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Supporting information for article:

Polarized X-ray Diffraction Anomalous Near-edge Structure Study on Orbital Physics of Thin WSe2 Layers

Shih-Lun Chen, Tai-Sing Wu, Hung-Lung Huang, Sheng-Fu Chen, Yun-Liang Soo, Horng-Tay Jeng and Hsueh-Hsing Hung

S1. X-ray diffraction measurements at different energy

Fig. S1 shows the measurements of few-layer WSe_2 (00·8) and (11·0) diffractions by changing the x-ray energy just below, above and well above of the absorption Se K-edge, 12658 eV. 2θ- θ scans of WSe_2 (00·8) at 12.61 (blue curve), 12.66 (black curve) and 12.71 keV (red curve) are shown in Fig. S1(a). The measurement of WSe_2 (11·0) is shown in Fig. S1(b). Notice that DANES measurements were therefore performed under the condition of $\boldsymbol{q}$ fixed (see dash lines), well centring at the peak of each diffraction profile.

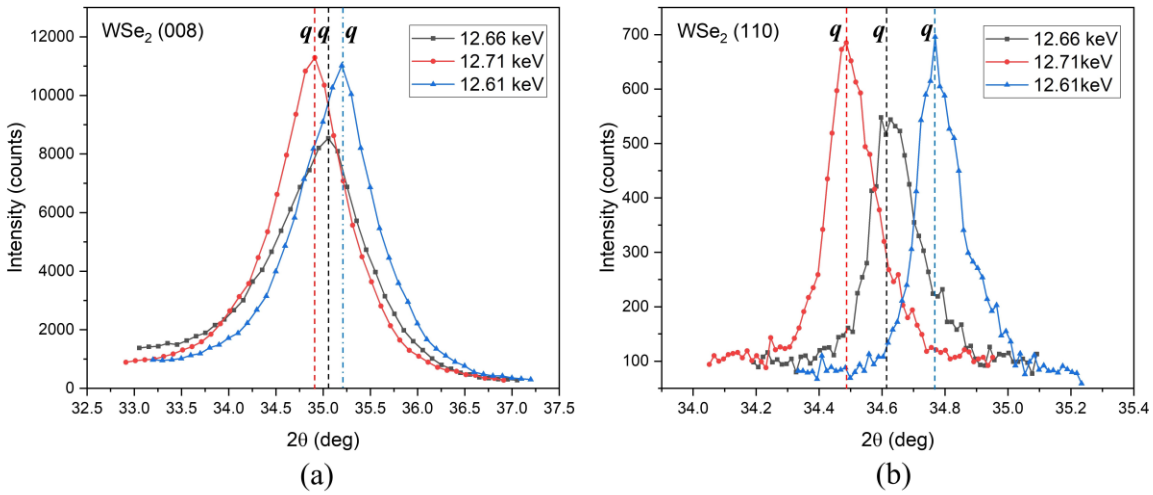

Figure S1 The 2θ- θ scans of WSe_2 for (a) (00·8) and (b) (11·0) at 12.61, 12.66 and 12.71 keV, respectively.

S2. Simulated DANES spectra to examine the spin-orbit coupling (SOC) effect

Table S1 lists the fractional atomic coordinates of bulk WSe_2. The parameters were input into FDMNES codes to simulate the XANES and DANES spectra. Fig. S2 shows the DANES spectra with SOC and without SOC at DANES (00·8) and (11·0), respectively. The minor systematic deviation of spectra weight after the absorption edge with SOC (red curve) from that without SOC (black curve) can be observed from both spectra. We only show the calculations with SOC in our article.

