Thermodynamics and superconductivity of $S_xSe_{1-x}H_3$

Maximilian Amsler$^{1,*}$

$^1$Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York 14853, USA

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The compression of SH$_2$ and its subsequent decomposition to SH$_3$, presumably in a cubic $Im\bar{3}m$ structure, has lead to the discovery of conventional superconductivity with the highest measured and confirmed $T_c$ to date, 203 K at 160 GPa. Recent theoretical studies suggest that a mixture of S with other elements of the chalcogen group could improve the superconducting temperature. Here, we present a detailed analysis of the thermodynamic properties of S and Se mixtures in the bcc lattice with $Im\bar{3}m$ symmetry using a cluster expansion technique to explore the phase diagram of $S_xSe_{1-x}H_3$. In contrast to earlier reports, we find that $S_{0.5}Se_{0.5}H_3$ is not stable in the pressure range between 150–200 GPa. However, phases at compositions $S_{0.2}Se_{0.8}H_3$, $S_{0.7}Se_{0.3}H_3$, and $S_{0.6}Se_{0.4}H_3$ are stable at 200 GPa, while additional phases at $S_{0.25}Se_{0.75}H_3$ and $S_{0.75}Se_{0.25}H_3$ are accessible at lower pressures. Electron-phonon calculations show that the values of $T_c$ are consistently lower for all ternary phases, indicating that mixtures of S and Se with H might not be a viable route towards compounds with improved superconducting properties.

Metallic hydrogen (1) has become the holy grail in high-pressure physics due to its predicted exotic properties, most notably the expected high-$T_c$ superconductivity in its molecular or atomic form, potentially above room temperature (2–5). Despite recent reports on the successful formation of metallic hydrogen in diamond anvil cells at static pressures close to 500 GPa (6), the findings still remain unconfirmed and are subject to controversial discussions (7–11). On the other hand, Ashcroft’s proposal (12) to lower the metalization pressure of hydrogen by adding heavier elements to exert chemical pressure in hydrogen-rich compounds has proven to be particularly fruitful. Theoretical studies based on structural searches and ab initio calculations have been performed to screen for many potential candidate materials, ranging from silicon (13–15), scandium (16), sulfur (17, 18), and phosphorus hydrides (19–21) to calcium, lanthanum and yttrium hydrides (22–24) with very high hydrogen content.

The existence of high-$T_c$ hydride compounds has been meanwhile reported in at least three chemical systems through high-pressure experiments, namely in PH$_3$ (25), LaH$_x$ (26, 27), and SH$_x$ (28–30). For the latter, compression of SH$_2$ up to 250 GPa (28) has led to the discovery of two distinct regimes of superconductivity, namely a low-$T_c$ phase (33-150 K) and a high-$T_c$ (203 K) phase, the highest measured and confirmed superconducting transition temperature to date. The different superconducting states emerge depending on the synthesis conditions, and the common consensus is that the high-$T_c$ phase can be attributed to a decomposition of SH$_2$ to SH$_3$ in annealed samples (30–39). According to crystal structure prediction (CSP) calculations (18, 36, 38) and in agreement with available experimental data (30), the structure of this SH$_3$ phase has a bcc lattice with $Im\bar{3}m$ symmetry, and is stable at pressures above about 150 GPa. The values of $T_c$ predicted from Eliashberg theory are very close to the experimental measurements (18, 32, 36). This excellent agreement between theory and experiment together with the isotope effect measurements (28) and the recent optical spectroscopy studies (40) confirm that SH$_3$ is indeed a conventional, phonon-mediated superconductor.

The success of ab initio calculations to accurately describe the fascinating properties of SH$_3$ has turned this system into a playground to test new ideas that could further enhance its properties. Heil et al. (41) replaced the S atoms with chalcogens (O, S, Se, Te) using the virtual crystal approximation in an attempt to identify trends that would increase the $T_c$, and found that a partial substitution of S with O could enhance its value. Ge et al. (42) proposed doping SH$_3$ with elements from neighboring groups in the periodic table, and concluded that a $T_c$ as high as 280 K could be reached at 250 GPa in $S_{0.9}P_{0.075}H_3$. Very recently, Liu et al. (43) performed CSP calculations at a fixed composition of $S_{0.5}Se_{0.5}H_3$ and found that the lowest enthalpy structures indeed correspond to different decorations of the cubic SH$_3$ lattice. Based on their electron-phonon calculations, the superconducting temperature decreases when S is replaced by Se, which the authors attribute to a decreasing strength of the covalent H–S or H-Se bonds.

