Electronic and optical properties of single crystal SnS$_2$: an earth-abundant disulfide photocatalyst†

Lee A. Burton,*a Thomas J. Whittles,b David Hesp,b Wojciech M. Linhart,b Jonathan M. Skelton,c Bo Hou,d Richard F. Webster,e Graeme O’Dowd,b Christian Reece,f David Cherns,e David J. Fermin,g Tim D. Veal,b Vin R. Dhanakb and Aron Walshch

Tin disulfide is attractive as a potential visible-light photocatalyst because its elemental components are cheap, abundant and environmentally benign. As a 2-dimensional semiconductor, SnS$_2$ can undergo exfoliation to form atomic layer sheets that provide high surface areas of photoactive material. In order to facilitate the deployment of this exciting material in industrial processes and electrolytic cells, single crystals of phase pure SnS$_2$ are synthesised and analysed with modern spectroscopic techniques to ascertain the values of relevant semiconductor properties. An electron affinity of 4.16 eV, ionisation potential of 6.44 eV and work function of 4.81 eV are found. The temperature dependent band gap is also reported for this material for the first time. We confirm the valence band is formed predominately by a mixture of 3p and 5s, while the conduction band consists of a mixture of 5s and 5p orbitals and comment on the agreement between experiment and theory for values of band gaps.

1 Introduction

Today, more than 50% of global primary oil demand is concentrated in the transport sector, compared with around 7% in power generation.1 As such, the greatest strides to be made in securing a sustainable future reside in the substitution of consumable transport fuels with a renewable energy vector. One candidate fuel to achieve this goal is hydrogen gas as it is light, compressible and abundant. However, an efficient and cost-effective way of producing H$_2$ on an industrial scale has yet to be found.

Water photolysis is a potential method of hydrogen production that relies on the energy of the sun to liberate hydrogen gas from water molecules. However, most modern photocatalytic systems are inefficient, and/or require the use of expensive and rare elements, such as Ir, Ga or Pt.

Recent studies have shown that the relatively cheap/abundant transition metal dichalcogenides (e.g. WSe$_2$, MoS$_2$) are promising candidates for photocatalysis and photoelectrochemistry.2,3 In these species the chalcogenide anions pack hexagonally between octahedrally coordinated metal cations, resulting in distinct layers bound by weak van der Waals (VdW) interactions.4,5 Not only do their band gaps typically correspond to regions of the terrestrial light spectrum with high photon intensities,6 but their valence and conduction band extrema also reside near to the energy levels associated with photoelectrochemical water splitting (−4.44 and −5.67 eV to the vacuum potential for reduction,7 and oxidation,8 respectively).9 Furthermore, the large surface area that can be obtained with these ultra-thin structures is a major driving force behind the increased activity in the field, not only because of the increased active area, but because in a 2D system, charges need not migrate to a surface before becoming available to the exterior medium. Tin disulfide (SnS$_2$) is of interest as it exhibits the same 2D structural motif, as shown in Fig. 1, and is expected to display similar electronic properties.10,11 It has been shown to exhibit a band gap of 2.18–2.44 eV,12,13 corresponding to a wavelength of light within the visible region of the electromagnetic spectrum. Here ca. 43% of available solar energy resides, as opposed to around 4% in the ultraviolet region, where the widely studied photocatalyst TiO$_2$ preferentially absorbs.14 Indeed, single atomic layers of SnS$_2$ have already

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Water photolysis is a potential method of hydrogen production that relies on the energy of the sun to liberate
been found to achieve an incident photon to current conversion efficiency of over 38%.\(^\text{16}\)

SnS\(_2\) is also of broader importance as a secondary phase in earth abundant photovoltaic applications, where spontaneous formation has been observed to occur during tin sulfide and copper zinc tin sulfide (CZTS) depositions.\(^\text{17,18}\) While such formation of tin disulfide ought to be carefully avoided in the photo-active bulk, it remains potentially useful as a n-type buffer layer in such applications, as the wide band gap allows for the transmission of visible light and the low lying conduction band minimum can accept migrating electrons from the photoabsorber.