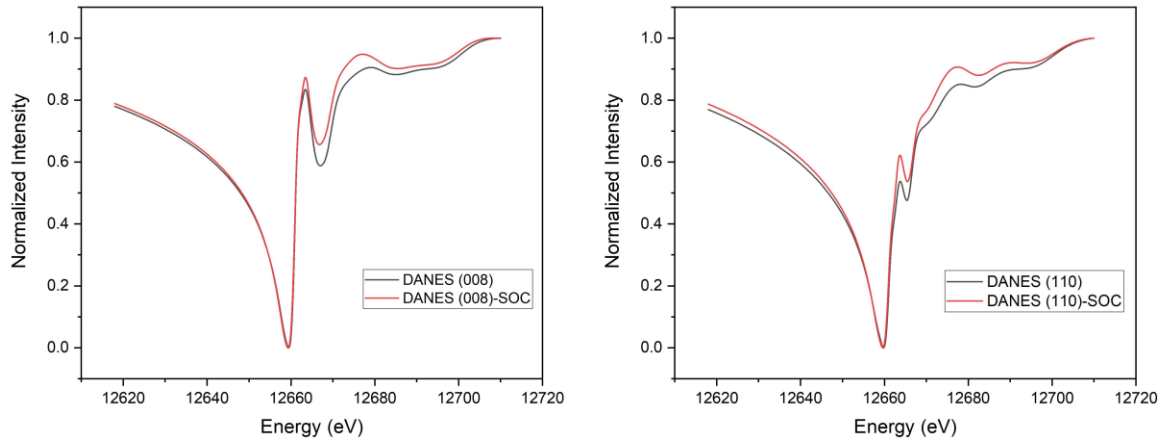

Figure S2 The simulated DANES (00·8) and (11·0) spectra with SOC are in comparison with the simulated spectra without SOC.

Table S1 The fractional atomic coordinates and lattice parameters of bulk WSe_2 in the FDMNES code to simulate the DANES and XANES spectra.

	a (Å)	***b*** (Å)	***c*** (Å)
	3.29	3.29	13.03
	x	*y*	*z*
W	0.33333	0.66667	0.25000
W	0.66667	0.33333	0.75000
Se	0.66667	0.33333	0.36160
Se	0.33333	0.66667	0.86160
Se	0.66667	0.33333	0.13840
Se	0.33333	0.66667	0.63840

S3. LDA vs. GGA functionals in FDMNES and VASP

The calculated partial density of states (pDOS) of WSe_2 in LDA and GGA functionals are compared in this section. Both functionals are applied in FDMNES and VASP packages. From Fig. S3, the calculation of pDOS in FDMNES which adopts GGA (a, b) and LDA (c, d) functionals. The black dash line show that the peaks of W-$d_{x^2-y^2}$, d_{xy} and Se-p_x, p_y in LDA and GGA calculations are lined up at

12661 eV. The orbital distributions above conduction band edge from LDA functional are in good agreement with the calculation by GGA functional. This consistence of overall features as shown in the orbital distributions also reflected in the geometry along the out-of-plane direction (b and d).

