First-principles calculations and thermodynamic modeling of the S-Se system and implications for chalcogenide alloys

Pinwen Guan,^{*a} Shun-Li Shang,^a Greta Lindwall,^{a,†} Tim Anderson,^b and Zi-Kui Liu^a

^a*Department of Materials Science and Engineering, The Pennsylvania State University,
University Park, Pennsylvania 16802, USA.*

^b*Department of Chemical Engineering, University of Florida, Gainesville, Florida 32611, USA*

* Corresponding author.

E-mail address: pxg928@psu.edu

Abstract:

The S-Se system is the key to many chalcogenide alloys. A thermodynamic model of the S–Se system is formulated using an integrated approach of first-principles calculations and the CALculation of PHase Diagram (CALPHAD) method, which is used to predict the vapor-liquid-solid S-Se phase diagram. An existing first-principles approach is modified through considering the contribution from the acoustic Grüneisen parameters to the thermodynamic properties, enabling more accurate prediction of thermodynamic properties of crystals with large unit cells. The approach is applied to all the stable and metastable phases with complex molecule structures within the S-Se system with the exception of an intermediate phase due to its unknown structure. The prediction of the transition temperature between α -S and β -S (428 K) is close to the

[†] Present address: National Institute of Standards and Technology, Gaithersburg, MD 20899

experimental value (369 K). Given the high complexity of solid solutions containing multiple molecular species, two models based on homogeneous and randomly substituted species are constructed and applied to give an interval estimation of solid mixing enthalpies. The CALPHAD approach is applied using both selected experimental measurements and thermodynamic properties predicted by first-principles calculations, reproducing experimental data and predictions reasonably well.

Keywords: First principles, Thermodynamics, Chalcogenide alloys, Theory, Molecular crystal

1. Introduction

There is considerable interest in chalcogenide-based materials for their applications in energy transformation, electronics and other fields. Notable examples include the photovoltaic (PV) absorber material $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ [1-3] and the 2-D transition metal dichalcogenides $\text{Mo}(\text{S},\text{Se})_2$, $\text{W}(\text{S},\text{Se})_2$ and $\text{Sn}(\text{S},\text{Se})_2$ [4, 5]. To synthesize high-quality materials, a thorough understanding of the underlying thermochemistry and phase equilibria would be helpful. The formation of solid solutions between metal sulfides and selenides is key to tuning their properties to achieve optimal performance, rendering the thermodynamics of metal S-Se systems especially important. To this end, the interaction between S and Se should be studied first. The S-Se system also deserves attention on its own merit as S-Se solutions or compounds find application in other fields. For example, selenium sulfides of composition SeS_2 and SeS are used as an antifungal agent in shampoos for the treatment of dandruff and seborrheic dermatitis[6]. In Na-S electrochemical cells, selenium is added to sulfur to reduce viscosity [7]. Interestingly amorphous S-Se alloys behave as p-type semiconductors that have application in optoelectronic and memory switching devices [8].

Surprisingly, a full model describing the thermochemistry and phase equilibria in the S-Se system has not been reported, likely due to both experimental and modeling challenges. Historically, most thermodynamic modeling studies have focused on metallic systems, while the methodology for non-metallic ones is much less developed. In addition, the complex molecular crystal structure exhibited in this system is difficult to model, requiring consideration of van der Waals forces. In the present work, the thermodynamic properties of the S-Se system are computed through developing an efficient and accurate approach based on first-principles calculations that is coupled with experimental data to produce an assessed phase diagram using the CALPHAD (CALculation

of PHase Diagram) method [9, 10]. Available experimental data in the literature are evaluated along with predicted properties using first-principles calculations to produce a thermodynamically consistent description of phase equilibria in the S-Se system.

The properties of elemental S [11] and Se [12] have been critically reviewed. Selected thermodynamic and equilibrium properties of the S-Se system have been measured by several investigators [13-16], however, these data show high uncertainty and inconsistencies. As noted previously, the system has not been assessed and modeled previously.

The first equilibrium measurements were reported by Ringer [13] in 1902. This work suggested the existence of four solid equilibrium phases in the S-Se system: the orthorhombic α phase with space group $Fddd$, the monoclinic β phase (ordered [17] below 198 K with space group $P2_1$ and disordered [17, 18] above 198 K with space group $P2/c$) on the S-rich side, the hexagonal δ phase with space group $P3_121$ on the Se-rich side, and an intermediate X phase with an unknown structure. This investigation also reported information on three invariant reactions: a peritectic reaction (liquid (L) + δ = X) at 160 °C, a eutectic reaction (L = β + X) at 105 °C and a eutectoid reaction (β = α + X) at 75 °C. In 1950, Klemm [14] suggested a similar phase diagram as the one proposed by Ringer [13], although detailed phase boundary data were not provided. In 1973, Nakagawa [15] investigated the liquidus on the Se-rich side, and found good agreement with the work by Ringer [13]. A reinvestigation of the full composition interval was performed by Bector and Kullerud [16] in 1987. The results differed from the previous studies in suggesting that the eutectoid reaction does not occur. In 1996, Sharma and Chang [19] constructed a phase diagram based on all available experimental information with the exception of the work by Bector and Kullerud [16], which the authors did not reference.

Although the type and number of equilibrium solid phases in the S-Se system have not been confirmed, the literature reports agree that the solid α , β and δ phases all are equilibrium phases. The situation in the intermediate composition region, however, is less understood. Sharma and Chang [19] assigned the intermediate region as one phase (they called it “ γ ”, named in the present work as “X” to avoid confusion with the sulfur allotrope, γ -S), yet several different structures have been reported, including but not limited to γ -S with space group $P2_1/c$ [20-23], α -Se with space group $P2_1/n$ [20-23], and β -Se with space group $P2_1/a$ [21]. The γ -S structure was found to form for compositions less than 50 at.% Se, while the α -Se structure was found to form for compositions greater than 50 at.% Se [23]. Whether these structures are stable or metastable is, however, unknown. In the present work, the crystal structure of the X phase is not assumed, and its thermodynamic parameters are determined solely from experimental phase boundary measurements.

The experimental data reported for the invariant reactions in the literature are not in good agreement. For the peritectic reaction ($L + \delta = X$), Ringer [13] reported a temperature of 160 °C and compositions 73.5, 83.0 and 87.0 at.% Se for the L, X and δ phases, respectively. Boctor and Kullerud [16] reported the corresponding values of 168 ± 2 °C and 73.5, 85.0, and 92.0 at.% Se, respectively. Nakagawa [15] measured the electrical conductivity of S-Se samples crystallized below 150 °C and reported that the conductivity decreased sharply when the S content was increased to about 6~7 at.%, suggesting a phase transition [16]. Ringer [13] also investigated the eutectic reaction ($L = \beta + X$) and reported an invariant temperature of 105 °C and compositions of 29.0, 40.0 and 48.7 at.% Se of β , L and X, respectively. The phase diagram measurements by

Klemm [14], however, indicates that the composition of L was lower than 40 at.% Se for this reaction. In addition, Boctor and Kullerud [16] reported a temperature of 102 ± 1 °C and a composition of 35 ± 1 at.% Se of L, which also deviates from Ringer's work [13]. In the case of the eutectoid reaction ($\beta = \alpha + X$), Ringer [13] reported a temperature of 75 °C and compositions of 12.0, 16.5, and 50.0 at.% Se of α , β and X, respectively, whereas the results by Boctor and Kullerud [16] do not show any evidence of the presence of this eutectoid reaction.

In the present work, we assume that α , β , δ and X are the four equilibrium solid phases in accordance with the conclusions drawn by Sharma and Chang [19]. Given the large number of measurements, the eutectic point reported by Boctor and Kullerud [16] is judged to be the most accurate and hence included in this work. The non-existence of the eutectoid reaction suggested by Boctor and Kullerud [16], however, is not accounted for since it is not supported by any of the other studies [13, 14, 19].

