



Phonon Engineering in Graphene Oxide: Effects of Pressure and Thermal Reduction



O. O. Romantsova^{2,1}, D. Szewczyk², Yu. Horbatenko¹,
M. Vinnikov¹, S. Cherednichenko¹, O. Krivchikov^{1,2}

¹B. Verkin Institute for Low Temperature Physics and Engineering of the NAS of Ukraine,
47 Nauky Ave., Kharkiv, 61103, Ukraine

²Institute of Low Temperature and Structure Research, PAS, 2 Okólna Str., 50-422, Wrocław, Poland

Graphene oxide (GO) and its thermally reduced derivatives (trGO) exhibit a wide range of vibrational behaviors arising from structural disorder, oxygen functional groups, and variable interlayer coupling. [1,2] Understanding how processing parameters influence their low-energy phonon spectra is essential for designing carbon-based materials with tailored thermal properties. In this work, we systematically investigate the effects of both mechanical compaction and thermal annealing on the low-temperature heat capacity of GO.

GO synthesized via a modified Hummers method was thermally reduced at 300°C, 500°C, and 700°C, leading to controlled removal of oxygen groups and progressive graphitization. Samples compacted under pressures from 0.75 to 1.25 GPa provided insight into the mechanical tuning of interlayer interactions. Low-temperature calorimetry (1.8–100 K), complemented by X-ray diffraction and TEM, reveals that the total heat capacity can be decomposed into four components: a Schottky-type anomaly, a linear T-term, a Debye T³ contribution, and a negative T⁵ term associated with flexural ZA phonons.

Samples:

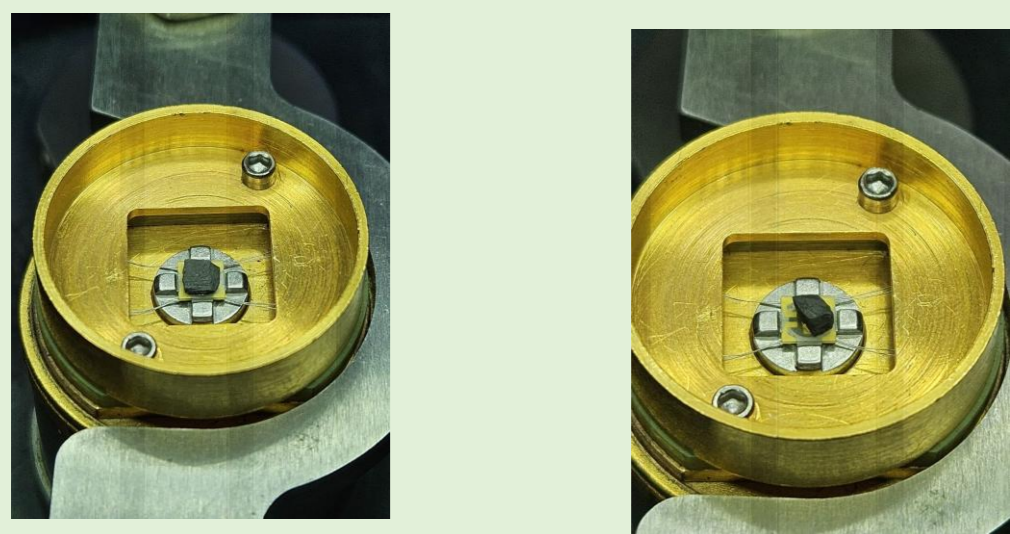


Fig. 1 Examples of investigated materials on the sample platform (PPMS)

