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# The surface stability of CoS$_2$(100)

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**Abstract**
The stability of various possible terminations of the CoS$_2$ (1 × 1) surface have been explored
and theoretical expectations are found to agree with experiment. With extensive annealing,
there is a phase separation at the (100) surface of CoS$_2$. Sulfur segregation to the surface leads
to a significant change in the largely sulfur bands due to changes in the hybridized bands, with
cobalt. Resonant photoemission spectra indicate clearly that the hybridized cobalt and sulfur
bands, characteristic of the CoS$_2$ bulk, lie at higher binding energies than those of
segregated sulfur layers. This is discussed in terms of the stability of various surface
structures.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

The pyrite-type transition metal compound CoS$_2$ is an
itinerant electron ferromagnet. In ground state band structure
calculations [1–6], CoS$_2$ is predicted to be highly spin
polarized and to be at least close to existing as a half-metallic
ferromagnet: i.e. a ferromagnet possessing only one spin
channel for conduction. An electron spin polarization of
about 56%, from point-contact Andréev reflection, has been
determined [7], consistent with a small distortion of the sulfur
positions [8].

While the alloy system of Fe$_{1-x}$Co$_x$S$_2$ systems will likely
suffer from Co segregation [9], the surface of CoS$_2$(100)
is a dense packed surface, with Co and S atoms in close
proximity, with the sulfur atoms outermost [10]. We have

found that the atoms in sublayer S and Co relax outward
(toward the vacuum) and inward (toward the bulk), along
the surface normal ('$x$'), approximately by 0.03 and 0.11 Å,
respectively [10]. The surface lattice relaxation suggests a
surface free enthalpy that differs from the bulk. With a
high surface energy, with simple bulk termination, surface
states and surface segregation are both likely, as has been
observed with many other high polarization materials [11].
The sulfur segregation has been studied in the iron-base
binary systems [12] and with adsorption on clean iron
surface [13–17].

As with all high polarization materials, surface stability
is a key issue [11] and here, the objective is the investigation
of the stability of various surface terminations as well as
possible compositional changes that may occur at the surface
of CoS$_2$(100). We have also begun an effort to characterize
the resulting changes in electronic structure in the surface and
selvedge of this system, that occur as a result of compositional
changes at the surface.

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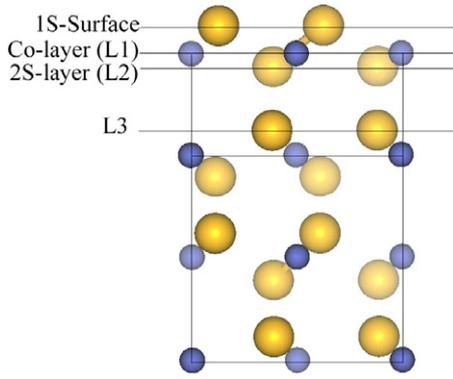Laboratory of Physics, University of Nebraska, Lincoln, NE 68588-0111,
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**Figure 1.** Schematic diagram of the 1S termination of the $CoS_2(100)$ surface (side view of the unit cell from the (100) direction). Large balls represent sulfur atoms, and small balls show cobalt atoms. The three surface layers are shown on top of the fcc unit cell (the interplane distances are summarized in table 1). These three layers are the possible ideal terminations of the (001) surface. 1S-structure is found to be the stable surface by dynamical low energy electron diffraction scattering [10].

## 2. Experiment

The crystals were prepared by chemical vapor transport, and have controlled stoichiometry well, as detailed in previous publications [18, 19]. Sample surfaces were initially prepared by the cleavage of sufficiently large $CoS_2(100)$ single crystal (millimeters in diameter) [8, 10]. The samples appear to be single crystal with no evidence of twinning or grain boundaries in the low energy electron diffraction (LEED) or x-ray diffraction [10, 18]. The surfaces prepared by cleavage alone result in stoichiometric surfaces [7], and the surface can be flash annealed up to 120 °C without the apparent loss of surface order or change in surface stoichiometry. Annealing the surface up to 200–300 °C may increase surface roughness as the mirror metallic 'finish' apparent after cleavage is lost with even modest annealing. Annealing to higher temperatures (in the vicinity of 350 °C and above) can alter the surface of $CoS_2$ significantly, principally through a surface enrichment of sulfur.