2. Methodology

2.1. First-principles calculations

First-principles calculations are used to determine the thermodynamic properties of various structures of pure elements, termed endmembers, as well as to estimate mixing enthalpies. Unfortunately, experimental data for these thermodynamic quantities are not available or incomplete. The calculated endmembers include structures of the α , β and δ phases. Additionally, the α -Se structure (hereafter denoted as α') is also calculated, since there is some experimental data for this phase to validate or correct calculations. In the present work, first-principles calculations are based on the density functional theory (DFT) [24], implemented with the Vienna

Ab-initio Simulation Package (VASP) [25-27]. The general gradient approximation (GGA) for exchange-correlation functional within the framework of the projector augmented wave (PAW) [28, 29] method is applied. Both GGA's of Perdew-Burke-Ernzerhof (PBE) functional [30] and PBEsol [31] are used, along with a dispersion correction using the D3 method [32] to describe the van der Waals force in the S-Se system based on our previous tests [33]. The plane wave energy cutoff is 360 eV for all calculations to ensure good convergence of energy and force according to our tests. The calculated energy converges to less than 5×10^{-7} and 5×10^{-6} eV/atom for each self-consistency step and relaxation of geometric configuration, respectively. Primitive cells of the α , β , δ and α' phases, containing 32, 48, 3 and 32 atoms, respectively, are used for calculations of 0 K properties. The k -point meshes are selected as $3 \times 4 \times 4$ for the α phase, $3 \times 3 \times 3$ for the β phase, $9 \times 9 \times 6$ for the δ phase, and $4 \times 4 \times 3$ for the α' phase. Denser meshes lead to change of the energy less than 10^{-3} eV/atom. The vibrational mode calculation is carried out on one primitive cell for the α , β and α' phases and on a $2 \times 2 \times 2$ supercell for the δ phase, while setting the convergence criterion identical to that used in the static structure calculation. For each direction of each atom, two displacements, ± 0.01 Å, are used to obtain vibrational properties.

The Debye model is often sufficient to estimate the finite temperature thermodynamic properties [34] for many simple solids, but this approach is not appropriate for the S-Se system [33] since it does not account for the internal degrees of freedom within a unit cell. These are needed for these complex molecular crystals. Estimation based on phonon calculations within the quasi-harmonic approximation (QHA) often describes finite temperature properties reasonably well, but is time-consuming, especially for the complex systems of this study. The unit cells of the α , β , and α' phases are quite large (32~48 atoms), and the symmetry is low, leading to a myriad of degrees of

freedom. In the usual phonon calculations, a supercell consisting of multiple unit cells is used. For the S-Se system, this is particularly demanding due to the structural features mentioned above. However, since the unit cells are large, and the interactions between them are attributed to van der Waals forces, it is expected that vibrations of a unit cell are not significantly influenced by the other unit cells. Consequently, it should be sufficient to constrain phonon calculations within one unit cell (i.e. at the Γ point). The three acoustic phonon branches, however, are limited to the Γ point with zero frequencies when one unit cell is used, and the acoustic phonon dispersion cannot be calculated, which introduces considerable error. To obtain the acoustic phonon dispersion, two widely used approaches are the linear dispersion assumption based on the Debye model, as successfully applied to ZrSiO_4 , USiO_4 , $\text{Ca}_5(\text{PO}_4)_3\text{F}$, and $\text{Pb}_5(\text{VO}_4)_3\text{I}$ [35], and the sine wave dispersion assumption based on the Kieffer model [36], as applied to $\text{Mg}_{14}\text{Si}_5\text{O}_{24}$ [37], CaCO_3 [38] and $\text{Al}_4\text{Be}_6\text{Si}_{12}\text{O}_{36}$ [39]. The latter approach is thought to be more accurate than the linear dispersion approach [36], and is adopted in the present work.

Treatment of anharmonicity is another issue. In the framework of QHA, this is usually accomplished by calculating phonons at several (at least five) volumes and fitting. Regardless of efficiency, sometimes this procedure fails, since imaginary frequencies may appear as volume changes. A method based on mode Grüneisen parameters, which represent the volume dependence of vibrational frequencies [37, 40, 41] has been applied to calculate finite temperature properties of silicates. In this method, anharmonicity is taken into account by mode Grüneisen parameters, and only calculations at three volumes are needed. In the applications referenced above, however, only the contribution from the optical Grüneisen parameters to thermal expansion was considered without stating a reason. Ignoring the contribution from the acoustic Grüneisen parameters,

however, will inevitably introduce errors that are not necessarily negligible. Considering the important role of the acoustic Grüneisen parameters, the acoustic contribution is derived and a more complete expression within QHA for the product of thermal expansion and bulk modulus is proposed as follows:

$$\alpha_T B_T = \frac{3k}{V_c} \left(\frac{2}{\pi}\right)^3 \sum_{i=1}^3 \gamma_i \int_0^{x_i} \frac{[\arcsin(x/x_i)]^2}{\sqrt{x_i^2 - x^2}} \frac{x^2 e^x}{(e^x - 1)^2} dx + \frac{k}{V_c} \sum_{i=4}^{3n} \gamma_i \frac{x_i^2 e^{x_i}}{(e^{x_i} - 1)^2} \quad (1)$$

where

$$x_i = \frac{\hbar \omega_i}{kT} \quad (2)$$

In the above expressions, α_T is the volume thermal expansion coefficient, B_T the bulk modulus, k the Boltzmann constant, V_c the volume of a unit cell, γ_i the mode Grüneisen parameter, n the number of atoms in a unit cell, and ω_i the vibrational frequency. On the right side of (1), the first term is related to the acoustic Grüneisen parameters, and the second term is related to the optical Grüneisen parameters. It is stressed that the inclusion of the contribution from the acoustic Grüneisen parameters is not only for theoretical completeness, but also has practical value. Neglecting the acoustic Grüneisen parameters leads to underestimation of the thermal expansion that produces further errors in other finite temperature properties.

The temperature-dependent bulk modulus can be calculated knowing its value at 0 K and its temperature derivative expressed as [40]:

$$\left(\frac{\partial B}{\partial T}\right)_p = -\alpha B^\infty (B' - q^{ht} + 1) \quad (3)$$

where αB^∞ is the limit of $\alpha_T B_T$ as T approaches infinity. Furthermore,

$$q^{ht} = \frac{\partial \ln \bar{\gamma}}{\partial \ln V} \quad (4)$$

$$\text{where } \bar{\gamma} = \frac{\sum_{i=1}^{3n} \gamma_i}{3n} \quad (5)$$

It is noted that the parameter q^{ht} , which describes the volume dependence of the macroscopic Grüneisen parameter at high temperature, cannot be reliably calculated from first-principles for the present system, possibly due to the inherent limitation of the D3 correction. For most solids, the value of q^{ht} lies between 1 and 2, and is largely dependent on the crystal structure [42-44]. Fortunately, such variation in q^{ht} will have only minor influence on the thermodynamic properties since q^{ht} is a high order effect of anharmonicity. For α , β and α' , we simply assign $q^{\text{ht}}=1$, which is close to the value calculated for 3D van der Waals crystals [45]. The δ phase consists of molecular chains and is treated as 2D van der Waals crystals. Thus 1.5 is a more appropriate value for q^{ht} (see details in Appendix). Knowing the temperature-dependent thermal expansion and bulk modulus, other finite temperature properties, such as entropy and enthalpy, can be deduced in the QHA framework (see details in Appendix).

The β -S phase consists of six molecules in one unit cell, each with two possible orientations. It was reported that there is an order-disorder transition at about 198 K [17, 18, 46]. The ordered phase at low temperature, denoted by β_1 in the present work, contains neighboring molecules in different orientations. In the disordered phase, two of six molecules are randomly oriented. Similar to our recent partition function approach [47], the disordered phase is considered to be a mixture of two ordered microstates, β_1 and β_2 . In β_2 , the orientations of neighboring molecules are the same. To further simplify this case, it is assumed that the β_1 and β_2 microstates have equal probability of existing, since the temperature range in which β -S is stable is well above the order-disorder transition temperature of 198 K [11]. Assuming ideal mixing, the Gibbs energy of the disordered phase can be written as:

$$G^\beta = \frac{G^{\beta 1} + G^{\beta 2}}{2} - TS_c \quad (6)$$

Here, $S_c = (R/24) \ln 2$ is the configurational entropy caused by disorder [46] due to the 2-fold disorder of 2 molecules in the 48-atom unit cell. Given the Gibbs energy, G^β , the thermal properties of the disordered phase can be calculated from those of the ordered phases.

