Supplementary Information for the paper entitled “Phase Diagram and High-Temperature Superconductivity of Compressed Selenium Hydrides”

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Supplementary Methods

Our structural prediction approach is based on a global minimization of free energy surfaces of given compounds by combining *ab initio* total-energy calculations with the particle swarm optimization (PSO) algorithm.\(^1,^2\) The structure search of each \(\text{H}_x\text{Se}_y\) \((x = 1−5\) and \(y = 1−3\)) stoichiometry is performed with simulation cells containing 1−4 formula units. In the first generation, a population of structures belonging to certain space group symmetries are randomly constructed. Local optimizations of candidate structures are done by using the conjugate gradients method through the VASP code\(^3\), with an economy set of input parameters and an enthalpy convergence threshold of \(1 \times 10^{-5}\) eV per cell. Starting from the second generation, 60% structures in the previous generation with the lower enthalpies are selected to produce the structures of next generation by the PSO operators. The 40% structures in the new generation are randomly generated. A structure fingerprinting technique of bond characterization matrix is employed to evaluate each newly generated structure, so that identical structures are strictly forbidden. These procedures significantly enhance the diversity of sampled structures during the evolution, which is crucial in driving the search into the global minimum. For most of cases, the structure search for each chemical composition is converged (evidenced by no structure with the lower enthalpy emerging) after 1000 \(\sim\) 1200 structures investigated (*i.e.* in about 20 \(\sim\) 30 generations).

The energetic stabilities of different \(\text{H}_x\text{Se}_y\) stoichiometries are evaluated by their formation enthalpies relative to the products of dissociation into constituent elements (*i.e. solidified phases of H\(_2\) and Se*):

\[
\Delta H = [h(\text{H}_x\text{Se}_y) -xh(\text{H}) -yh(\text{Se})]/(x+y)
\]

(1)

where \(h\) represents absolute formation enthalpy. By regarding H and Se as the binary variables, with these \(\Delta H\) values we can construct the convex hull at each pressure (Fig. 1 in the main text). It is known that the zero-point energy plays an important role in determining the phase stabilities of the compounds containing light elements such as
H. We hence examine the effect of zero-point energy on the stability of the stoichiometries on the convex hull (Fig. S9), by using the calculated phonon spectrum with the supercell approach as implemented in the Phonopy code.

The electron-phonon coupling calculations are carried out with the density functional perturbation (linear response) theory as implemented in the QUANTUM ESPRESSO package. We employ the norm-conserving pseudopotentials with 1s\(^1\) and 4s\(^2\)4p\(^4\) as valence electrons for H and Se. The kinetic energy cutoff for wave-function expansion is chosen as 70 Ry. To reliably calculate electron-phonon coupling in metallic systems, we need to sample dense \(k\)-meshes for electronic Brillouin zone integration and enough \(q\)-meshes for evaluating average contributions from the phonon modes. Dependent on specific structures of stable compounds, different \(k\)-meshes and \(q\)-meshes are used: 16 x 16 x 16 \(k\)-meshes and 4 x 4 x 4 \(q\)-meshes for HSe\(_2\) in the \(C2/m\) structure, 18 x 18 x 24 \(k\)-meshes and 3 x 3 x 6 \(q\)-meshes for HSe with the \(P4/nnm\) structure, 24 x 24 x 24 \(k\)-meshes and 6 x 6 x 6 \(q\)-meshes H\(_3\)Se with the \(Im-3m\) structure. Note that the calculated EPC strength is affected by two critical parameters associated with the broadening technique: one broadening parameter (\(\delta\)) is to account for the Fermi surface of metals; the other broadening parameter (\(\sigma\)) is for evaluating the integration of the double-delta function within the expression of phonon linewidth. In principle, the values of \(\delta\) and \(\sigma\) can be chosen as small as possible (approaching to zero) when the dense enough \(k\)-meshes are used. This ideal case is difficult to be achieved since the finite \(k\)-meshes are always adopted in the calculations. Here for safety we used the relatively large values of \(\delta\) (0.05 Ry) and \(\sigma\) (0.04 Ry). They thus give a rather conservative evaluation of total EPC constant \(\lambda\).

