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Electronic Supplementary Information

Pressure-induced Mott-insulator–metal crossover at ambient temperature in an overexpanded fulleride

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Table S1. Refined parameters for the fcc $Rb_{0.5}Cs_{2.5}C_{60}$ phase (space group $Fm\bar{3}m$, phase fraction refined to 70.61(9)%) obtained from the Rietveld analysis of the synchrotron X-ray powder diffraction data collected at 0.14 GPa and at ambient temperature (λ = 0.3738 Å). Estimated errors in the last digits are given in parentheses. The weighted-profile and expected *R*-factors are R_{wp} = 2.91% and R_{exp} = 5.95%. The lattice constant and unit cell volume are: *a* = 14.6298(3) Å and *V* = 3131.3(2) Å^3. The sum of the fractional occupancies of the Rb and Cs(1) atoms residing in the tetrahedral holes were fixed to the values refined from the ambient pressure data for the same sample. The fractional occupancy of the Cs(2) atom residing in the octahedral hole was fixed to 1. This resulted in a refined stoichiometry of the fcc-phase of $Rb_{0.426(8)}Cs_{2.574(8)}C_{60}$, which was kept fixed in subsequent refinements at higher pressures. The thermal displacement parameters of the C atoms and the tetrahedral interstitial sites could not refine to physically meaningful values, so they were fixed to values of appropriate magnitude. The fraction of the co-existing orthorhombic (space group *Pmnn*) CsC_{60} phase is 29.4(1)%.

***P* = 0.14 GPa**	***x/a***	***y/b***	***z/c***	***N***	B_{iso} (Å^2)
Rb	0.25	0.25	0.25	0.2125	1.97
Cs(1)	0.25	0.25	0.25	0.7875	1.97
Cs(2)	0.5	0.5	0.5	1.0	7.0(2)
C(1)	0	0.04861	0.23574	0.5	0.79
C(2)	0.20577	0.07858	0.09702	0.5	0.79
C(3)	0.17560	0.15700	0.04861	0.5	0.79

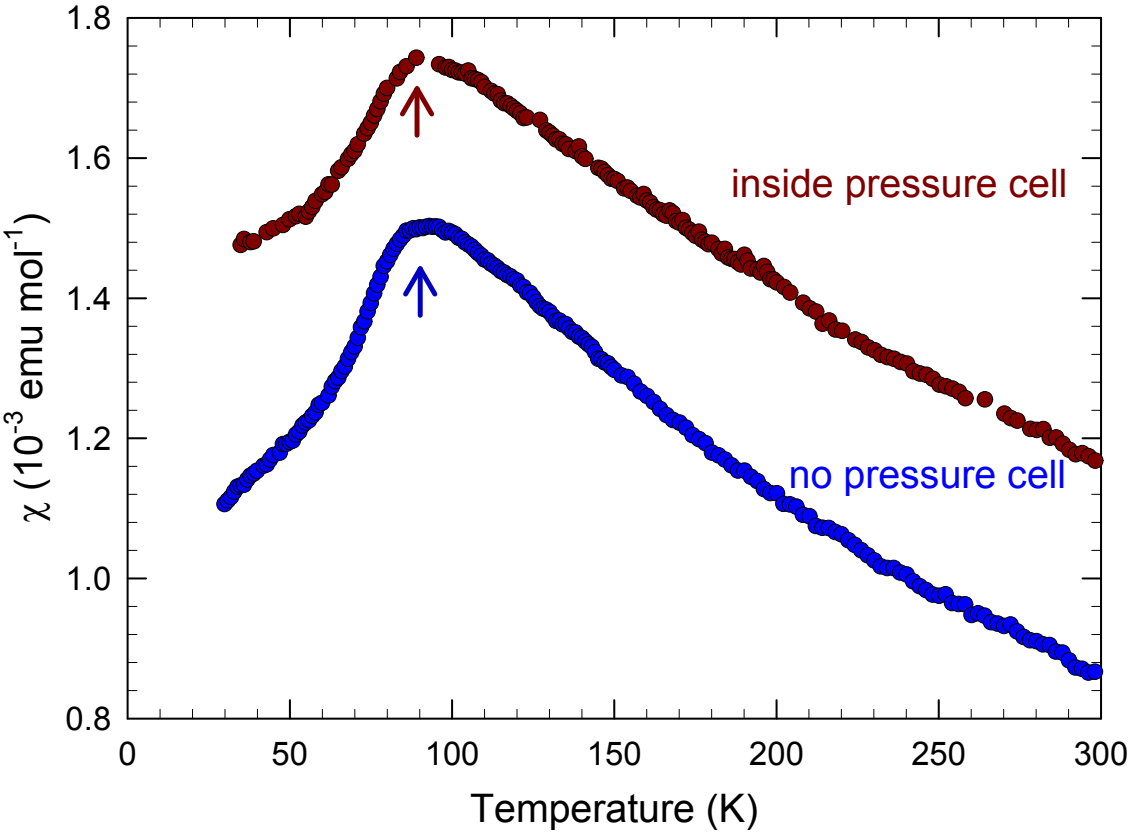

Fig. S1 Temperature dependence of the paramagnetic susceptibility, χ(T), of $Rb_{0.5}Cs_{2.5}C_{60}$ at ambient *P* measured inside and outside the Mcell10 pressure cell (dark red and blue circles, respectively). Arrows mark the temperatures, *T*′, at which maxima are observed.