2.2. CALPHAD modeling

The CALPHAD method uses thermochemical data and phase equilibrium information subject to the phase equilibrium constraints to estimate the optimal set of parameters describing the Gibbs energy of each individual phase in a thermodynamic system. In the present system, the Gibbs energy of the pure component end-members, α -S, β -S and δ -Se, are represented by the same expressions as developed and recommended by the Scientific Group Thermodata Europe (SGTE) [48]. To describe the Gibbs energy of the pure elements in phases that are not available in the SGTE database, the following approximate function is used:

$${}^0G_i^\varphi = {}^0G_i^\theta + a_i^\varphi + b_i^\varphi T + c_i^\varphi T \ln T + d_i^\varphi T^2 \quad (7)$$

Here, φ indicates a specific phase (α , β , δ or X), i represents an element (i.e. S or Se), and ${}^0G_i^\theta$ is the Gibbs energy of the stable phase at room temperature, namely, $\theta = \alpha$ for S and $\theta = \delta$ for Se. Using first-principles calculations, the Gibbs energy of a phase with respect to that of the stable phase can be obtained and used to evaluate the parameters in Eq. (7).

The one-sublattice model treats one atomic position as one site and is used for all random solution phases, since all sites have a similar chemical environment. Another way to construct a sublattice model is to treat the position of one molecule as one site. This would, however, require

multiple species to account for all the different possibilities and thus is not adopted in the present work. The Gibbs energy of each solution phase (α , β , δ , X and liquid) is described by:

$$G_m^\varphi = x_S {}^0G_S^\varphi + x_{Se} {}^0G_{Se}^\varphi + RT(x_S \ln x_S + x_{Se} \ln x_{Se}) + {}^{xs}G^\varphi \quad (8)$$

The first two terms are simply the Gibbs energy of the pure elements in amounts proportional to the mixture composition prior to mixing and the third term accounts for the entropy of mixing the pure the elements to form an ideal solution. The last term, ${}^{xs}G^\varphi$, captures the excess Gibbs energy, which is described functionally by the Redlich–Kister polynomial [49]:

$${}^{xs}G^\varphi = x_S x_{Se} \sum_{k=0} {}^kL_{S,Se} (x_S - x_{Se})^k \quad (9)$$

The coefficient ${}^kL_{S,Se} = {}^kA + {}^kBT$ describes the non-ideal interaction between S and Se, where kA and kB are model parameters. These model parameters are estimated by optimizing selected experimental thermochemical and phase equilibrium data as well as incorporating the thermodynamic property values suggested by the present first-principles calculations. The optimization is carried out using the PARROT module of the Thermo-Calc software [50].

The gas phase is described by an ideal substitutional model with the molar Gibbs energy given as

$$G_m^{gas} = \sum_i y_i {}^0G_i + RT \sum_i y_i \ln y_i + RT \ln \frac{P}{P_0} \quad (10)$$

where 0G_i is the Gibbs energy of the individual constituents, i the constituents (S, S₂, S₃, S₄, S₅, S₆, S₇, S₈, Se, Se₂, Se₃, Se₄, Se₅, Se₆, Se₇, Se₈, and SSe), P the total pressure and the P_0 the standard pressure, 1 bar. 0G_i is taken from the available data in the SGTE database [48]. It is possible that there are the other species in the gas phase, but including all of them is out of the scope of the present work.

3. Results and discussion

3.1. First-principles calculations

The results of first-principles calculations of the pure elements at 0 K are listed in Table 1. The properties for each phase include energy (the stable phase at 0 K is set as the reference state), volume, bulk modulus (B) and its pressure derivative (B'). Where available, experimental information is included in the table for comparison. It is seen that the different DFT functionals lead to different results and the functional that best represents the experimental data is different for each element.

For sulfur, PBEsol+D3 represents the experimental data better than PBE+D3. As an example, PBE+D3 predicts a negligible energy difference between α -S and β -S, just 15.7 J/mol (considering the accuracy of the present DFT calculations, 0.1 kJ/mol, this number is essentially 0), while the experimental transition enthalpy is about 400 J/mol or even larger [51-53]. The transition enthalpy does not differ considerably from 0 K energy difference, thus it can be concluded that PBE+D3 seriously underestimates the stability of α -S with respect to β -S. In contrast, PBEsol+D3 predicts an energy difference of 0.4 kJ/mol, agreeing well with experiment. Moreover, PBE+D3 incorrectly predicts α' -S to be the stable phase of sulfur at 0 K with energy of -18.3 J/mol compared to α -S. Again, this minor difference is beyond the accuracy of the present DFT calculations, though it is clear that PBE+D3 predicts that α -S has almost no stability compared to α' -S. As for volume, both methods have acceptable accuracy. It is noted that PBEsol+D3 tends to underestimate volume while PBE+D3 tends to overestimate volume. Related to such tendency, the bulk modulus of α -S is predicted to be 5.804 and 12.242 GPa by PBE+D3 and PBEsol+D3, respectively. Most of the corresponding experimental values are in the range of 7~10 GPa (at room temperature) [54-57].

Considering temperature effects, it is concluded that PBEsol+D3 gives a fairly good prediction while PBE+D3 does not. Finally, the pressure derivative of the bulk modulus predicted by PBEsol+D3 is 8.123, closer to the experimental measurements (5.433~8.324) [54, 55, 57] than the value predicted using PBE+D3, i.e. 11.403. This conclusion is consistent with previous observations [33], where PBEsol+D3 was determined to be the better X-C functional to compute the thermodynamic properties of α -S.

In contrast to pure sulfur, the better functional for prediction of the thermochemical properties of pure selenium was the opposite, PBE+D3. PBEsol+D3 predicts very large energy differences between δ -Se and the other selenium phases. For example, it yields an energy difference of 8.6 kJ/mol between δ -Se and α' -Se, which is much higher than the experimental transition enthalpies, especially the two most recent values (1200 and 2100 J/mol) [58-60]. PBE+D3 predicts a corresponding value of 3.0 kJ/mol. As for volume, PBE+D3 performs quite well, while PBEsol+D3 underestimates volume severely, by -13.1% and -10.4% for δ -Se and α' -Se, respectively. Moreover, PBEsol+D3 overestimates the bulk modulus of δ -Se, predicting a value of 34.163 GPa, which is significantly outside the experimental range (about 7~15 GPa) [54, 55, 61], while PBE+D3 predicts a much more agreeable value, 14.359 GPa. It appears that the main reason for the large error when calculating the selenium phases with PBEsol+D3 is that PBEsol+D3 overbinds δ -Se severely.

Since PBE+D3 incorrectly predicts the stable phase of sulfur at 0 K (Table 1), PBEsol+D3 was employed for the continued study. Available experimental data were used to correct the calculation

results for the selenium phases using PBEsol+D3, thus relieving the overbinding problem, which is discussed later.

Solid solutions in the S-Se system are very complex. They consist of molecules, which may contain both sulfur and selenium of different ratios [23, 62-68]. The interactions within and between the molecules are also very different, being covalent bonds or van der Waals force. Three phases, α , β and α' , contain molecular (S, Se)₈ rings. Each ring contains eight atom sites and is crown-shape. Each atom site can be occupied by either sulfur or selenium, leading to 30 ring configurations [66]. A strict treatment would take all 30 species as constituents of this system. Calculations for such a large system, however, are beyond the scope of the present work and hence, it is necessary to look for an approximation. From Raman and NMR spectroscopic experiments, it was found that within a molecule, the same kind of atoms tend to neighbor each other [64, 67]. The reason for this is that the homonuclear bonds (S-S, Se-Se) are energetically more favorable (~ 7.4 kJ per mole pair of a S-S bond and a Se-Se bond) than the heteronuclear bonds (S-Se), as supported by several computational studies [69-71]. As temperature increases, of course, ordering of the sulfur and selenium atoms becomes more random, increasing the entropy. Relative population of different species depends on three factors: intra-molecule covalent bonds, inter-molecule van der Waals forces, and entropy. To bound the Gibbs energy, the homo-species model and the random solid solution model are constructed for DFT calculations to describe the low and high temperature behavior of solid solutions, respectively.

