I. Possibility of contamination above 80 GPa

Electrical resistance measurements were repeated with similar set-ups made but using different gasket materials. When the gasket material was switched to epoxy-free diamond powder measurements were performed by two point contact method using Pt thin foils as electrodes. The result is shown in Fig.S1. The electrical resistivity showed sudden increase and then the semiconducting character (negative $d\rho/dT$ value) near 80 GPa in agreement with our previous measurements. As pressure was unloaded, the resistivity decreased along with the curve for pressure loading, and then Li recovered the metallic temperature dependence of resistivity and superconductivity at 76 GPa. This result gives strong evidence that the metal-to-semiconductor transition is not due to any chemical reactions between Li and surrounding materials such as epoxy.
Figure S1. Pressure and temperature dependence of the electrical resistance through pressure loading and unloading. The resistance is plotted as a function of temperature. The resistance value is normalized at 20 K. Inset shows the pressure dependence of the resistance at 25 K. The marks ▲ (black) and ▼ (blue) indicate the data for pressure loading and unloading, respectively. Li shows metal character at 27 GPa and superconducting transition at 39 GPa. At 86 GPa, the resistance shows the semiconducting character, accompanied with a large increase in its value. After decreasing pressure to 76 GPa, Li clearly recovers metal character and superconductivity. The resistance was measured by two-point contact method. Measured resistance contains the resistance of sample itself and contact resistance between sample and electrodes. Arrows are guides for eyes.