In this work, we investigate the thermodynamic and superconducting properties of the complete compositional range of $S_xSe_{1-x}H_3$. Using a cluster expansion (CE) of the cubic lattice of SH$_3$, we sample all phases with up to 56 atoms/cell at pressures between 150 and 200 GPa. In contrast to earlier reports, we discover that $S_{0.5}Se_{0.5}H_3$ is not thermodynamically stable at any pressure. However, phases with compositions $S_{0.2}Se_{0.8}H_3$, $S_{0.7}Se_{0.3}H_3$, and $S_{0.6}Se_{0.4}H_3$ are stable at 200 GPa, while $S_{0.25}Se_{0.75}H_3$ and $S_{0.75}Se_{0.25}H_3$ are stable at lower pressures. Our calculations reveal that all phases are superconductors, but exhibit $T_c$ values significantly lower than pure SH$_3$ and SeH$_3$.

We start out by showing the conventional unit cell of the high-pressure phase of SH$_3$ and SeH$_3$ with $Im\bar{3}m$ symmetry in Fig. 1, where the large spheres denote the S and Se sites, and the small spheres represent the H atoms. Recent theoretical studies report that the phase...
Formation enthalpy (meV)

The central motivation in the recent work of Liu et al. (43) was to address the issue that so far all studies in the S–Se–H system have been only treated within the virtual crystal approximation, without explicitly taking into account any potential changes in the underlying crystal structure. To this end, the authors performed CSP calculations at a fixed composition of $S_{0.5} Se_{0.5} H_3$. Their results showed that an ordered structure was preferred over structural disorder. However, all low-enthalpy phases that they found during their structural search are merely different decorations of the S/Se sites in the $Im3m$ parent lattice.

These findings raise the question if other decorations of the lattice with different compositions might have lower formation enthalpies. To address this issue, we use the cluster expansion technique (44, 45), which is frequently employed to study metals and alloys, and provides a convenient means to expand the enthalpy in terms of short-range structural arrangements. We use the Alloy-Theoretic Automated Toolkit (ATAT) (46–48) to perform a CE based on the formation enthalpies from first principles DFT calculations. In a CE, sites $i$ in a lattice are assigned an occupation variable $\sigma_i$, depending on the atom type. A specific arrangement of these $\sigma_i$, called a configuration, is encoded in a vector $\sigma$, and the energy (or enthalpy) of said configuration is expressed in terms of “clusters” $\alpha$ through

$$E(\sigma) = \sum_\alpha m_\alpha J_\alpha \left( \prod_{i \in \alpha} \sigma_i \right)$$  \hspace{1cm} (1)

$\alpha$ represents a set of sites $i$ that are symmetrically inequivalent, and for every $\alpha$ we take the average over all clusters $\alpha'$ which are symmetrically equivalent to $\alpha$ with multiplicity $m_\alpha$. The effective cluster interactions (ECI) $J_\alpha$ are fitted from a rather small set of configurations and their DFT enthalpies. In this way, the enthalpy of any configuration $\sigma$ can be quickly evaluated through equation (1), allowing a fast exploration of the enthalpy as a function of compositions. Here, we use occupational variation on the S/Se sites of the $Im3m$ lattice, keeping the H atoms fixed and fully occupied.

The DFT calculations to fit the ECI are performed with the Vienna Ab initio Simulation Package (VASP) (49–51) within the projector augmented wave (PAW) formalism (52, 53), using the PBE parameterization of the generalized gradient approximation to the exchange correlation functional (54). For the CE, we use $k$-point meshes with about 8000 $k$-points per reciprocal atom together with a plane-wave cutoff energy of 500 eV. The structural relaxations are carried out by taking into account the atomic and cell degrees of freedom until the force components on the atoms are within 0.01 eV/Å, and stresses are within a few kbar. For phases that are predicted to be the ground states from the CE, we refine the enthalpies by performing iterative variable cell shape relaxations until the forces are smaller than 0.002 eV/Å.