The homo-species model consists of only two species, S₈ and Se₈, thus there are no heteronuclear bonds. Although this model has the van der Waals energy penalty imposed by size mismatch

between S_8 and Se_8 , it is plausible since the covalent bond is considerably stronger than the van der Waals forces. In the random solid solution model, each atom site is randomly occupied by sulfur or selenium to achieve maximum entropy. It is expected that the real situation should be between these two models. Consequently, by applying both models, an estimation of the mixing enthalpy bounds for a given composition (in terms of selenium concentration) can be obtained. When temperature increases, the mixing enthalpies should approach the random values, since the degree of disorder increases.

The success in calculating 0 K properties discussed above gives confidence in calculating thermodynamic quantities. Fig. 1 shows the finite temperature properties (heat capacity at constant pressure, C_p , thermal expansion coefficient (TEC), entropy, enthalpy, and Gibbs energy) of the elemental phases α -S, β -S, δ -Se and α' -Se using DFT. The calculated results for the α -S phase are compared with SGTE data [48] and other experimental data [72, 73]. The calculated temperature dependence of C_p , entropy, enthalpy and Gibbs energy are each in excellent agreement with experiment [48, 72]. The agreement for TEC [73] in the low-temperature range is also good, but deviates in the high-temperature range (above 300 K, note that the melting temperature of sulfur is 388 K). This is partially attributed to the invalidity of QHA near the melting temperature where atoms can move away significantly from their equilibrium positions. The same calculations are also performed for β -S, which is a disordered phase and treated as a mixture between two ordered structures in this study. Again, the agreement with experiment [48, 72] is good, noting that a comparison of TEC is absent due to the lack of experimental data.

Using the calculated finite temperature properties of α -S and β -S, the Gibbs energy difference between these two phases is obtained and plotted in Fig. 2. The α -S $\rightarrow\beta$ -S transition temperature is predicted to be 428 K, which is reasonably close to the experimental value, 369 K [74]. The deviation may be partly due to the approximation made when calculating the properties of β -S, i.e., the β_1 and β_2 microstates have equal probability of existing. To the best of our knowledge, such a prediction has no successful precedents, although sulfur is a common and important element in the everyday life of human beings.

As previously mentioned, application of the DFT functional PBEsol+D3 has the problem of overbinding δ -Se. This affects not only the 0 K properties (e.g. overestimating the binding energy of δ -Se), but also the finite temperature properties. Fig. 1 shows the calculated finite temperature properties of δ -Se. The calculated values for C_p are in good agreement with experiment [12, 48] below 400 K. However, above this temperature the disagreement is not negligible, with the calculated values being smaller than the experimental observations. This is not surprising since the TEC is also seriously underestimated [73] and that C_p is dependent on TEC. The agreement is better for entropy, enthalpy, and Gibbs energy [48], but small deviation is observable at higher temperature. A substantial improvement requires a DFT functional that can describe δ -Se well, which is beyond the scope of the present work.

Also shown in Fig. 1 is the calculated finite temperature properties of α' -Se. C_p and entropy are in good agreement with experiments whereas the enthalpy and Gibbs energy show large systematic errors [12]. The main source of the disagreement is the overestimation of the enthalpy at 0 K. Note that the reference state is the most stable phase at 0 K, δ -Se, thus this overestimation comes from

the problem of overbinding δ -Se. In fact, for α' -Se itself, C_p and entropy, for which δ -Se does not need to be used as reference state, are both well reproduced. This suggests that this phase can be well described by the present methodology. The systematic errors can be corrected by requiring match to experimental data [12]. The quantity used for this correction is the difference between Gibbs energies of δ -Se and α' -Se, $\Delta G = {}^0G_{Se}^{\delta} - {}^0G_{Se}^{\alpha'}$, which is calculated from DFT and experiment [12] respectively. The correction term is (to reduce round-off error, the significant figures in the following expression are beyond the accuracy of both the experiment and the DFT calculation)

$$\widetilde{{}^0G_{Se}^{\delta}} - {}^0G_{Se}^{\delta} \equiv G_{cor} = \Delta G(\text{exp}) - \Delta G(\text{DFT}) = 6413.525 - 1.989T \quad (10)$$

where $\widetilde{{}^0G_{Se}^{\delta}}$ and ${}^0G_{Se}^{\delta}$ are the corrected and uncorrected Gibbs energies (in J/mol) of δ -Se, respectively, and T is the temperature (in K). The correction term is taken as a linear function determined by two data points at 298 K and 420 K which is the highest temperature studied for α' -Se in the experiments [12].

The δ -S, α' -S and β -Se phases are metastable, and thus their properties have not been measured. Their calculated finite temperature properties are listed in Fig. 3. In addition, the α -Se phase is unstable and cannot be treated within the framework of QHA. Thus, its finite temperature properties are not calculated with DFT in the present work. There is overall consistency between the first-principles predictions and the results of the CALPHAD modeling presented in the next section after the above described correction is made to the Gibbs energy of δ -Se, which demonstrates the usefulness of *ab initio* thermodynamic approach for metastable phases.

In summary, it is concluded that the present first-principles calculations of finite temperature properties, based on the proposed approach, are successful for the S-Se system. Not only properties of individual phases are well reproduced, but also the relationship between different phases is described with satisfactory accuracy, as illustrated for the α -S $\rightarrow\beta$ -S transition temperature. While necessary for the thermodynamic modeling of the S-Se system, using first principles calculations to suggest thermodynamic properties that describe phase equilibria is not trivial due to the subtle energetics in this complex crystal system.

3.2. Thermodynamic modeling

Table 2 summarizes the evaluated parameters used to describe the Gibbs energy of the pure components that were fixed using the calculated finite temperature properties (i.e. phases other than the reference phases and unstable X phase). The corrected parameters based on Eq. (10) are also listed. The interaction parameters were evaluated using the available phase boundary measurements [13, 15, 16] along with estimations for mixing enthalpies from application of DFT. Using the parameters shown in Table 3, the assessed low temperature phase diagram was calculated (Fig. 4). As shown in this figure between 298 and 500 K at 1 bar, the experimental phase boundary data show some scatter, however, the general agreement between the calculated phase diagram and experimental data is evident. The peritectic reaction temperature predicted by this assessment is 433.1 K, which is in excellent agreement with the value observed by Ringer [13] (433.16 K). The predicted eutectic reaction temperature, 372.3 K, is slightly lower than the values reported by Ringer [13] (378.16 K) and by Boctor and Kullerud [16] (375.16 ± 1 K). The predicted eutectoid reaction temperature, 337.7 K, is lower than that observed by Ringer [13] (348.16 K).

Comparing the three invariant reaction temperatures, the discrepancy on eutectoid reaction temperature is relatively large. It was not possible to satisfactorily reproduce the other data in addition to this reaction without over parameterizing. Sluggish solid state reaction kinetics at lower temperature can obfuscate measurements. Moreover, the existence of this eutectoid reaction needs further experimental verification [16]. The phase diagram in the lower plot in Fig. 4 spans the temperature range 298 to 1300 K at 1 bar, revealing the gas phase at higher temperatures. Due to possible incompleteness of species considered (for species containing both sulfur and selenium atoms, only SSe is considered), the modeling of the gas phase may deviate from reality to some extent. In addition, experimental data for the phase equilibria between the mixed S-Se gas and liquid/solid is lacking. Thus, more works are needed to elucidate the thermodynamics of the mixed S-Se gas. However, as long as the temperature is sufficiently high, the present description of the gas phase should be accurate, since the small SSe molecules are dominant among the mixed S-Se species. The present assessment indicates a congruent volatilization temperature at 1029 K and composition 76 at.% Se at 1 bar, which is suitable for experimental verification as well as evaluating the accuracy of the present description of the gas phase.

