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SUPPLEMENTARY INFORMATION
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Supplementary material for "Aluminum at terapascal pressures"

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LIST OF STRUCTURES

File name	Space group	x	Pressure (TPa)
Al40-P4mnc-5TPa.cif	$P4/mnc$	2	5
Al21-P1-5TPa.cif	$P1$	$2\frac{1}{2}$	5
Al42-P4mnc-5TPa.cif	$P4/mnc$	$2\frac{1}{2}$	5
Al16-B2n-5TPa.cif	$B2/n$	$2\frac{2}{3}$	5
Al16-I4mcm-5TPa.cif	$I4/mcm$	$2\frac{2}{3}$	5
Al86-P4212-3TPa.cif	$P42_12$	$2\frac{3}{4}$	3
Al11-P-1-5TPa.cif	$P\bar{1}$	3	5
Al22-P4mbm-5TPa.cif	$P4/mbm$	3	5
Al46-P4mbm-5TPa.cif	$P4/mbm$	$3\frac{1}{2}$	5
Al1-P6mmm-10TPa.cif	$P6/mmm$	–	10
Al4-Cmma-20TPa.cif	$Cmma$	–	20

TABLE I: Aluminum structures studied in this work. The full structures are given in the accompanying CIF files.

The Ba-IV host-guest structure has x guest atoms per 8 host atoms. Some papers report instead the (irrational) ratio $\gamma = c_H/c_G$ of the host to guest "repeat" lengths along the axis of the guest chain. The average number of guest atoms per 8 host atoms is given by $2c_H/c_G$, and therefore $x = 2c_H/c_G = 2\gamma$.

NEAREST NEIGHBOUR DISTANCES IN THE AL16 STRUCTURE

The closest host and guest atoms in Al16 at 3 TPa are about 1.6 Å apart, while the guest chains are dimerised with bond lengths of 1.41 and 1.45 Å. The closest host atoms are separated by 1.51 Å.

PHASE STABILITY AT PRESSURES OF 10–30 TPA

The relative stabilities of phases in the range 10–30 TPa are shown in Fig. S1. The high pressure searches were performed at 25 TPa using a pseudopotential of core radius 1.1 a.u. The $Cmma$ and $Imma$ phases are also "electride" phases.

FINDING THE EQUILIBRIUM VALUES OF x

The enthalpies of various host-guest structures are plotted against x in Fig. S2 at pressures of 3 and 8 TPa. Similar calculations calculations were performed at 4, 5, 6 and 7 TPa. The equilibrium value of x at each pressure was obtained from the minimum in the quadratic fit.

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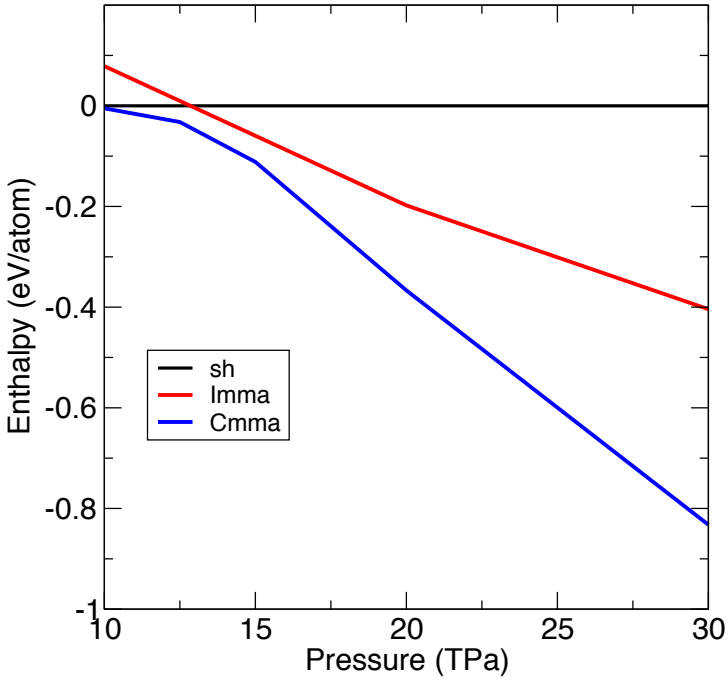

FIG. 1: Enthalpy differences between Al phases and the sh phase as a function of pressure in the range 10–30 TPa.