Angle-resolved photoemission spectra were obtained using plane polarized synchrotron light dispersed by a 3 m toroidal grating monochromator, at the Center for Microstructures and Devices (CAMD) [20]. The measurements were made in a UHV chamber, with a pressure of $1 \times 10^{-10}$ Torr, employing a hemispherical electron analyzer with an angular acceptance of $\pm 1°$, as described elsewhere [21, 22]. The combined resolution of the electron energy analyzer and monochromator is 120–150 meV for high kinetic photon energies (50–120 eV), but higher resolution (about 80 meV) was obtained at lower photon energies of 25–40 eV. The photoemission experiments were undertaken with a light incidence angle of 45° with respect to the surface normal and with the photoelectrons collected along the surface normal. All binding energies are referenced to the Fermi level, as determined from clean gold.

The scanning tunnel microscopy (STM) measurements were done with the base pressure lower than $2 \times 10^{-10}$ Torr. A sharp W tip was used to obtain atomic resolution images

**Table 1.** Interlayer distances for three surface terminations (in Å). Relaxed values are given in the brackets. The results derived from experimental low energy electron diffraction are in the last column.

|         | Co            | 1S           | 2S            | LEED |
|---------|---------------|--------------|---------------|------|
| Surf.-L1 | 0.234 (0.446) | 0.736 (0.75) | 1.285 (1.587) | 0.75 |
| L1-L2   | 1.479 (1.545) | 0.355 (0.38) | 0.691 (0.726) | 0.38 |
| L2-L3   | 0.673 (0.746) | 1.686 (1.65) | 0.557 (0.506) | 1.65 |
| L3-L4   | 0.626 (0.679) |              |               |      |

and all the STM studies reported herein were done at room temperature in an Omicron variable-temperature scanning tunnel microscopy (STM).

## 3. Modeling the surface termination of $CoS_2(100)$

Stability of the $CoS_2$ surface is analyzed from the comparison of surface energies obtained by first-principle calculations using the projector augmented-wave (PAW) method implemented in the Vienna *ab initio* simulation package (VASP) [23]. The exchange–correlation potential is treated in the generalized gradient approximation (GGA). We use the energy cut-off of 350 eV for the plane wave expansion of the PAWs and a $10 \times 10 \times 1$ Monkhorst–Pack grid for $k$-point sampling. Other details of the calculations can be found elsewhere [23, 24]. All the structural relaxations are performed until the Hellman–Feynman forces on the relaxed atoms become less than 10 meV Å$^{-1}$.

The (100) surface has three possible surface terminations which can be viewed as the various truncations of the unit cell by the (100) plane. We will follow the notations given by Jin and Lee [25] to describe terminations as Co-terminated (L1 in figure 1), 2S-terminated by two planes of sulfur (L2 in figure 1) and 1S-terminated by sulfur atoms nearest to Co-plane (see figure 1). We used a slab model where we included four full unit cells of $CoS_2$ (each unit cell contains four Co and eight S atoms) and additional layers to form particular termination. For example, 1S termination has 4.5 unit cells with 54 atoms in our calculations. This corresponds to about 9 composite $Co_2S_4$ layers with average interlayer distance of 2.76 Å.

As with the theoretical study by Jin and Lee [25], we found that the 1S-terminated surface is the most stable surface, consistent with the experimental surface structural determination [10]. This surface is not however a simple termination of the bulk structure.

The calculated interplanar distances for the three different surface terminations are presented in table 1. The agreement of calculated interlayer spacing for 1S termination with the low energy electron diffraction (LEED) results is also very good, while the two other possible terminations [10, 25] are not consistent with experimental findings. The stability of the 1S-terminated surface is also corroborated by the smaller relaxation of surface atom position compared to the ideal positions of atoms in the bulk unit cell.

