Supplementary informations

Raman Scattering Experiments on Unfilled Skutterudite $CoSb_3$ under High Pressure and High Temperature

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X-ray diffraction experiments

A piece of $CoSb_3$ single crystal was cut and has approximate dimensions 0.042 mm x 0.097 mm x 0.183 mm, was used for the X-ray crystallographic analysis using a Bruker D8 venture. The X-ray intensity data were measured using Mo $K_{\alpha1}$ and $K_{\alpha2}$ wavelengths.

The total exposure time was 2.56 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. [S1] The integration of the data using a cubic unit cell yielded a total of 19067 reflections to a maximum θ angle of 72.47° (0.37 Å resolution), of which 1339 were independent (average redundancy 14.240, completeness = 97.9%, R_{int} = 4.70%, R_{sig} = 2.32%) and 1322 (98.73%) were greater than $2\sigma(F^2)$. The final lattice parameters of a = b = c = 9.0369(3) Å, volume = 738.00(7) $Å^3$, are based upon the refinement of the XYZ-centroids of 7349 reflections above 20 σ(I) with 11.25° < 2θ < 156.3°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). [S2] The ratio of minimum to maximum apparent transmission was 0.411. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.0880 and 0.4100. The structure was solved and refined using the Bruker SHELXTL Software Package, [S3] using the space group I m -3, with Z = 8 for the formula unit, $CoSb_3$. The final anisotropic full-matrix least-squares refinement on F^2 with 12 variables converged at R1 = 2.42%, for the observed data and wR2 = 5.61% for all data. The goodness-of-fit was 1.404. The largest peak in the final difference electron density synthesis was 4.300 $e^-/Å^3$ and the largest hole was -3.155 $e^-/Å^3$ with an RMS deviation of 0.813 $e^-/Å^3$. On the basis of the final model, the calculated density was 7.633 g/cm^3 and F(000), 1440 e^-.

Atom	site	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Co	8c	0.00423(5)	U_{11}	U_{11}	-0.00021(3)	- U_{23}	U_{23}
Sb	24g	0.00430(3)	0.00735(3)	0.00555(3)	-0.00070(2)	0.000	0.000

Table S1 : Anisotropic atomic displacements parameters U_{ij} (in) obtained from analysis of the single-crystal data of $CoSb_3$.

The polycrystalline $CoSb_3$ sample was measured with an Xpert X-ray diffraction apparatus using copper $K_{\alpha 1}$ and $K_{\alpha 2}$ wavelengths and a 0.008356° step. Lattice parameter and atomic positions were derived from Rietveld refinement of the XRD patterns using the Fullprof software. [S4] We find that our polycrystalline sample contain 76 % of $CoSb_3$ and 24 % of Sb. For $CoSb_3$, we derive the lattice parameter a = b = c = 9.03890(6) Å, volume = 738.493(8) $Å^3$.