Over 70 stacking polytypes of SnS\(_2\) have been reported to date,\(^\text{19}\) with thin films grown by spray pyrolysis,\(^\text{20}\) chemical bath,\(^\text{21}\) chemical vapour deposition,\(^\text{22}\) and SILAR methods.\(^\text{14}\) Numerous nano-forms of SnS\(_2\) have also been synthesised, including nano-flowers,\(^\text{23}\) nano-flakes,\(^\text{24}\) nano-tubes,\(^\text{25}\) and quantum dots.\(^\text{26}\) In addition, a number of other tin sulfide phases (i.e. SnS and Sn\(_2\)S\(_3\)) are known to exist,\(^\text{27}\) with anisotropic properties of their own.\(^\text{27}\) Unsurprisingly then, reported properties vary with synthesis conditions,\(^\text{26}\) and thus it is important to identify and analyse the ground state, phase pure SnS\(_2\) not just with regards to photocatalytic applications, but all manner of two dimensional devices and metamaterial applications.\(^\text{29}\)

We report the valence band maximum and conduction band minimum energies with respect to the vacuum level and temperature dependent band gaps for phase pure single crystal SnS\(_2\), compare these directly with density functional theory and conclude on the applicability of this system for photocatalysis.

2 Methods

2.1 Experimental details

Single crystals were obtained using the chemical vapour transport (CVT) method, which involved the placement of solid iodine and 1:2 stoichiometric amounts of tin and sulfur in a sealed and evacuated quartz ampoule. A temperature gradient between 850 and 600 °C was enforced across this ampoule for twelve days in order to drive the reaction. Full details of the experimental procedure can be found in Ref. 28, along with additional characterisation such as energy dispersive spectroscopy.

X-ray diffraction (XRD) patterns were taken of the as prepared single crystals to confirm their structures. These were collected on a Bruker D8 instrument with Cu K\(_\alpha\) radiation (\(\lambda = 1.54 \) Å) with the samples being held with a Si XRD holder.

Transmission electron microscopy (TEM) results were prepared by dispersing the sample in toluene and drop casting the solution onto a thin carbon support film on a copper grid. The samples were examined at 200 kV in a JEOL 2010 TEM. Selected area electron diffraction (SAED) and convergent beam electron diffraction (CBED) were performed on samples clamped in a folding grid in a Philips EM430 TEM at an accelerating voltage of 200 kV.

Fourier-transform infra-red (FTIR) absorption spectroscopy was performed using a Bruker Vertex 70 V Fourier transform IR spectrometer using a tungsten lamp, a silicon diode detector and a quartz beam splitter. Measurements were performed between 4 and 350 K using a continuous flow helium cryostat. Reflectance and transmittance measurements were performed at an incident angle of 11° relative to the surface normal from which the absorption spectra were calculated.

X-ray photoelectron spectroscopy (XPS) measurements were carried out using a SPECS monochromated Al K\(_\alpha\) source (1486.6 eV) at 200 W power with a PSP Vacuum Technology electron analyser. The spectrometer was calibrated using standard Ag 3d\(_{5/2}\) peak at 368.3 eV binding energy with a full-width-half-maximum of 0.6 eV and operated in constant pass energy mode. Low resolution survey spectra were taken at 50 eV pass energy, with regions of interest measured at a higher resolution 10 eV pass energy.

The valence band was also probed by XPS, with the crystals held at a constant sample bias, arbitrarily chosen, of ~10.0 V. The conduction band was probed by using inverse photoemission spectroscopy (IPES), using a BaO cathode dispenser electron source and an isochromat NaCl photon detector (PSP Vacuum Technology) to measure the photon energies resulting from the decay of absorbed low energy electrons. Analysis of the measured Fermi edge of a polycrystalline Ag foil indicated instrumental resolutions of 0.3 eV and 0.9 eV for XPS and IPES measurements respectively.

Binding energy scales for the spectra are referenced to the Fermi level determined from the Fermi edge position of polycrystalline Ag foil. Prior to measurement, the single crystals were cleaved by splitting with a steel blade \textit{ex situ} and vacuum prepared by 500 eV Ar\(^+\) ion bombardment for 5 minutes, and annealing at 230 °C for 5 h, to remove surface contaminants.