To examine the reliability of the adopted projected-augmented-wave (PAW) pseudopotentials for H and Se, the formation enthalpy calculations of H\(_3\)Se with other types of pseudopotentials (contained in the VASP code) are performed. The results are shown in Table S0. As seen different pseudopotentials generally give consistent results, though the LDA ones turns out to overcount the magnitude of formation enthalpy. The reliabilities of the pseudopotentials at high pressures are also crosschecked with the full-potential linearized augmented plane-wave (LAPW)
method as implemented in the WIEN2k code\textsuperscript{9}. By using the two different methods, we calculate total energies of H\textsubscript{3}Se in the \textit{Im}-3\textit{m} structure with varying pressures, and then fit the obtained energy-volume data into the Birch-Murnaghan equation of states. Figure S0 shows the resulted fitted equation of states. We can see the results derived from two methods are almost identical, which clearly indicates the suitability of the PAW pseudopotentials for describing the energetics of Se hydrides at megabar pressures.

\textbf{Table S0.} Calculated formation enthalpy (in eV) per formula unit of H\textsubscript{3}Se with respect to solid H\textsubscript{2} and Se using different PAW pseudopotentials at 150 GPa.

|       | PBE  | LDA  |
|-------|------|------|
|       | H    | H    | H | H | H | H |
| Se    | -0.0092 | -0.0193 | -0.0105 | -0.0105 | Se_GW | -0.0079 | -0.0180 | -0.0093 | -0.0093 |
| Se_GW | -0.1531 | -0.1538 | -0.1536 | -0.1538 | Se_GW | -0.1528 | -0.1534 | -0.1533 | -0.1534 |
Figure S0. Comparison of the fitted Birch-Murnaghan equation of states for H$_3$Se in the $Im$-$3m$ structure by using the calculated results from the PAW pseudopotentials and the full-potential LAPW methods.
Supplementary Figures

Figure S1. (a) Phase stabilities of various H-Se compounds at the low pressure range of 0 and 50 GPa. The formation enthalpies of H-Se compounds are relative to the enthalpies of elemental decomposition into solidified phases of H₂ and Se. Dashed lines connect data points, and solid lines denote the convex hull. Compounds corresponding to data points located on the convex hull are stable against decomposition. (b) Calculated enthalpies per atom of various structures for stoichiometry H₂Se in the pressure range of 0–350 GPa with respect to H₂+Se. (c) Predicted structure of H₂Se with P3121 symmetry at 0 GPa.
Figure S2. The metastable structures for stoichiometries H$_2$Se, HSe$_2$ and H$_3$Se at selected pressures. The corresponding detailed structural information is summarized in Table S2.
Figure S3. Calculated electronic band structure (left panels) and projected density of states (right panels) for the predicted H-rich compounds at the lower boundary of respective stable pressure region: (a) HSe$_2$(C2/m) at 125 GPa, (b) HSe(P4/nmm) at 250 GPa, and (c) H$_3$Se(Im-3m) at 175 GPa.
**Figure S4.** Two-dimensional plots of the electron localization function (ELF) for HSe$_2$(C2/m), HSe(P4/nmm) and H$_3$Se(Im-3m) at 300 GPa.

**Figure S5.** Calculated enthalpies per atom of various structures for stoichiometry HSe$_2$ in the pressure range of 50–350 GPa with respect to 1/2H$_2$+2Se.
**Figure S6.** Calculated enthalpies per atom of various structures for stoichiometry HSe as functions of pressure between 50 and 350 GPa with respect to $1/2\text{H}_2+\text{Se}$.

**Figure S7.** Calculated enthalpies per atom of various structures for stoichiometry $\text{H}_3\text{Se}$ as functions of pressure between 50 and 350 GPa with respect to $3/2\text{H}_2+\text{Se}$.
**Figure S8.** Fermi surfaces for HSe in the $P4/nmm$ structure at 250 GPa.

