Structure and optical properties of $\alpha$- and $\gamma$- cerium sesquisulfide

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Abstract

Structural and electronic properties of the $\alpha$- and $\gamma$-phases of cerium sesquisulfide, Ce$_2$S$_3$, are examined by first-principles calculations using the GGA+U extension of density functional theory. The strongly correlated $f$-electrons of Ce are described by a Hubbard-type
on-site Coulomb repulsion parameter. A single parameter of $U' = 4$ eV yields excellent results for crystal structures, band gaps, and thermodynamic stability for both Ce$_2$S$_3$ allotropes. This approach gives insights in the difference in color of brownish-black $\alpha$-Ce$_2$S$_3$ and dark red $\gamma$-Ce$_2$S$_3$. The calculations predict that both Ce$_2$S$_3$ modifications are insulators with optical gaps of 0.8 eV ($\alpha$-phase) and 1.8 eV ($\gamma$-phase). The optical gaps are determined by direct electronic excitations at $k = \Gamma$ from localized and occupied Ce 4$f$-orbitals into empty Ce 5$d$-states. The $f$-states are situated between the valence and conduction bands. The difference of 1 eV between the optical gaps of the two Ce$_2$S$_3$ modifications is explained by different coordinations of the cerium cations by sulfur anions. For both Ce$_2$S$_3$ modifications the calculations yield an effective local magnetic moment of 2.6 $\mu_B$ per cerium cation, which is in agreement with measurements. The electronic energy of the $\alpha$-phase is computed to be 6 kJ mol$^{-1}$ lower than that of the $\gamma$-phase, which is consistent with the thermodynamic stability of the two allotropes.

**Key words:** rare earth alloys and compounds, crystal structure, electronic band structure, computer simulations

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1 Introduction

Rare earth (RE) elements are essential ingredients in a large variety of materials of vital technological, economic, and ecological importance. This includes energy-efficient lighting systems, plasma displays, medical imaging, automotive catalysts, permanent magnets, and pigments [1]. These applications depend on the unique structural, electronic, optical, magnetic, and chemical properties of RE compounds. The origin for many of these properties is the presence of localized 4\(f\)-electrons interacting with the valence electrons. In this context, the present work focuses on cerium sesquisulfide (Ce\(_2\)S\(_3\)), which is used as an environmentally responsible pigment with high temperature stability [2]. Beyond this specific application, Ce\(_2\)S\(_3\) can be seen as a representative of a large class of RE compounds containing 4\(f\)-electrons. Therefore, the approach and results of the present work have implications for many RE-containing compounds and their applications.

The localization of the 4\(f\)-electrons involves strong correlation effects which are not captured by current standard methods within density functional theory (DFT). The result is that these DFT calculations fail to reproduce, e.g. the non-metallic ground state of Ce\(_2\)S\(_3\) [3, 4] and overestimate the mass density of crystal structures of other cerium compounds [5, 6, 7]. Hence, approaches beyond conventional DFT methods are required to describe Ce\(_2\)S\(_3\) realistically from first principles. The present work demonstrates the usefulness of a DFT method extended by a Hubbard-type on-site Coulomb repulsion parameter for treating the Ce 4\(f\)-electrons (the GGA+U approach).

Cerium sesquisulfide exists in three allotropic forms [8, 9]. The \(\alpha\)-phase is the
low-temperature modification and has a brownish-black (rusty) hue [10]. Above 
\(\sim900^\circ\text{C}\) \(\alpha\)-Ce\(_2\)S\(_3\) transforms irreversibly into the dark red (maroon) colored 
\(\beta\)-phase. The \(\beta\)-modification has been described as an oxysulfide with the formula 
Ce\(_{10}\)S\(_{15-x}\)O\(_x\) [11]. The oxygen can be partially replaced by sulfur. However, a 
complete substitution appears to be impossible [11], despite other assertions of 
Picon et al. [10]. The structure of the \(\beta\)-phase has been described as complex, but 
has not been resolved. For these reasons, the \(\beta\)-phase is not considered in the 
present computational work. The high-temperature allotrope, \(\gamma\)-Ce\(_2\)S\(_3\), is 
preferentially formed between 1100\(^\circ\text{C}\) and 1200\(^\circ\text{C}\). However, \(\gamma\)-Ce\(_2\)S\(_3\) can be 
stabilized at temperatures below 800\(^\circ\text{C}\) [12, 2]. The melting point of the \(\gamma\)-phase is 
at \(\sim2100^\circ\text{C}\) [10, 13].

The \(\gamma\)-phase of Ce\(_2\)S\(_3\) is a nontoxic inorganic high performance pigment of dark red (burgundy) hue, which is used on an industrial scale in the coloration of 
plastics, paints, and coatings [2]. Optical studies [14, 15] suggest that the dark red color of \(\gamma\)-Ce\(_2\)S\(_3\) arise from dipole-allowed excitations of electrons from 4\(f\)-states into the empty 5\(d\)-states \((4f^15d^0 \rightarrow 4f^05d^1)\) of the same cerium cation. The three 
modifications of Ce\(_2\)S\(_3\) have an insulating nature, as is already clear from their color.

The magnetic susceptibility of \(\alpha\)-Ce\(_2\)S\(_3\) and \(\gamma\)-Ce\(_2\)S\(_3\) at room temperature are 
similar [10]: \(2.9 \times 10^7\) (\(\alpha\)-phase) and \(2.7 \times 10^7\) (\(\gamma\)-phase), in SI units. The \(\gamma\)-phase 
exhibits ferromagnetism below 3 K and the measured effective magnetic moment 
of each cerium cation is \(\mu_{\text{eff}} = 2.5 \mu_B\) [16, 17, 18]. The magnetic moment is 
equivalent to that of an isolated Ce\(^{3+}\) ion which has the electron configuration 
[Xe]4\(f^1\) and the ground state \(^2F_{5/2}\) [19]. Thorough literature searches did not 
yield anything about a magnetic ordering of \(\alpha\)-Ce\(_2\)S\(_3\) at low temperatures. The \(\alpha\)-
and \(\gamma\)-phases of Gd\(_2\)S\(_3\) have the same magnetic ordering at low temperatures [20].
Moreover, $\alpha$-Gd$_2$S$_3$ and $\gamma$-Gd$_2$S$_3$ are isomorphic to $\alpha$-Ce$_2$S$_3$ and $\gamma$-Ce$_2$S$_3$, respectively. For these reasons, we shall assume in the following that both $\alpha$-Ce$_2$S$_3$ and $\gamma$-Ce$_2$S$_3$ are ferromagnetic at low temperatures.