Fig. 2 shows the results of our CE of the $S_{x}Se_{1-x}H_3$ system at 200 GPa. Some 170 configurations are used to fit the ECI, giving rise to a very accurate cross-validation score of 10 meV/site. The filled yellow circles denote
the configurations that are evaluated with DFT calculations, while the crosses and squares correspond to the predicted enthalpies from the CE. The convex hull construction shows that configurations at the compositions $S_{0.2}S_{0.8}H_3$, $S_{0.7}S_{0.3}H_3$, and $S_{0.5}S_{0.5}H_3$ are thermodynamically stable, but not at the composition $S_{0.5}S_{0.5}H_3$ explored by Liu et al. (43) (see Supplementary Materials for all ground state structures). However, we find that the lowest energy structure at $S_{0.5}S_{0.5}H_3$ corresponds to the putative ground state determined through the CSP exploration of Liu et al. with $P6_3m$ symmetry, providing additional confidence that the cluster expansion is well converged.

Further CE calculations at 175 and 150 GPa show that additional phases become thermodynamically stable at lower pressures (see Supplementary Materials). In particular, the compositions $S_{0.75}S_{0.25}H_3$ and $S_{0.75}S_{0.25}H_3$ are stable at 150 GPa. However, at no pressure does $S_{0.5}S_{0.5}H_3$ touch the convex hull of stability. Since DFT calculations have shown that a rhombohedral $R3m$ phase of $SH_3$ becomes stable below 150 GPa (36), the CE results for the $Im3m$ parent lattice might not be representative at these pressures. Therefore, all further discussions will be restricted to calculations at 200 GPa.

In addition to the CE calculations, we perform structural searches at 200 GPa using the Minima Hopping Method (MHM) (59, 60) at the three stable compositions. The MHM implements a reliable algorithm to explore the low-lying portions of the enthalpy landscape given the chemical composition. Consecutive, short molecular dynamics (MD) escape trials to overcome enthalpy barriers are followed by local geometry optimizations. The Bell-Evans-Polanyi principle is exploited by aligning the initial MD velocities along soft-mode directions in order to accelerate the search (61, 62). In the past, the MHM has been successfully employed to predict or resolve the structure of a wide class of materials, including superconducting materials at high pressures (15, 63–70). At least two distinct MHM runs are performed at each relevant composition, using both random structures and the ground states from the CE as the initial seeds. We find no structures with lower enthalpies than the ground states predicted through the CE, confirming that we correctly identify the lowest enthalpy structures at the given stoichiometries.

The three ternary phases above are not only stable along the constrained compositions $S_xS_{1-x}H_3$ in the phase diagram, but also with respect to all other competing phases in the S–Se–H system. The complete Gibbs triangle convex hull is shown in Fig. 3, where the formation enthalpies are encoded in a color plot as a function of composition. The yellow line connecting Se$H_3$ and SH$_3$ corresponds to the compositions sampled with the CE. Note that all phases along this line on the complete, three-dimensional convex hull of the S–Se–H system are thermodynamically stable, as indicated by the blue circles.

Among the phases that constitute the convex hull within the CE, $S_{0.7}S_{0.3}H_3$ is exceptional due to several reasons. First, we observe the lowest enthalpy among all phases at this composition. Further, in contrast to both $S_{0.2}S_{0.8}H_3$ and $S_{0.6}S_{0.4}H_3$ which barely touch the convex hull (especially $S_{0.2}S_{0.8}H_3$), $S_{0.7}S_{0.3}H_3$ also denotes the point inflicting the strongest change in the slope of the hull. Second, the enthalpy gap between the ground

![FIG. 3. The Gibbs triangle convex hull of the ternary phase space of H–S–Se at 200 GPa. Large blue and small red circles denote thermodynamically stable and unstable phases, respectively, and grey lines indicate tie lines on the convex hull. The compositional space investigated here with the CE approach is indicated by the yellow line connecting Se$H_3$ and SH$_3$. The structures of the phases SH$_3$ ($Cmca$) and Se$_2$H$_2$ ($C2/m$) are taken from Refs. (17) and (55), respectively. The S and Se sites were substituted in both phases to compute Se$H_2$ and Se$_2$H$_2$, respectively. The elemental reference phases are S in the $\beta$-Po structure type (56), Se in the bcc structure type (57), and the $C2/c$ phase of molecular H$_2$ (58).](image)