Finally, Raman spectra were recorded at room temperature with a Raman microscope (Renishaw inVia), using a 532 nm wavelength laser focused through an inverted microscope (Leica), via a 50× objective lens (Leica).

2.2 Theoretical details

The room temperature atomic structure of the SnS\(_2\) single crystals, obtained from the XRD analysis, was relaxed using
Kohn–Sham density functional theory (DFT),\textsuperscript{30,31} within the plane-wave project-augmented wave formalism as implemented in the Vienna ab initio simulation package (VASP).\textsuperscript{32,33} Electron exchange and correlation were described with the generalized gradient approximation (GGA) within the functional of Perdew, Burke and Ernzerhof (PBE).\textsuperscript{34,35}

To account for van der Waals interactions, the D3 correction with Becke–Johnson damping was included,\textsuperscript{36,37} which has been shown to provide superior agreement with experiment over other such relaxation schemes.\textsuperscript{38} A plane-wave basis set with a 500 eV kinetic energy cut-off, was employed with well-converged k-point sampling of at least $8 \times 8 \times 6$. For the electronic structure and band gap results, hybrid-DFT was employed, incorporating 25% screened Hartree–Fock exchange, i.e. the HSE06 functional.\textsuperscript{39}

3 Results

3.1 Materials characterisation

Single crystal XRD confirmed that the SnS$_2$ crystals had the standard hexagonal crystal structure with $P3m1$ symmetry (space group 164) corresponding to the ground state 2H polytype with the lattice constants $a = 3.649$ Å and $c = 5.899$ Å.\textsuperscript{28} This is shown as ESI, Fig. S1.†

Fig. 2 (top-left) shows a TEM micrograph of a thin area of a sample which displays twist dislocations. It can be inferred that the crystals are composed of narrow platelets, highlighted by the termination of the dislocations at the platelet edges, as corroborated by the physical appearance of the macroscopic crystals (bottom-centre). Fig. 2 (top-right) also shows the obtained diffraction patterns for a convergent beam electron diffraction in the [0001] direction, from this the lattice parameter $a = 3.61 \pm 0.04$ Å has been determined, which agrees with the average value determined from XRD and simulated TEM for the 2H SnS$_2$ polytype. A CBED pattern in the [0001] direction, shown as the inset of top-right Fig. 2, shows the 6-fold symmetry expected from this direction.

$$\frac{1}{H} = \frac{2}{\lambda G^2}$$  \hspace{1cm} (1)

A first order Laue zone (FOLZ) ring was observed which is formed by the intersection of the Ewald sphere with the reciprocal lattice of the crystal in the direction of the incident electron beam, in this case the [0001] direction of the crystal. Using Eqn (1) (where $H$ is the height of the unit cell in real space, $G_1$ is the measured radius of the FOLZ ring and $\lambda$ is the wavelength of the electrons used), which is derived from the geometry in reciprocal space, the lattice parameter in the [0001] direction can be determined. This was found to be $c = 5.3 \pm 0.8$ Å, which is consistent with the 2H structure. There is however no sign of any higher order Laue zone rings apart from the FOLZ ring, likely owing to the reduced elastic scattering and the increased inelastic background expected at higher scattering angles.

The absence of an inner Laue ring between the zero order reflections (central spot) and the clear higher order Laue zone ring, indicate that phase pure 2H polytype is obtained (see full-size, annotated image in ESI, Fig. S2†). An inner Laue ring would be present because of the larger $c$ lattice parameter for alternate polytypes as the 2H structure has the smallest $c$ lattice parameter possible for this system.\textsuperscript{40}

Fig. 3 shows unpolarized Raman spectra recorded in back-scattering geometry. Two peaks are visible, one intense peak at 316.2 cm$^{-1}$ and a weaker one at 207.9 cm$^{-1}$. These features are assigned to the two Raman active phonon modes of the 2H

![Fig. 2](image_url) Top left – Bright field transmission electron microscopy of a SnS$_2$ platelet, image near the [0001] zone axis. Top right – Convergent beam electron diffraction pattern near the [0001] zone axis and, inset, detail of the zero order Laue zone from the same sample. Bottom centre – Macroscopic single crystals synthesised from the CVT method, with the scale in centimetres.