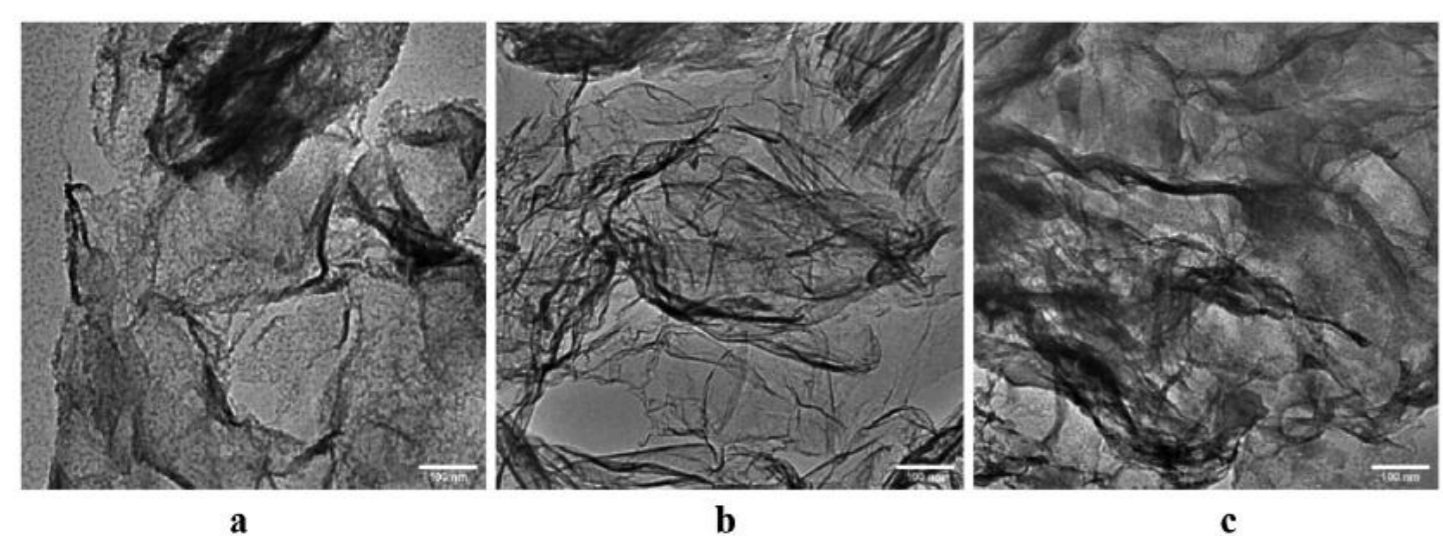


Fig. 2 TEM images of GO powder sample after thermo-vacuum exfoliation and subsequent annealing: (a) trGO₃₀₀ (reduced at 300°C), (b) trGO₅₀₀, and (c) trGO₇₀₀, additionally annealed at 500°C and 700°C, respectively. Progressive annealing leads to increased sheet compaction and structural ordering.