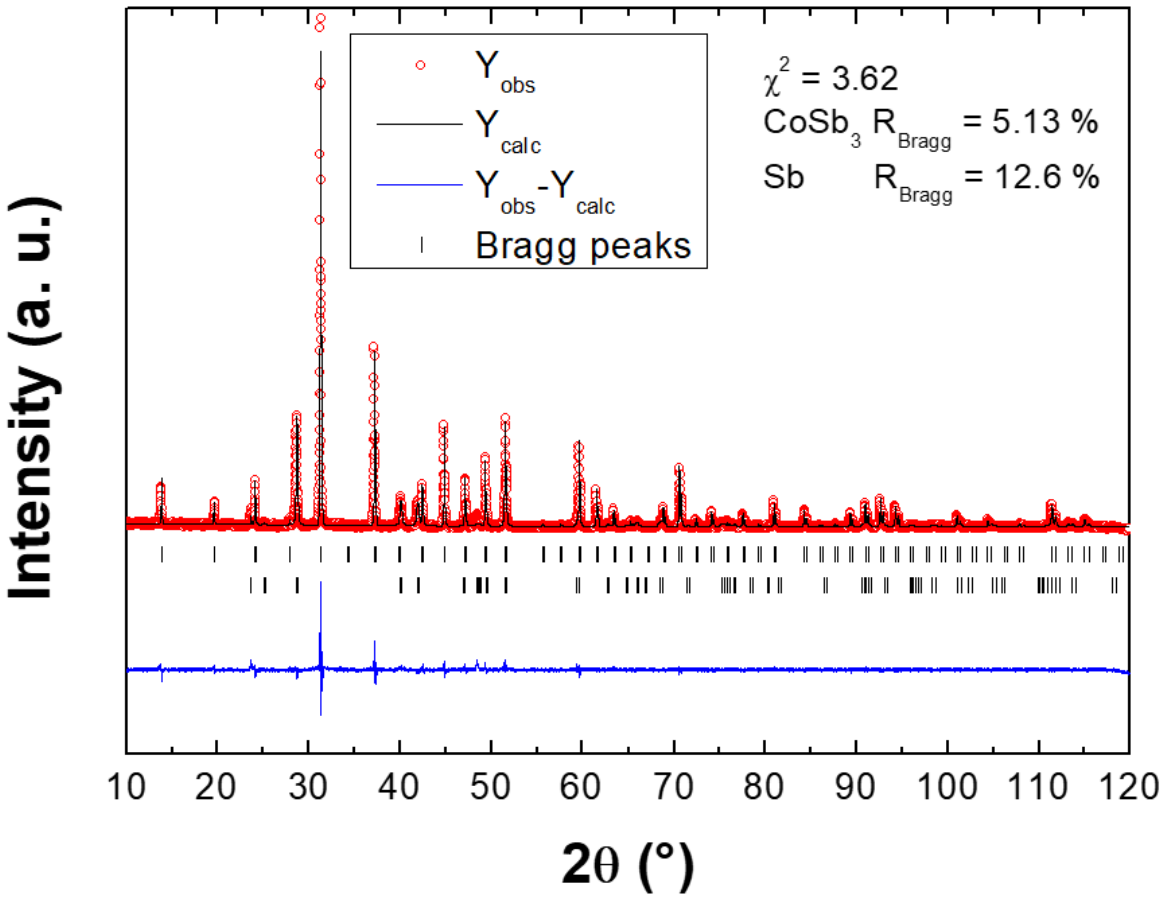

Figure S1 : Rietveld refinement of the powder X-ray pattern of $CoSb_3$. The upper vertical ticks of the Bragg peaks correspond to $CoSb_3$ whereas the lower vertical ticks of the Bragg peaks correspond to Sb.

Raman scattering experiments under pressure

Figures below show pressure-dependent Raman experimental results evidencing the irreversibility of the structural change at 27 GPa. If the pressure is elevated to 36 GPa (left hand side), the spectrum does not recover after decompression. On the other hand, for the pressurization up to 24 GPa (right hand side), the Raman spectrum shows reversible change.

