

Supporting information to
“Electronic structure and electron-transport properties of three metal hexacyanoferrates”

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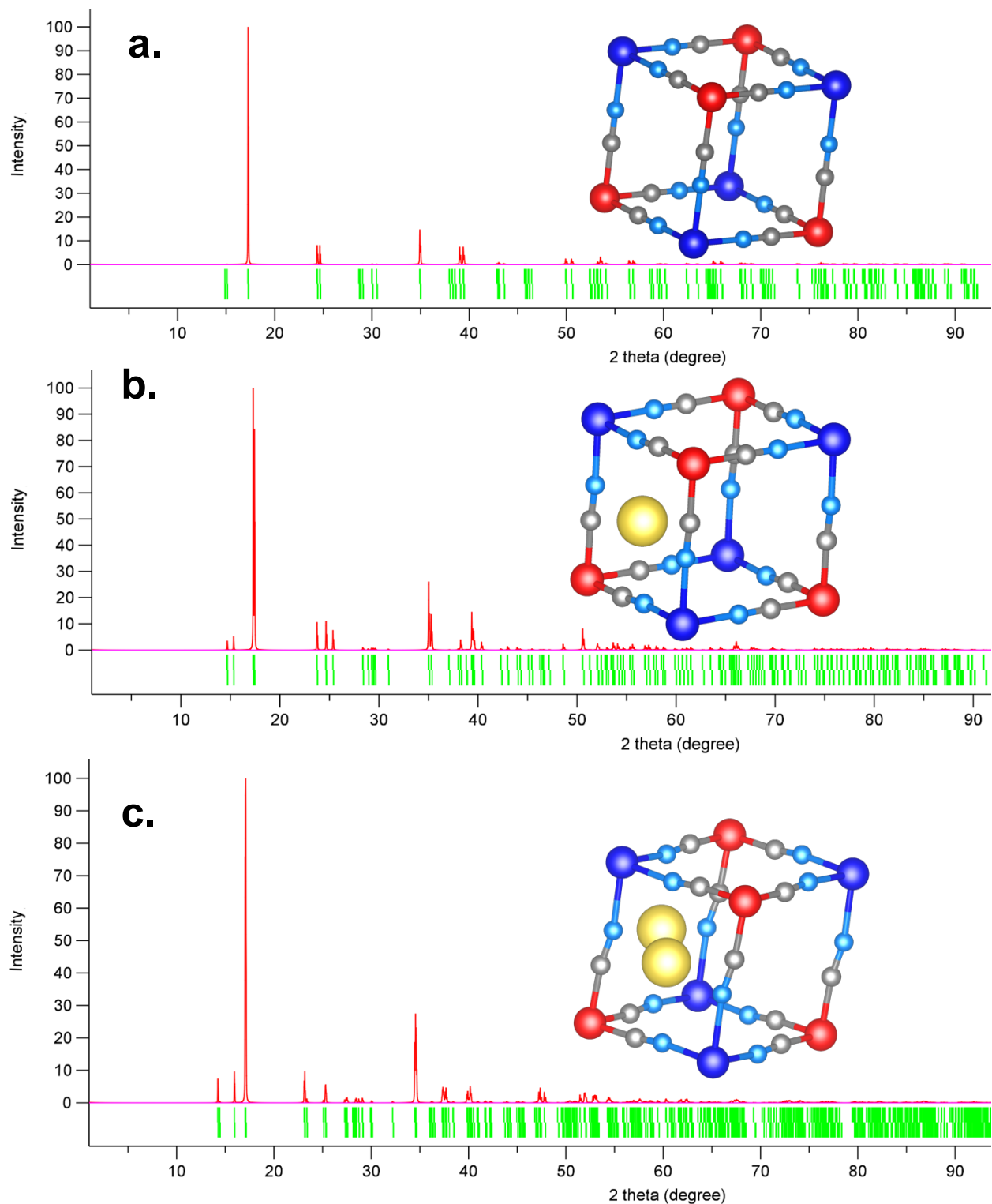


Figure SI.1: Simulated X-ray diffractograms of different oxidation states. These are the XRD patterns for a. $\text{Fe}[\text{Fe}(\text{CN})_6]$, b. $\text{NaFe}[\text{Fe}(\text{CN})_6]$, and c. $\text{Na}_2\text{Fe}[\text{Fe}(\text{CN})_6]$. All are the (1s, hs) configuration calculated to the level of the HSE functional. The cubic-to-rhombohedral phase change is observed experimentally, too, in low-vacancy, dehydrated PBA cathodes.