The conduction band (cb) of $\gamma$-Ce$_2$S$_3$ is mainly formed by empty Ce 5$d$-states while the valence band (vb) consists predominantly of sulfur 3$p$-orbitals \[3, 4, 14, 15, 21\]. Due to their rather extended character and large energy dispersion Ce 6$s$-states contribute to both the vb and the cb. The measured gap between the upper edge of the vb and the lower edge of the cb of $\gamma$-Ce$_2$S$_3$, $E_g$, is between 2.7 eV \[15, 22, 23\] and 3.3 eV \[15\]. In agreement with group-theoretical arguments \[24\] the smaller band gap has been assigned to phonon-assisted (indirect) electronic excitations. The larger band gap is associated with direct electronic transitions. The temperature dependence of $E_g$ between 250 and 350 K is approximately $-0.1 \mu$eV K$^{-1}$, which has been derived from $\gamma$-La$_2$S$_3$ and $\gamma$-Dy$_2$S$_3$ \[24\]. Both compounds have the same structural topology as $\gamma$-Ce$_2$S$_3$. The corresponding values of typical semiconductors like CdS and CdSe are around $-4 \mu$eV K$^{-1}$.

Photoconductivity spectra \[25\] as well as measurements of the photoluminescence \[26\] of $\gamma$-Ce$_2$S$_3$ indicate that the occupied 4$f$-states of cerium cations are energetically located between the vb and the cb. The gap between the 4$f$-states and the cb obtained from these measurements is in agreement with the optical gap of 1.8–2.0 eV derived from the dielectric function \[14, 15\]. Up to now, photoemission spectroscopy studies of $\gamma$-Ce$_2$S$_3$ have not been able to resolve precisely the energetic position of the occupied Ce 4$f$-states with respect to the vb \[27, 15\]. However, the measurements of Mauricot et al. \[25\] reveal that the occupied Ce 4$f$-states are energetically 0.8 eV above the vb.
Earlier band structure calculations within DFT in the local density approximation (DFT-LDA) on model structures for $\gamma$-Ce$_2$S$_3$ demonstrated qualitatively the importance of 4$f$-electrons for the optical properties [3, 4]. However, these calculations have several limitations, which hamper quantitative predictions. These limitations mostly stem from the well known inability of DFT-LDA methods to describe correctly the localized 4$f$-states. First, when the 4$f$-states are treated in the valence, DFT-LDA calculations predict a metallic (Kohn-Sham) band structure for Ce$_2$S$_3$, with $f$-states at the Fermi level, in contradiction with the insulating nature of this material. The fact that, within DFT-LDA, these $f$-bands are found to be split off from the sulfur $p$-bands is indeed suggestive that the optical transitions from 4$f$ to 5$d$ bands are playing an important role in the optical properties. But it is clearly not possible to go beyond this qualitative observation in a pure DFT-LDA framework, let alone to reach a quantitative description of the optical gaps of Ce$_2$S$_3$ derivatives [3, 4]. Second, the models used to describe $\gamma$-Ce$_2$S$_3$ in Refs. [3, 4] did not capture the electrostatics of the real compound adequately. The charges of the cations in the model significantly deviate from that of trivalent cerium. The deviation was one of the factors for the DFT-LDA calculations to underestimate the energy difference between the 4$f$-states and the vb. The result was an overestimation of the overlap between the 4$f$-states and the vb and an artificially large splitting of band states on top of the vb [3]. Third, the previous LDA-DFT calculations did not perform structural relaxation studies or attempt to predict crystal structures. However, the electronic structure and, hence, optical properties are very sensitive to interatomic distances. Furthermore, it is widely documented that DFT-LDA and even the generalized gradient approximation (GGA), an extension of DFT-LDA, severely overestimate the mass density of $f$-electron compounds when the $f$-states are treated in the valence [5, 28, 29]. Our own experience with alkali-doped cerium sesquisulfides is that GGA calculations
underestimate the unit cell volume of these compounds by as much as 6% [30].

The main goal of the present study is to gain a deeper understanding of the relations between the chemical composition, the crystal structure, and the optical properties of both \(\alpha\)-Ce\(_2\)S\(_3\) and \(\gamma\)-Ce\(_2\)S\(_3\). Our study addresses both the crystal structure as well as the electronic properties quantitatively within a single computational framework, namely the GGA+U approach. Analogue to the LDA+U method [31], the GGA+U approach uses the DFT framework but extends the GGA description of exchange-correlation effects in the localized 4\(f\)-shell by a many-body interaction term. This term is then treated in a mean-field like manner, allowing for a simple description of strong correlation effects within the Ce 4\(f\)-states. The GGA+U approach allows for a full optimization of the crystallographic parameters of Ce\(_2\)S\(_3\), and captures the role of the 4\(f\)-electrons in the optical transitions. As we shall see, Ce\(_2\)S\(_3\) is found to be an \(f\)-electron Mott insulator, in which the Ce 4\(f\)-states are split into lower occupied and upper unoccupied sub-bands by the strong on-site Coulomb repulsion. Optical transitions responsible for the color of these compounds are between the lower unoccupied Ce 4\(f\)-states and the bottom of the Ce 5\(d\)-like cb.