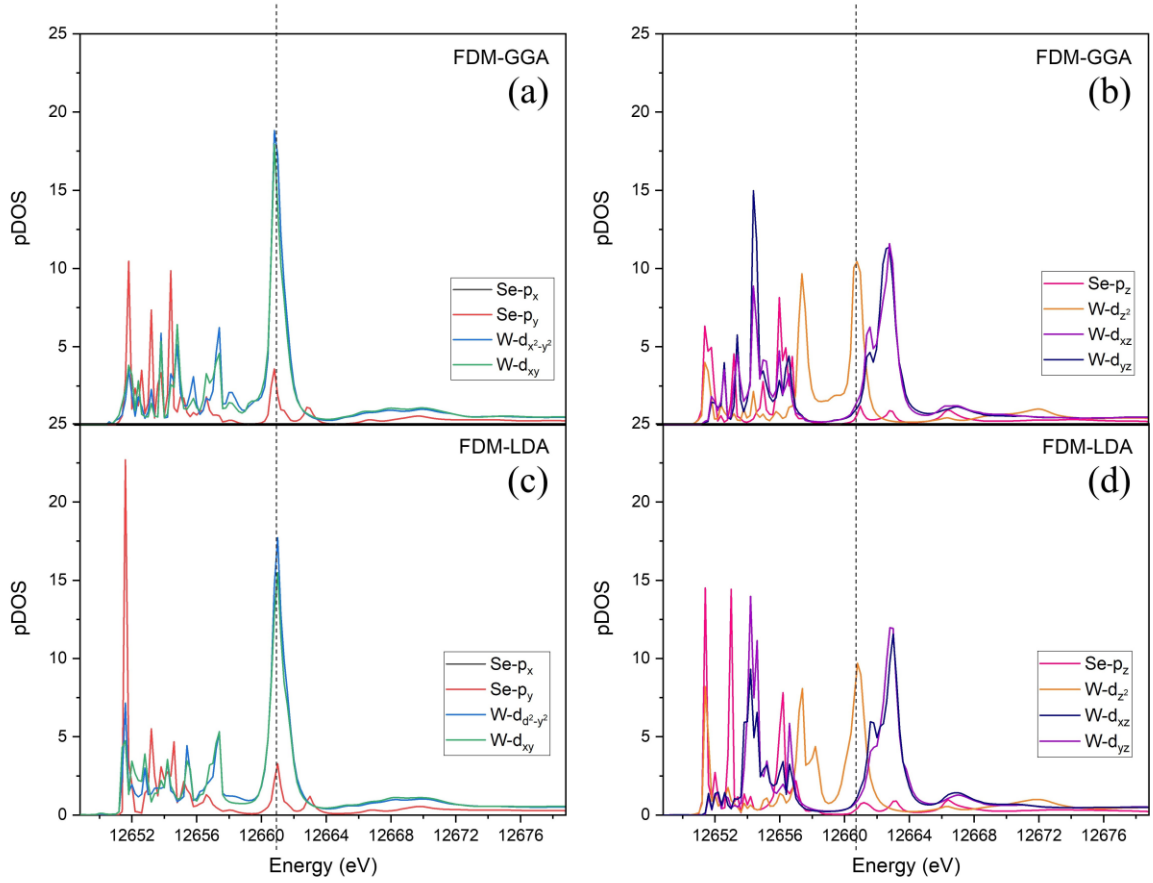

Figure S3 Fig. S3 The pDOS of WSe_2 derived by using FDMNES in GGA functional (a, b) are in comparison with the result calculated by LDA functional (c, d).

Calculations of pDOS by using VASP package in which LDA (a, b), GGA (c, d) and GGA-SOC (e, f) functionals are adopted in Fig. S4. Because the orbital distributions among them are quite similar, we believe that the pDOS by GGA functional can be employed to interpreted XANES and DANES spectra which are just based on LDA functional.