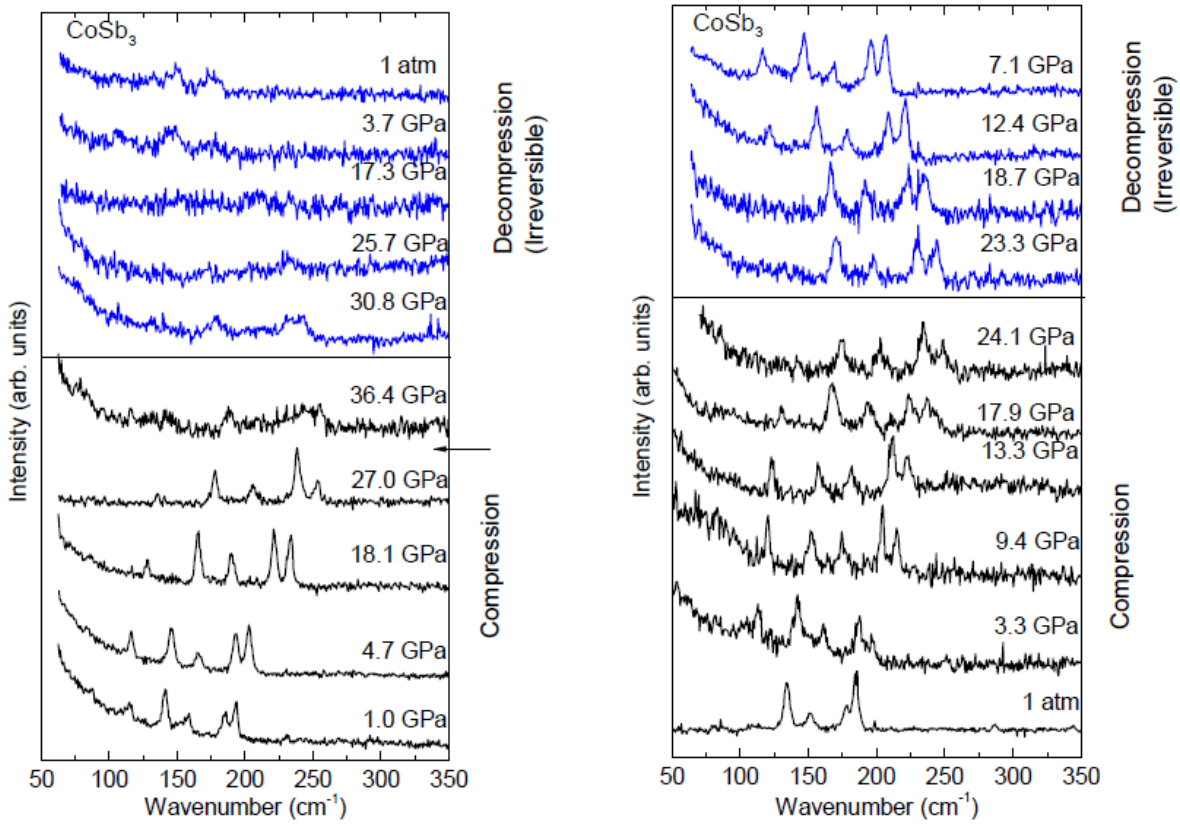

Figure S2 : Raman spectra of $CoSb_3$ upon compression and subsequent decompression. Left, maximum pressure is 36.4 GPa. Right, maximum pressure is 24.1 GPa.

DFT calculations of $SbCo_4Sb_{12}$

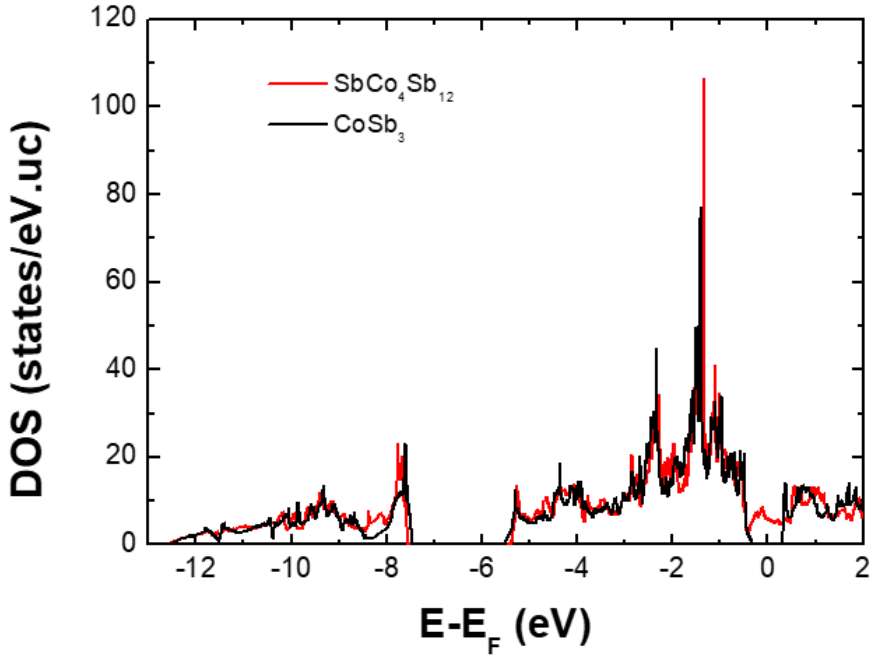

Figure S3 : Electronic density of states of $CoSb_3$ and $SbCo_4Sb_{12}$ at 0 GPa calculated with the DFT.