Fig. 5 shows the pressure-temperature diagram of the S-Se system at 25 at.% Se, 50 at.% Se and 75 at.% Se. According these diagrams, it is found that when the pressure is relatively high, the solid phase transforms into the liquid phase and then into the gas phase with increasing temperature. When the pressure is relatively low, the liquid phase disappears and the solid phase sublimates into the gas directly. For the composition 25 at.% Se and 50 at.% Se, the transformation from the liquid to the gas is accompanied by the gradual temperature change, while for the composition 75 at.% Se, the temperature is almost unchanged during the transformation, indicating a congruent volatilization, in consistence with the previous observation from the temperature-

composition diagram. In addition, the congruent volatilization temperature decreases when the pressure gets lower.

Fig. 6 shows the enthalpy of mixing S and Se as a function of composition for each of the four phases considered in the present work. As expected, the mixing enthalpy for the α phase from CALPHAD modeling is approximately bounded by the values from the homo-species model and the random solid solution model. In addition, the homo-species model is closer to the CALPHAD modeling result than the random solid solution model, suggesting a low degree of disorder. For the β phase, the mixing enthalpy from the CALPHAD assessment is very close to that from the random solid solution model, but quite different from the homo-species model, suggesting a high degree of disorder in this phase. This is probably because of the narrow stability range of the β phase at temperatures near the melting temperature. For the δ phase, the enthalpy of mixing from the CALPHAD modeling, the homo-species model and the random solid solution model are close to each other, which is quite different compared with phases consisting of molecular rings. In addition, the δ phase has the highest mixing enthalpy among all the phases considered in the present work. For the liquid phase, excellent agreement with the experimental data [75] is evident using a simple substitutional solution model. This is somewhat unexpected since it seems reasonable to assume that molecular species should be found in the liquid due to the complex crystallographic aspect of the solid phase structures as well as their physical-chemical build up as discussed above. However, the suitability of the simple substitutional solution model may be due to the fact that the two elements are next to each other in the same column in the periodic table, resulting in similar bonding energies in various complex clusters.

The formation enthalpy and entropy at 298 K at 1 bar are shown in Fig. 7. The reference states are the α -S and δ -Se at the same conditions. When the Se content increases, the system undergoes transitions as $\alpha \rightarrow \alpha + X \rightarrow X \rightarrow X + \delta \rightarrow \delta$, which are reflected by the kinks of the formation enthalpy and entropy. The formation enthalpy and Gibbs energy can be measured in experiments and compared with the calculated results in the present work.

4. Conclusions

The thermodynamic properties of solid phases in the S-Se system (except the X phase due to its unknown crystal structure) at finite temperatures have been predicted by first-principles calculations with the vibrational properties obtained by a modified approach that includes both acoustic and optical contributions. The accuracy of this new approach is demonstrated. The Gibbs energy function of each phase is modeled, enabling calculation of a phase diagram that is in agreement with experimental data using a minimal number of model parameters. It is expected that the methodology in the present work can be applied to other complex crystal systems, and the resulted model will make significant contribution to understanding the thermodynamics of the chalcogenide alloys.

Acknowledgements

This work was financially supported by NSF with Grant Nos. CHE-1230924 and CHE-1230929. First-principles calculations were carried out on the LION clusters at the Pennsylvania State University. Calculations were also carried out on the CyberStar cluster funded by the NSF through Grant No. OCI-0821527.

Appendix: details of calculation for finite temperature properties

Within the quasi-harmonic approximation (QHA), finite temperature properties are determined by phonon density of states (DOS). In the present work, phonons are separated into the acoustic and optical branches. The three acoustic branches are assumed to have a sine wave dispersion, following the Kieffer model [36]. The maximum frequency of each acoustic branch is calculated from the sound velocity, using the following equation [36]:

$$\omega_i = 4v_i \left(\frac{3}{4\pi V_c} \right)^{\frac{1}{3}} \quad (10)$$

In the above equation, ω_i is the maximum angular frequency of an acoustic branch, v_i the sound velocity, and V_c the volume of one unit cell.

The sound velocity is calculated by [37, 76]:

$$v_1 = v_2 = \bar{v}_s = \sqrt{\frac{G_H}{\rho}} \quad (11)$$

$$v_3 = \bar{v}_l = \sqrt{\frac{K_H + \frac{4}{3}G_H}{\rho}} \quad (12)$$

where

$$K_H = \frac{1}{2}(K_R + K_V) \quad (13)$$

$$G_H = \frac{1}{2}(G_R + G_V) \quad (14)$$

$$K_R = \frac{1}{s_{11} + s_{22} + s_{33} + 2(s_{12} + s_{23} + s_{13})} \quad (15)$$

$$K_V = \frac{c_{11} + c_{22} + c_{33} + 2(c_{12} + c_{23} + c_{13})}{9} \quad (16)$$

$$G_R = \frac{15}{4(s_{11} + s_{22} + s_{33}) - 4(s_{12} + s_{23} + s_{13}) + 3(s_{44} + s_{55} + s_{66})} \quad (17)$$

and

$$G_V = \frac{c_{11} + c_{22} + c_{33} - (c_{12} + c_{23} + c_{13}) + 3(c_{44} + c_{55} + c_{66})}{15} \quad (18)$$

Here, $\bar{v}_s$ is the average shear sound velocity, $\bar{v}_l$ is the average longitudinal sound velocity, ρ is the density, c_{ij} are the elastic constants, and s_{ij} are the compliances.

The optical phonon branches are approximated by vibration modes, since the large unit cell and the weak van der Waals force lead to weak coupling between atoms in different unit cells. Elastic constants and optic vibration frequencies are calculated using VASP directly. With values for these frequencies, finite temperature properties are calculated within QHA. In the present work, an expression is proposed for the product of the thermal expansion and bulk modulus as shown Eq. (1) in the main text. Then, finite temperature properties are then calculated with Eq. (2), (3), and (4) in the main text and the following equations [37]:

$$C_V = \frac{3R}{n} \left(\frac{2}{\pi}\right)^3 \sum_{i=1}^3 \int_0^{x_i} \frac{[\arcsin(x/x_i)]^2}{\sqrt{x_i^2 - x^2}} \frac{x^2 e^x}{(e^x - 1)^2} dx + \frac{R}{n} \sum_{i=4}^{3n} \frac{x_i^2 e^{x_i}}{(e^{x_i} - 1)^2} \quad (19)$$

$$C_p = C_V + T \alpha_T^2 B_T V_T \quad (20)$$

$$S_T = \frac{3R}{n} \left(\frac{2}{\pi}\right)^3 \sum_{i=1}^3 \int_0^{x_i} \frac{[\arcsin(x/x_i)]^2}{\sqrt{x_i^2 - x^2}} \left[\frac{x}{e^x - 1} - \ln(1 - e^{-x}) \right] dx + \frac{R}{n} \sum_{i=4}^{3n} \left[\frac{x_i}{e^{x_i} - 1} - \ln(1 - e^{-x_i}) \right] + \frac{R}{n} \ln Q_e + \int_0^T \alpha_T^2 B_T V_T dT' \quad (21)$$

$$H_T = E_0 + \frac{3RT}{n} \left(\frac{2}{\pi}\right)^3 \sum_{i=1}^3 \int_0^{x_i} \frac{[\arcsin(x/x_i)]^2}{\sqrt{x_i^2 - x^2}} x \left(\frac{1}{e^x - 1} + \frac{1}{2} \right) dx + \frac{RT}{n} \sum_{i=4}^{3n} x_i \left[\frac{1}{e^{x_i} - 1} + \frac{1}{2} \right] + \int_0^T T' \alpha_T^2 B_T V_T dT' \quad (22)$$

$$G_T = H_T - TS_T \quad (23)$$

In the above equations, αB^∞ is the limit of $\alpha_T B_T$ as T approaches infinity, R the gas constant, C_V the molar specific heat capacity at constant volume, C_p the molar specific heat capacity at constant pressure, $\frac{R}{n} \ln Q_e$ the electronic contribution to entropy (here equal to 0), and S_T the entropy, H_T the enthalpy, and G_T the Gibbs energy at temperature T.