2 Crystal structures

The \(\alpha\)-phase of Ce\(_2\)S\(_3\) crystallizes in an orthorhombic lattice (crystallographic space group \textit{Pnma}). The unit cell contains four formula units with two and three symmetry inequivalent cerium and sulfur ions, respectively [11]. Figure 1(a) illustrates two different kinds of interlocked Ce–S skeletons which are the
coordination polyhedra of the four Ce1 and the four Ce2 cations. The coordination polyhedra (Ce1)S$_8$ and (Ce2)S$_7$ have the shapes of a bi-capped trigonal prism and a rather distorted mono-capped octahedron, respectively. The corners of the trigonal prism are S2, S3, and S3’ whereas the vertices of the two caps are the sulfur ions S1’. The cap tip of the octahedron is the sulfur ion S2’. Two of the three symmetry inequivalent sulfur anions (S2 and S3) are bound to five cerium cations. The cations form a rectangular pyramid. The five cerium cations encompassing the remaining symmetry inequivalent sulfur anion (S1) form an axial distorted trigonal bipyramid. The Ce–S distances of the two coordination polyhedra are in the range of 2.85–3.14 Å with average distances of 3.01 Å [(Ce1)S$_8$] and 2.93 Å [(Ce2)S$_7$].

The crystal structure of $\gamma$-Ce$_2$S$_3$ has a body-centered cubic lattice. It is isomorphic to the Th$_3$P$_4$ structure and contains vacancies on the cationic sublattice \[ \{ \text{11} \} \; [32] \; [33]. \] The cerium cations are located on the 12$a$ positions which have the point group symmetry $S_4$; the sulfur anions occupy sites with $C_3$ symmetry (16$c$ positions). Each cerium cation is coordinated by eight sulfur anions forming a triangular dodecahedron as depicted in Fig. 1(b), with two different nearest-neighbor distances \[ 34]: r(\text{Ce–S})=2.89 \text{ Å} \text{ and } r(\text{Ce–S'})=3.09 \text{ Å}. \] Each sulfur anion is located on a threefold axis and surrounded by six nearest cerium cations, provided all 12$a$ positions are occupied. The six cations form a distorted octahedron. However, when all the 16$c$ and 12$a$ position are occupied with cations and anions, respectively, the stoichiometry would be Ce$_3$S$_4$. In order to achieve the stoichiometry of $\gamma$-Ce$_2$S$_3$ one out of nine cations has to be removed and vacancies on the cerium sublattice, V$_\text{Ce}$, have to be created \[ 33]:

\[
3 \times [\text{Ce}_3\text{S}_4] \equiv \text{Ce}_9\text{S}_{12} \xrightarrow{\text{Ce}_8\text{V}_\text{Ce}\text{S}_{12}} \equiv 4 \times [\text{Ce}_2\text{S}_3]
\]
Note that both, $\gamma$-Ce$_2$S$_3$ and Ce$_3$S$_4$ have very similar lattice parameters differing only by 0.06% [32, 34]. The tiny volume difference is evidence for a rather rigid Ce-S framework.

Raman spectra of several RE sesquisulfides in the $\gamma$-phase give evidence for randomly distributed vacancies [35]. However, simple electrostatic energy calculations predicted that a completely random distribution of the voids on the cerium sublattice yields an energetically less stable ground state than a vacancy ordering such that the resulting crystal structure of $\gamma$-Ce$_2$S$_3$ has the symmetry of the space group $I\bar{4}2d$ [33]. A highly symmetric ordering of the vacancies is likely in well-annealed $\gamma$-phases whereas rapidly quenched samples might have a random distribution of vacancies [33]. Vacancies in the sulfur sublattice are rather unlikely [36].

Figure 1(c) depicts the smallest conventional crystallographic supercell that accommodates the stoichiometry of $\gamma$-Ce$_2$S$_3$. The supercell is three times as big as the conventional unit cell of Ce$_3$S$_4$ and has the composition $4 \times$ [Ce$_8$V$_{Ce}$S$_{12}$]. The distances of a cerium cation to its first, second and third nearest cations in $\gamma$-Ce$_2$S$_3$ are 7.5, 4.8 and 4.0 Å [34]. In this structure the voids on the cation sublattice create three symmetry inequivalent cerium cations. The supercell can be transformed into a primitive unit cell half as large as the conventional cell shown in Fig. 1(c).

3 Computational Method

All GGA+U calculations have been performed with the Vienna ab initio simulation package (VASP) [37, 38, 39, 40, 41] as integrated in the MedeA environment [42]. VASP uses the projector-augmented wave (PAW) method [43].
in the implementation of Kresse and Joubert [39]. Exchange- and correlation effects are described within the GGA by the density functional of Perdew, Burke and Ernzerhof [44]. The PAW potentials take into account 12 valence electrons of each Ce \((5s^25p^66s^25d^14f^1)\) and six valence electrons of each S \((3s^23p^4)\) atom. The plane wave energy cutoff has been set to 333 eV and 299 eV for \(\alpha\)-Ce\(_2\)S\(_3\) and \(\gamma\)-Ce\(_2\)S\(_3\), respectively.

Within the present GGA+U approach [40, 45] the strong electron correlation among the 4\(f\)-states is described with the parameter \(U' = U - J\). In the latter term, \(U\) is the spherically averaged screened Coulomb repulsion energy required for adding an extra electron into the Ce 4\(f\)-states and \(J\) represents the corresponding screened exchange energy. The GGA+U one-electron potential is defined as

\[
V_{ij}^\sigma = \frac{\partial E_{GGA}}{\partial \rho_{ij}^\sigma} + U'(0.5\delta_{ij} - \rho_{ij}^\sigma),
\]

whereby \(E_{GGA}\) is the GGA electronic energy, \(\rho_{ij}^\sigma\) is the density matrix of \(f\)-electrons with spin \(\sigma\), and \(\delta_{ij}\) is the delta function. The double counting correction applied is equivalent to that of the fully-localized limit. The case \(U' = 0\) is the limit of pure GGA.

