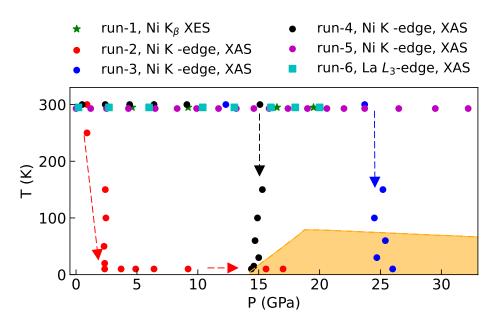


Figure S2: Experimental conditions and routes mapped onto the phase diagram of La<sub>3</sub>Ni<sub>2</sub>O<sub>7</sub> reported by H. Sun et al (Nature 621, 493, 2023).

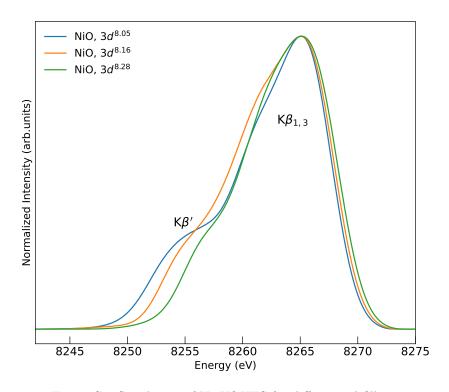


Figure S3: Simulation of Ni  $K\beta$  XES for different 3d filling.

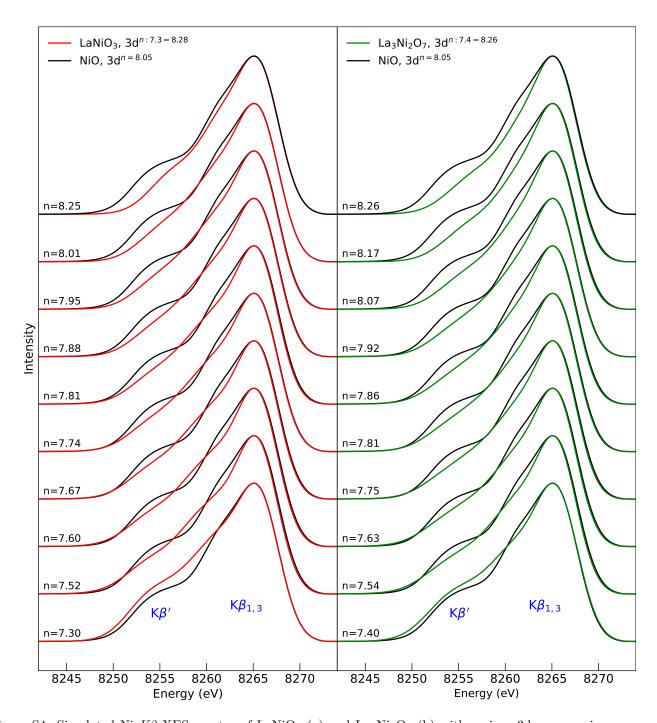


Figure S4: Simulated Ni  $K\beta$  XES spectra of LaNiO<sub>3</sub> (a) and La<sub>3</sub>Ni<sub>2</sub>O<sub>7</sub> (b) with various 3d occupancies, compared with the spectrum of NiO calculated for a 3d<sup>8.05</sup> configuration.

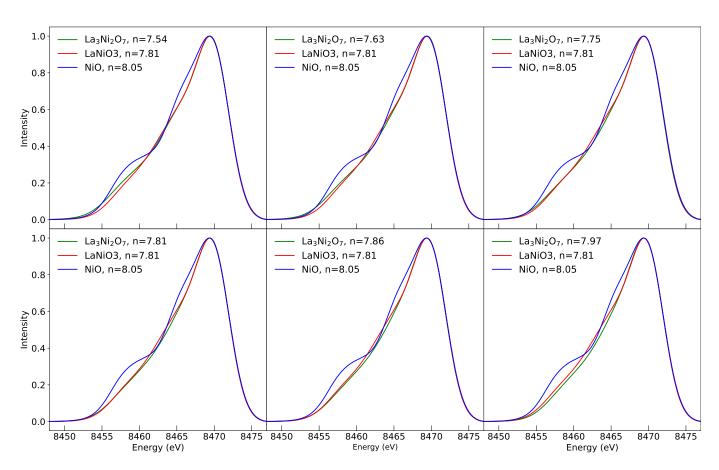


Figure S5: Simulated Ni  $K\beta$  XES spectra of La<sub>3</sub>Ni<sub>2</sub>O<sub>7</sub> with various 3d occupancies, compared with those of NiO and LaNiO<sub>3</sub>, calculated for 3d<sup>8.05</sup> and 3d<sup>7.81</sup> configurations, respectively.