As mentioned in the main text, for the S-Se system, q^{ht} cannot be reliably calculated based on the present functionals, thus requiring approximation. The three phases, α , β , and α' , are formed by 3D stacking of molecular rings, and approximated as 3D van der Waals crystals with $q^{ht} \approx 1$, which is close to the value calculated for rare-gas crystals using an intermolecular potential [45]. The

other phase, δ , is formed by 2D arrangement of molecular chains, and approximated as 2D van der Waals crystals. With the other factors fixed, there is a correspondence between q^{ht} and dimensionality. For 3D solids, $V \propto a^3$, $q^{ht} = \frac{\partial \ln \bar{y}}{\partial \ln V} = \frac{1}{3} \frac{\partial \ln \bar{y}}{\partial \ln a}$ (a is the lattice parameter). For 2D solids, $V \propto a^2$, $q^{ht} = \frac{\partial \ln \bar{y}}{\partial \ln V} = \frac{1}{2} \frac{\partial \ln \bar{y}}{\partial \ln a}$. Thus, $q^{ht}(2D) = 1.5 q^{ht}(3D)$. To be consistent with the other phases, $q^{ht} \approx 1.5$ is used for the δ phase.

References

- [1] W. Wang, M.T. Winkler, O. Gunawan, T. Gokmen, T.K. Todorov, Y. Zhu, D.B. Mitzi, Device characteristics of CZTSSe thin-film solar cells with 12.6% efficiency, *Advanced Energy Materials*, 4 (2014) 1301465.
- [2] S. Chen, A. Walsh, J.H. Yang, X.G. Gong, L. Sun, P.X. Yang, J.H. Chu, S.H. Wei, Compositional dependence of structural and electronic properties of $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ alloys for thin film solar cells, *Phys Rev B*, 83 (2011) 125201.
- [3] H. Katagiri, K. Jimbo, S. Yamada, T. Kamimura, W.S. Maw, T. Fukano, T. Ito, T. Motohiro, Enhanced conversion efficiencies of $\text{Cu}_2\text{ZnSnS}_4$ -based thin film solar cells by using preferential etching technique, *Applied Physics Express*, 1 (2008) 041201.
- [4] M. Chhowalla, H.S. Shin, G. Eda, L.J. Li, K.P. Loh, H. Zhang, The chemistry of two-dimensional layered transition metal dichalcogenide nanosheets, *Nature Chemistry*, 5 (2013) 263-275.
- [5] D. Jariwala, V.K. Sangwan, L.J. Lauhon, T.J. Marks, M.C. Hersam, Emerging device applications for semiconducting two-dimensional transition metal dichalcogenides, *ACS Nano*, 8 (2014) 1102-1120.
- [6] E.J. Matson, Selenium sulfide as an antidandruff agent, *J Cosmet Sci*, 7 (1956) 459-466.
- [7] V. Berbenni, A. Marini, V. Massarotti, D. Capsoni, A DSC characterization of sulfur selenium interaction phenomenology, *Thermochim Acta*, 237 (1994) 253-260.
- [8] K.D. Machado, D.F. Sanchez, G.A. Maciel, S.F. Brunatto, A.S. Mangrich, S.F. Stolf, Vibrational, optical and structural studies of an amorphous $\text{Se}_{0.90}\text{S}_{0.10}$ alloy produced by mechanical alloying, *J Phys-condens Mat*, 21 (2009) 195406.
- [9] L. Kaufman, The lattice stability of metals. 1. Titanium and zirconium, *Acta Metallurgica*, 7 (1959) 575-587.
- [10] Z.K. Liu, First-Principles Calculations and CALPHAD Modeling of Thermodynamics, *J. Phase Equilib. Diff.*, 30 (2009) 517-534.
- [11] R. Steudel, B. Eckert, Solid sulfur allotropes, in: R. Steudel (Ed.) *Elemental sulfur and sulfur-rich compounds I*, 2003, pp. 1-79.
- [12] U. Gaur, H.C. Shu, A. Mehta, B. Wunderlich, Heat capacity and other thermodynamic properties of linear macromolecules. 1. Selenium, *J Phys Chem Ref Data*, 10 (1981) 89-117.
- [13] W.E. Ringer, Mixed crystals of sulphur and selenium, *Zeitschrift Fur Anorganische Chemie*, 32 (1902) 183-218.
- [14] W. Klemm, Einige probleme aus der physik und der chemie der halbmatalle und der metalmatalle, *Angewandte Chemie*, 62 (1950) 132-142.
- [15] T. Nakagawa, The physico-chemical properties of the Se-S crystals, *Nippon Kagaku Kaishi*, (1973) 1822-1826.
- [16] N.Z. Boctor, G. Kullerud, Phase-relations and equilibrium copolymerization in the Se-S system, *J Solid State Chem*, 71 (1987) 513-521.
- [17] L.M. Goldsmith, C.E. Strouse, Molecular dynamics in solid state: the order-disorder transition of monoclinic sulfur, *J Am Chem Soc*, 99 (1977) 7580-7589.
- [18] L.K. Templeton, D.H. Templeton, A. Zalkin, Crystal structure of monoclinic sulfur, *Inorg Chem*, 15 (1976) 1999-2001.
- [19] R.C. Sharma, Y.A. Chang, The S-Se (sulfur-selenium) system, *J Phase Equilib*, 17 (1996) 148-150.

- [20] J.E. Fergusson, G.M. Pratt, G.A. Rodley, C.J. Wilkins, Selenium-sulphur solid solutions, *Journal of Inorganic & Nuclear Chemistry*, 24 (1962) 157.
- [21] Y.M. Dehaan, M.P. Visser, Structures of sulfur-selenium mixtures, *Acta Crystallographica*, 13 (1960) 1023-1023.
- [22] R. Laitinen, L. Niinisto, R. Steudel, Structural studies on the sulfur selenium binary-system, *Acta Chem Scand*, A33 (1979) 737-747.
- [23] R. Steudel, Cyclic selenium sulfides, *Top Curr Chem*, 102 (1982) 177-197.
- [24] W. Kohn, L.J. Sham, Self-consistent equations including exchange and correlation effects, *Physical Review*, 140 (1965) 1133-1138.
- [25] G. Kresse, J. Furthmuller, Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set, *Phys Rev B*, 54 (1996) 11169-11186.
- [26] G. Kresse, J. Furthmuller, Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set, *Comp Mater Sci*, 6 (1996) 15-50.
- [27] G. Kresse, J. Hafner, Abinitio molecular-dynamics for liquid-metals, *Phys Rev B*, 47 (1993) 558-561.
- [28] P.E. Blochl, Projector augmented-wave method, *Phys Rev B*, 50 (1994) 17953-17979.
- [29] G. Kresse, D. Joubert, From ultrasoft pseudopotentials to the projector augmented-wave method, *Phys Rev B*, 59 (1999) 1758-1775.
- [30] J.P. Perdew, K. Burke, M. Ernzerhof, Generalized gradient approximation made simple, *Phys Rev Lett*, 77 (1996) 3865-3868.
- [31] J.P. Perdew, A. Ruzsinszky, G.I. Csonka, O.A. Vydrov, G.E. Scuseria, L.A. Constantin, X. Zhou, K. Burke, Restoring the density-gradient expansion for exchange in solids and surfaces, *Phys Rev Lett*, 100 (2008) 136406.
- [32] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu, *J Chem Phys*, 132 (2010) 154104.
- [33] S.L. Shang, Y. Wang, P. Guan, W.Y. Wang, H. Fang, T. Anderson, Z.K. Liu, Insight into structural, elastic, phonon, and thermodynamic properties of alpha-sulfur and energy-related sulfides: a comprehensive first-principles study, *Journal of Materials Chemistry A*, 3 (2015) 8002-8014.
- [34] S.L. Shang, Y. Wang, D.E. Kim, Z.K. Liu, First-principles thermodynamics from phonon and Debye model: Application to Ni and Ni₃Al, *Comp Mater Sci*, 47 (2010) 1040-1048.
- [35] J.L. Fleche, Thermodynamical functions for crystals with large unit cells such as zircon, coffinite, fluorapatite, and iodoapatite from ab initio calculations, *Phys Rev B*, 65 (2002).
- [36] S.W. Kieffer, Thermodynamics and lattice-vibrations of minerals. 3. Lattice-dynamics and an approximation for minerals with application to simple substances and framework silicates, *Rev Geophys*, 17 (1979) 35-59.
- [37] G. Ottonello, B. Civalleri, J. Ganguly, W.F. Perger, D. Belmonte, M.V. Zuccolini, Thermochemical and thermo-physical properties of the high-pressure phase anhydrous B (Mg₁₄Si₅O₂₄): an ab-initio all-electron investigation, *Am Mineral*, 95 (2010) 563-573.
- [38] C.G. Ungureanu, M. Prencipe, R. Cossio, Ab initio quantum-mechanical calculation of CaCO₃ aragonite at high pressure: thermodynamic properties and comparison with experimental data, *Eur J Mineral*, 22 (2010) 693-701.