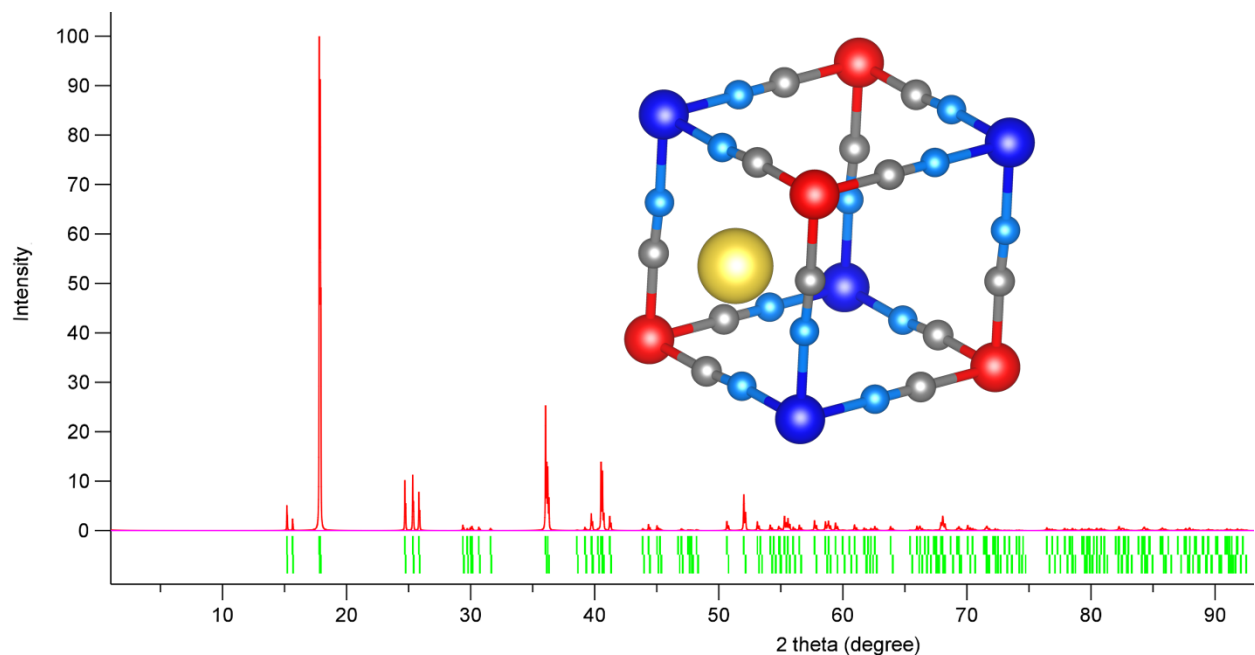


Figure SI.2: Simulated X-ray diffractogram for (ls, ls) NaFe[Fe(CN)₆] with crystal structure inset. This pattern is qualitatively similar to that in Figure SI.1.b (for (ls, hs) NaFe[Fe(CN)₆]), but the peaks here are shift to higher angles 2θ because the lattice parameter, and therefore the volume, of the (ls, ls) phase is smaller than that of the (ls, hs) phase.

	(ls, ls)	(ls, hs)
Fe_N – N / Å	1.92	2.06
N – C / Å	1.16	1.17
C – Fe_C / Å	1.89	1.89

Table SI.1: Average bond lengths in NaFe[Fe(CN)₆]. The cyanide bond length and the Fe_C – C bond lengths are mostly unchanged, but the Fe_N – N bond length increases by 7.3% in the (ls, hs) phase versus the (ls, ls) phase.