![FIG. 4. The ground state structure of $S_{0.7}S_{0.3}H_3$ with $P6_3m$ symmetry from three different perspectives. The small (white) spheres denote the H atoms, while the large yellow (light) and orange (dark) spheres correspond to the S and Se atoms.](image)
state and the next higher enthalpy configuration at that
given composition is especially large, namely 58 meV/f.u.
(here, the chemical formula is \(\text{SSe}_2\text{H}_6\)). In fact, this
enthalpy gap is the largest among all compositions constit-
tuting the convex hull from the CE. These two criteria
are strong evidences that \(\text{S}_{0.3}\text{Se}_{0.7}\text{H}_3\) is thermodynami-
cally particularly stable.

The corresponding ground state structure of
\(\text{S}_{0.3}\text{Se}_{0.7}\text{H}_3\) has \(\text{P}\text{Tm}1\) symmetry and is shown in
Fig. 4. The view along the \(c\)-axis shows that the Se
atoms form a channel-like geometry, surrounding units
of \(\text{SH}_6\) at its center. Each S is surrounded by six H
atoms at the identical distance of 1.386 Å which form
bridges to surrounding Se atoms, S–H···Se. Note that
this S–H bond length is slightly shorter than in pure
\(\text{SH}_3\) (1.491 Å), but is close to the S–H bond in molecular
\(\text{SH}_2\) (1.336 Å). On the other hand, the Se atoms are
surrounded by H atoms with two distinct bond lengths,
namely three with 1.555 Å for the Se–H···Se bonds, and
three with 1.701 Å for the Se–H···S bonds. In comparison,
the Se–H bond length in SeH\(_3\) has an intermediate value of 1.573 Å.

We can explain the particularly high stability of
\(\text{S}_{0.3}\text{Se}_{0.7}\text{H}_3\) in terms of the properties of its electronic
structure. Both \(\text{SH}_3\) and \(\text{SeH}_3\) exhibit a rather high den-
sity of states (DOS) at the Fermi level, \(N_{E_F}\). This high
\(N_{E_F}\) can be attributed to a van Hove singularity in the
DOS very close to the Fermi level, which stems predomi-
nantly from the anti-bonding states of the S–H and Se–H
interactions, respectively, as we see from a COHP analy-
sis using the Lobster package (71–73) (see Supplementary
Materials). Such high occupations of states at the Fermi
level is electronically unfavorable, and lowering the value
of \(N_{E_F}\) can lead to a decrease of the band energy, and
consequently to a lower formation enthalpy. Providing
the additional chemical degree of freedom to the system
by allowing the mixing of S with Se allows a rearrange-
ment of the atoms and their bonds to decrease the value
of \(N_{E_F}\), thereby leading to an improved stability. We
observe exactly this behavior in the \(\text{S}_{0.3}\text{Se}_{1-x}\text{H}_3\) system.
Tab. I lists the normalized values of \(N_{E_F}\) for all relevant
phases, and all ternary compounds exhibit significantly
lower \(N_{E_F}\), reaching a minimum of \(N_{E_F} = 0.038\ \text{eV}^{-1}\)
for \(\text{S}_{0.3}\text{Se}_{0.7}\text{H}_3\).

This change in the electronic structure also affects the
superconducting behavior in \(\text{S}_{x}\text{Se}_{1-x}\text{H}_3\). We assess the
superconducting properties with the Allan-Dynes mod-
dified McMillan’s approximation of the Eliashberg equa-
tion (74). The electron-phonon parameters are computed
within a linear response framework as implemented in
the Quantum Espresso package (75). The values for the
Coulomb pseudopotential \(\mu^*\) is chosen to be 0.10, which
has been shown to give \(T_c\) in good agreement with ex-
periments for hydride superconductors, and a Gaussian
smearing parameter of \(\sigma = 0.03\ \text{Ry}\) is used for the dou-
ble delta integration over the Fermi surface to compute
the electron-phonon interactions. We use norm conserving
pseudopotentials (76) and a plane-wave cutoff energy
of 60 Ry, together with dense \(k\)-point meshes to ensure
convergence of the \(T_c\) values (see Supplemental Materials
for details).