- [39] M. Prencipe, I. Scanavino, F. Nestola, M. Merlini, B. Civalleri, M. Bruno, R. Dovesi, High-pressure thermo-elastic properties of beryl ($\text{Al}_4\text{Be}_6\text{Si}_{12}\text{O}_{36}$) from ab initio calculations, and observations about the source of thermal expansion, *Phys Chem Miner*, 38 (2011) 223-239.
- [40] G. Ottonello, M.V. Zuccolini, B. Civalleri, Thermo-chemical and thermo-physical properties of stishovite: an ab-initio all-electron investigation, *Calphad*, 33 (2009) 457-468.
- [41] D. Belmonte, G. Ottonello, M.V. Zuccolini, Ab initio thermodynamic and thermophysical properties of sapphirine end-members in the join $\text{Mg}_4\text{Al}_8\text{Si}_2\text{O}_{20}$ - $\text{Mg}_3\text{Al}_{10}\text{SiO}_{20}$, *Am Mineral*, 99 (2014) 1449-1461.
- [42] R.W. Roberts, R. Rupp, Volume dependence of Gruneisen parameter of alkali halides, *Phys Rev B*, 4 (1971) 2041.
- [43] R. Boehler, J. Ramakrishnan, Experimental results on the pressure-dependence of the Gruneisen-parameter - a review, *J Geophys Res*, 85 (1980) 6996-7002.
- [44] O.L. Anderson, Determination of volume dependence of Gruneisen parameter gamma, *J Geophys Res*, 79 (1974) 1153-1155.
- [45] A.C. Holt, M. Ross, Calculations of Gruneisen parameter for some models of solid, *Phys Rev B*, 1 (1970) 2700.
- [46] Montgome.RI, Monoclinic sulfur: heat capacity anomaly at 198 degrees K caused by disordering of crystal-structure, *Science*, 184 (1974) 562-563.
- [47] Z.K. Liu, Y. Wang, S.L. Shang, Thermal Expansion Anomaly Regulated by Entropy, *Scientific Reports*, 4 (2014) 7043.
- [48] A.T. Dinsdale, SGTE data for pure elements, *Calphad*, 15 (1991) 317-425.
- [49] O. Redlich, A.T. Kister, Algebraic representation of thermodynamic properties and the classification of solutions, *Industrial and Engineering Chemistry*, 40 (1948) 345-348.
- [50] J.O. Andersson, T. Helander, L.H. Hoglund, P.F. Shi, B. Sundman, THERMO-CALC & DICTRA, computational tools for materials science, *Calphad*, 26 (2002) 273-312.
- [51] G.N. Lewis, M. Randall, The heat content of the various forms of sulfur, *J Am Chem Soc*, 33 (1911) 476-488.
- [52] R.T. Grimley, J.A. Forsman, Mass-spectrometric determination of the heats of slow transitions - orthorhombic-monoclinic sulfur system, *International Journal of Mass Spectrometry and Ion Processes*, 30 (1979) 389-391.
- [53] E.D. West, The heat capacity of sulfur from 25-degrees to 450-degrees, the heats and temperatures of transition and fusion, *J Am Chem Soc*, 81 (1959) 29-37.
- [54] P.W. Bridgman, Linear compressions to 30,000 kg/cm², including relatively incompressible substances, *Proceedings of the American Academy of Arts and Sciences*, 77 (1949) 189-234.
- [55] S.N. Vaidya, G.C. Kennedy, Compressibility of 22 elemental solids to 45 kBar, *J Phys Chem Solids*, 33 (1972) 1377.
- [56] G.A. Saunders, Y.K. Yagurtcu, J.E. Macdonald, G.S. Pawley, The elastic behavior of orthorhombic sulfur under pressure, *P Roy Soc Lond A Mat*, 407 (1986) 325-342.
- [57] H. Luo, A.L. Ruoff, X-ray diffraction study of sulfur to 32 GPa - amorphization at 25 GPa, *Phys Rev B*, 48 (1993) 569-572.
- [58] G. Gattow, G. Heinrich, Thermochemie des selens. 2. Die umwandlungen der kristallinen selen-modifikationen, *Z Anorg Allg Chem*, 331 (1964) 256-274.
- [59] K.E. Murphy, M.B. Altman, B. Wunderlich, Monoclinic-to-trigonal transformation in selenium, *J Appl Phys*, 48 (1977) 4122-4131.

- [60] M. Meissner, A. Tausend, D. Wobig, Heat capacities and thermodynamic properties of alpha-monoclinic selenium in range 3 to 300 K, *Phys Status Solidi A*, 49 (1978) 59-66.
- [61] R. Keller, W.B. Holzapfel, H. Schulz, Effect of pressure on atom positions in Se and Te, *Phys Rev B*, 16 (1977) 4404-4412.
- [62] R. Cooper, J.V. Culka, Interchalcogen compounds. I. Sulphur-selenium system, *Journal of Inorganic & Nuclear Chemistry*, 29 (1967) 1217.
- [63] C.R. Ailwood, P.E. Fielding, Sulphur-selenium compounds, *Aust J Chem*, 22 (1969) 2301-2307
- [64] R. Laitinen, R. Steudel, Vibrational spectroscopic investigations of SnSe_{8-n} molecules, *J Mol Struct*, 68 (1980) 19-32.
- [65] R.S. Laitinen, T.A. Pakkanen, Se-77 NMR-study of the sulfur selenium binary-system, *Journal of the Chemical Society, Chemical Communications*, (1986) 1381-1382.
- [66] R.S. Laitinen, Selenium sulfide ring molecules, *Acta Chem Scand*, A41 (1987) 361-376.
- [67] R.S. Laitinen, T.A. Pakkanen, Se-77 NMR spectroscopic characterization of selenium sulfide ring molecules SenS_{8-n}, *Inorg Chem*, 26 (1987) 2598-2603.
- [68] R.S. Laitinen, P. Pekonen, Y. Hiltunen, T.A. Pakkanen, The Se-77 NMR spectroscopic identification of heterocyclic selenium sulfides prepared by the reactions of chlorosulfanes and dichlorodisilane with potassium-iodide, *Acta Chem Scand*, 43 (1989) 436-440.
- [69] R.O. Jones, D. Hohl, Structure, bonding, and dynamics in heterocyclic sulfur selenium molecules, *SexSy*, *J Am Chem Soc*, 112 (1990) 2590-2596.
- [70] J. Taavitsainen, H. Lange, R.S. Laitinen, An ab initio MO study of selenium sulfide heterocycles Se(n)S(8-n), *J Mol Struct-theochem*, 453 (1998) 197-208.
- [71] J. Komulainen, R.S. Laitinen, R.J. Suontamo, A theoretical study of the Se-77 NMR and vibrational spectroscopic properties of SenS_{8-n} ring molecules, *Can J Chem*, 80 (2002) 1435-1443.
- [72] M.W. Chase, Jr., NIST-JANAF Thermochemical Tables, National Institute of Standards and Technology, 1998.
- [73] Thermal expansion, in: R. K. Kirby, T. A. Hahn, B.D. Rothrock (Eds.) *American Institute of Physics Handbook*, McGraw-Hill, New York, 1972.
- [74] E.M. Hampton, J.N. Sherwood, Self-diffusion in alpha-sulfur crystals, *Philosophical Magazine*, 29 (1974) 763-769.
- [75] T. Maekawa, T. Yokokawa, K. Niwa, Enthalpies of binary-mixtures of chalcogen elements, *B Chem Soc Jpn*, 46 (1973) 761-765.
- [76] O.L. Anderson, A simplified method for calculating debye temperature from elastic constants, *J Phys Chem Solids*, 24 (1963) 909.
- [77] S.J. Rettig, J. Trotter, Refinement of the structure of orthorhombic sulfur, alpha-S₈, *Acta Crystallogr C*, 43 (1987) 2260-2262.
- [78] W.C. Hamilton, B. Lassier, M.I. Kay, Phonon spectra of trigonal selenium at 77 and 298 degree K, *J Phys Chem Solids*, 35 (1974) 1089-1094.
- [79] R.D. Burbank, The crystal structure of alpha-monoclinic selenium, *Acta Crystallographica*, 4 (1951) 140-148.