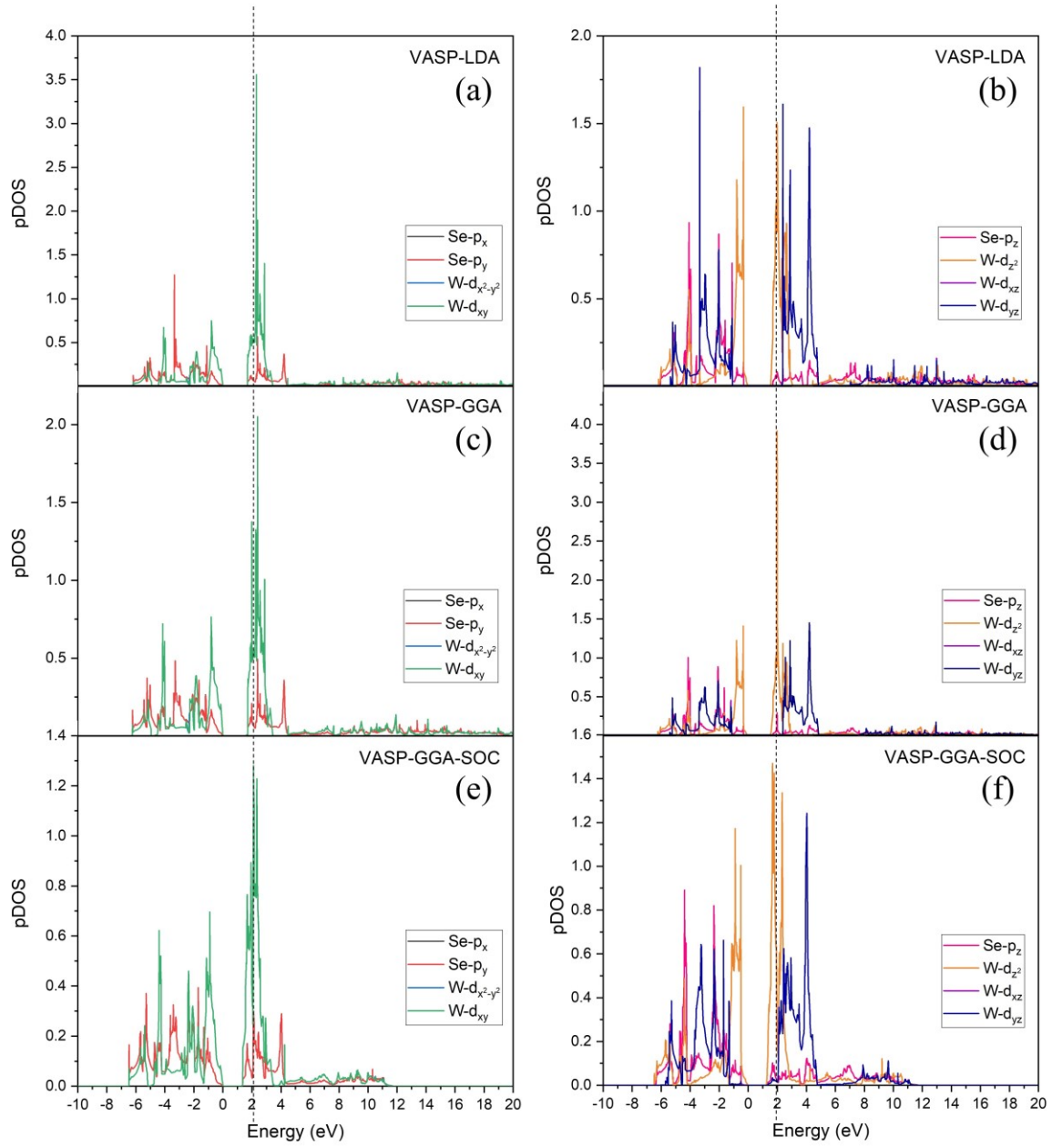

Figure S4 Fig. S4 The calculated pDOS of WSe_2 from VASP package with LDA functional: (a) and (b) are compared to (c) and (d) with GGA-functional, and (e) and (f) with GGA-functional with SOC.

S4. Core-hole effect on calculations of partial density of states

We demonstrate the calculated pDOS of WSe_2 (Fig. S5) from FDMNES package in non-excited (a, b) and excited states (c, d) by using GGA functional. The incorrect Fermi level obtained from excited state is not accurate due to the core-hole effect. Therefore, the Fermi level obtained from non-excited state is more reliable and, thus, this value is utilized to realign with 12658.8 eV. The peak of W-$d_{x^2-y^2}$ in non-excited state has energy difference of 0.2 eV to the peak of W-$d_{x^2-y^2}$ in excited state. This energy

shift between two peaks describes the existence of core-hole effect that the pDOS of excited state is more closed to Fermi level. However, the core-hole effect on WSe_2 at Se K-edge seems not significant. The features of pDOS above the conduction band edge show that no apparent difference appears between the calculations with and without the core-hole effect. We infer that the reduced influence of the core-hole effect is due to the excited electrons far from the core hole when the electrons are excited from 1*s* to 4*p* orbital. Besides, the screening from the core and valence electrons might also contribute the reduction of this effect as well.

