Supplementary Materials Submitted to *Physical Chemistry Chemical Physics* X-ray absorption spectroscopy insights on the structure anisotropy and charge transfer in Chevrel Phase chalcogenides

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### Materials

 $MoS_2$  powder (99%, ~325 mesh), Cu powder (99.995%, ~100 mesh),  $MoSe_2$  powder (99.999%, ~200 mesh) and Ni powder (99.8%, ~325 mesh) were used as purchased from Alfa Aesar. Mo powder (99.99%, ~100 mesh) and Te powder (99.8%, ~200 mesh) were used as purchased from Sigma Aldrich. Fused quartz tubes (2 mm thick) were purchased from AdValue Technology and made into round-bottom tubes with an in-house oxy-hydrogen torch.

### Synthesis and characterization

Cu<sub>2</sub>Mo<sub>6</sub>S<sub>8</sub>, Mo<sub>6</sub>Se<sub>8</sub>, Cu<sub>2</sub>Mo<sub>6</sub>Se<sub>8</sub>, Mo<sub>6</sub>Te<sub>8</sub> and NiMo<sub>6</sub>Te<sub>8</sub> were all synthesized through a microwave-assisted solid-state synthesis approach described in detail in our previous work.<sup>1–3</sup> In short, precursors powders were stoichiometrically mixed in an N<sub>2</sub> filled glovebox and ball milled overnight. The mixed powders were pressed into a pellet, packed in a quartz tube under inert atmosphere and heated inside a graphite bath in a conventional microwave oven for up to 10 minutes. CP sulphides and selenides were obtained after 10min of heating at a power of up to 1000 W, reaching temperatures between 1000-1200°C. The power level was adjusted accordingly to maintain a temperature between 900 and 1000°C for the telluride phase to avoid synthesizing a mixture of CP telluride and metallic Mo that is observed at higher temperatures due to Te loss. Owing to the metastability of Mo<sub>6</sub>S<sub>8</sub> through chemically etching in O<sub>2</sub>-bubbled 6.0 M HCl according to literature methods.<sup>4</sup> Phase purity of each CP was confirmed through PXRD using a Bruker D8 Advance diffractometer with Cu K-alpha radiation (1.5406 Å), while morphology was evaluated using a FEI (Hillsboro, OR) 430 Nano Scanning Electron Microscope (SEM).



Figure S1. a) SEM Micrographs of a)  $Mo_6S_8$ , b)  $Mo_6Se_8$  and c)  $Mo_6Te_8$  along their corresponding PXRD diffractograms d) - f).



**Figure S2**. Changes in 2 $\theta$  values for the diffraction peak in the (101) plane upon metal intercalation in CP sulphides **a**) and selenides **b**). Metal intercalation in CP tellurides results in a triclinic distortion, in which the diffraction peak ~2 $\theta$  = 12.5° corresponds to diffraction in the (101) and (010) for binary CP telluride and metal intercalated CP telluride, respectively **c**).

### XAS data analysis of Chevrel-phases

To ensure the resulting amplitude within the k-space is accurate, samples were first ground down into fine powder using a mortar and pestle. Subsequently, acetone was added to the resulting powder to create a suspension of the smaller particles. The suspension was then drop cast onto a glass slide and allowed to dry. Once dried, the powder was scrapped onto Kapton tape used as a transparent film for X-ray analysis. Mo<sub>6</sub>S<sub>8</sub>, Cu<sub>2</sub>Mo<sub>6</sub>S<sub>8</sub>, Mo<sub>6</sub>Se<sub>8</sub>, Cu<sub>2</sub>Mo<sub>6</sub>Se<sub>8</sub>, Mo<sub>6</sub>Te<sub>8</sub>, NiMo<sub>6</sub>Te<sub>8</sub> were all screened at their respective Mo K-edge, corresponding chalcogen edges: Te L<sub>III</sub>-edge, S K-edge, Se K-edge, and their metal promoter K-edge (Cu and Ni). CPs were screened at Mo, T, and M K- and L- edges at SSRL beamline 4-1 (Mo K-edge, Cu K-edge, Ni K-edge, Se K-edge, and Te L-edge), SSRL beamline 4-3 (S K-edge, Mo L-edge), and NSLS 6-BM (Mo K-edge). For each analysis, a reference foil of the corresponding element edge was placed downstream from the sample chamber in transmission data acquisition mode and fluorescence signal was taken simultaneously to allow for post-analysis calibration of the beam energy. For S K-edge scans, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> powder was used as a standard where the position of the white line peak was set to 2472.04 eV.<sup>5–7</sup> It is to be noted that multiple standards have been used in previous studies (such as the peak position of the elemental sulfur S K-edge<sup>8</sup> and molybdenum foil L<sub>3</sub>-edge<sup>9</sup>).