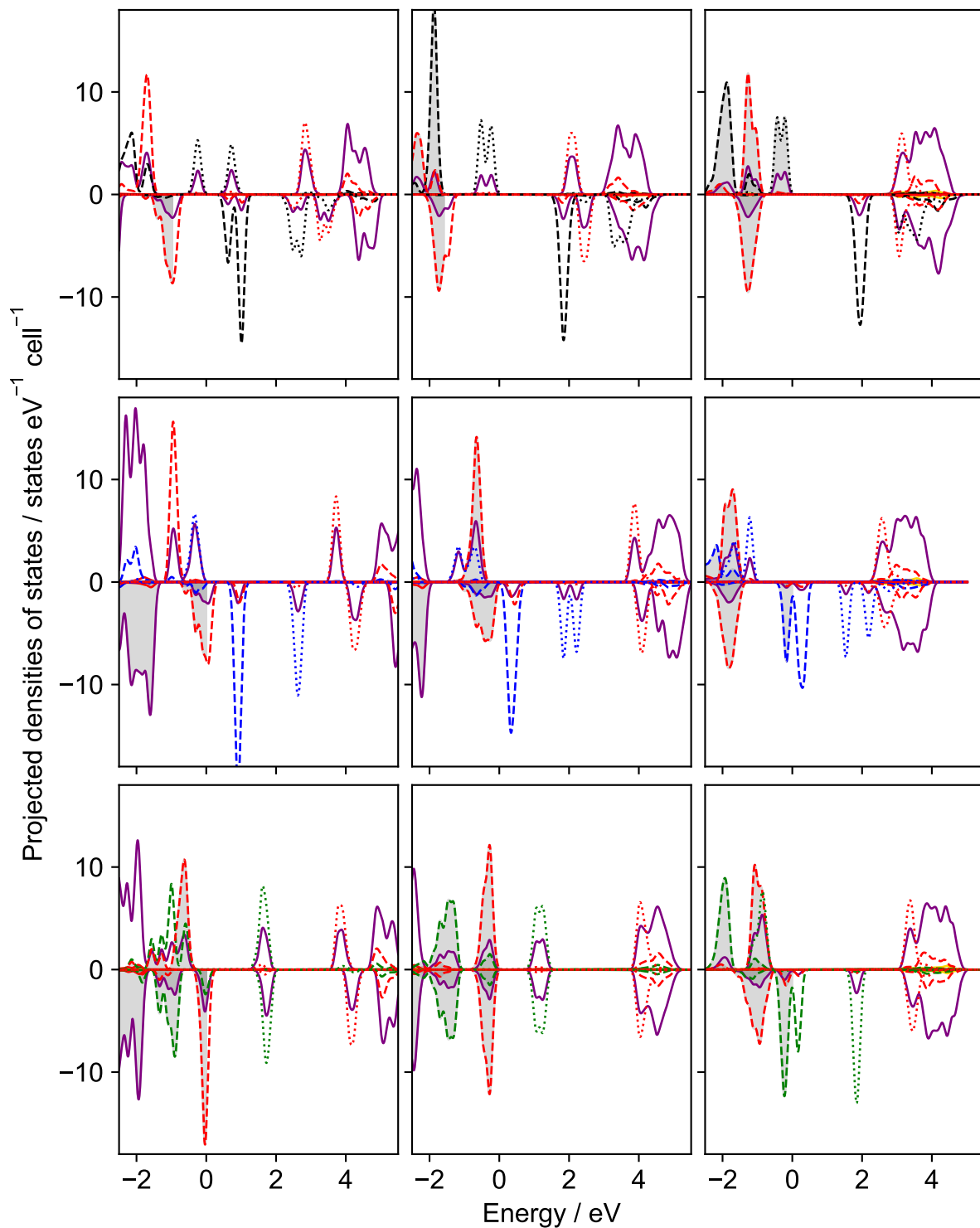


Figure SI.3: PDOS as calculated by the PBE functional. Note that these are all the (ls, hs) configuration (except for $\text{Co}[\text{Fe}(\text{CN})_6]$ and $\text{NaCo}[\text{Fe}(\text{CN})_6]$ which are (ls, ls)) for ease of comparison with the PDOS figure in the main text; the PBE functional predicts a (ls, ls) ground state for all compounds except $\text{Na}_2\text{Mn}[\text{Fe}(\text{CN})_6]$.

		$k_x / 2\pi/a$	$k_y / 2\pi/a$	$k_z / 2\pi/a$
Mn	0	-0.49	0.00	0.0
	1	-0.23	0.23	-0.25
	2	-0.02	-0.02	0.49

Fe	0	-0.51	0.00	0.00
	1	0.00	0.00	0.51
	2	0.00	0.00	0.00

Co	0	-0.53	0.00	0.00
	1	0.00	0.00	0.53
	2	0.00	0.00	0.00

Table SI.2: Wavevectors of the valence-band tops used for the evaluation of hole effective masses.