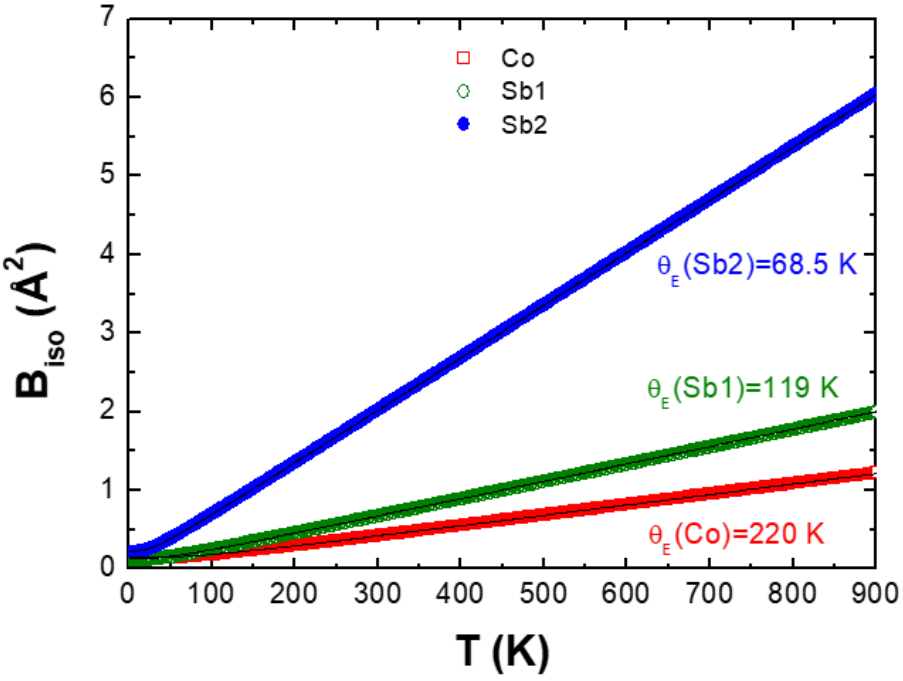

Figure S4 : Atomic displacement parameters of the Co and Sb1 atoms of the cage framework and of the Sb2 guest atom in $SbCo_4Sb_{12}$ at 0 GPa calculated with the DFT (symbols). The solid lines correspond to fit results with the Einstein model.