Each edge scan <5000 eV was performed under He to mitigate beam interactions with  $O_2/N_2$  which can diminish the fluorescence signal intensity, while edge scans >5000 eV were performed under ambient atmospheric conditions. Spectra were acquired in triplicate and averaged prior to data analysis to improve signal-to-noise ratio. All reported results correspond to fluorescence data collected with a Lytle detector.

#### EXAFS analysis

Full X-ray absorption (including XANES and EXAFS regions) spectra for each of the elements in the six Chevrel-phases that were investigated were first averaged in *SixPack*. Postprocessing of data was performed in *Athena*<sup>10</sup> version 0.9.26 including normalization of spectra resulting from the pre- and post-edge regions of each respective edge. Mo K-edge X-ray absorption spectra were used fully after averaging. In cases where there was edge overlap, for example in  $Mo_6S_8$  where the Mo L<sub>3</sub>-edge is located 50 eV past the S K-edge, data was truncated to properly delimit each edge region. The processed data was then imported into *Artemis*, version 0.9.26, where the corresponding real-space data was fit with theoretical models that were established using structural information from the International Crystallographic Structure Database using IFEFFIT model for numerical calculations.<sup>10,11</sup>

Amplitude reduction factors  $(S_0^2)$  which account for multiple-electron excitations of an absorbing atom were treated as empirical parameters in the EXAFS analysis, and were calculated using the appropriate metal reference.<sup>12</sup> Debye-Waller factors ( $\sigma^2$ ) which relate to the thermal motion of a system, specifically thermal disorder of crystalline solids were defined as being identical for any species that had similar bonding environments (e.g. Mo – S<sub>1</sub> and Mo – S<sub>2</sub> paths were treated with the same Debye-Waller factor).  $\Delta E_0$  is the relative difference between the edge

position of the element and the edge position calculated by FEFF. This parameter has a strong correlation with  $\Delta r$  for various paths. Identification of each edge energy, E<sub>0</sub>, was ascribed to the first derivative of the Mo K-edge plot shown in **Figure S3**. **Table S1** showcases the scattering element, scattering pathway with the corresponding path label associated with **Figure 3**, and the distance that was calculated for the scattering paths, all of which show good agreement with previously reported crystallographic data.<sup>13</sup>

Path length information from the EXAFS region of the Mo-K edge was acquired for all Chevrel-phase samples. The values obtained through this analysis were used to calculate the % anisotropy of the materials which is shown in **Table 1**.



Figure S3. First derivative of the Mo K-edge

Chevrel-Phase	Scattering Path	Distance (Å)
	Mo-Mo <sub>intra</sub>	2.78, 3.05
Mo <sub>6</sub> S <sub>8</sub>	Mo-S <sub>inter</sub>	2.52
	Mo-S <sub>intra</sub>	2.40
	Mo-Mo <sub>intra</sub>	2.58, 2.70
Cu <sub>2</sub> Mo <sub>6</sub> S <sub>8</sub>	Mo-S <sub>inter</sub>	2.28
	Mo-S <sub>intra</sub>	2.42
	Mo-Mo <sub>intra</sub>	2.72, 2.88
Mo <sub>6</sub> Se <sub>8</sub>	Mo-Se <sub>inter</sub>	2.65
	Mo-Se <sub>intra</sub>	2.65, 2.54
	Mo-Mo <sub>intra</sub>	2.60, 2.70
Cu <sub>2</sub> Mo <sub>6</sub> Se <sub>8</sub>	Mo-Se <sub>inter</sub>	2.56
	Mo-Se <sub>intra</sub>	2.51, 2.52
	Mo-Mo <sub>intra</sub>	2.62, 2.75
Mo <sub>6</sub> Te <sub>8</sub>	Mo-Te <sub>inter</sub>	
	Mo-Te <sub>intra</sub>	2.79, 2.97
	Mo-Mo <sub>intra</sub>	2.74, 3.08
NiMo <sub>6</sub> Te <sub>8</sub>	Mo-Te <sub>inter</sub>	
	Mo-Te <sub>intra</sub>	2.79

**Table S1.** Scattering path distances obtained through Mo K-edge EXAFS data fitting for the sulphide, selenide and telluride CPs. Path labels correspond to those represented graphically in Figure 4.