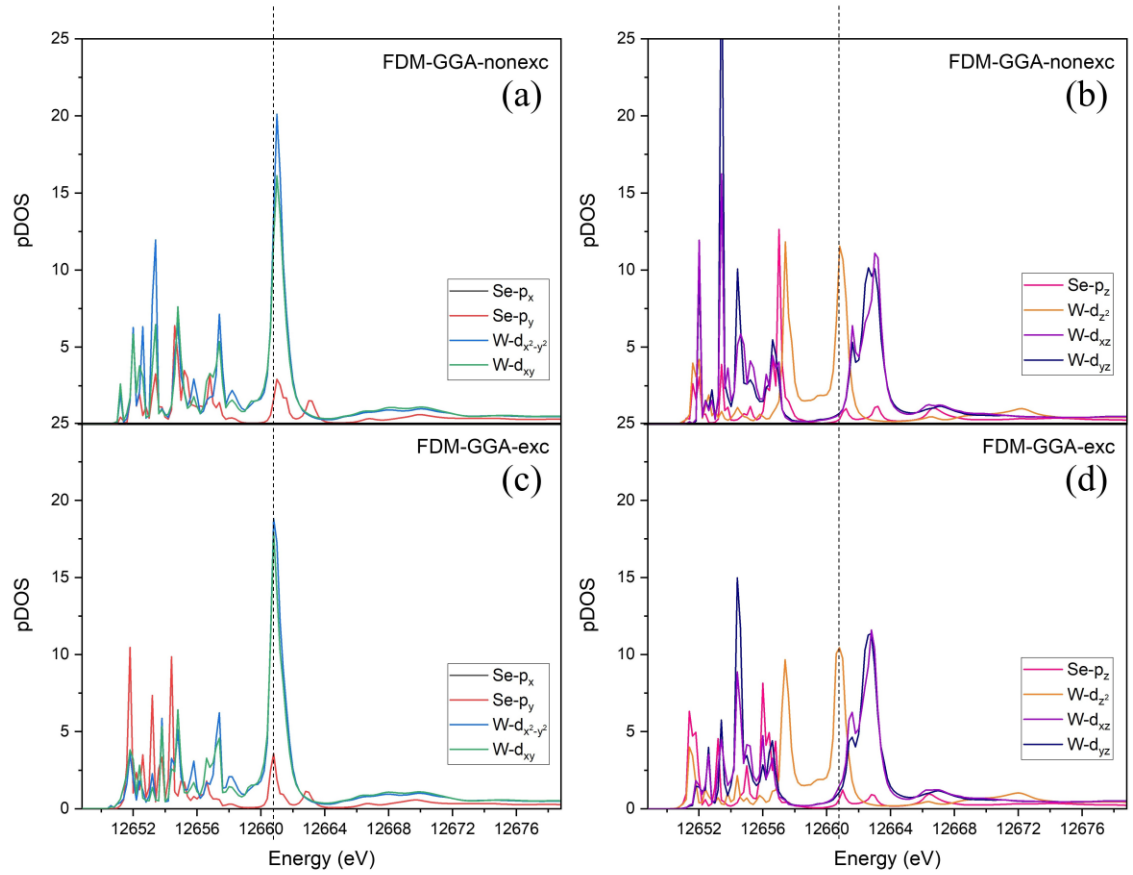

Figure S5 The pDOS of WSe_2 of non-excited state shown in (a) and (b) is compared to the case of excited state, (c) and (d).

S5. pDOS comparison between FDMNES and VASP

The pDOS of WSe_2 from FDMNES compared to VASP calculation is demonstrated in Fig. S6. The Fermi level is aligned at 12658.8 eV. Despite the existence of core-hole effect, the orbital distributions derived from ground-state DFT calculations are good enough to describe our DANES spectra. To deal with the energy shift due to core-hole and compare the VASP-based pDOS to DANES spectra, we move Fermi level from VASP and align with the DANES spectra at 12658.6 eV.