X-ray diffraction

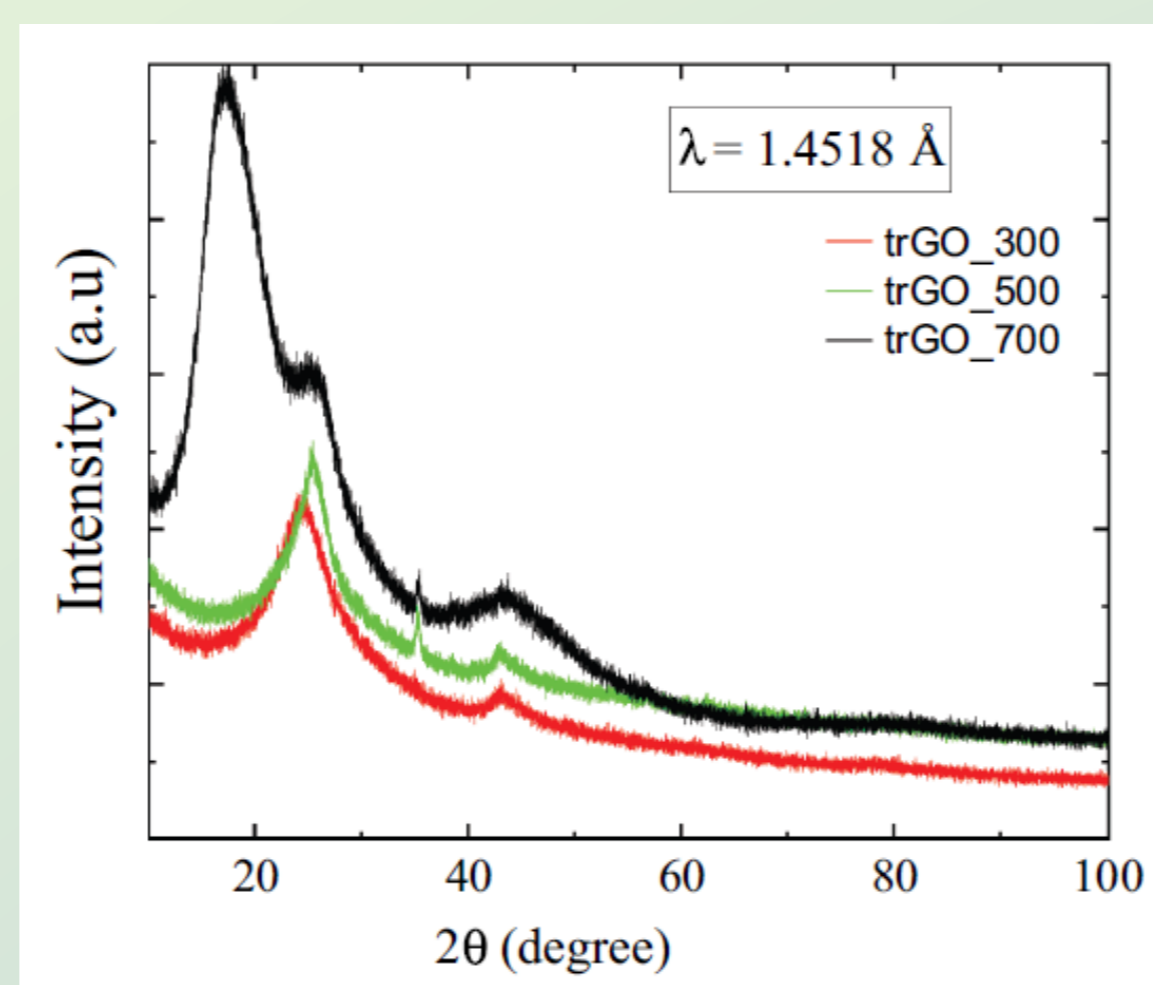


Fig. 3 X-ray diffraction patterns of GO sample after thermo-vacuum exfoliation and annealing: trGO₃₀₀ (red), trGO₅₀₀ (green), and trGO₇₀₀ (black). The systematic shift and sharpening of diffraction features reflect a reduction in interlayer spacing and enhanced stacking order with increasing annealing temperature.

Measurement setup



Fig. 4 The specific heat was determined using the method of thermal relaxation on a commercially available Physical Properties Measurement System (PPMS, Quantum Design Inc.)

Experimental results:

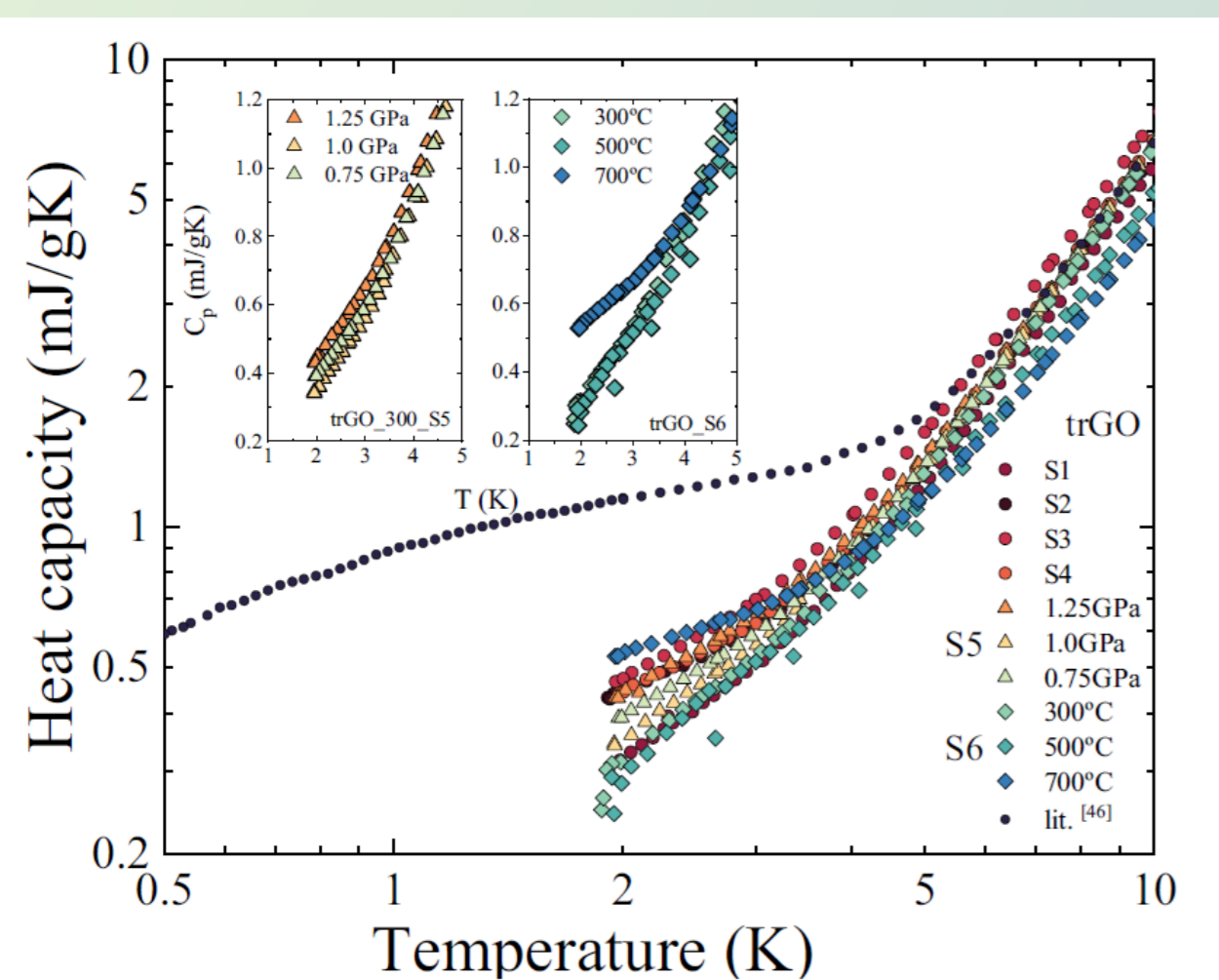


Fig. 5. Temperature dependence of the heat capacity $C_p(T)$ for GO samples: S1–S4 (●), S5 (▲), S6 (◆), and literature data (●). Insets show the low-temperature region for (left) compacted samples S5 under different pressures and (right) annealed samples S6.