### **Cluster anisotropy calculation**

The Mo<sub>6</sub> cluster anisotropy was determined as the difference between the longest and shortest Mo-Mo interatomic distances (obtained from EXAFS analysis and detailed in **Table S1**) following Levi and Aurbach,<sup>13</sup> equation 1:

$$\% Anisotropy = \frac{R_{long} - R_{short}}{R_{long}} 100\%$$
<sup>(1)</sup>

The uncertainty in the anisotropy values shown in Table 1 of the manuscript was obtained through the error propagation detailed in equation 2:

$$\Delta Anisotropy = \sqrt{\left(\frac{R_{short}}{R_{long}^2} x \ 100 \ x \ \Delta R_{long}\right)^2 + \left(-\frac{100}{R_{long}} x \ \Delta R_{short}\right)^2} \tag{2}$$

#### XANES analysis

Interpretation of edge position can give insight into oxidation state changes, or the effect of polarization of the ions. Figure S4a and b identify the red shift observed in cases of metal intercalation for CP sulphides and selenides. In contrast, the tellurides experience a blue shift upon intercalation of Ni (Figure S4c).



**Figure S4.** Mo L<sub>3</sub>-edge XANES spectra corresponding to the binary and ternary  $M_XMo_6T_8$ Chevrel phases demonstrating the effect of intercalation. Comparison between: **a**)  $Mo_6S_8$  and  $Cu_2Mo_6S_8$ , **b**)  $Mo_6Se_8$  and  $Cu_2Mo_6Se_8$ , **c**)  $Mo_6Te_8$  and  $NiMo_6Te_8$ , and insets highlight the observed energy shifts with dotted lines through peak maxima.



Figure S5. First derivative plots of the normalized Mo  $L_3$ -edge containing insets detailing the maxima for each binary Chevrel-phase.

As detailed in Figure S5, there is a relative shift in the white-line position that agrees with relative shifts observed in the first derivative analysis of the Mo  $L_3$ -edge. Specifically, the peak maxima detailed in Figure S5 are listed in Table S2.

Table S2. Peak maximum of the first derivative of the Mo L<sub>3</sub>-edge.

Material	First Derivative Peak Maxima (eV)	
Mo <sub>6</sub> S <sub>8</sub>	2522.1	
Cu <sub>2</sub> Mo <sub>6</sub> S <sub>8</sub>	2521.95	
Cu <sub>2</sub> Mo <sub>6</sub> Se <sub>8</sub>	2121.5	
Mo <sub>6</sub> Se <sub>8</sub>	2121.35	
Cu <sub>2</sub> Mo <sub>6</sub> Te <sub>8</sub>	2521.2	
NiMo <sub>6</sub> Te <sub>8</sub>	2521.35	

To further interpret the edge-position, the second derivative of each edge scan was analyzed. **Figure S3a** highlights the unique observation of a pre-edge feature in the sulfur K-edge which arises due to the empty orbitals of predominant chalcogen character present in the binary CPs.<sup>14</sup> Upon metal intercalation, the S is fully coordinated which results in a more degenerate species and a lessened or lack of pre-edge feature dependent upon the number of ions inserted in the framework.<sup>14</sup>

The selenides and tellurides were also analyzed using the same second derivative method to understand pre-edge features that may arise but difficult to discern from the absorption edges alone. While no pre-edge features were present, both selenide and telluride CPs show a substantial shift in their respective chalcogen edge. **Figure S6b** identifies the second derivative of the XANES for the selenide CP before and after intercalation, where a subtle difference in the inflection point is observed. This inflection point can be defined as the true edge position, and present in both selenide and telluride data.