There is a key difference between the model calculations here and the prior surface structural models. Unlike Jin and Lee [25], we find that not only does the terminal surface layer retain a complete S–Co–S sandwich structure but that
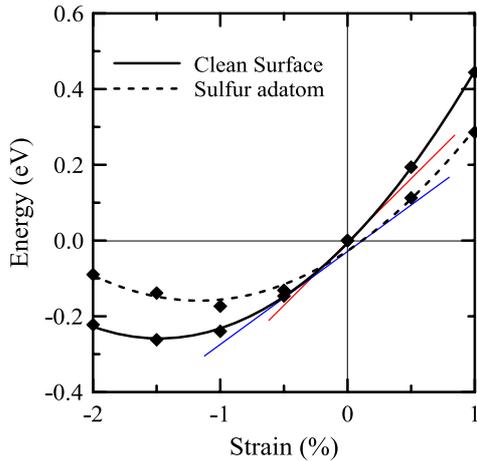
**Figure 2.** The total energies as function of in-plane strain (using the epitaxial Bain path (EBP) model) for 1S termination: clean (solid line) and S-adatom (dotted line) for the (100) surfaces of $CoS_2$. The slope of energy at zero strain is substantially higher in case of the 'clean' (100) surface than the slope for the surface containing a sulfur adatom.



**Figure 3.** 1S termination of the $CoS_2(100)$ surface: side view of the slab from the (100) direction (left panel), top view of the slab (right panel). The sulfur adatom is shown in a darker color.

the surface S atoms move outwards towards the vacuum while the subsurface Co atoms move towards the bulk. This is consistent with experiment [10], as seen in table 1. Prior work by Jin and Lee [25] suggested that both the topmost sulfur and the topmost cobalt layers should contract towards the bulk by roughly 8% and 34% respectively, which is not observed in experiment. We believe the main reason for the different outcomes in the model calculations undertaken here and those undertaken by Jin and Lee [25] is that the calculations presented here follow from allowing all the atoms in the slab to relax perpendicularly into the bulk with fixed in-plane parameter. Jin and Lee [25], on the other hand, only varied the top two layers, i.e. the top Co–S layer. By 'fixing' or constraining the positions of the sulfur layer right under the surface Co, an inappropriate surface relaxation is calculated (in spite of the sufficient accuracy of the calculation) because the subsurface sulfur is a part of the combined S–Co–S surface layer.

We have estimated the surface energy by using the epitaxial Bain path (EBP) approach [26, 27]. Uniform compressive strain was applied in the plane of the slab to find the elastic response of the system. The slab is allowed to relax in the perpendicular direction. The total energy as a function of the applied strain is shown in figure 2. The surface stress of 1S-terminated surface is equal to 8.5 N m$^{-1}$ for the (100) estimated by the slope of the EBP energy derivative at zero strain (i.e. the bulk lattice parameter). The 1S termination, despite being stable, still has a large calculated surface tension which suggests that additional mechanisms of surface relaxation are possible. Partial segregation of sulfur at the surface is one probable outcome. We have performed this slab calculation with the presence of the sulfur adatom at the (100) surface. We find that the adatom forms a 'dimer' structure (figure 3) with another sulfur atom, and bond formation between the two sulfur atoms is observed. This means that excess (segregated) sulfur may partly fill the
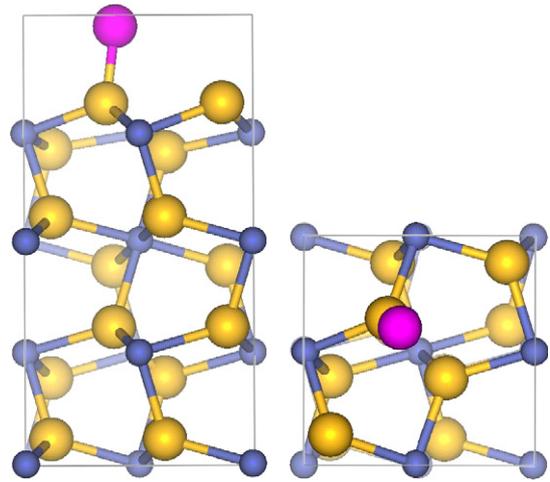
'overlayer' on top of the 1S termination, and a stable sulfur rich surface is possible. The formation of a dimer is expected from the crystal structure of a bulk $CoS_2$. Sulfur atoms form dimer structures on an fcc lattice which is embedded in the Co fcc lattice. When a fresh surface is obtained by (100) plane cleavage, there is a stretching of these dimers in the case of the 1S termination to 0.218 nm from 0.212 nm in the bulk. These dimers would tend to be naturally restored over time. The length of the newly formed dimer on top of the surface is equal to 0.194 nm which is shorter than in the bulk.