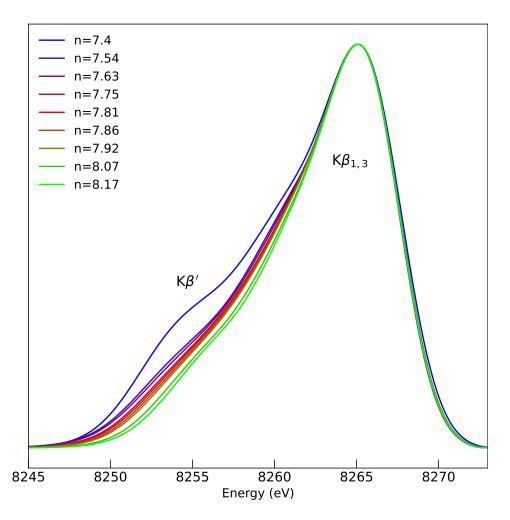


Figure S6: Simulated Ni  $K\beta$  XES spectra of La<sub>3</sub>Ni<sub>2</sub>O<sub>7</sub> with various 3d occupancies, plotted on the same scale (without y-offset) for better comparison.

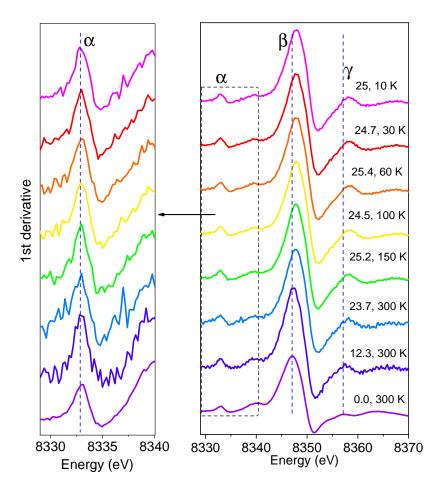


Figure S7: First derivative of the Ni K-edge XANES measured along the 2nd experimental run (run-2). Pre-edge range was shown with magnification at the left panel. Stable energy position and nearly similar line shapes of pre-edge peak  $\bf A$  can be seen from the behavior of feature  $\alpha$  in the first derivative spectra (left panel). Shift of the edge energy is evident from the movement of the main peak (feature  $\beta$ ), while the enhancement of feature  $\bf C$  is captured by the appearance of feature  $\gamma$  in the first derivative spectra (right panel). The absence of spectral modifications upon cooling at  $23.7 \sim 25$  GPa (see Fig. 4d in the main text) is further confirmed by the identical line shapes of the first derivative spectra.

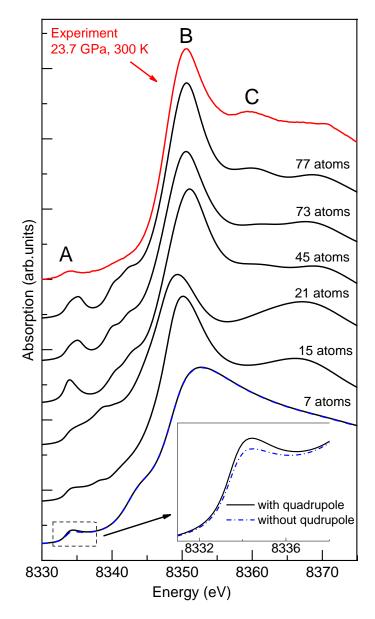


Figure S8: XANES simulations performed for various atomic cluster sizes. Experimental spectra (red curve) was measured at P=23.7 GPa under room temperature.

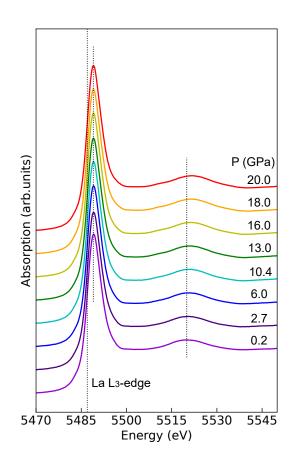


Figure S9: La  $L_3$ -edge XANES of La<sub>3</sub>Ni<sub>2</sub>O<sub>7</sub> measured along run-5 up to 20 GPa under room temperature.