**Figure S6.** Second derivative of the respective chalcogen K- (S and Se) and L-edge (Te) spectra in **a**)  $Mo_6S_8$  and  $Cu_2Mo_6S_8$ , **b**)  $Mo_6Se_8$  and  $Cu_2Mo_6Se_8$  and **c**)  $Mo_6Te_8$  and  $NiMo_6Te_8$ . **a**) the twin peaks located at 2470 which unify into a single signal upon copper intercalation and the sulfur atoms along the threefold rotation are fully coordinated. **b**) focuses on the slight Se K-edge shift which occurs upon metal intercalation.

**Table S3.** Fitting parameters for the Mo K-edge of  $Mo_6Se_8$ .  $S_0^2$  is the amplitude reduction factor,  $\Delta E_0$  is the energy offset of the white line between the  $E_0$  from Table S2 and that calculated by FEFF,  $\sigma^2$  is the Debye-Waller factor, N is the scattering path degeneracy. The distances obtained

Chevrel-phase	Parameter	Value		R-factor
	S <sub>0</sub> <sup>2</sup>	0.8	Set	
	ΔE <sub>0</sub>	5.9	Set	
	$\sigma^2_{Mo}$	0.009	+/- 0.007	
	$\sigma^2_{Se}$	0.001	+/- 0.001	
	Mo-Se1	2.54 Å	+/- 0.01	
	Mo-Se2	2.65 Å	+/- 0.02	
Ma Ca	Mo-Mo1	2.72 Å	+/- 0.04	0.00166193
MO <sub>6</sub> Se <sub>8</sub>	Mo-Mo2	2.88 Å	+/- 0.05	
	N (Mo-Se1)	3	Set	
	N (Mo-Se2)	2	Set	
	N (Mo-Mo1)	2	Set	
	N (Mo-Mo2)	2	Set	
	R-range	1.6 – 3.2 Å	Set	
	k-range	3 – 14.6 Å <sup>-1</sup>	Set	

from the EXAFS analysis are listed as Absorber-Scatterer pairs.

Chevrel-phase	Parameter	Value		R-factor
	S <sub>0</sub> <sup>2</sup>	0.8	set	
	ΔE <sub>0</sub>	5	set	
	$\sigma^2_{Mo}$	0.001	+/- 0.0004	
	$\sigma^2{}_s$	0.016	+/- 0.002	
	Mo-S1	2.52 Å	+/- 0.02	
	Mo-S2	2.40 Å	+/- 0.00	
Mo <sub>6</sub> S <sub>8</sub>	Mo-Mo1	2.78 Å	+/- 0.02	0.0084271
	Mo-Mo2	3.05 Å	+/- 0.05	
	N (Mo-S1)	1	Set	
	N (Mo-S2)	4	Set	
	N (Mo-Mo1)	4	Set	
	R-range	1.5 – 3.5 Å	Set	
	k-range	3 – 13.2 Å <sup>-1</sup>	Set	

# Table S4. Fitting parameters for the Mo K-edge of $Mo_6S_8$

Chevrel-phase	Parameter	Value		R-factor
	S <sub>0</sub> <sup>2</sup>	0.85	set	
	ΔE <sub>0</sub>	5.0	set	
	$\sigma^2_{Mo}$	0.023	+/- 0.001	
	$\sigma^2_{Te}$	0.024	+/- 0.002	
Mo <sub>6</sub> Te <sub>8</sub>	Mo-Te1	2.79 Å	+/- 0.01	
	Mo-Te2	2.97 Å	+/- 0.02	
	Mo-Mo1	2.62 Å	+/- 0.01	0.0018176
	Mo-Mo2	2.75 Å	+/- 0.01	
	N (Mo-Te1)	2	Set	
	N (Mo-Te2)	2	Set	
	N (Mo-Mo1)	2	Set	
	N (Mo-Mo2)	2	Set	
	R-range	1 – 3.5 Å	Set	
	k-range	3 – 14.6 Å <sup>-1</sup>	Set	