![Fig. 3](image_url) Raman spectrum from SnS$_2$, with $A_{1g}$ and $E_g$ modes indicative of the 2H polytype. The inset shows a 20 times magnification of the $E_g$ mode.
polytype of SnS$_2$; that is, with A$_{1g}$ and E$_g$ symmetry, respectively.\textsuperscript{40,41} The 4H and 18R polytypes are ruled out, as they give three peaks within the 190–225 cm$^{-1}$ range rather than the single peak observed here.\textsuperscript{41}

We conclude from the combined X-ray, electron diffraction and Raman results that the single crystals are the ground state 2H polytype of phase-pure SnS$_2$.

### 3.2 Electronic structure: experiment

XPS core level spectra confirmed both the phase purity of the crystals, and also the successful removal of surface contaminants by sputtering and annealing (see Fig. S3 in ESI). The combination of valence band XPS and IPES measurements allows the positions of the valence band maximum ($E_{\text{VBM}}$), conduction band minimum ($E_{\text{CBM}}$), and Fermi level ($E_F$) to be determined with respect to the vacuum level ($E_{\text{vac}}$).\textsuperscript{42} These positions were determined by linear extrapolation of the band edges and secondary electron cut-off, to the baseline, and yielded an ionisation potential ($E_{\text{vac}} - E_{\text{VBM}}$) of 6.44 ± 0.07 eV and an electron affinity ($E_{\text{vac}} - E_{\text{CBM}}$) of 4.16 ± 0.17 eV. A bandgap ($E_{\text{CBM}} - E_{\text{VBM}}$) of 2.28 ± 0.15 eV is thus found that corresponds to the indirect band gap. All of these values are schematically represented in Fig. 4. Given that these techniques have an approximate surface sampling depth of 5 atomic layers it is expected that these values will also be relevant for exfoliated layers and thin films as well as the bulk solid.

The macroscopic single crystals of yellow SnS$_2$ were analysed with FTIR spectroscopy between the temperatures 4–350 K, in order to report the temperature dependence of the band gap. The optical absorption spectra are shown in Fig. 5(a) in the form of absorption coefficient squared versus photon energy. The linear portion of these curves is extrapolated to zero to estimate the direct band gap as a function of temperature. These values are then shown as squares in Fig. 5(b). The room temperature (300 K) direct band gap is 2.38 ± 0.01 eV. The indirect band gap was estimated by plotting the square root of the absorption coefficient versus photon energy (see Fig. S4 in ESI) and extrapolating the linear part of the curves to zero. The values are plotted as circles in Fig. 5(b). It has previously been noted that these methods should be applied with caution to the determination of direct and indirect band gaps that are close in energy.\textsuperscript{43} However, some support for the methodology is provided here by the relatively close agreement between the 300 K indirect band gap value from absorption of 2.25 eV and the room temperature value determined from XPS and IPES of 2.28 eV.

The direct band gap data have been fitted by the standard expressions for the temperature dependence of band gaps, namely the Varshni, Bose–Einstein, and O’Donnell equations.\textsuperscript{44,45} These models account in different ways for the lattice dilation and electron–phonon interactions. All three methods produce a good fit to the data. The coefficients obtained from the fitting procedures are given in Table 1, along with the 0 K band gaps ($E_{\text{go}}$) from extrapolation that allow, in principle, for direct comparison with DFT methods. The 0 K direct and indirect band gaps are found to be 2.56 ± 0.01 eV and 2.48 ± 0.01 eV, respectively. The Varshni parameters for the indirect band gap are $\alpha = 1.61 \times 10^{-3}$ eV K$^{-1}$, $\beta = 312.2$ K and $E_{\text{go}} = 2.485$ eV. The previously determined direct and indirect band gap values for 2H-SnS$_2$ at 273 and 77 K fall close to the fit lines presented here.\textsuperscript{45}

![Fig. 4](image) The energy levels of SnS$_2$ as determined by XPS/IPES in this work, showing the desirable band placements for water splitting.\textsuperscript{7,8}