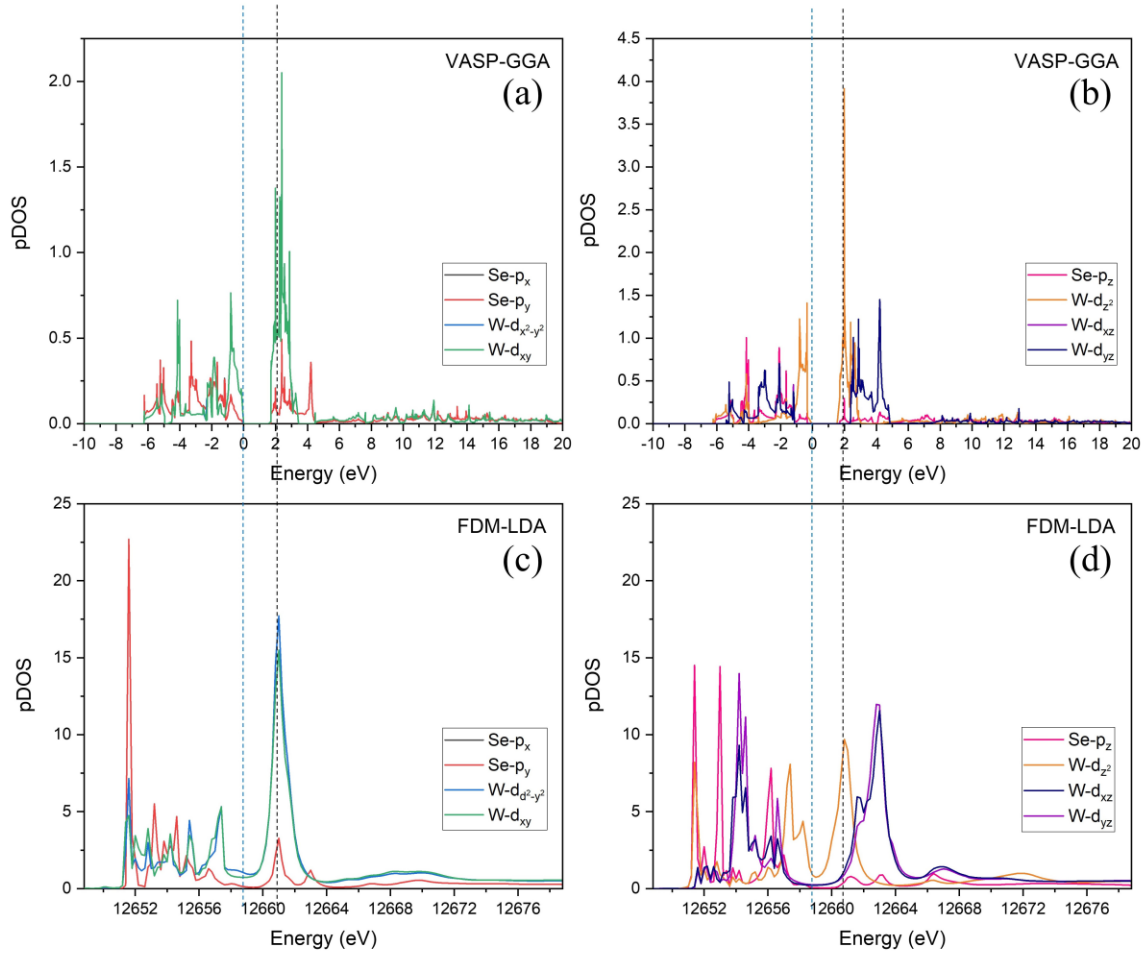

Figure S6 The pDOS of WSe_2 derived from VASP shown in (a) and (b) is compared to FDMNES, (c) and (d).