## Table S5. Fitting parameters for the Mo K-edge of $Mo_6Te_8$

Chevrel-phase	Parameter	Value		R-factor
	S <sub>0</sub> <sup>2</sup>	0.85	set	
	ΔE <sub>0</sub>	4.5	set	
	σ² <sub>Mo</sub>	0.001	+/- 0.001	
	$\sigma^2$ s	0.001	+/- 0.003	
	$\sigma^2_{Cu}$	0.008	+/- 0.008	
	Mo-S1	2.28 Å	+/- 0.05	
	Mo-S2	2.42 Å	+/- 0.02	
	Mo-S3	2.42 Å	+/- 0.02	-
	Mo-Mo1	2.58 Å	+/- 0.04	-
Cu <sub>2</sub> Mo <sub>6</sub> S <sub>8</sub>	Mo-Mo2	2.70 Å	+/- 0.02	0.024248
	Mo-Cu1	3.27 Å	+/- 0.07	-
	N (Mo-S1)	1	Set	-
	N (Mo-S2)	2	Set	-
	N (Mo-S3)	2	Set	
	N (Mo-Mo1)	2	Set	
	N (Mo-Mo2)	2	Set	
	N (Mo-Cu1)	2	Set	
	R-range	1 – 3.2 Å	Set	
	k-range	3 – 13.2 Å <sup>-1</sup>	Set	

Table S6. Fitting parameters for the Mo K-edge of  $Cu_2Mo_6S_8$ 

Chevrel-phase	Parameter	Value		R-factor
	<b>S</b> <sub>0</sub> <sup>2</sup>	0.8	set	
	ΔE <sub>0</sub>	4.2	set	
	σ² <sub>Mo</sub>	0.005	+/- 0.002	
	σ² <sub>Se</sub>	0.007	+/- 0.006	
	Mo-Se1	2.56 Å	+/- 0.22	
Cu₂Mo <sub>6</sub> Se <sub>8</sub>	Mo-Se2	2.51 Å	+/- 0.17	
	Mo-Se3	2.52 Å	+/- 0.02	
	Mo-Mo1	2.60 Å	+/- 0.04	0.0089445
	Mo-Mo2	2.70 Å	+/- 0.01	
	N (Mo-Se1)	1	Set	
	N (Mo-Se2)	2	Set	
	N (Mo-Se3)	2	Set	
	N (Mo-Mo1)	2	Set	
	N (Mo-Mo2)	2	Set	
	R-range	1.5 – 3.5 Å	Set	
	k-range	3 – 14.9 Å <sup>-1</sup>	Set	

## Table S7. Fitting parameters for the Mo K-edge of CuMo<sub>6</sub>Se<sub>8</sub>

Chevrel-phase	Parameter	Value		R-factor
	S <sub>0</sub> <sup>2</sup>	0.8	set	
	ΔE <sub>0</sub>	4.6	set	
	$\sigma^2_{Mo}$	0.001	+/- 0.001	-
NiMo <sub>6</sub> Te <sub>8</sub>	σ <sup>2</sup> <sub>Te</sub>	0.003	+/- 0.007	0.0323450
	Mo-Te1	2.79 Å	+/- 0.01	
	Mo-Mo1	2.74 Å	+/- 0.01	
	Mo-Mo2	3.08 Å	+/- 0.01	
	N (Mo-Te1)	4	Set	
	N (Mo-Mo1)	3	Set	
	N (Mo-Mo2)	1	Set	-
	R-range	1.55–4 Å	Set	-
	k-range	3 – 13.2 Å <sup>-1</sup>	Set	-

## Table S8. Fitting parameters for the Mo K-edge of NiMo<sub>6</sub>Te<sub>8</sub>



Figure S7. Molybdenum K-edge fits in k-space corresponding to a)  $Mo_6S_8$ , b)  $Cu_2Mo_6S_8$ , c)  $Mo_6Se_8$ , d)  $Cu_2Mo_6S_8$ , e)  $Mo_6Te_8$ , and f)  $NiMo_6Te_8$ .

#### • Computational Details:

We calculated the spectra and the Bader charges of Mo<sub>6</sub>S<sub>8</sub> and Cu<sub>2</sub>Mo<sub>6</sub>S<sub>8</sub> using Kohn-Sham Density Functional Theory (DFT). Spectral calculations were carried out using the manybody X-ray absorption spectroscopy (MBXAS) formalism<sup>15–17</sup> which computes the transition dipole moment by approximating the final (initial) state as a Slater determinant composed of KS orbitals obtained in absence (presence) of the relevant core electron. This is accomplished with the help of a transformation matrix connecting the spectrum of orbitals from the initial and final state self-consistent fields. The final-state Slater determinant is constructed from frozen orbitals obtained using the eXcited-electron and Core-Hole (XCH) approach which essentially computes the lowest-energy neutral KS state compatible with the presence of the relevant core-hole. In our calculations, the effects of the core-hole are incorporated by employing a modified pseudopotential.