The parameter \(U'\) can be calculated from first principles without knowledge of experimental data [46]. In this work however, instead of performing such calculations (which are computationally heavy because of the large numbers of atoms in the unit cell), we have investigated whether \(U'\) can be chosen in such a way to reproduce with reasonable accuracy both the experimentally measured unit cell volume, as well as the optical gap of the \(\gamma\)-Ce\(_2\)S\(_3\) allotrope. We found that the value \(U' = 4\) eV achieves this goal. This value is in agreement with Coulomb repulsion parameters calculated for other cerium compounds [47, 48].

The Kohn-Sham equations are solved self-consistently in their spin-polarized form employing an iterative matrix diagonalization (blocked Davidson scheme) and the
spin interpolation of Vosko et al. [49]. The convergence criterion to obtain the energy is $10^{-5}$ eV. The integration over the first Brillouin-zone is performed using symmetry adapted Monkhorst-Pack grids [50] of $k$-point sets of various size. To calculate energies, energy gradients (atomic forces as well as the stress tensors), and charge densities the $k$-point sets are $3 \times 7 \times 3$ ($\alpha$-Ce$_2$S$_3$) and $3 \times 3 \times 3$ ($\gamma$-Ce$_2$S$_3$). All $k$-point sets as well as the plane wave energy cutoff has been determined within a convergence test to yield to a numerical precision of $5 \times 10^{-3}$ eV.

The crystal structures of $\alpha$-Ce$_2$S$_3$ and $\gamma$-Ce$_2$S$_3$ as described in Sec. 2 have been optimized such that atomic positions and the crystallographic cell parameters are relaxed simultaneously. The optimization procedure has two steps. In the first step, the conjugate-gradient algorithm is used and the optimization stops when all energy gradients are smaller than 0.02 eV Å$^{-1}$. Then the crystal structures are further refined within a quasi-Newton algorithm with a very tight convergence criterion of 0.002 eV Å$^{-1}$.

Energy gradients have been calculated with a Gaussian integration method and a smearing of $\sigma = 10^{-3}$ eV. The linear tetrahedron method with Blöchl corrections has been used to obtain accurate energies and the self-consistent charge densities. (This integration scheme is inappropriate for calculating energy gradients.) The self-consistent charge densities are used to calculate the band structures and the densities of states (DOS’s). All DOS’s have been calculated using the linear tetrahedron method without corrections and the same $k$-point sets applied to calculate the energies (see above).

Since the calculations correspond to zero temperature, the two Ce$_2$S$_3$ phases adopt the ferromagnetic state. In all calculations the ferromagnetic state is described
with all $f$-electron spins aligned parallel (spin-up). The band structures and DOS’s have been created from the charge density of the electrons with spin-up. This is sufficient since in the present approach only the spin-up states contain occupied $f$ states while the $S\,3p$-$vb$ and Ce $5d/6s$-conduction states are similar for both spin orientations.

4 Results and discussion

4.1 $\alpha$-Phase

Table 1 summarizes calculated lattice parameters and interionic distances of the two interlocked (Ce1)S$_8$ and (Ce2)S$_7$ skeletons shown in Fig. 1a. As announced above, the chosen value $U' = 4$ eV yields a relative error on the unit cell volume which is smaller than 1% in comparison to experiments. A comparison with the corresponding experimental distances reveals remarkable agreement. Most of the calculated distances are less than 0.9% larger than those determined from x-ray diffraction measurements. Exceptions are the calculated cell length $c$ and the bond lengths $r$(Ce1–S1’) and $r$(Ce2–S3) which are nearly equal or smaller, respectively, than the corresponding measured distances. The discrepancies are almost zero for $c$, −0.1% ($r$(Ce2–S3), and around −1.2% for the longest of the two Ce1–S1’ distances. The calculations tend to strengthen one of the Ce1–S1’ bonds at the expense of the other thereby slightly decreasing the sulfur coordination of Ce1. Note that the measurements and the calculations yield for the two distances $r$(Ce1–S1’) average values of 3.12 and 3.11 Å, respectively. The average of the calculated distances between cerium and sulfur within the (Ce1)S$_8$ and (Ce2)S$_7$ skeletons are 3.02 and 2.94 Å, respectively. Both distances are only between 0.4
and 0.7% larger than the corresponding distances of the x-ray structure. Apart from $r(\text{Ce}1–\text{Ce}1)$ all other calculated Ce–Ce distances are larger than the measured values with deviations not larger than 0.5%.

The energy of formation, $E_{\text{form}}$, is a measure for the stability and is the difference between the energy of the entire system and the energies of the electronic ground state of the constitutive elements in their standard state. For $\alpha$-Ce$_2$S$_3$ the calculations yield $E_{\text{form}} = -820 \text{ kJ mol}^{-1} \text{Ce}_2\text{S}_3$.

Figure 2 shows the band structure and the corresponding partial DOS (PDOS) calculated for the fully optimized crystal structure of $\alpha$-Ce$_2$S$_3$. The electronic bands are drawn along the standard pathway within the irreducible wedge of the Brillioun zone of simple orthorhombic lattices. The PDOS illustrates that the vb, i.e. the occupied and evenly dispersed electron bands below approximately $-0.8$ eV, are mainly formed by S 3$p$-orbitals with contributions of Ce 3$d$-orbitals. This indicates a significant covalent contribution to the bonding in $\alpha$-Ce$_2$S$_3$.

On top of the vb, i.e. the occupied electron bands between $-0.8$ eV and zero energy are two kinds of occupied 4$f$-orbitals namely those of the cations Ce1 and Ce2, respectively. In the following occupied 4$f$-states are termed as lower Hubbard bands (LHB’s). Both LHB’s have rather large admixtures of S 3$p$-states. This indicates a participation of Ce 4$f$-orbitals in the covalent bonding. The PDOS of Fig. 2(b) shows that the LHB of the Ce1 cations is located at a lower energy than the LHB of the Ce2 cations. The main reason for the different positions must be the different sulfur environments of the Ce1 and Ce2 cations as depicted in Fig. 1(a). The calculations yield almost one 4$f$-electron localized on each cerium cation. The computed occupation numbers of the 4$f$-states, $n_f$, of the two symmetry inequivalent cerium cations are 1.12 (Ce1) and 1.14 (Ce2).
Occupation numbers of $n_f > 1$ are consistent with admixtures of $S\;3p$-states to $Ce\;4f$-orbitals. Assuming that the total orbital moment of the electronic ground state of all cerium cations is $J = 5/2$ the effective local magnetic moment is around 2.6 $\mu_B$ per cerium cation. This is consistent with experiment.