		$k_x / 2\pi/a$	$k_y / 2\pi/a$	$k_z / 2\pi/a$
Mn	0	0.00	0.00	0.00
	1	0.00	0.00	0.00
	2	0.00	0.00	0.00

Fe	0	0.00	0.00	0.00
	1	-0.25	0.25	0.00
	2	0.25	0.25	0.23

Co	0	0.00	0.00	0.00
	1	0.00	0.00	0.53
	2	-0.23	0.25	-0.25

Table SI.3: Wavevectors of the conduction-band bottoms used for the evaluation of electron effective masses.

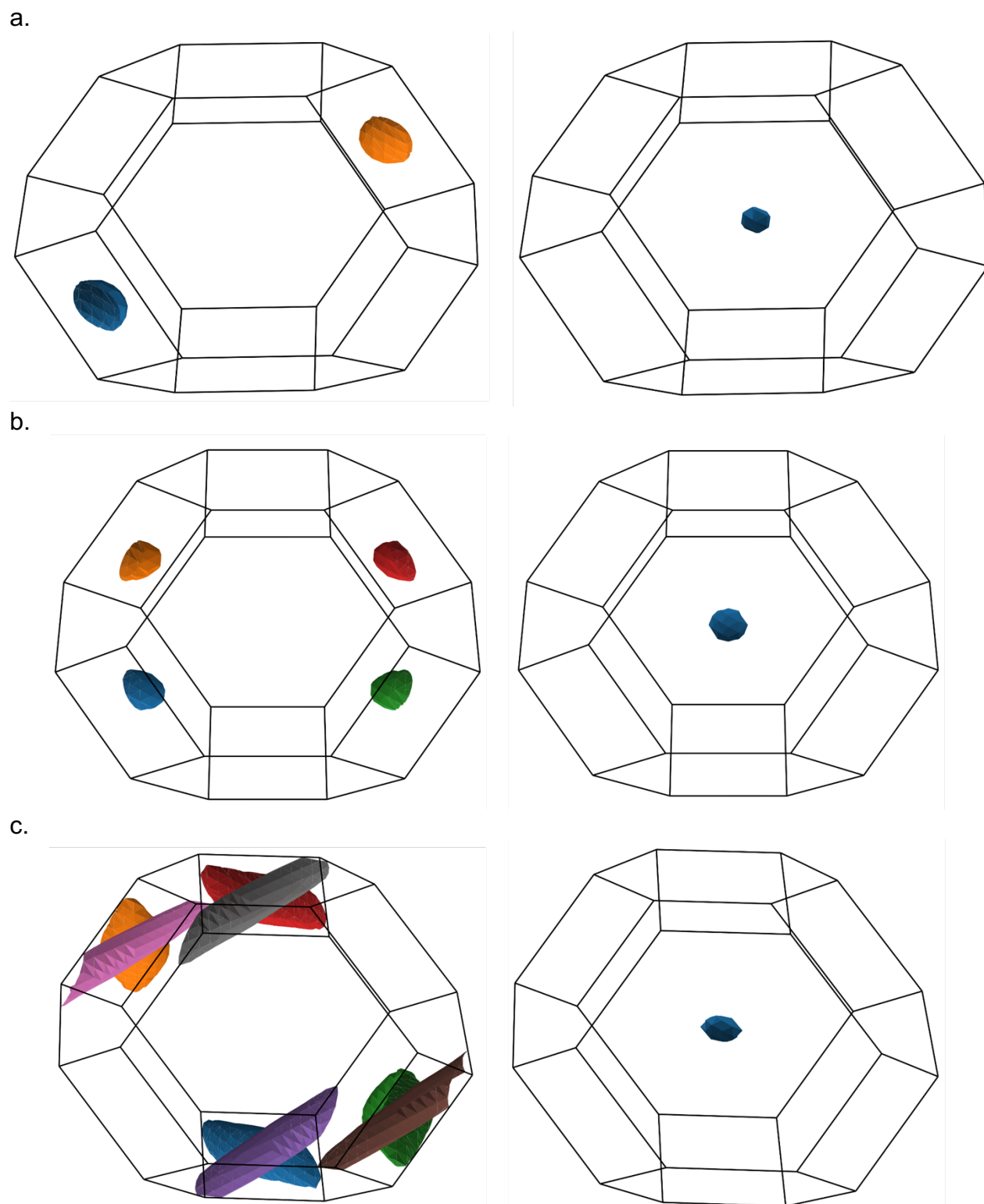
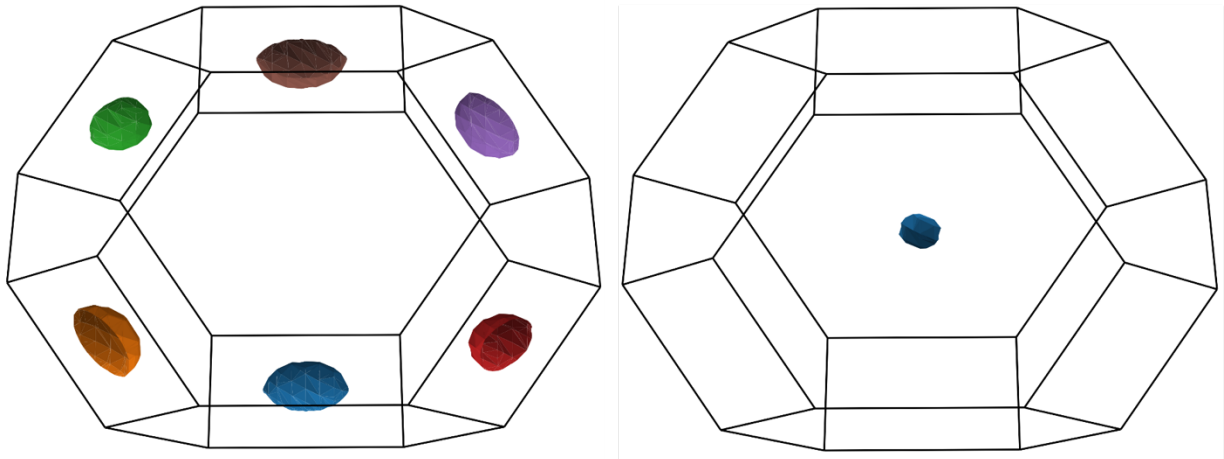