The atomic model for  $Mo_6S_8$  was obtained from the Materials Project: mp-2164; while the structure for  $Cu_2Mo_6S_8$  was calculated with DFT, as described in Ref. 18. In order to reduce the impact of spurious interactions among periodic images of the core-excited atoms, we ensure that the supercells used in our calculations have a dimension at least of 1 nm in each direction. The Perdew-Burke-Ernzerhoff (PBE) exchange-correlation functional,<sup>19</sup> in conjunction with ultrasoft pseudopotentials<sup>20</sup> was used in all calculations. In order to account for strong onsite Coulomb interactions and associated electron-localization in the d-orbitals, Hubbard U values of 4.0 eV<sup>21</sup> and 3.16 eV<sup>8,22–25</sup> were used for Cu and Mo, respectively. Plane-wave kinetic energy cut-offs of 35 and 280 Ry were found necessary for KS orbitals and charge density, respectively, to obtain converged spectra, together with first Brillouin zone sampling using a 3x3x3 k-point grid. Finally, a rigid empirical energy-shift of 2468 eV (dependent on the pseudopotential, functional, cut-offs, etc.) is added to all spectra.

The Bader charges were calculated with the Bader Charge Analysis Code<sup>26</sup> using the ground state charge density obtained from the spectral simulations, and recover 100% of the valence electrons. The charge in each atom is calculated as the difference between the valence charge in the pseudopotential for each element and their Bader valence charge.



Figure S8. Spectra of the  $S_1$  and  $S_2$  atoms in  $Mo_6S_8$  and  $Cu_2Mo_6S_8$ ; note that the starkly different pre-edge in  $S_1$  and  $S_2$  spectra (red and blue, respectively) in  $Mo_6S_8$  become more similar in  $Cu_2Mo_6S_8$ .

 $\begin{array}{l} \textbf{Table S9. Calculated Bader charges (Lowdin charges in parentheses) on Mo-tetracoordinated (S_1) and Mo-tricoordinated (S_2) sulfur atoms and Mo atoms in Mo_6S_8 and Cu_2Mo_6S_8. \end{array}$ 

Туре	Mo <sub>6</sub> S <sub>8</sub>	Cu₂Mo <sub>6</sub> S <sub>8</sub>	Difference
S <sub>1</sub>	-0.73 (0.42)	-0.75 / -0.80 (0.45 / 0.42)	-0.02 / -0.07 (0.03 / 0.00)
S <sub>2</sub>	-0.63 (0.26)	-0.79 (0.34)	-0.16 (0.08)
Мо	0.94 (-0.41)	0.86 / 0.87 (–0.36 / –0.40)	-0.08 / -0.09 (0.05 / 0.01)

### • Effect of geometric changes and charge transfer on spectra

Spectral differences that result from intercalation could be attributed to the presence of the intercalant, as well as the geometric changes associated with it. Here, we discuss the case of copper intercalation in the S K-edge spectra of  $Mo_6S_8$ . As mentioned in the main text, the key difference between the S K-edge spectra of the Non-Intercalated structure and the Intercalated one (Fig. 5 in the main text) is the decrease in pre-peak intensity. Comparing the individual spectra of the four-fold and three-fold coordinated (Type 1 and 2) sulfur atoms, we see that overall pre-peak intensity decrease results from a *decrease in the pre-peak* intensity of the  $S_1$  spectrum and an overall *blue-shift* in the  $S_2$  spectrum (Fig. S8).

In order to separate the effects of geometry changes and charge transfer due to presence of the intercalant in the spectra of  $S_1$  and  $S_2$ , we have investigated the following structures:

- 1. Non-Intercalated Mo<sub>6</sub>S<sub>8</sub>;
- 2. Intercalated Cu<sub>2</sub>Mo<sub>6</sub>S<sub>8</sub>;
- 3. Artificial intermediate: Non-Intercalated structure 1 with added copper ( $Mo_6S_8 + 2Cu$ ) in which only the positions of the Cu atoms have been optimized;
- 4. Artificial intermediate: Intercalated structure 2 with all the copper atoms removed.