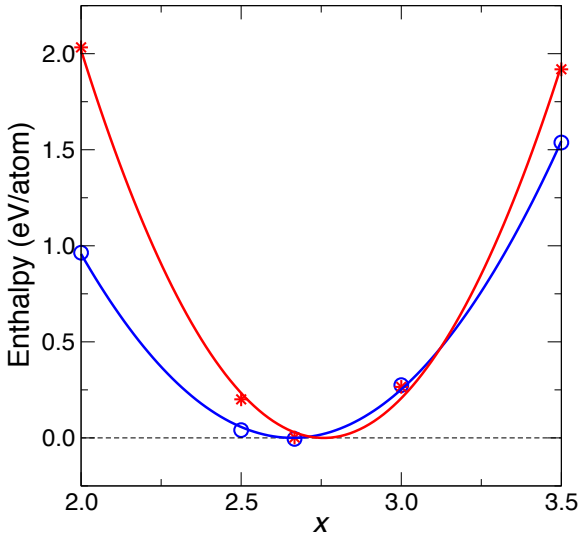

FIG. 2: Enthalpy per atom as a function of the number of guest atoms per 8 host atoms at 3 TPa (blue circles) and 8 TPa (red stars). The lines are quadratic fits to the data points.

ELECTRONIC DENSITIES OF STATES

The electronic densities of states (e-DoS) of the Al11, Al16, and bcc phases at 5 TPa are shown in Fig. S5, including the semi-core 2*s* and 2*p* derived energy levels, while the valence e-DoS of the Al11, Al42, Al16, bcc and sh phases at 5 TPa are shown in Fig. S6. The valence bandwidth calculated within the free-electron model at the density of Al16 at 5 TPa is 40.6 eV, but the DFT calculations with an accurate description of the atomic cores give a bandwidth of about half this size at 21.9 eV. The valence bandwidths of the other host-guest structures and the bcc and hcp phases are similar. The 2*s* orbitals lie within the range -116 to -104 eV, the 2*p* orbitals lie within the range -82 to -65

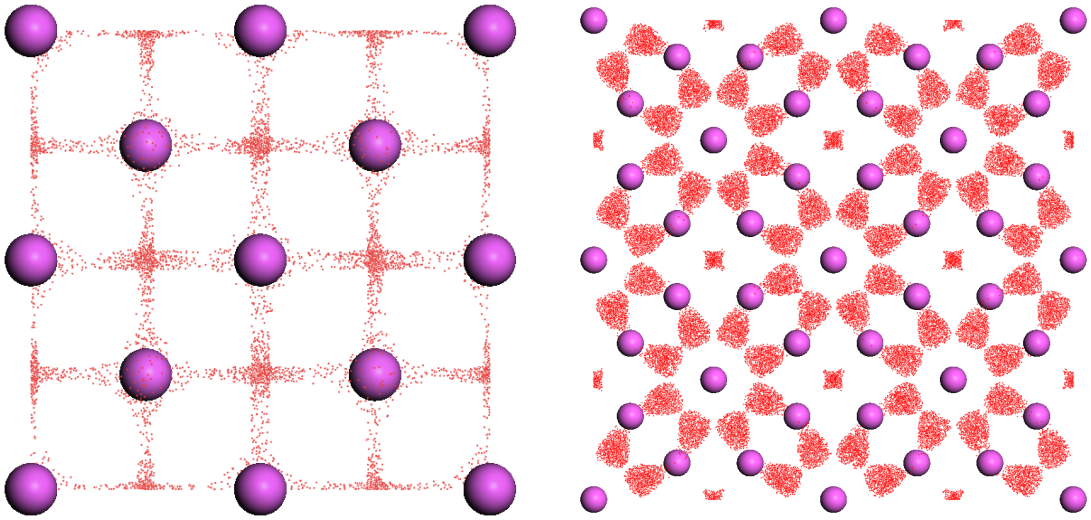

FIG. 3: The valence charge density (red) of the bcc structure (left) and Al16-I4mcm host-guest structure (right) at 5 TPa. The ions are shown in purple. The lines of maxima in the charge are clearly visible in the bcc structure. Note that in Al16-I4mcm some of the electron "blobs" shown are at different heights.