The LHB’s have different features within the chosen part of the Brillouin zone. On the one hand the LHB’s have significant dispersion (on the scale of $\sim 0.5$ eV) between $k = T$ and the center of the line between $k = \Gamma$ and $k = X$ (\Sigma line). On the other hand the LHB’s are rather flat between the center of the $\Sigma$ line and $k = Y$ and along the line between $k = R$ and $k = T$. The LHB’s are almost degenerate at $k = R$ and $k = S$.

The smallest gap between the upper edge of the LHB of Ce2 and the lower edge of the unoccupied states (cb) is 0.8 eV and is at $k = \Gamma$. At the same $k$-point is the smallest separation between the vb and the cb (1.34 eV). The cb has predominantly Ce $5d$-character with small contributions of $S\;3p$-orbitals. Like the LHB’s but more distinct, the cb exhibits a strong dispersion between $k = T$ and $k = X$. The PDOS of the cb at its lower edge is tiny and increases in small steps between 0.7 and 1.8 eV.

The inset of Fig.2(b) depicts the presence of Ce $6s$- and Ce $6p$-orbitals in the relevant electron bands of Fig.2(a). Their contributions within the relevant energy range around the Fermi energy are relatively small because the $6s$- and $6p$-states are spatially extended and energetically dispersed. Inside the cb between 2.0 and 4.2 eV are unoccupied Ce $4f$-orbitals which form the upper Hubbard band (UHB).

The band dispersions of the LHB and the cb are examined in terms of an orbital-projected band-structure (sometimes called “fat-band” representation). Figure3 illustrates contributions of atomic states to relevant energy bands of Fig.
between $k = T$ and $k = X$ at different $k$-points. The three lowest unoccupied states at $k = \Gamma$ are due to anti-bonding interactions between cerium 5$d$- and sulfur 3$p$-states. The contribution of S 3$p$-orbitals to the three states is between 5 and 15% whereby only states of the atoms S2 and S3 are involved. Admixtures of 3$p$-orbitals of S1 are negligibly small. The corresponding bonding states are located between $-1.9$ and $-2.3$ eV. The splitting between bonding and antibonding states of Ce1 and S3 is between 0.7 and 1.4 eV smaller than that of Ce2 and S2. The smaller splitting and, hence, the distinct dispersion of the two lowest unoccupied bands is due to smaller overlap between 5$d$- and 3$p$-orbitals of Ce1 and S3, respectively.

The dispersions at the upper edge of the LHB are also due to admixtures of S 3$p$-orbitals to the Ce 4$f$-states. The two highest occupied electronic states of the LHB contain at $k = \Gamma$ both 44% of S 3$p$-orbitals whereby all sulfur ions contribute equally. The remaining contributions come from the 4$f$-states of Ce1 and Ce2, respectively (cf. Fig. 3). The contributions of all cerium cations is consistent with the small tails of the 4$f$-states in the PDOS of Fig. 2(b) at zero energy. In fact the entire vb contains contributions of 4$f$-states which decrease towards lower energies.

The calculated GGA+U band structure yields insight into the optical properties of $\alpha$-Ce$_2$S$_3$ and its color. The dispersion at the lower edge of the cb at $k = \Gamma$ causes the rather small direct band gap of 0.8 eV. However, this gap is between states of Ce1 and Ce2. Since the color of the cerium sesquisulfides is determined by the excitations $4f^15d^0 \rightarrow 4f^05d^1$ taking place on the same site we have to distinguish between two optical transitions. The orbital-projected band-structure of Fig. 3 reveals that the smallest 4$f$–5$d$ gaps of Ce1 and Ce2 are about 1.0 and 1.7 eV, respectively. Consequently, the reason why $\alpha$-Ce$_2$S$_3$ has a brownish-black color is
twofold. The cerium cations Ce2 absorb photons with energies larger than 1.7 eV which would lead to a dark red color. The smaller gap of \(~1.0\) eV (Ce1 cations) is responsible that all radiation of the visible range is absorbed. However, the absorption of radiation with an energy between 0.7 and 1.8 eV (near infrared and red light) is relatively low because the density of states is rather small in this region [compare Fig. 2(b)]. This effect leads to the black shade. Dark red mixed with black yields a brown-black hue.

4.2 \(\gamma\)-Phase

Table 2 summarizes lattice parameters and selected interionic distances calculated for \(\gamma\)-Ce\(_2\)S\(_3\) and compares the values with that of the x-ray structure of Ref. [34]. Again, the chosen value of \(U'\) yields a calculated unit-cell volume which is less than 1\% larger than that determined from experiment. The deviation between the calculated and measured average Ce–S bond lengths is negligibly small. The smallest calculated Ce–Ce distance which is 2\% smaller than that determined from the x-ray structure. The reason for the cell expansion is a growth of the voids located on the cation sublattice [\textit{cf.} red spheres of Fig. 1(c)]. The calculated structure has distances between the center of the voids, Q, and the nearest sulfur anions which are between 3.1\% and 4.0\% larger than those of the experimental structure.

The \(I\overline{4}2d\) structure of Fig. 1(c) has three symmetry inequivalent cerium cations and sulfur anions, respectively. Two of the symmetry inequivalent cerium cations have clearly distinguishable bond distances of \(r(\text{Ce–S})\sim2.90\) and \(r(\text{Ce–S'})\sim3.10\) Å. However, the third kind of cations has an almost continuous spectrum of bond length to its eight nearest sulfur anions in the range of 2.90 and 3.30 Å. Due to the
vacancies two of the three symmetry inequivalent sulfur anions are bound to five cerium cations only. All the penta-coordinated sulfur anions have three Ce–S bonds and two Ce–S’ bonds [cf. Fig. 1(b)]. The six-fold coordinated sulfur anions have Ce–S distances, which are between 1 and 2% larger than the calculated average bond lengths of Tab. 2. The calculated energy of formation for the γ-phase is $\Delta E_{form} = -814 \text{ kJ mol}^{-1} \text{ Ce}_2\text{S}_3$.