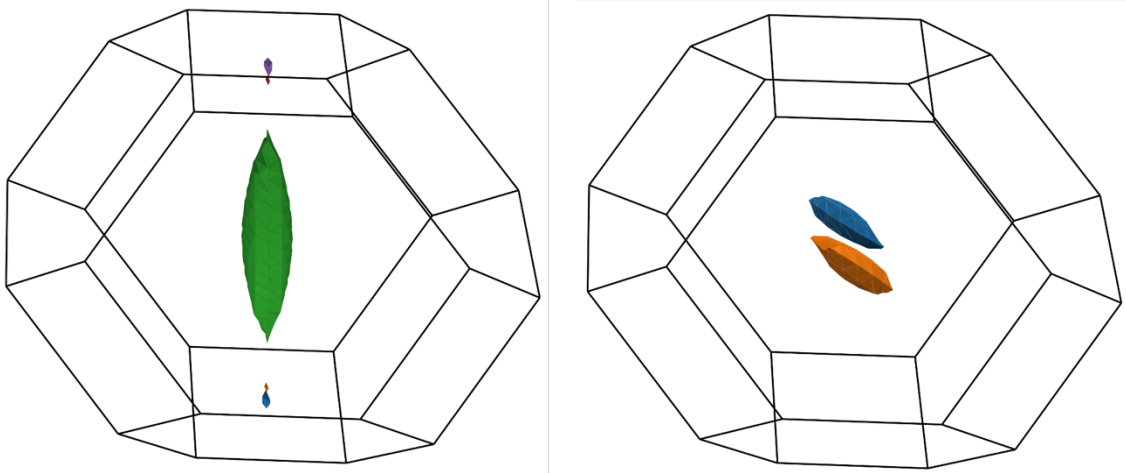


Figure SI.4: Energy isosurfaces. The energy isosurfaces in the first Brillouin zone at 10 meV below the valence-band top (left) and 10 meV above the conduction-band bottom (right) for (a) $\text{Na}_0\text{Mn}[\text{Fe}(\text{CN})_6]$, (b) $\text{Na}_1\text{Mn}[\text{Fe}(\text{CN})_6]$, and (c) $\text{Na}_2\text{Mn}[\text{Fe}(\text{CN})_6]$.

a.



b.



c.