![Fig. 5](image) (a) Optical absorption spectra as a function of temperature and (b) corresponding direct (closed squares) and indirect (open circles) band gaps for the same single crystal of tin disulphide. Also shown are Varshni, Bose–Einstein and O’Donnell fits to the direct band gaps and a Varshni fit to the indirect band gaps.
observed alongside direct comparison to single crystal experi-
ments. Such consideration allows, uniquely in this study,
from experiment and by relaxation with various common DFT
functionals. Indeed, for the similar, pseudo-2-dimensional SnS
materials band gaps,
accuracy of density functional theory presents itself.

3.3 Electronic structure: calculation

2-Dimensional semiconductors present both an interesting
opportunity and a challenging problem for materials simulation.
The failure of DFT to accurately account for long range van
der Waals, or London dispersion interactions, is well known, as
is the difficulty in calculating accurate values for band gaps.

These two dimensional systems are problematic because their
band gap and inter-bonding layer distance are intrinsically
linked and accurate modelling of such sensitive parameters has
yet to be demonstrated.

SnS2 provides a unique opportunity to study these effects in
the absence of exotic physical phenomena, such as Dirac cones
or topological effects, which can arise from partially filled d-
orbitals in other systems. With the accurate and well-behaved
properties reported for the confirmed ground state structures in
the previous section, the opportunity to appraise suitable levels
of density functional theory presents itself.

The HSE06 functional has been shown to be superior to
other, even higher levels of theory, when it comes to predicting
materials band gaps, without the need for empirical (+U)
parameters. Indeed, for the similar, pseudo-2-dimensional SnS
case, this level of theory has been shown to give exceptional
agreement with electronic properties of single crystals. As
such, we assess the performance of HSE06 for electronic-
structure calculations on atomic structures obtained directly
from experiment and by relaxation with various common DFT
functionals. Such consideration allows, uniquely in this study,
for the effect of the VdW spacing on electronic structure to be
observed alongside direct comparison to single crystal experimental
results.

Table 2 compares the lattice parameters and band gaps ob-
tained from HSE06 calculations on the crystal structure ob-
tained at room temperature from single-crystal XRD both
without relaxation, and after relaxation with several common
DFT functionals. These results show that while the D3 corre-
cction is more successful than PBE at reproducing the interlayer
spacing in the structure, the subsequent application of HSE06
to this structure yields overestimated band gaps (direct 2.68 eV,
indirect 2.14 eV). On the other hand, relaxation with the PBE
level of theory greatly overestimates the interlayer spacing by
more than 15% but does allow for relatively accurate band gaps
when compared to experiment (direct 2.62 eV, indirect 2.32 eV).
The converged atomic coordinates from the HSE06 level gave
band gap values of 2.77 eV and 2.46 eV for direct and indirect
gap respectively. The fundamental gap is the closest value to
experiment reported here but the direct transition is somewhat
overestimated. The full electronic structure at this level yielded
the band structure diagram for SnS2 as shown in Fig. 6. From
this, it is possible to see the highly dispersed conduction band,
corroborating the use of this material as an n-type component
in electrochemical applications, as band dispersion is inversely
proportional to charge effective mass. Similarly the relatively
flat valence band between Γ and A shows the low degree of
bonding between the distinct layers. The direct band gap of 2.77
eV can be seen, in Fig. 6, to occur at M and the fundamental
band gap of 2.25 eV is between the VBM at Γ and the CBM at L.
The valence band is found to be composed of a mixture of S 3p
and Sn 5s, while the conduction band consists of a mixture of
Sn 5s and 5p orbitals, for all HSE06 calculations.

All of the methods implemented in this work yield band gap
energies that are simultaneously over and under estimated for
the direct and indirect gap respectively. This behaviour shows
that more than a scissor operator is required to correct the
single-particle Kohn–Sham density functional theory descrip-
tion, i.e. a more rigorous description of many body effects may
be required for 2D systems. Our results indicate therefore that
in order to recover properties for these 2D systems that are as
accurate as possible, more sophisticated implementations of
DFT are necessary, for example the self consistent screening
approach described by Lucero et al., and the explicit treat-
ment of electron–phonon coupling. This is due to the sensitivity
of the electronic structure on the VdW spacing that is, as of yet,
poorly described, even with modern corrections. For now, the
most optimal method appears to be allowing structural relaxa-
tion with the HSE06 level of theory. While this is the most

Table 1 Coefficients for the fitting procedures illustrated in Fig. 5 relating band gap to temperature, as listed. $E_{g0}$ denotes the extrapolated 0 K band gaps.