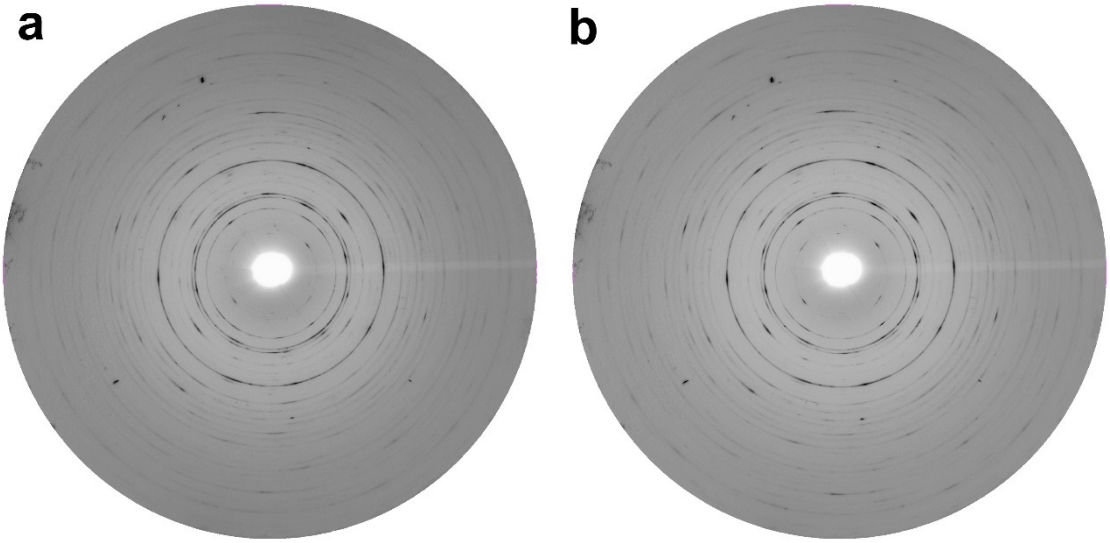

Fig. S2 Two-dimensional X-ray diffraction images of the $Rb_{0.5}Cs_{2.5}C_{60}$ sample, contained in a MDAC, recorded at ambient temperature and at (a) 0.28 and (b) 0.75 GPa with a MARCCD detector (X-ray wavelength = 0.3738 Å).

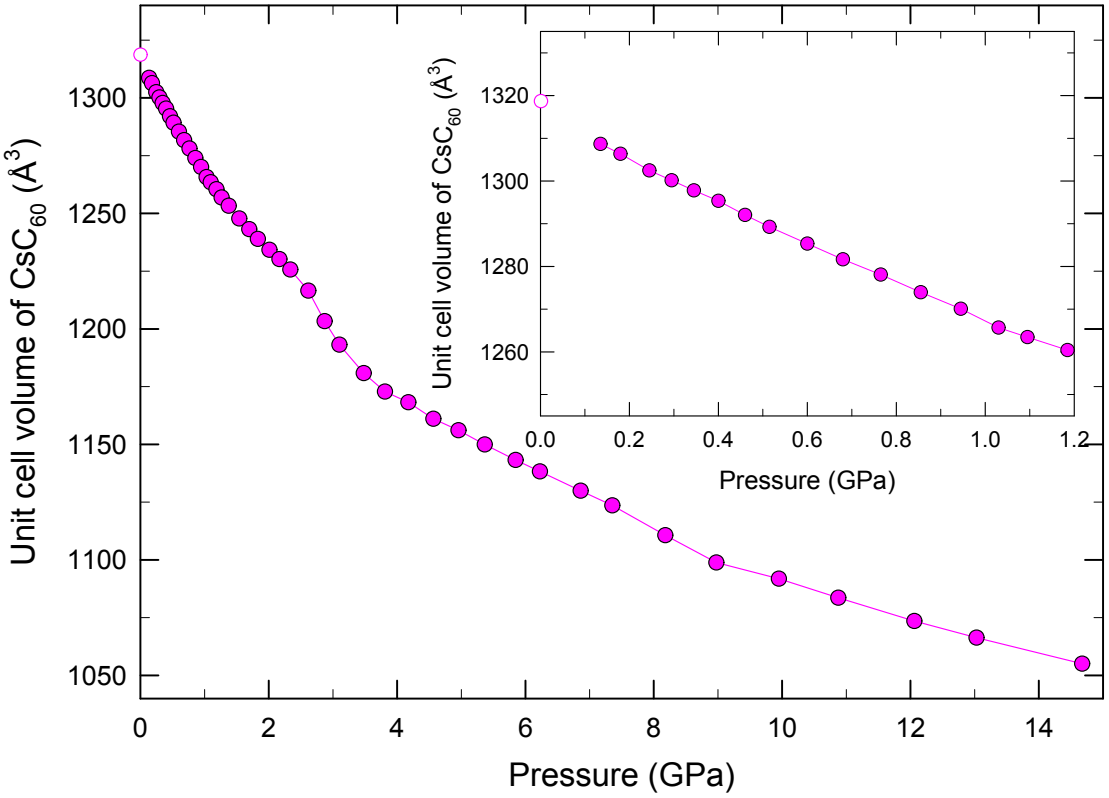

Fig. S3 Pressure evolution of the unit cell volume (pink circles) for CsC_{60}, at ambient temperature, up to an applied pressure of 14.7 GPa. *Inset*: expanded view of the low-pressure data. The open circle is the unit cell volume measured at ambient pressure at the ID31 diffractometer at the ESRF.