It should be noted that in **3**, due to the structural constraints in this artificial series, the S2 atom is coordinated with one copper atom and not two, as in the Intercalated phase (2). Here, we consider a coordination cutoff of 2.7 Å. This series of structures facilitates investigating structural effects by comparing **1** and **4**, or **2** and **3**. On the other hand, charge-transfer effects can be investigated by comparing **1** and **3**; or **2** and **4**.

The atomic Bader charges for each structure are shown in Figure S9. The Non-Intercalated structure (1) and the Intercalated structure with removed Cu atoms (4) have a similar charge distribution, with a clear difference in charge on the S atoms, depending on their four-fold (Type 1) or three-fold (Type 2) coordination with the surrounding Mo atoms (Fig. S9 a and c). In contrast, Type 2 sulfur atoms get reduced in the structures with copper (2 and 3, Fig. S9 b and c). In the Intercalated phase, their charges become similar to those of Type 1 sulfur atoms. That is, most of the Cu charge redistributes in the S<sub>2</sub> atoms rather than in the Mo, independently of the charges in the geometry of the Mo<sub>6</sub>S<sub>8</sub> lattice when Cu is added. When copper is removed, the charges on the sulfur atoms return to values closer to those in the Non-Intercalated structure (4).



**Figure S9.** Change in Bader charge with respect to the neutral atom in structures 1-4, colored according to the element and coordination around the given atom.

Next, we compare the spectra of structures 1-4. Let us look separately at  $S_1$  and  $S_2$  spectra to understand the above-mentioned *decrease in the pre-peak* of the  $S_1$  spectrum and an overall *blue-shift* in the  $S_2$  spectrum.



Figure S10. Structural and charge transfer effects in the spectra of S<sub>1</sub> for structures 1-4.

In Figure S10, the  $S_1$  spectra of structures 1-4 are shown in pairs to ease the comparison of the effects that result from geometry changes (a and b) and from the presence of Cu (c and d). Now, we can carry out a thought experiment of the step-wise spectral changes between 1 and 2: starting from the Non-Intercalated phase (1), let us change the geometry of the  $Mo_6S_8$  lattice to match that of the Intercalated phase (4). This results in a red-shift and intensity decrease of the pre-peak (Fig. S10 a), due to the Mo-S<sub>1</sub> distances changing from 2.44-2.45 to 2.40, 2.45, 2.47 and 2.51 A. This is consistent with a tight-binding picture in which longer Mo-S bonds lead to red-shifted peaks due to reduced orbital repulsion. Then, we introduce the Cu atoms to produce the Intercalated phase (2). The pre-peak intensity decreases again, but strongly blue-shifts (Fig. These changes in the spectra are due to Pauli exclusion - filling of previously S10 d). unoccupied orbitals that contributed to the pre-peak due to the rising the Fermi level. An alternative pathway from the same starting point (1) can be taken by adding Cu first to produce **3**. This leads to a blue-shift and intensity decrease of the pre-peak (Fig. S10c). Once **3** is "expanded" to the Intercalated phase (2), a slight red-shift and further intensity decrease are observed (Fig. S10b). In conclusion, the pre-peak intensity decrease in  $S_1$  results from cooperation of structural effects and electronic effects, while they mostly cancel each other out in terms of energy shift.



Figure S11. Structural and charge transfer effects in the spectra of S<sub>2</sub> for structures 1-4.

A similar set of plots for the Type 2 S is shown in Figure S11. Let us repeat the thought experiment: this time, changing the Non-intercalated structure (1) to match the Intercalated

 $Mo_6S_8$  lattice (4) leads to red-shift and intensity increase in the pre-peak (Fig. S11a), again due to the elongation of Mo-S<sub>2</sub> distances (2.43 to 2.45, 2.49, 2.51 A). Once Cu atoms are added to produce the Intercalated phase (2), an overall blue-shift and strong intensity decrease in the prepeak follow (Fig. S11c). If we take the alternative route, adding Cu to 1 first leads to an overall blue-shift and strong intensity decrease in the pre-peak of 3 (Fig. S11c). From here, "expanding" the geometry to match the intercalated phase 2 results in a slight red-shift of the pre-peak. Hence, for Type 2 S, pre-peak intensity results from the canceled out effects of change in geometry and charge transfer. The strongest change, that is, the overall **blue shift**, is entirely due to the **presence of the Cu**.