Tables and Table Captions

Table 1

Calculated 0 K equilibrium properties of phases of the pure elements (S, Se) from DFT using PBE+D3 and PBEsol+D3, including energy, volume, bulk modulus (B_0) and its pressure derivative (B'_0). Note that (i) the percent errors of the calculated volumes with respect to experimental data are also shown; (ii) all the calculated properties do not consider the zero point vibrational energy.

Element	Phase	Method	Energy(J/mol) ^a	Volume(Å ³ /atom)	%Error	B_0 (GPa)	B'_0
S	α	Expt.	0	25.76 [77]	-	7.692~14.5 ^b	5.433~8.324 ^c
		PBE+D3	0	27.29	5.9	5.804	11.403
		PBEsol+D3	0	23.51	-8.7	12.242	8.123
	$\beta 1$	Expt. ^d	470 [51],396 [52],401.7±2 [53]	25.50 [17]	-	-	-
		PBE+D3	15.7	27.81	9.1	7.046	5.597
		PBEsol+D3	423.6	24.22	-4.8	10.867	8.432
	$\beta 2$	Expt.	-	-	-	-	-
		PBE+D3	-	-	-	-	-
		PBEsol+D3	561.3	24.35	-	10.393	8.712
	δ	Expt.	-	-	-	-	-
		PBE+D3	3369.3	26.86	-	7.252	5.790
		PBEsol+D3	3181.3	22.20	-	9.349	5.610
	α'	Expt.	-	-	-	-	-
		PBE+D3	-18.3	27.49	-	6.383	7.893
		PBEsol+D3	95.9	23.66	-	10.265	7.973
Se	α	Expt.	-	-	-	-	-
		PBE+D3	3681.4	32.13	-	9.058	9.420
		PBEsol+D3	10022.1	28.19	-	15.142	6.954
	β	Expt.	-	-	-	-	-
		PBE+D3	3576.9	32.52	-	8.393	6.962
		PBEsol+D3	9750.3	27.74	-	14.033	7.381
	δ	Expt.	0	26.57 [78]	-	7.085~14.9 ^e	5.828 [55],6.317 [54]
		PBE+D3	0	25.99	-2.2	14.359	10.435
		PBEsol+D3	0	23.08	-13.1	34.163	8.447
	α'	Expt.	6700 [58],2100 [59],1200 [60]	29.78 [79]	-	-	-
		PBE+D3	3019.0	31.49	5.7	7.737	6.157
		PBEsol+D3	8579.5	26.68	-10.4	13.342	7.248

^a The energy is relative to that of the stable phase, and the experimental values are conversion enthalpies. ^b Fitted with modified Murnaghan equation: 7.692 [54], 9.373 [55]; fitted with Murnaghan equation: 8.239 [54], 8.843 [55]; 9.7 [56], 14.5 [57].

^c Fitted with modified Murnaghan equation: 8.324 [54], 5.433 [55]; fitted with Murnaghan equation: 7.106 [54], 6.547 [55]; 7 [57].

^d Experimental values are of the β phase.

^e Fitted with Murnaghan equation: 7.085 [54], 7.90 [55]; 8.974 [55], 14.9 [61].

Table 2

Parameters of Gibbs energies for phases of pure elements (except the unstable phase α -Se, the unknown X phases and the reference phases, α -S and δ -Se) based on DFT calculation using PBEsol+D3.

Element	S			Se	
Phase	β	δ	α'	β	α'
a_i^g	482.420	3013.008	142.825	9668.747	8502.029
b_i^g	-1.001	-1.319	-1.993	3.269	3.093
c_i^g	0.078	0.400	0.545	-1.575	-1.563
d_i^g	-0.00139	-0.00916	-0.00284	0.00395	0.00380
a_i^g (modified)				3255.222	2088.504
b_i^g (modified)				5.258	5.082
c_i^g (modified)				-1.575	-1.563
d_i^g (modified)				0.00395	0.00380

Table 3

Parameters used to describe the S-Se system from CALPHAD modeling. Values are expressed in J/mol-atom.

Phase	Parameter	Expression
L	0L	$5030-11.414T$
α	${}^0G_{Se}^{\alpha}$	$6018+{}^0G_{Se}^{\delta}$
	0L	$2000-15.500T$
β	${}^0G_{Se}^{\beta}$	$3255.222+5.258T-1.575T\ln T+0.00395T^2+{}^0G_{Se}^{\delta}$
	0L	$9500-25.550T$
δ	${}^0G_S^{\delta}$	$3013.008-1.319T+0.400T\ln T-0.00916T^2+{}^0G_S^{\alpha}$
	0L	$13000-25.000T$
X	${}^0G_S^X$	$100+1.800T+{}^0G_S^{\alpha}$
	${}^0G_{Se}^X$	$1300-2.300T+{}^0G_{Se}^{\delta}$
	0L	$1000-0.300T$

Fig. 1. Heat capacity at constant pressure (C_p), linear thermal expansion coefficient (LTEC), entropy, enthalpy and Gibbs energy of α -S, β -S, δ -Se and α' -Se (in the α -Se structure) predicted by DFT using PBEsol+D3, in comparison with those from the CALPHAD model (taken from the SGTE database [48] directly for α -S, β -S and δ -Se) and experimental data [12, 72, 73].

Fig. 2. Gibbs energy difference between the β -S and the α -S predicted by PBEsol+D3.

Fig. 3. Heat capacity at constant pressure (C_p), linear thermal expansion coefficient (LTEC), entropy, enthalpy and Gibbs energy of δ -S, α -S and β -Se predicted by DFT using PBEsol+D3, in comparison with those from the CALPHAD model.

Fig. 4. Calculated S-Se phase diagrams in the range 298 to 500 K at 1 bar and compared with phase boundary data from Ringer [13], Nakagawa [15], Boctor et al. [16] (upper plot) and the same diagram in the extended range 298 and 1300 K at 1 bar showing the gas phase (lower plot).

Fig. 5. The pressure-temperature diagram of the S-Se system at the composition (a) 25 at.% Se (b) 50 at.% Se (c) 75 at.% Se based on the CALPHAD assessment.

Fig. 6. Mixing enthalpy calculated by DFT using homo-molecules model and random solid solution model shown with the results of CALPHAD modelling from the present work and the experimental data [75].

Fig. 7. The formation enthalpy (upper plot) and the formation entropy (lower plot) as a function of composition at 298 K and 1 bar based on the CALPHAD assessment.