Figure 2 shows the epitaxial Bain path (EBP) model results for the case of sulfur adatoms on the 1S-surface termination. Clearly, the curvature of the energy dependence and the slope at zero strain are smaller in the presence of an adatom. This means that the segregation of sulfur atoms will reduce the surface energy (tension) and produce a more stable surface. The surface stress in the presence of the sulfur adatom is equal to 5.5 N m$^{-1}$, which is 35% lower than that of a clean surface.

We have considered other possible surface modifications in order to explore possible mechanisms for sulfur segregation, such as exchange of sulfur and cobalt atoms, and sulfur atom diffusion outwards to the surface. First, we find that the formation of vacancies on the 1S surface with excess of sulfur diffusing out is not likely because the sulfur adatoms have no potential barrier to 'back diffusion' and migrate back to the ideal position upon relaxation. We also find that the Co-terminated surface (which can be considered as a sulfur depleted 1S surface) is unstable with respect to the exchange of a Co atom from the surface layer with a S atom in the subsurface layer. The total energy is reduced upon the exchange of Co and S by more than 2 eV per slab of 54 atoms (which was used to calculate this surface). This means that S would segregate on top of the Co layer making the surface effectively similar to a 1S termination.
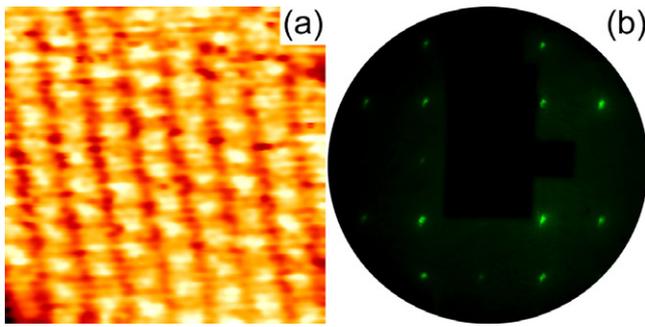
**Figure 4.** The surface structure, as imaged by STM (a) and (b) LEED at room temperature, respectively. The STM image was taken on an area of 3.8 nm × 3.8 nm with sample bias $V_{bias} = 0.55$ V and tunneling current $I_t = 0.48$ nA. A slight sample drift during imaging was not corrected. The LEED diffraction image was taken at an incident electron kinetic energy of 107 eV.

## 4. Other possible surface terminations of $CoS_2(100)$

The surface composition and order of $CoS_2(100)$ were seen to be strongly dependent upon surface preparation. Both the low energy electron diffraction (LEED) and the scanning tunneling microscopy (STM) indicate that the $1 \times 1$ surface structure dominates the cleaved surface, as seen in figure 4. For such a surface, the surface sulfur dimer pairs, associated with each surface unit cell, is the likely source of the STM images. Without LEED I(V) analysis [10], the glide plane symmetry of the $CoS_2(100)$ surface region is not apparent and the LEED appears to be 4-fold symmetric. As noted in the prior sections, the surface terminated as in the structure shown in figure 1 or figure 3, less the sulfur adatom, is the favored surface. This is not the only possible surface termination observed however.

Sulfur segregation could be easily obtained after annealing above 650 K *in vacuo*, although it was difficult to control the surface formation by controlling annealing temperature. With sulfur segregation or compositional phase separation at the surface, the clarity of the $1 \times 1$ LEED patterns diminished but a sulfur $c(2 \times 2)$ superstructure was not observed in the LEED. This could mean disorder, a multiplicity of surface binding sites for sulfur, or that the adlayer of sulfur is highly mobile on the close packed 1S-terminated $CoS_2(100)$ surface.

Figure 5 illustrates the normal emission photoemission spectra for a photon energy 40 eV, as a function of annealing. The broad photoemission features spread between $-3$ and $-7$ eV, are ascribed to the S 3p bands [8]. The sharp photoemission peak around $-0.8$ eV is attributed to the fully occupied very narrow band width Co 3d (bulk $t_{2g}$) band. The partially occupied Co 3d (bulk $e_g$) band can be seen as a shoulder to the prominent Co peak, near the Fermi level. Higher resolution photoemission spectra show that the Co 3d ($e_g$) band is around $-0.15$ eV binding energy, generally consistent with theory [1–3].