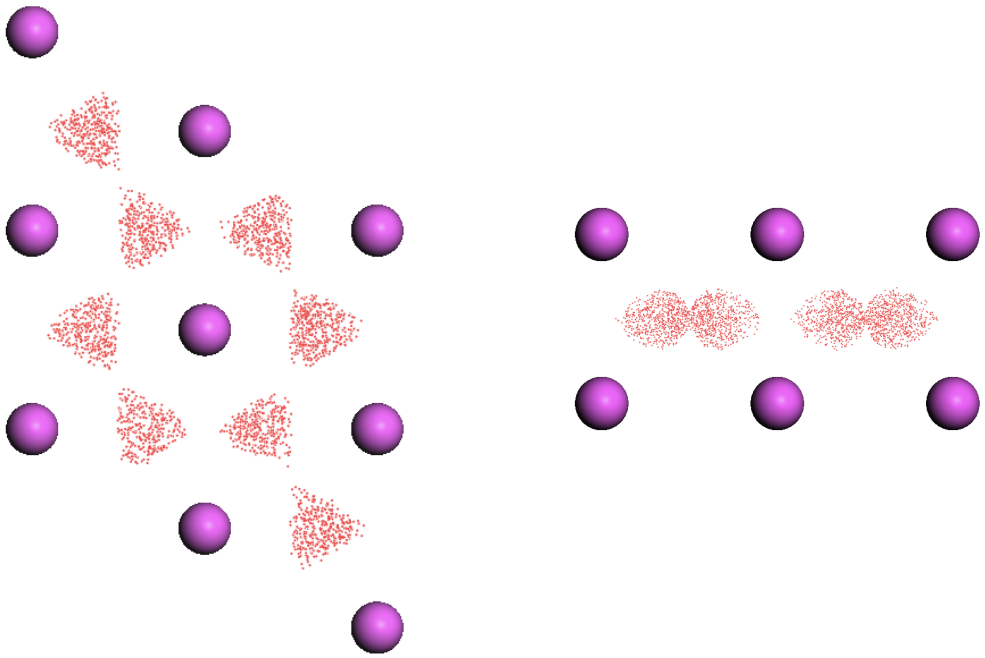

FIG. 4: The valence charge density (red) of the sh structure, with the ions shown in purple. A view perpendicular to the hexagonal layers is shown on the left and a view within the layers is shown in the right. The layers of valence electron charge density are clearly visible in the right hand view.

eV, and the occupied valence orbitals lie within the range -22.5 to 0 eV. The bandwidths of the $2s$, $2p$ and occupied valence orbitals are narrowest for the bcc structure and widest for Al11.

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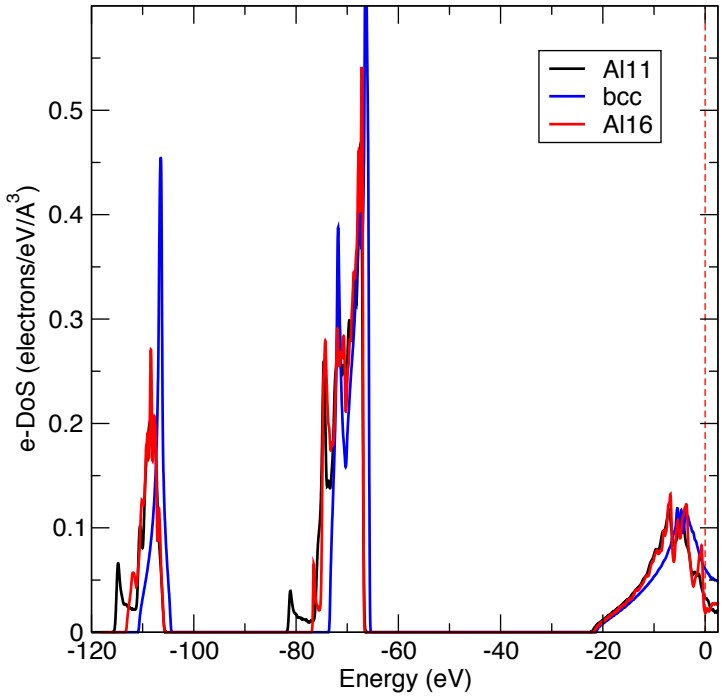

FIG. 5: Electronic densities of states of the Al11, Al16, and bcc phases at 5 TPa showing the $2s$ and $2p$ semi-core states and the valence states. The zero of energy is placed at the Fermi energy.

VOLUME-PRESSURE RELATIONS

The volume-pressure relations for the bcc, Al16, and sh phases shown in Fig. 3 of the main text are given by:

$$\begin{aligned}
\text{bcc} \qquad & V = 7.0774 - 2.7213\,p + 0.67007\,p^2 - 0.06293\,p^3; \\
\text{Al16} \qquad & V = 4.9705 - 0.82279\,p + 0.084728\,p^2 - 0.0033708\,p^3; \\
\text{sh} \qquad & V = 4.1265 - 0.4735\,p + 0.034535\,p^2 - 0.0010017\,p^3.
\end{aligned}$$

where V is in Å^3 per atom and p is in TPa. These expressions should only be used within the stability ranges indicated in Fig. 3 of the main text.