Figure 4 depicts the band structure and PDOS calculated for the fully optimized Ce$_{16}$S$_{24}$ supercell which is the primitive cell of that shown in Fig. 1(c). Comparison with Fig. 2 reveals similarities between the electronic structures of the α-phase and the γ-modification, but also significant differences which will be addressed in more details in Sec. 5. Up to an energy of $-1.0$ eV, the vb is mainly formed by S 3p-orbitals with small contributions of Ce 4f-states. Between $-1.2$ and $-0.5$ eV the vb has increasing admixtures of Ce 4f-states. The region of the occupied states above $-0.5$ eV (directly on top of the vb) is dominated by the LHB with significant components of S 3p-states. The difference to the PDOS of the α-phase is that the LHB of γ-Ce$_2$S$_3$ has one maximum only at around $-0.4$ eV. The width of the LHB is around 0.5 eV without any distinct dispersion. The location of the 4f LHB is in good agreement with available photoelectron spectroscopy data, but inferring its width from these experiments is difficult given the resolution [15].

The single maximum of the LHB in the PDOS is evidence for cerium cations which are electronically and magnetically equivalent. This is consistent with the fact that the calculations yield for each cerium cation occupation numbers of $n_f = 1.14$. Occupation numbers larger than one indicate admixtures of other band states, mainly S 3p-orbitals. As in the case of α-Ce$_2$S$_3$ the cerium cations of the γ-phase have a local effective magnetic moment of $2.6 \mu_B$. 

The cb has predominantly Ce 5d character with small admixtures of S 3p-states and has its largest dispersion around \( k = \Gamma \). At the same \( k \)-point is the smallest direct gap between the maximum of the LHB and the cb minimum of around 1.8 eV which is in fact in the range of measured optical gaps between 1.8 and 2.0 eV [15, 22, 51, 52]. Thus the present calculations on \( \gamma \)-\( \text{Ce}_2\text{S}_3 \) result in a dark red color.

The rather weak dispersion of both the LHB and of the Ce 5d bands at the bottom of the cb [see Fig. 4(a)] implies a rather sharp absorption edge. This is in contrast with the \( \alpha \)-allotrope in which both the LHB and the 5d cb are more disperse. The smallest gap between the vb and the cb is 2.3 eV, also at \( k = \Gamma \). The minimum of the lower edge of the UHB is located approximately 2.8 eV above zero energy.

5 Comparison between the \( \text{Ce}_2\text{S}_3 \) modifications

Both allotropes have crystal structures with a relatively high average coordination of eight sulfur atoms around each Ce atom. The mass density of the two \( \text{Ce}_2\text{S}_3 \) phases calculated from the optimized crystal structures is similar: 5.10 Mg m\(^{-3}\) (\( \alpha \)-phase) and 5.13 Mg m\(^{-3}\) (\( \gamma \)-phase). For comparison the experimentally determined mass densities for \( \alpha \)-\( \text{Ce}_2\text{S}_3 \) and \( \gamma \)-\( \text{Ce}_2\text{S}_3 \) are 4.95 and 5.18 Mg m\(^{-3}\) [10]. The calculations predict that the electronic energy of the \( \alpha \)-phase is 6 kJ mol\(^{-1}\) \( \text{Ce}_2\text{S}_3 \) lower (i.e. more stable) than that of the \( \gamma \)-phase. This is in agreement with the fact that \( \alpha \)-\( \text{Ce}_2\text{S}_3 \) is the low temperature configuration. In order to be more stable at higher temperatures the \( \gamma \)-phase must have a larger entropy than the \( \alpha \)-modification. This is plausible because the \( \gamma \)-phase contains vacancies on the cationic sublattice. The voids might cause more low energy lattice phonons in the \( \gamma \)-phase than in the \( \alpha \)-phase. A lowering of phonon frequencies leads to a higher vibrational entropy. Furthermore, the distribution of
voids in the lattice adds a configurational entropy, which also tends to stabilize the \( \gamma \)-phase at elevated temperatures.

Figure 5 compares the partial density of states of \( \alpha \)-Ce\(_2\)S\(_3\) and \( \gamma \)-Ce\(_2\)S\(_3\) in the energy range of \(-37\) to \(10\) eV. Overall, the electronic structures of the two allotropes have common features. The bonding between Ce and S atoms has significant covalent components. It is dominated by the interaction between Ce 5\(d\)- and S 3\(p\)-orbitals. The centers of the bonding and anti-bonding \(p\)-\(d\) bands are approximately \(7\) eV apart in both compounds (cf. Fig. 5).

In both modifications, the effective one-particle energy of this LHB is at the top of the S 3\(p\) vb. This leads to a hybridization between Ce 4\(f\)- and S 3\(p\)-orbitals. Electronic excitations in the visible part of the spectrum involve transitions from the occupied LHB into the cb, which is dominated by Ce 3\(d\)-levels.