With increased annealing, the photoemission features attributable to the largely sulfur weighted bands in $CoS_2$ diminish in intensity, while there is an increase in the density of states in the vicinity of 4 eV binding energy (figure 5). We attribute this to a decrease in sulfur to cobalt hybridization with increased annealing.
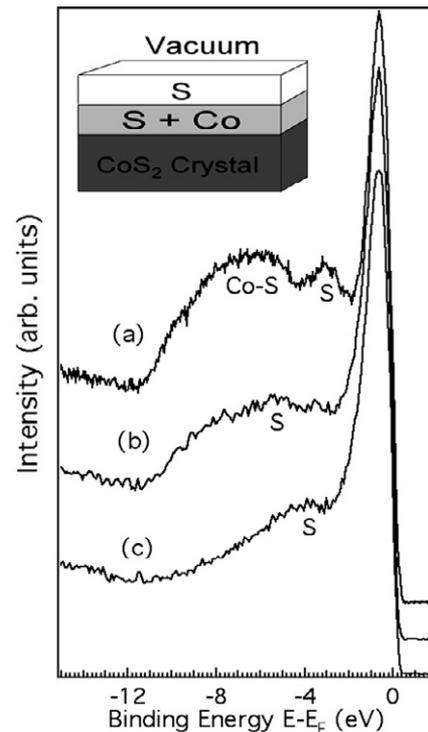


**Figure 5.** The photoemission spectra of $CoS_2(100)$ for photon energies 40 eV, taken at normal emission ($k_\parallel = 0$), for the stoichiometric clean surface (a), after first annealing (b), after second annealing (c). The inset shows a schematic diagram of the segregated sample with sulfur and cobalt layers.

In a previous photoemission study of sulfur segregation on clean iron surfaces, it has been shown that the sulfur band is very weak in photoemission and to a great extent depends on the incident photon energy [14]. Because surface bands with strong sulfur weight are very sensitive to the photon energy, if the bands have little or no cobalt weight, then at 40 eV photon energy, such bands should be very weak, which is not the case for the photoemission spectrum for clean $CoS_2(100)$, shown in figure 5(a). For the stoichiometric surface, there are some broad features of the S 3p band that can be resolved into a number of subbands in the vicinity of $-3$ and $-9$ eV, all with appreciable cross section at 40 eV. These bands have been demonstrated to have some cobalt character [8], and thus can retain some appreciable cross section to 40 eV.

After first time 'flash' annealing, to approximately 600 K, the segregation of sulfur resulted in the photoemission spectrum shown in figure 5(b). The hybridized Co–S bands and another sulfur band are suppressed. The hybridized Co–S bands are completely destroyed in figure 5(c), after an annealing cycle to approximately 600 K, additional sulfur is driven to the surface. We still can see the $-3$ eV sulfur valence band though this photoemission feature is not as obvious as for the 'fresh' surface. After each annealing treatment to approximately 600 K or more, an additional 'excess' of sulfur is evident at the surface, although the surface sulfur band due to the 'adlayer' surface sulfur is weak due to the low cross section of sulfur at a photon energy of 40 eV [28]. On the other hand, the hybridized band of $CoS_2(100)$ vanishes because of sulfur
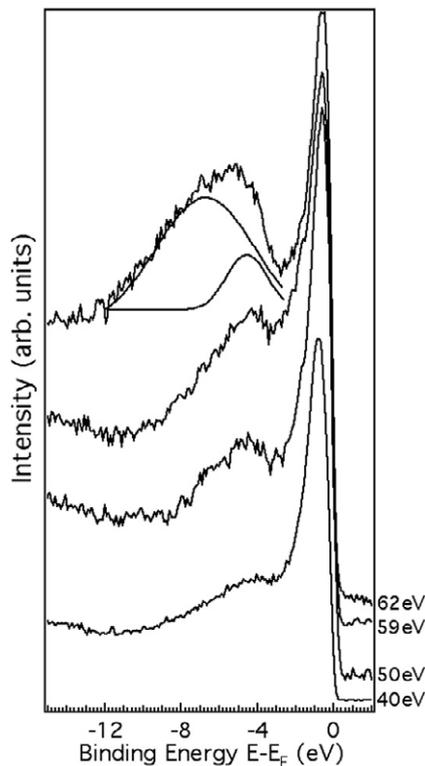
**Figure 6.** The photoemission spectra of segregated (heavily annealed) $CoS_2(100)$ for photon energies 40, 50, 59 and 62 eV. The intensity enhancement for the hybridized band indicates that the resonance phenomenon can still be seen in the S segregation at the surface of $CoS_2(100)$. The components of the heavily weighted sulfur 3p bands associated with $CoS_2$ (at higher binding energies) and for the sulfur rich surface layer (lower binding energy) are indicated.

segregation and consequently less bonding is evident between sulfur and cobalt in the bulk (at least the several topmost layers in the $CoS_2$ system).