<table>
<thead>
<tr>
<th>Fitting procedure</th>
<th>Parameter</th>
<th>Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>Varshni $^{46}$</td>
<td>$\alpha$ (eV K$^{-1}$)</td>
<td>$2.12 \times 10^{-3}$</td>
</tr>
<tr>
<td></td>
<td>$\beta$ (K)</td>
<td>797</td>
</tr>
<tr>
<td>Bose–Einstein $^{47}$</td>
<td>$a$ (eV)</td>
<td>0.151</td>
</tr>
<tr>
<td></td>
<td>$\theta$ (K)</td>
<td>304.7</td>
</tr>
<tr>
<td>O’Donnell $^{48}$</td>
<td>$\Delta$</td>
<td>5.76</td>
</tr>
<tr>
<td></td>
<td>$h$ (eV)</td>
<td>0.026</td>
</tr>
<tr>
<td></td>
<td>$E_{g0}$ (eV)</td>
<td>2.559</td>
</tr>
</tbody>
</table>

Table 2 The band gaps found from the DFT calculation procedures in this work and their comparison with single crystal data. The difference from experiment in each case is indicated in brackets (%).

<table>
<thead>
<tr>
<th>Ionic procedure</th>
<th>Electronic procedure</th>
<th>Direct gap (eV)</th>
<th>Indirect gap (eV)</th>
<th>$c$ lattice parameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>HSE06</td>
<td>2.74 (7.03)</td>
<td>2.29 (−7.66)</td>
<td>5.899 (0.00)</td>
</tr>
<tr>
<td>PBE</td>
<td>HSE06</td>
<td>2.62 (2.34)</td>
<td>2.32 (−6.45)</td>
<td>6.859 (16.3)</td>
</tr>
<tr>
<td>PBE-D3</td>
<td>HSE06</td>
<td>2.68 (4.69)</td>
<td>2.14 (−13.7)</td>
<td>5.808 (−1.54)</td>
</tr>
<tr>
<td>HSE06</td>
<td>HSE06</td>
<td>2.77 (8.20)</td>
<td>2.46 (−0.81)</td>
<td>6.561 (11.2)</td>
</tr>
<tr>
<td>Experiment</td>
<td></td>
<td>2.56</td>
<td>2.48</td>
<td>5.899</td>
</tr>
</tbody>
</table>
It is also expected that these results will have impacts beyond photocatalysis. For example, the energy levels of SnS$_2$ are similar to those found in the n-type material cadmium sulfide (band gap of 2.41 eV and electron affinity of 4.5 eV), commonly used in photovoltaic devices. In this way SnS$_2$ could facilitate the elimination of cadmium from these devices, decreasing costs and increasing the deployment of such an important renewable energy source.

We also report the temperature dependent electronic structure relationship for the first time. Extrapolation to a value at 0 K ($E_{g0} = 2.56$ eV, Bose–Einstein fit) provides a reliable reference point for first principles electronic structure calculations. Such realistic benchmarks can greatly facilitate the development of new van der Waals corrections and subsequent improvements of simulation accuracy that we show are currently lacking in the field.

Finally, DFT analysis shows that while many corrections to DFT exist, the optimal method of analysing the electronic structure of such systems is the HSE06 level of theory relaxation of crystal structures. That is to say that in this study, the DFT band gap that is closest in value to the single crystal data, from the several common methods deployed in this work, is the one in which HSE06 was used to fully converge atomic and electronic configurations.

The physical properties reported in this work, combined with the high surface areas readily obtainable with this class of 2-dimensional semiconductors, show that phase pure SnS$_2$ is certainly one of the most promising candidates for water splitting considered to date.

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### References