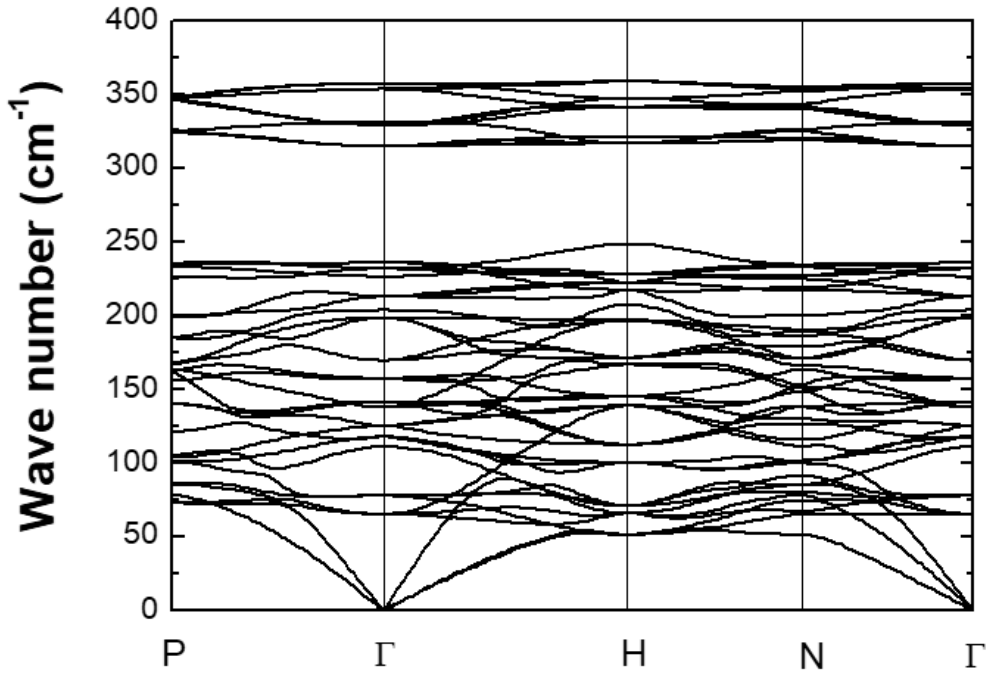

Figure S5 : Phonon dispersion curves of $SbCo_4Sb_{12}$ at 30 GPa calculated with the DFT.

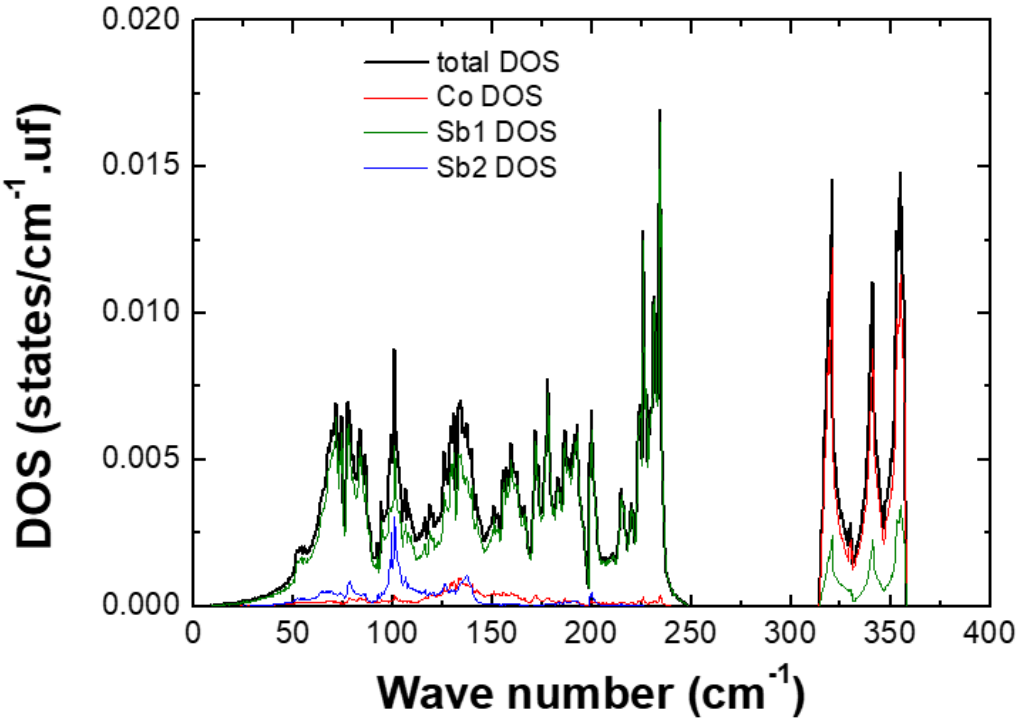

Figure S6 : Total and atom-projected phonon density of states of $SbCo_4Sb_{12}$ at 30 GPa calculated with the DFT.

References

[S1] Bruker. APEX3, SAINT and SADABS. Bruker AXS Inc., Madison, Wisconsin, USA (2015).

[S2] Harker, D. ; Kasper, J. S., Phases of Fourier coefficients directly from crystal diffraction data. *Acta Cryst*. **1948**, *1*, 70-75.

[S3] Sheldrick, G. M., SHELXT - Integrated space-group and crystal-structure determination. *Acta Cryst. A* **2015**, *71*, 3-8.

[S4] Rodriguez-Carvajal, J., Recent advances in magnetic-structure determination by neutron powder diffraction. *Phys. B* **1993**, *192*, 55-69.