To ascertain the extent of the sulfur segregation, after extensive annealing, we changed photon energy to enhance the hybridized Co–S bands of $CoS_2(100)$. The photoemission intensity of the hybridized Co–S −6 eV binding energy bands increases drastically at incident photon energy of 62 eV, which is near the Co 3p shallow core edge. The photoemission resonance is shifted towards higher photon energies than observed for pure cobalt (around 59 eV) due to the strong hybridization between sulfur and cobalt [8]. Figure 6 shows the normal emission photoemission spectra for a $CoS_2$ sample that has sulfur segregation layers after three annealing treatments to approximately 600 K or more. For the purpose of comparison, we show the spectra at four different photon energies: 40, 50, 59 and 62 eV.

Since this $CoS_2$ sample has extensive sulfur segregation at the surface, we can only see the broad sulfur 3p weighted bands, and the Co–S hybridized band of $CoS_2(100)$ is not very obvious in the photoemission spectra taken at photon energies below 60 eV. However, the resonance phenomenon still exists because the photoemission intensity at −4 to −6 eV binding energy ($E-E_F$) is enhanced at photon energy 62 eV. The broad sulfur features can be resolved into two bands by a simple Gaussian lineshape fitting. The photon energy dependent photoemission spectra suggest that the −4 eV binding energy photoemission feature does not change very much for different photon energies. The intensity enhancement of the sulfur 3p weighted photoemission features at −4 to −6 eV binding energy ($E − E_F$) in the region of a photon energy of 62 eV, is largely photoemission resonance of the −6 eV binding energy photoemission feature, which must therefore contain some Co weight. This −6 eV binding energy ($E − E_F$) photoemission feature is observed in the clean $CoS_2(100)$ system. Although the Co–S hybridized bands of $CoS_2(100)$ are suppressed in the photoemission spectra by the sulfur segregation, the hybridized Co–S bands of $CoS_2(100)$ at −6 eV binding energy ($E − E_F$) can still be seen by resonance photoemission.

This behavior may indicate that there is a mixed layer of cobalt and sulfur between segregated sulfur layers and the clean $CoS_2$ surface, schematically indicated in the inset of figure 5, or that the sulfur rich layer that is evident at the $CoS_2(100)$ surface following multiple annealing treatments is no thicker than the escape depth of the photoelectron (the photoelectron mean free path) at about 55 eV kinetic energy (through sulfur, about 4–8 Å). After sulfur segregates to the surface, the photoemission spectra of our sample are very similar to those of clean iron with segregated/absorbed sulfur [12, 13].

Such sulfur segregation is very likely to lead to a huge decrease in surface spin polarization, much the observations that the surface enrichment of NiMnSb, with either Sb or Mn, leads to a huge decrease in measured spin asymmetry [29, 30]. The details of the sulfur surface segregation at the surface of $CoS_2(100)$, such as the extent and stable site locations must, however, be determined before model calculations can be undertaken, although the sulfur segregation observed remains consistent with our theoretical expectations as noted in the prior theoretical discussion. Compared with sulfur segregation from clean iron, more sulfur atoms could segregate to the surface of $CoS_2(100)$ due to large amount of sulfur atoms in the $CoS_2$ bulk, but there is no evidence as yet that this is the case.

## 5. Summary

Two different stable or metastable surface phases have been identified; one associated with the surface after a fresh 'cleaved surface', and the other occurring after annealing the $CoS_2(100)$ single crystals. Sulfur segregates to the surface and causes vanishing of the hybridized band, which can only be seen at resonance photoemission at Co 3p shallow core edge (after the Co to S bonding of $CoS_2$ is taken into account). With sulfur segregation, the photoemission suggests that a near surface hybridized Co–S selvedge region is still preserved, although there does appear to be phase separation at the surface of $CoS_2(100)$. For the stoichiometric surface, the calculated surface S–Co–S atomic layer relaxations are seen to be in agreement with experiment if all the surface layers are allowed to relax.

## Acknowledgments

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