The values of \(\lambda\) and \(\omega_{\text{ph}}\) for all ground states are
listed in Tab. I, including the superconducting transition
temperature estimated within the Allan-Dynes mod-
dified McMillan’s approximation of the Eliashberg equa-
tion (74). Note that for the composition \(\text{S}_{0.6}\text{Se}_{0.4}\text{H}_3\), the
ground state and the first excited state are very close in
enthalpy, merely 6 meV/f.u. apart (i.e., 0.3 meV/atom).
Since both phases are essentially degenerate in enthalpy,
we report here the superconducting properties of only the
one with a smaller unit cell (1 f.u., 20 atoms per cell)

FIG. 5. The electron-phonon properties of the thermody-
namically stable \(\text{S}_x\text{Se}_{1-x}\text{H}_3\) phases. Each panel corresponds
to a specific stoichiometry, with the top part showing the
Eliashberg spectral function \(\alpha^2F\) together with the inte-
grated electron-phonon coupling constant \(\lambda\), and the lower
part showing the partial phonon density of states (PHDOS).
to reduce the computational cost. Overall, the superconducting parameters are in agreement with the values found in the literature for the previously reported phases of SH$_3$ (18) and the metastable phase S$_{0.5}$Se$_{0.5}$H$_3$ (43).

We find that SeH$_3$ has a lower $T_c$ than SH$_3$, a behavior that has been previously attributed to the larger ionic size of Se which leads to a larger electronic screening of the hydrogen vibrations (36). However, the change in $T_c$ as a function of composition does not follow a monotonic interpolation between the values of SeH$_3$ and SH$_3$, as one would rather expect from a virtual crystal approximation (41, 42). Instead, we observe a marked minimum in $T_c$ as we move along the S/Se concentration in S$_x$Se$_{1-x}$H$_3$, with the lowest value for S$_{0.3}$Se$_{0.7}$H$_3$. This trend in $T_c$ is strongly correlated with the value of $N_{E_F}$, which in turn directly affects $\lambda$. Hence, the property that leads to a high thermodynamic stability is essentially responsible for a reduced superconducting transition temperature.

The detailed features of the Eliashberg spectral function $\alpha^2 F(\omega)$, the integrated electron-phonon coupling constant $\lambda$, and the partial phonon density of states (PHDOS) are shown in Fig. 5. As expected, none of the phases exhibit imaginary phonons, and are therefore dynamically stable. Note how the phonon spectra are roughly split in three regions: the low-frequency Se vibrations, the intermediate S vibrations, and the high-frequency H vibrations. All three regions contribute to the electron-phonon coupling in all phases. However, SH$_3$ exhibits a spectral function $\alpha F(\omega)$ with especially strong contributions from all phonons of a rather continuous PHDOS distribution. This unique property of SH$_3$ does not carry over to the ternary mixtures, contributing as a further factor to their reduced $T_c$ values.

In summary, we study the thermodynamic and superconducting properties in the ternary S$_x$Se$_{1-x}$H$_3$ system. We identify three new thermodynamically stable phases at 200 GPa, namely S$_{0.3}$Se$_{0.7}$H$_3$, S$_{0.7}$Se$_{0.3}$H$_3$, and S$_{0.6}$Se$_{0.4}$H$_3$. The particularly high DOS due to a van Hove singularity at the Fermi level of SH$_3$ and SeH$_3$, which strongly contributes to their high superconducting temperature, is significantly reduced for all ternary compounds. We attribute this change of the electronic structure to the additional, chemical degree of freedom that allows for a lowering of $N_{E_F}$. As a consequence, the electron-phonon coupling constant $\lambda$ is reduced as well, leading to lower superconducting transition temperatures. Hence, alloying SH$_3$ with Se might not be a viable route towards new compounds with improved superconducting properties, which essentially disrupts the key factors responsible for its high $T_c$. In fact, similar arguments could be applied to other mixtures with elements Y of the form S$_x$Y$_{1-x}$H$_3$, and the chemical constraint to binary SH$_3$ is essential for the high $T_c$.

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* amsler.max@gmail.com

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