It is important to note here that the blue-shift in the  $S_2$  spectra contradicts the typical expectation that the spectrum of a reduced species (with lower oxidation state) is red-shifted due to the increased screening of the core electrons provided by the extra valence electrons. The reason for this relates to the interesting electron-deficient band structure of  $Mo_6S_8$ . In  $Mo_6S_8$ , adding electrons raises the Fermi level, bringing it closer to the pseudo-gap (Fig. S12). The downward slope in the electronic density of states (DOS) implies a decrease in the number of free carriers near the Fermi level as it rises, and, therefore, a decrease in electronic screening. This is consistent with the increases in (pseudo) band gap upon intercalation (Fig. S12). The reduced screening will also increase the binding energy of the S 1s core electrons and shift the unoccupied S<sub>2</sub> orbitals with p character higher in energy, resulting in the blue-shift of the S<sub>2</sub> spectra.



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**Figure S12.** Projected density of states for the Non-Intercalated (a) and Intercalated (b) phases, aligned with reference to each's Fermi level - marked by a vertical line.

In summary, while pre-peak intensity decrease in  $S_1$  is due to cooperative structural and charge transfer effects, the blue-shift in  $S_2$  is solely due to charge transfer.

### Atomic structures used in the calculations (POSCAR format):

Mo18 S24

1.0 9.288858 0.000000 0.000000 -4.644429 8.044387 0.000000 0.000000 0.000000 10.984105 Mo S 18 24 direct 0.016027 0.177204 0.389330 Mo 0.822796 0.838822 0.389330 Mo 0.161178 0.983973 0.389330 Mo 0.983973 0.822796 0.610670 Mo 0.177204 0.161178 0.610670 Mo 0.838822 0.016027 0.610670 Mo 0.682693 0.510538 0.722664 Mo 0.489462 0.172156 0.722664 Mo 0.827844 0.317307 0.722664 Mo 0.650640 0.156129 0.944003 Mo 0.843871 0.494511 0.944003 Mo 0.505489 0.349360 0.944003 Mo 0.349360 0.843871 0.055997 Mo 0.156129 0.505489 0.055997 Mo 0.494511 0.650640 0.055997 Mo 0.317307 0.489462 0.277336 Mo 0.510538 0.827844 0.277336 Mo 0.172156 0.682693 0.277336 Mo 0.714999 0.029741 0.418033 S

0.970259 0.685257 0.418033 S 0.314743 0.285001 0.418033 S 0.285001 0.970259 0.581967 S 0.029741 0.314743 0.581967 S 0.685257 0.714999 0.581967 S 0.000000 0.000000 0.221041 S 0.000000 0.000000 0.778959 S 0.381665 0.363075 0.751367 S 0.636925 0.018591 0.751367 S 0.981409 0.618335 0.751367 S 0.951668 0.303592 0.915300 S 0.696408 0.648076 0.915300 S 0.351924 0.048332 0.915300 S 0.6666667 0.333333 0.554374 S 0.666667 0.333333 0.112292 S 0.048332 0.696408 0.084700 S 0.303592 0.351924 0.084700 S 0.648076 0.951668 0.084700 S 0.618335 0.636925 0.248633 S 0.363075 0.981409 0.248633 S 0.018591 0.381665 0.248633 S 0.333333 0.666667 0.887708 S 0.333333 0.666667 0.445626 S Cu2 Mo6 S8

1.0

6.543083 -0.306105 -0.119756

-0.453054 6.405233 0.234909

-0.756782 - 0.570508 6.479792

Cu Mo S

268

direct

0.939188 0.161709 0.905066 Cu

0.060808 0.838287 0.094920 Cu

0.219229 0.544697 0.399739 Mo

0.780776 0.455307 0.600269 Mo

0.408031 0.226173 0.543638 Mo

0.591985 0.773820 0.456356 Mo

0.534632 0.406577 0.222425 Mo

0.465370 0.593419 0.777571 Mo

0.140730 0.371154 0.715454 S

 $0.859255\; 0.628857\; 0.284548\; \mathrm{S}$ 

0.715263 0.138399 0.384125 S

0.284734 0.861601 0.615879 S

0.381325 0.729891 0.122170 S

0.618678 0.270116 0.877835 S

0.190204 0.204510 0.196348 S

0.809792 0.795484 0.803656 S

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