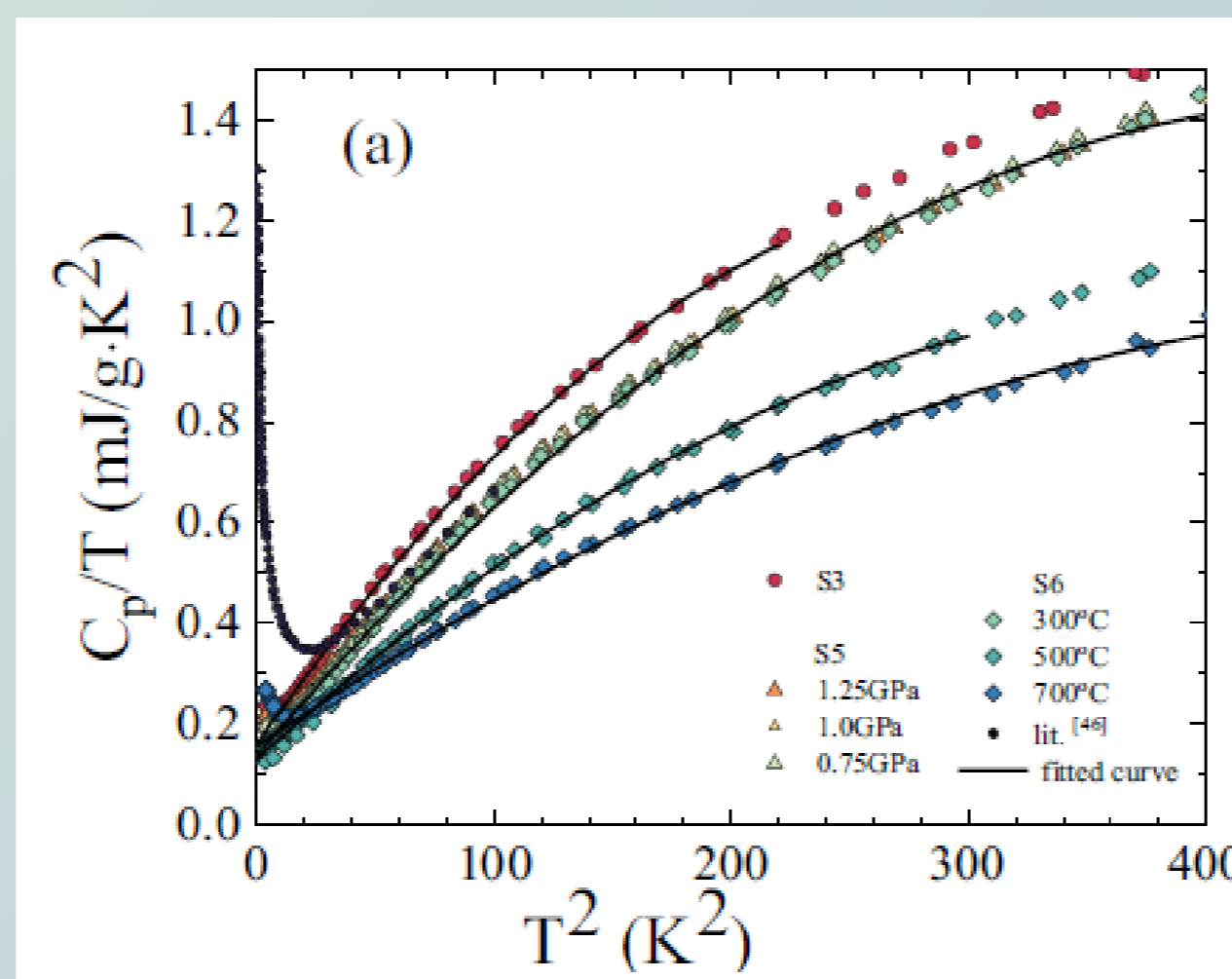


Fig. 6. C_p/T vs T^2 , used to extract the linear (A_1T) and phonon contributions.