However, the present calculations reveal a major distinction between the \( \alpha \)- and \( \gamma \)- allotropes, due to the structural differences. The presence of two different coordination environments of the cerium cations in the \( \alpha \)-phase causes a splitting near the minimum of the cb and also within the occupied 4\(f\)-states at the top of the vb (Figs. 2 and 5). As a consequence, the optical transitions at 1.8 eV responsible for the red color are superimposed by transitions, which start around 0.8 eV. Furthermore, this distinction between the two types of Ce cations in the \( \alpha \)-phase is noticeable also in the Ce 5\(s\)- and Ce 5\(p\)-semi-core states at \(-34\) and \(-17\) eV, respectively (Fig. 5). Both states are split by about 0.5 eV whereby the 5\(s\) and 5\(p\)-states of Ce1 are located at lower energies than that of Ce2. This implies that the effective potential for electrons around Ce1 is more attractive than around Ce2.
6 Summary and conclusions

The present GGA+U calculations yield a very good description of the crystal structures and of the chromatic properties of $\alpha$-Ce$_2$S$_3$ and $\gamma$-Ce$_2$S$_3$ involving 4$f$-electrons explicitly. With a Coulomb repulsion parameter of $U' = 4$ eV the calculated cell volume and most of the interionic distances for both Ce$_2$S$_3$ phases are less than 1% larger than that determined from x-ray diffraction measurements. This is comparable to the accuracy of standard GGA calculations as applied to systems without $f$-electrons. This is a major improvement over standard GGA calculations, which underestimate the cell volume of Ce$_2$S$_3$ derivatives by as much as 6% and fail to predict their semiconducting character [30].

With the same $U'$ parameter the present calculations yield effective one-electron energies, which allow a quantitative interpretation of optical transitions and thus accounts for the colors of the two Ce$_2$S$_3$ allotropes in a satisfactory manner. The vb and cb of both allotropes are dominated by S 3$p$ and Ce 5$d$-states, respectively. In both phases the occupied Ce 4$f$-states are energetically located between the vb and cb, whereby the smallest gap between the occupied Ce 4$f$- and the empty 5$d$-states ($\Delta_{4f-5d}$) is direct and located at $k = \Gamma$.

For the $\alpha$-phase the calculations yield $\Delta_{4f-5d} = 0.8$ eV and a rather small density of states in the range of 0.8–1.5 eV above the vb. The small density of states is due to three low-lying unoccupied bands with strong dispersion and corresponds to low absorption of radiation. The dispersion is related to the (Ce1)S$_8$ coordination polyhedron and it is the reason for the smaller optical band gap and explains the brownish-black hue $\alpha$-Ce$_2$S$_3$. The dark red color (burgundy) of the $\gamma$-Ce$_2$S$_3$ is due to $\Delta_{4f-5d} = 1.8$ eV and a rather steep increase of the density of states around the
lower edge of the cb. The γ-allotrope is characterized by somewhat less dispersive bands and hence a sharper absorption edge.

Thus, the present calculations provide an explanation for the difference of 1 eV in the optical gaps of α-Ce$_2$S$_3$ and γ-Ce$_2$S$_3$. The main factor is the presence of two types of Ce cations in the α-phase with two different coordination environments and the related difference of 3% between the average Ce–S bond distances in the two allotropes. Despite the different sulfur environments the calculations yield for cerium cations effective local magnetic moments of 2.6 $\mu_B$ which is in agreement with magnetic measurements.

It is gratifying that the computed electronic energy of the low-temperature modification (α-Ce$_2$S$_3$) is lower by 6 kJ mol$^{-1}$ (per formula unit) than that of the high-temperature modification (γ-Ce$_2$S$_3$). At low temperatures, the Gibbs free energy, which determines phase stabilities, is therefore lower for the α-phase. At elevated temperatures, the presence of vacancies in the γ–phase is expected to enhance the vibrational and configurational entropy, thus stabilizing the high-temperature phase.

The present GGA+U approach offers a satisfactory description of the Ce 4$f$-states in terms of structural and optical properties. However, the introduction of the on-site Coulomb repulsion does not cure the drawback of standard DFT methods of underestimating the gap between the itinerant S 3$p$- and the Ce 5$d$-band states. The smallest calculated direct gaps between the vb and the cb of γ-Ce$_2$S$_3$ is computed to be 2.3 eV. This is approximately 1 eV smaller than the value determined from optical, photoconductivity, and photoluminescence spectra. The same band gap calculated for α-Ce$_2$S$_3$ is about 1.3 eV and probably also underestimated by 1 eV. A remedy of this problem might be the combination of
GGA+U and GW techniques [53].

In conclusion, the present work demonstrates that the GGA+U approach is successful in describing quantitatively the structural and electronic properties of $\alpha$-Ce$_2$S$_3$ and $\gamma$-Ce$_2$S$_3$. The GGA+U approach overcomes a major shortcoming of standard GGA band structure calculations, which incorrectly yields a metallic bandstructure with $4f$-states at the Fermi level. Instead, we found Ce$_2$S$_3$ to be an $f$-electron Mott insulator, in which strong correlation effects open up a Mott gap within the $4f$-states, between a LHB and an UHB. The LHB is found to play a key role in the physical properties of these compounds, since the optical transitions responsible for their color are between the top of the LHB and the bottom of the $5d$ cb. Furthermore, subtle differences in the calculated electronic structure of the two allotropes (most notably the presence of two inequivalent cerium sites in the $\alpha$-modification, as well as more dispersive bands) give insight into the differences in the optical properties and color of these materials. The present GGA+U methodology applied here to RE compounds, could also be used to predict structural and opto-electronic properties of materials where RE elements are used as dopants. This capability will be particularly useful in the design and improvements of materials for lighting and display technologies with major benefits for our society and the environment.

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1 (color online) Structural features of cerium sesquisulfide allotropes. Blue and yellow spheres represent cerium cations and sulfur anions, respectively. (a) Coordination polyhedra of the symmetry inequivalent cerium cations Ce1 and Ce2 of $\alpha$-Ce$_2$S$_3$. (b) Coordination polyhedron of Ce cations in $\gamma$-Ce$_2$S$_3$. The sulfur anions S and S’ are within and out of the drawing plane, respectively. (c) Smallest conventional unit cell of $\gamma$-Ce$_2$S$_3$ with a stoichiometric amount of cerium vacancies (red spheres). The composition of the super cell is Ce$_{32}$S$_{48}$ and has the highest symmetry possible (space group I$\bar{4}2d$).

2 (color online) Electronic structure of $\alpha$-Ce$_2$S$_3$ around the Fermi energy; (a) band structure and (b) partial DOS calculated for the fully optimized crystal structure. Arrows indicate relevant direct band gaps. The energy axes are labeled relative to the energy of the highest occupied band state. The latter is set to zero and is denoted by dashed lines. VB – valence band, CB – conduction band, UHB and LHB – upper and lower Hubbard bands, respectively.