S6. The comparison of DANES spectra in different radius of clusters

To examine the convergence of our calculations and simulated spectra by FDMNES, we increased the radius of clusters from 5 to 7.1 Å , as shown in Fig. S7 below. Fig. S7(a) and S7(b) are, respectively, the simulated DANES spectra of (00·8) and (11·0) reflections without spin-orbit coupling (SOC) effect, and S7(c) as well as S7(d) is each of the case considering SOC for comparison. From these results, we could confirm that the spectra were almost unchanged at the radius of clusters 6.95 Å (black line) in comparison with the one at 7.1 Å (red line). Therefore, the simulated spectra by building the radius of clusters at 6.95 Å in FDMNES package could be considered convergent.

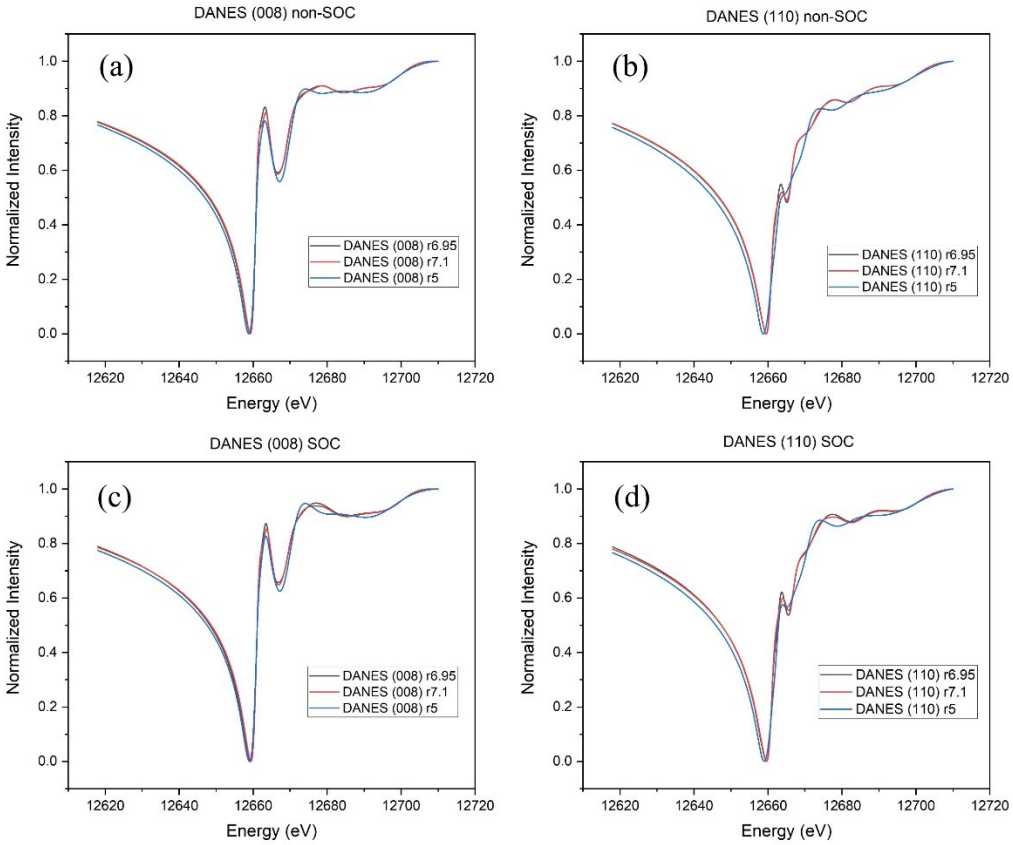

Figure S7 The simulated DANES spectra by building the radius of clusters from 5 to 7.1 Å are in comparison. (a) The spectra of DANES (00·8) and (b) (11·0) diffractions without SOC effect. (c) DANES (00·8) and (d) (11·0) diffractions with SOC effect.