**Figure S9.** Relative formation enthalpies of the predicted stable stoichiometries, e.g. HSe$_2$, HSe and H$_3$Se at 200 and 300 GPa with (filled symbols and solid lines) and without (open symbols and dash lines) the inclusion of zero-point energy contribution. One clearly sees that the introduction of zero-point energy does not change energetic stabilities of these stable stoichiometries.
**Figure S10.** The dependence of $T_c$ on $\mu^*$ for H$_3$Se($Im$-$3m$) and HSe($P4/nmm$) at 250 GPa.

**Figure S11.** Calculated electronic band structure for H$_3$Se($Im$-$3m$) at 250 GPa without (a) and with (b) the inclusion of spin-orbit coupling (SOC) contribution.
Supplementary Tables

**Table S1.** Detailed structural information of the predicted stable H-Se compounds at selected pressures.

| Phases     | Pressure (GPa) | Lattice parameters (Å, °) | Atomic coordinates (fractional) |
|------------|----------------|---------------------------|---------------------------------|
| HSe₂-C₂/m  | 300            | a = 7.580                 | H(4i) 0.376 0.000 0.288        |
|            |                 | b = 3.222                 | Se(4i) 0.105 0.000 0.842       |
|            |                 | c = 3.858                 | Se(4i) 0.355 0.000 0.672       |
|            |                 | a = γ = 90.000            |                                 |
|            |                 | β = 120.320               |                                 |
| HSe-P₄/nmm | 300            | a = b = 3.014             | H(2b) 0.500 0.500 0.500        |
|            |                 | c = 2.373                 | Se(2c) 0.500 0.000 0.817       |
|            |                 | a = β = γ = 90.000        |                                 |
| H₂Se-Im-3m | 300            | a = b = c = 3.025         | H(6b) 0.500 0.000 0.500        |
|            |                 | a = β = γ = 90.000        | Se(2a) 0.500 0.500 0.500       |
| HSe₂-C₂/m  | 200            | a = 7.897                 | H(4i) 0.376 0.000 0.288        |
|            |                 | b = 3.310                 | Se(4i) 0.105 0.000 0.842       |
|            |                 | c = 4.048                 | Se(4i) 0.355 0.000 0.672       |
|            |                 | a = γ = 90.000            |                                 |
|            |                 | β = 120.341               |                                 |
| H₂Se-Im-3m | 200            | a = b = c = 3.148         | H(6b) 0.500 0.000 0.500        |
|            |                 | a = β = γ = 90.000        | Se(2a) 0.500 0.500 0.500       |
| H₂Se-P₃,21 | 0              | a = b = 5.873             | H(6c) 0.900 0.450 0.030        |
|            |                 | c = 6.871                 | Se(3b) 1.320 0.320 0.500       |
|            |                 | a = β = 90.000            |                                 |
|            |                 | γ = 120.000               |                                 |
**Table S2.** Detailed structural information of the predicted metastable H-Se compounds at selected pressures.