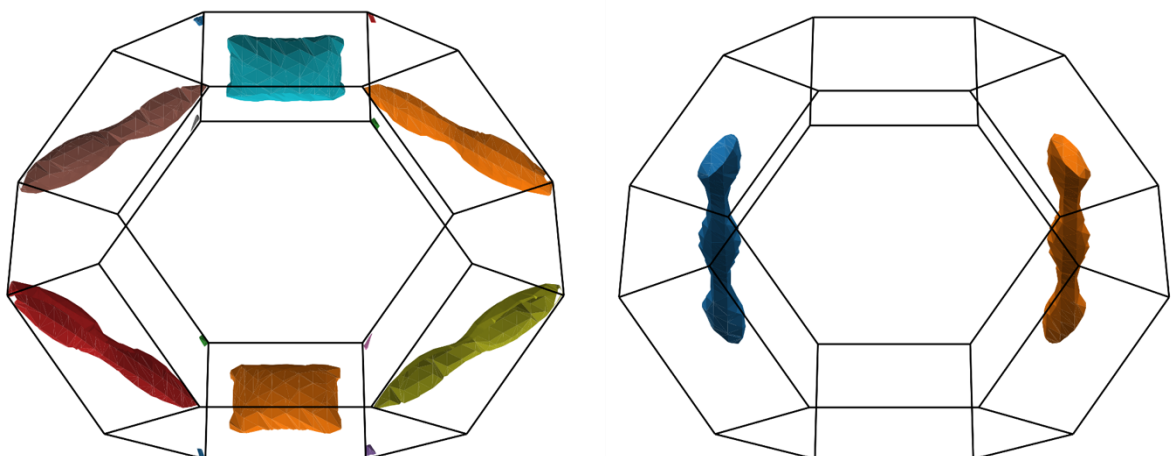
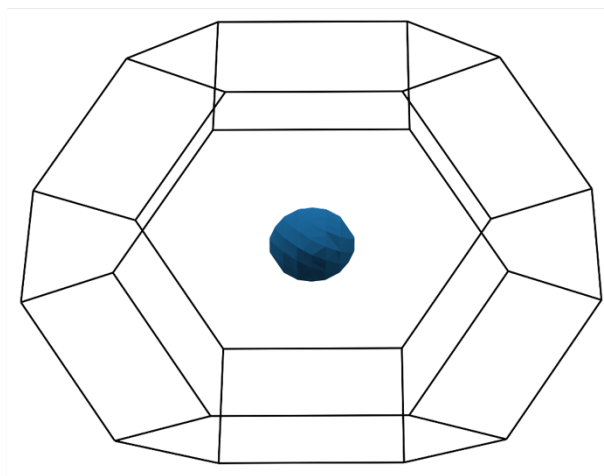
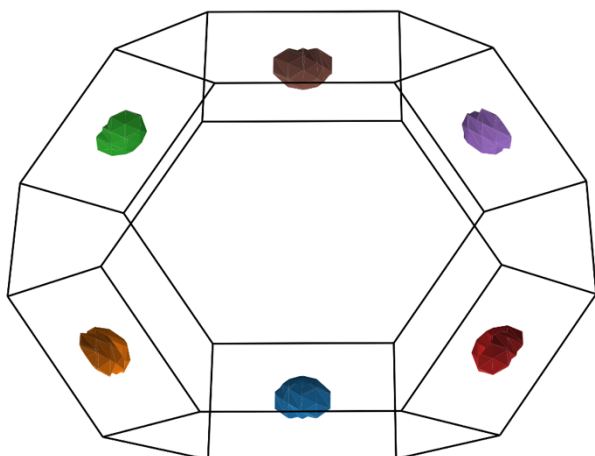
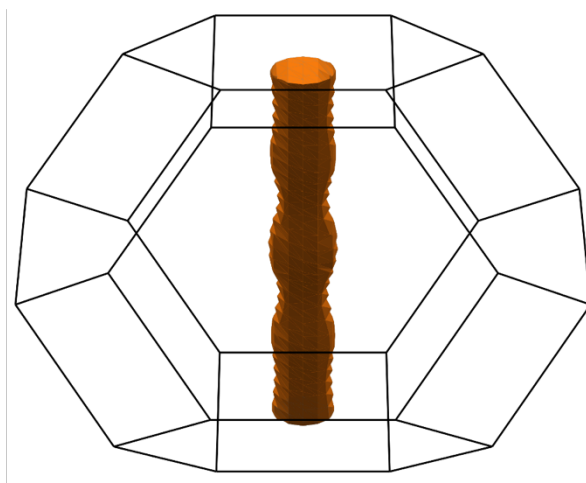
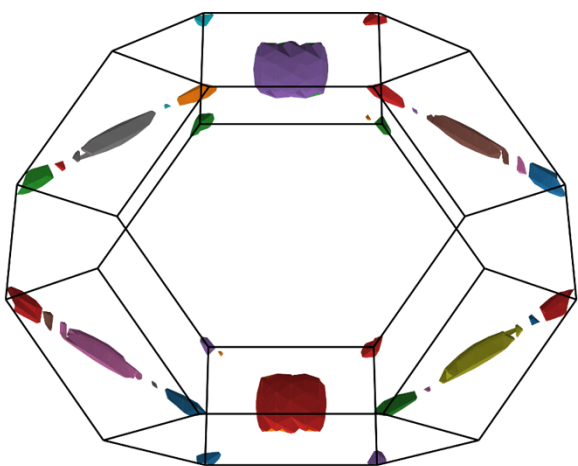