The data for the EoS of Lomonosov with the temperature set to zero were obtained from equation (5) of Ref. 2, using the parameters given in Table 1 of that paper. The zero-pressure value of the parameter $V_{0c} = 0.3614$ cm^3/g corresponds to a zero-temperature fcc lattice constant of $a_0 = 4.01595$ Å. We also used the EoS from Holian[2] with the values of the isothermal bulk modulus and its pressure derivative reported in that paper. For simplicity we used the same zero-temperature fcc lattice constant as for the Lomonosov EoS.[1] Using instead the density of 2.7 g/cm^3 (corresponding to $a_0 = 4.049$ Å) reported in Holian's paper moves the EoS even further from our DFT data. Our EoS for the bcc phase is in very good agreement with Lomonosov's, the differences at higher pressures arise from our discovery of denser phases.

SIMPLE PAIRWISE POTENTIAL

The simple pairwise potential used to generate the structure shown in Fig. 2(b) of the main text is given by

$$V_{ij}(r) = \epsilon \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \beta_{ij} \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right] \tag{1}$$

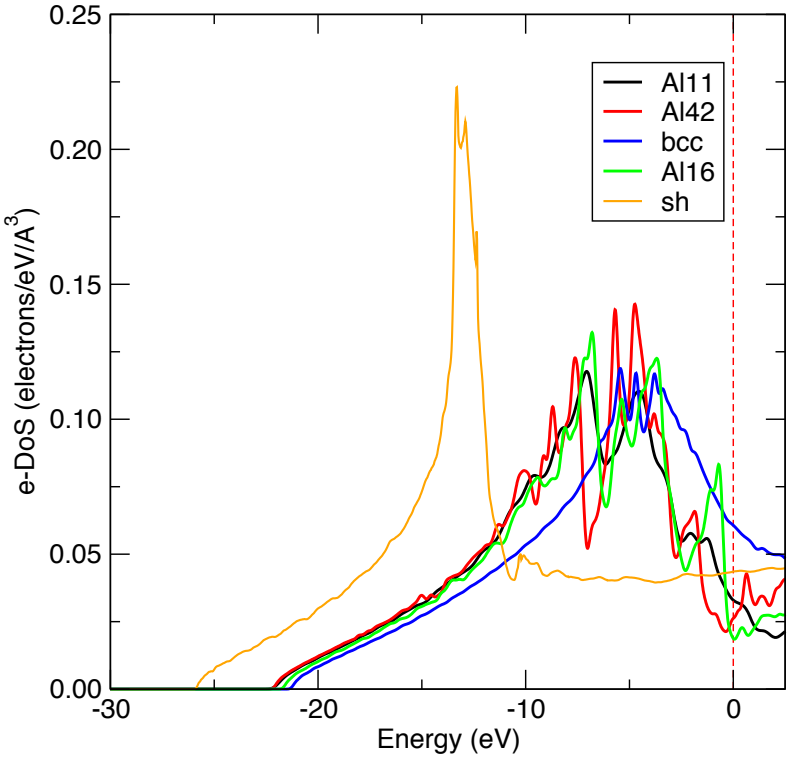

FIG. 6: Valence electronic densities of states of the Al11, Al42, Al16, bcc and sh phases at 5 TPa. The zero of energy is placed at the Fermi energy. Note that the e-DoS of Al11, Al42, Al16 and bcc are quite similar while that of sh is somewhat different. The stability of the host-guest and bcc phases follows the density of states at the Fermi energy. At 5 TPa in order of increasing stability we have bcc, Al11, Al42, Al16. The transfer of substantial weight in the e-DoS of sh to lower energies is clearly visible.

where $\epsilon = 1$ eV, $\sigma_{11} = 2$ Å, $\sigma_{22} = 1.25$ Å, $\sigma_{12} = 1.625$ Å, $\beta_{11} =$ -1, $\beta_{22} =$ -1, $\beta_{12} = 1$. The subscript "1" denotes the "Al" atom and "2" denotes the "electron" blobs. Random structure searches with 16 "Al" atoms and 28 "electron" blobs at 100 GPa gave Al16 as the most stable structure. The prefactor ϵ does not affect the structures obtained, but it can be used to scale the pressure to any desired value.

[1] Lomonosov, I. V. Multi-phase equation of state of aluminum. *Laser and Particle Beams* **25**, 567-584 (2007); Vladimirov, A. S., Voloshin, N. P., Nogin, V. N., Petrovtsev, A. V. & Simonenko, V. A. Shock compressibility of aluminum. *Sov. Phys. JETP Lett.* **39**, 85-88 (1984).
[2] Holian, K. S. A new equation of state for aluminum. *J. Appl. Phys.* **59**, 149-157 (1986).