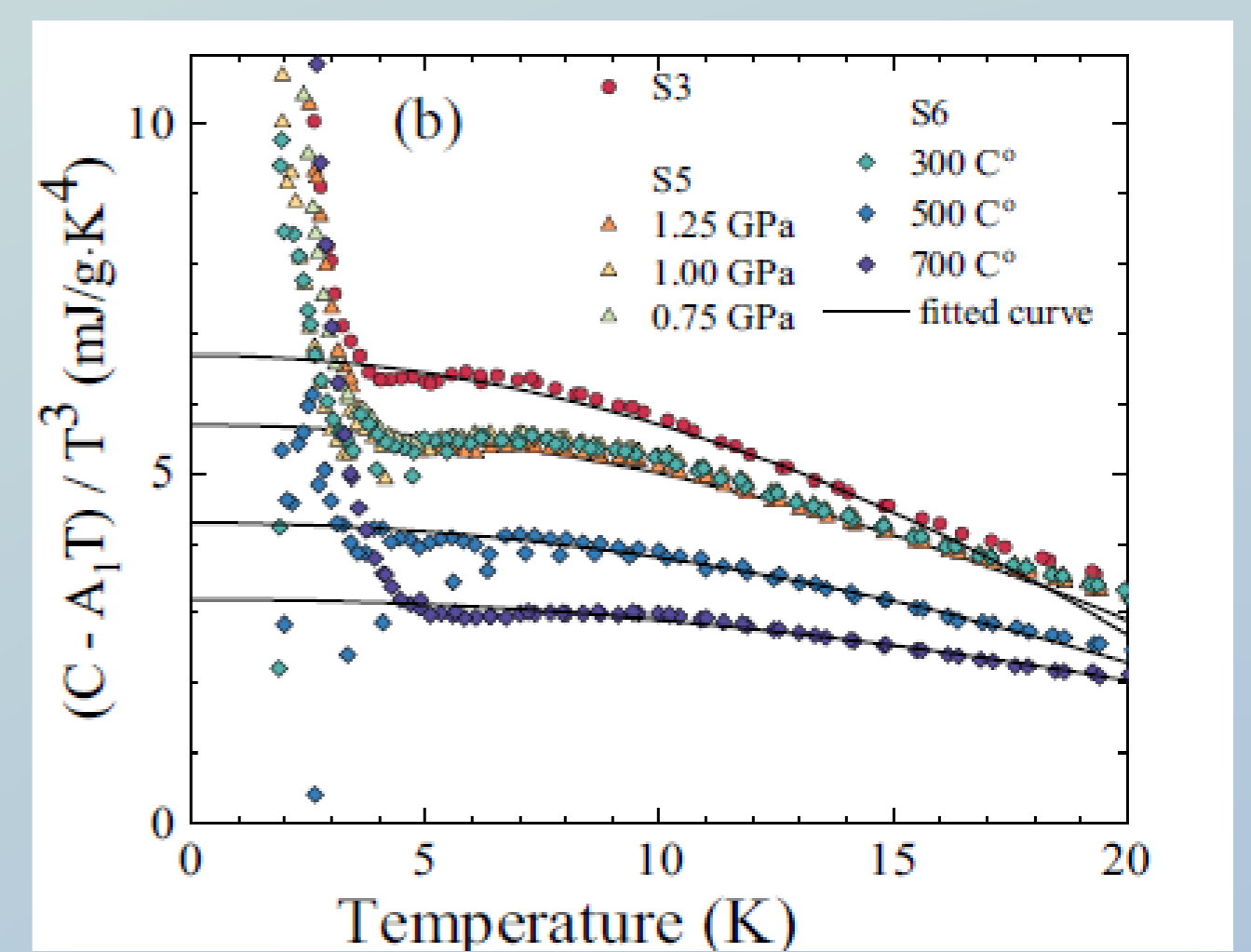


Fig. 7. $C_p - A_1T / T^3$ versus T , highlighting deviations from pure Debye behavior.