Figure SI.5: Energy isosurfaces. The energy isosurfaces in the first Brillouin zone at 10 meV below the valence-band top (left) and 10 meV above the conduction-band bottom (right) for (a) $\text{Na}_0\text{Fe}[\text{Fe}(\text{CN})_6]$, (b) $\text{Na}_1\text{Fe}[\text{Fe}(\text{CN})_6]$, and (c) $\text{Na}_2\text{Fe}[\text{Fe}(\text{CN})_6]$.

a.



b.



c.

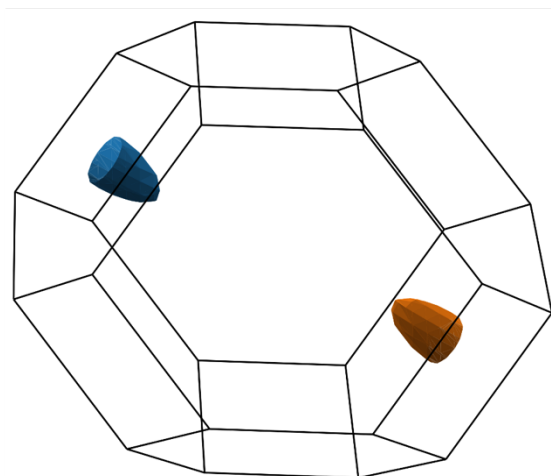
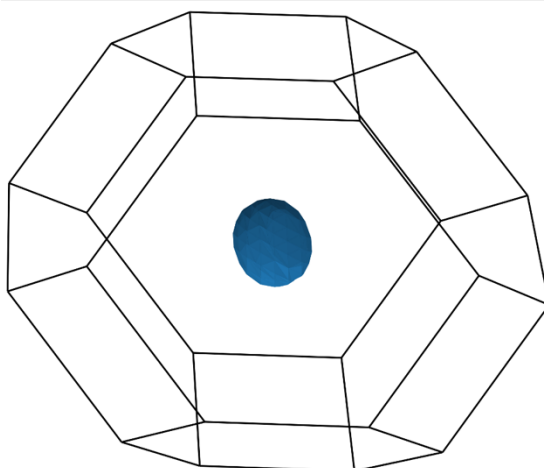


Figure SI.6: Energy isosurfaces. The energy isosurfaces in the first Brillouin zone at 10 meV below the valence-band top (left) and 10 meV above the conduction-band bottom (right) for (a) $\text{Na}_0\text{Co}[\text{Fe}(\text{CN})_6]$, (b) $\text{Na}_1\text{Co}[\text{Fe}(\text{CN})_6]$, and (c) $\text{Na}_2\text{Co}[\text{Fe}(\text{CN})_6]$.