3 (color online) Contributions of atomic states per $\mathbf{k}$-point to particular electronic bands of $\alpha$-Ce$_2$S$_3$ between $k = T$ and $X$ as shown in Fig. 2. The thicker the electronic bands the larger the contribution of particular atomic states. Significant contributions of specific atomic states are indicated at $k = \Gamma$. Asterisks denote anti-bonding interactions. More details are given in the legend of Fig. 2.

4 (color online) Electronic structure of pure $\gamma$-Ce$_2$S$_3$ around the Fermi energy. (a) Band structure and (b) partial density of states calculated for the fully optimized system Ce$_{16}$S$_{24}$ (space group I$\bar{4}2d$). More details are given in the legend of Fig. 2.

5 (color online) Calculated partial density of states of two Ce$_2$S$_3$ modifications in the energy range between $-37$ and $10$ eV.
Fig. 1. (color online) Structural features of cerium sesquisulfide allotropes. Blue and yellow spheres represent cerium cations and sulfur anions, respectively. (a) Coordination polyhedra of the symmetry inequivalent cerium cations Ce1 and Ce2 of α-Ce₂S₃. (b) Coordination polyhedron of Ce cations in γ-Ce₂S₃. The sulfur anions S and S’ are within and out of the drawing plane, respectively. (c) Smallest conventional unit cell of γ-Ce₂S₃ with a stoichiometric amount of cerium vacancies (red spheres). The composition of the super cell is Ce₃₂S₄₈ and has the highest symmetry possible (space group I42d).
Fig. 2. (color online) Electronic structure of $\alpha$-Ce$_2$S$_3$ around the Fermi energy; (a) band structure and (b) partial DOS calculated for the fully optimized crystal structure. Arrows indicate relevant direct band gaps. The energy axes are labeled relative to the energy of the highest occupied band state. The latter is set to zero and is denoted by dashed lines. VB – valence band, CB – conduction band, UHB and LHB – upper and lower Hubbard bands, respectively.
Fig. 3. (color online) Contributions of atomic states per \textbf{k}-point to particular electronic bands of $\alpha$-Ce$_2$S$_3$ between $k = T$ and $X$ as shown in Fig. 2. The thicker the electronic bands the larger the contribution of particular atomic states. Significant contributions of specific atomic states are indicated at $k = \Gamma$. Asterisks denote anti-bonding interactions. More details are given in the legend of Fig. 2.
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1  Calculated lattice parameters and selected interionic distances, Ce1–X and Ce2–X, of α-Ce$_2$S$_3$ compared with data obtained from the x-ray diffraction measurements of Ref. [11]. The notation is according to that of Fig. 1(a). All distances are given in Å.  

2  Comparison of calculated and measured lattice parameters and selected interionic distances of γ-Ce$_2$S$_3$. The calculated data have been obtained from the fully optimized supercell of Ce$_{16}$S$_{24}$ as depicted in Fig. 1(c). The experimental data has been taken from Ref. [34]. All values are given in Å.
Table 1
Calculated lattice parameters and selected interionic distances, Ce1–X and Ce2–X, of α-
Ce2S3 compared with data obtained from the x-ray diffraction measurements of Ref. [11].
The notation is according to that of Fig. 1(a). All distances are given in Å.

| Parameters | Exp.  | Calc. | Exp.  | Calc. | Exp.  | Calc. |
|------------|-------|-------|-------|-------|-------|-------|
| a          | 7.532 | 7.565 | S1    |       |       | 2.850 | 2.872 |
| b          | 4.097 | 4.119 | S1'   | 3.100 | 3.062 | 3.040 | 3.056 |
|            |       |       |       |       |       | 3.135 | 3.161 |
| c          | 15.728| 15.722| S2    | 2.983 | 2.998 | 2.883 | 2.893 |
| ΔV/V_{exp} [%] | 0.95  |       | S2'   | 4.727 | 4.761 | 2.976 | 2.988 |
|            |       |       |       |       |       | S3    | 3.006 | 3.018 | 2.897 | 2.893 |
|            |       |       |       |       |       | S3'   | 2.850 | 2.853 | 4.696 | 4.719 |
|            |       |       |       |       |       | Ce1   | 4.031 | 4.029 | 4.015 | 4.035 |
|            |       |       |       |       |       | Ce2   | 4.015 | 4.035 | 4.097 | 4.119 |
Table 2
Comparison of calculated and measured lattice parameters and selected interionic distances of $\gamma$-Ce$_2$S$_3$. The calculated data have been obtained from the fully optimized supercell of Ce$_{16}$S$_{24}$ as depicted in Fig. 1(c). The experimental data has been taken from Ref. [34]. All values are given in Å.

| Lattice (Quasi cubic) | Distances       |
|-----------------------|-----------------|
| Parameter             | Exp. | Calc.     | Exp. | Calc.     |
| $a$                   | 8.637| 8.677     | 4.040| 3.958     |
| $c$                   | 8.637| 8.641     | 2.896| 2.898     |
| $\Delta V/V_{exp} \times 100$ | 0.97 |           | 3.087| 3.086     |
| $r_{min}(\text{Ce} \cdots \text{Ce})$ |       |           | 2.896| 2.988     |
| $\langle r(\text{Ce} \cdots \text{S}) \rangle$ |       |           | 3.087| 3.208     |
| $r(\text{Q} \cdots \text{S})$ |       |           | 2.896| 2.988     |
| $r(\text{Q} \cdots \text{S'})$ |       |           | 3.087| 3.208     |
| $r_{min}(\text{Q} \cdots \text{Q})$ |       |           | 7.785| 7.779     |

$a)$ $c/3$ of the tetragonal supercell of Fig. 1(c).

$b)$ Q is the center of the voids on the cation sublattice.

$c)$ The notation is according to Fig. 1(b).