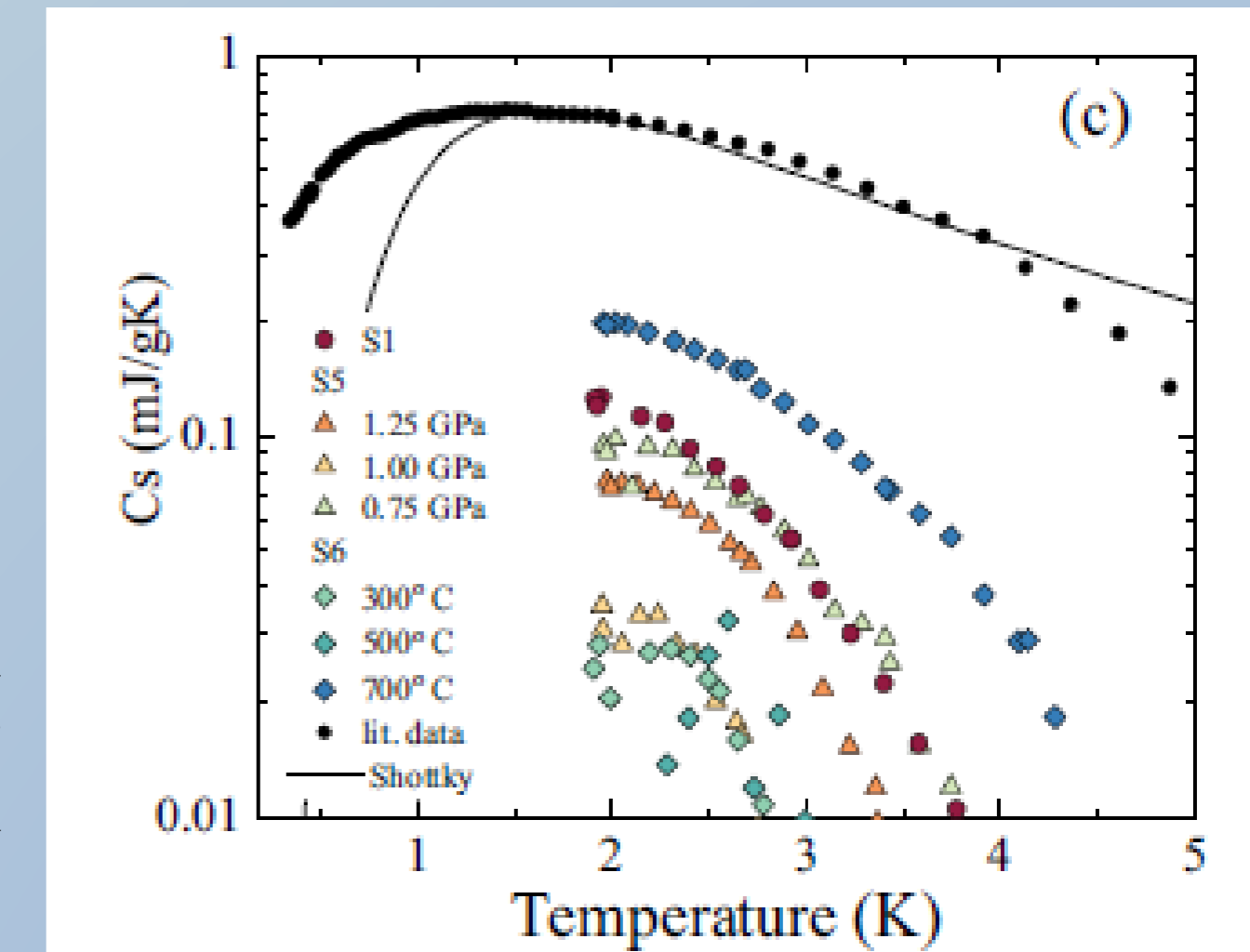


Fig. 8. Extracted Schottky-type contribution $C_s(T)$. The solid line shows the calculated Schottky heat capacity for a two-level system with an energy splitting of 4 K.

It is observed that thermal annealing strongly suppresses both Debye and flexural phonon contributions, indicating reduced disorder and enhanced stacking order with increasing graphitization. In contrast, the linear term remains nearly invariant, suggesting an intrinsic origin related to persistent low-energy excitations in quasi-2D GO layers. The Schottky anomaly displays a pronounced dependence on compaction pressure, highlighting its sensitivity to interlayer contacts, residual oxygen groups, and defect-related two-level systems.

A universal power-law correlation between Debye and ZA phonon coefficients places graphene oxide within the same vibrational framework as carbon nanotubes and graphite, demonstrating that low-temperature calorimetry serves as a precise probe of dimensionality, disorder, and interlayer coupling. These results provide a predictive foundation for engineering phonon spectra in graphene-based materials, with implications for cryogenic applications, composite design, and nanoscale thermal management.