| Phases       | Pressure (GPa) | Lattice parameters (Å, °) | Atomic coordinates (fractional) |
|--------------|----------------|--------------------------|---------------------------------|
| H$_2$Se-C2/m | 300            | $a = 6.983$               | H(4i) 0.064 0.000 0.596       |
|              |                | $b = 2.937$               |                                 |
|              |                | $c = 2.389$               |                                 |
|              |                | $a = \gamma = 90.000$    |                                 |
|              |                | $\beta = 95.442$         |                                 |
| HSe$_2$-C2/c | 300            | $a = 8.253$               | H(4e) 0.000 0.523 0.250        |
|              |                | $b = 2.363$               |                                 |
|              |                | $c = 4.286$               |                                 |
|              |                | $a = \gamma = 90.000$    |                                 |
|              |                | $\beta = 104.475$        |                                 |
| HSe$_2$-Pmna | 300            | $a = 5.899$               | H(4g) 0.250 0.200 0.250        |
|              |                | $b = 2.342$               |                                 |
|              |                | $c = 5.869$               |                                 |
|              |                | $a = \beta = \gamma = 90.000$ |                                 |
| H$_3$Se-C2/m | 50             | $a = 6.476$               | H(2b) 0.000 0.500 0.000        |
|              |                | $b = 4.875$               |                                 |
|              |                | $c = 4.503$               |                                 |
|              |                | $a = \gamma = 90.000$    |                                 |
|              |                | $\beta = 136.386$        |                                 |
| H$_3$Se-R3m  | 200            | $a = b = 4.451$           | H(9b) 0.500 0.500 0.298        |
|              |                | $c = 2.728$               |                                 |
|              |                | $a = \beta = 90.000$     |                                 |
|              |                | $\gamma = 120.000$       |                                 |
| H$_3$Se-P-1  | 300            | $a = 2.588$               | H(2i) 0.335 0.010 0.505        |
|              |                | $b = 2.565$               |                                 |
|              |                | $c = 4.279$               |                                 |
|              |                | $a = 91.920$              |                                 |
|              |                | $\beta = 94.937$         |                                 |
|              |                | $\gamma = 73.627$        |                                 |
| HSe-P2$_1$| c 300          | $a = 4.081$               | H(1a) 0.924 0.412 0.193        |
|              |                | $b = 4.456$               |                                 |
|              |                | $c = 2.563$               |                                 |
|              |                | $a = \gamma = 90.000$    |                                 |
|              |                | $\beta = 78.453$         |                                 |
|              |                | $Se(1a) 0.697 0.640 0.631$ |                                 |
|              |                | $Se(1a) 0.302 0.359 0.368$ |                                 |
|              |                | $Se(1a) 0.802 0.140 0.868$ |                                 |
|              |                | $Se(1a) 0.197 0.859 0.131$ |                                 |
Table S3. Calculated electron-phonon coupling parameter $\lambda$, logarithmic average frequency $\omega_{\text{log}}$, electronic density of states at the Fermi level $N(E_f)$ and critical temperature $T_c$ of predicted H-Se compounds and H$_3$S.

| Phases       | Pressure (GPa) | $\lambda$ | $\omega_{\text{log}}$ (K) | $N(E_f)$ states/spin/Ry/cell | $T_c$ (K) |
|--------------|---------------|-----------|--------------------------|------------------------------|-----------|
| HSe$_2$-C2/m | 300           | 0.45      | 647                      | 8.09                         | 5         |
| HSe-P2$_1$/c | 300           | 0.65      | 832                      | 9.55                         | 23        |
| HSe-P4/nmm   | 250           | 0.81      | 813                      | 5.62                         | 39        |
|              | 300           | 0.80      | 885                      | 5.75                         | 42        |
| H$_3$Se-Im-3m| 200           | 1.09      | 1477                     | 3.19                         | 116       |
|              | 250           | 1.04      | 1498                     | 3.13                         | 111       |
|              | 300           | 1.04      | 1492                     | 3.09                         | 110       |
| H$_3$S-Im-3m | 200           | 1.61      | 1484                     | 3.27                         | 171       |
|              | 250           | 1.33      | 1708                     | 3.25                         | 172       |
|              | 300           | 1.20      | 1774                     | 3.23                         | 160       |

Table S4. Calculated electron-phonon coupling parameter $\lambda$, logarithmic average frequency $\omega_{\text{log}}$, electronic density of states at the Fermi level $N(E_f)$ and critical temperature $T_c$ for H$_3$Se(Im-3m) at 250 GPa with/without the inclusion of spin-orbit coupling (SOC) contribution.

| Phases       | $\lambda$ | $\omega_{\text{log}}$ (K) | $N(E_f)$ states/spin/Ry/cell | $T_c$ (K) |
|--------------|-----------|--------------------------|------------------------------|-----------|
| H$_3$Se-Im-3m| 1.04      | 1498                     | 3.13                         | 111       |
| non-SOC      | 1.10      | 1386                     | 3.13                         | 111       |
| SOC          |           |                          |                              |           |
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