Supporting Information for

The "Electron Crystal" Behavior in Copper Chalcogenides Cu_2X (X=Se, S)

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This supporting information includes:

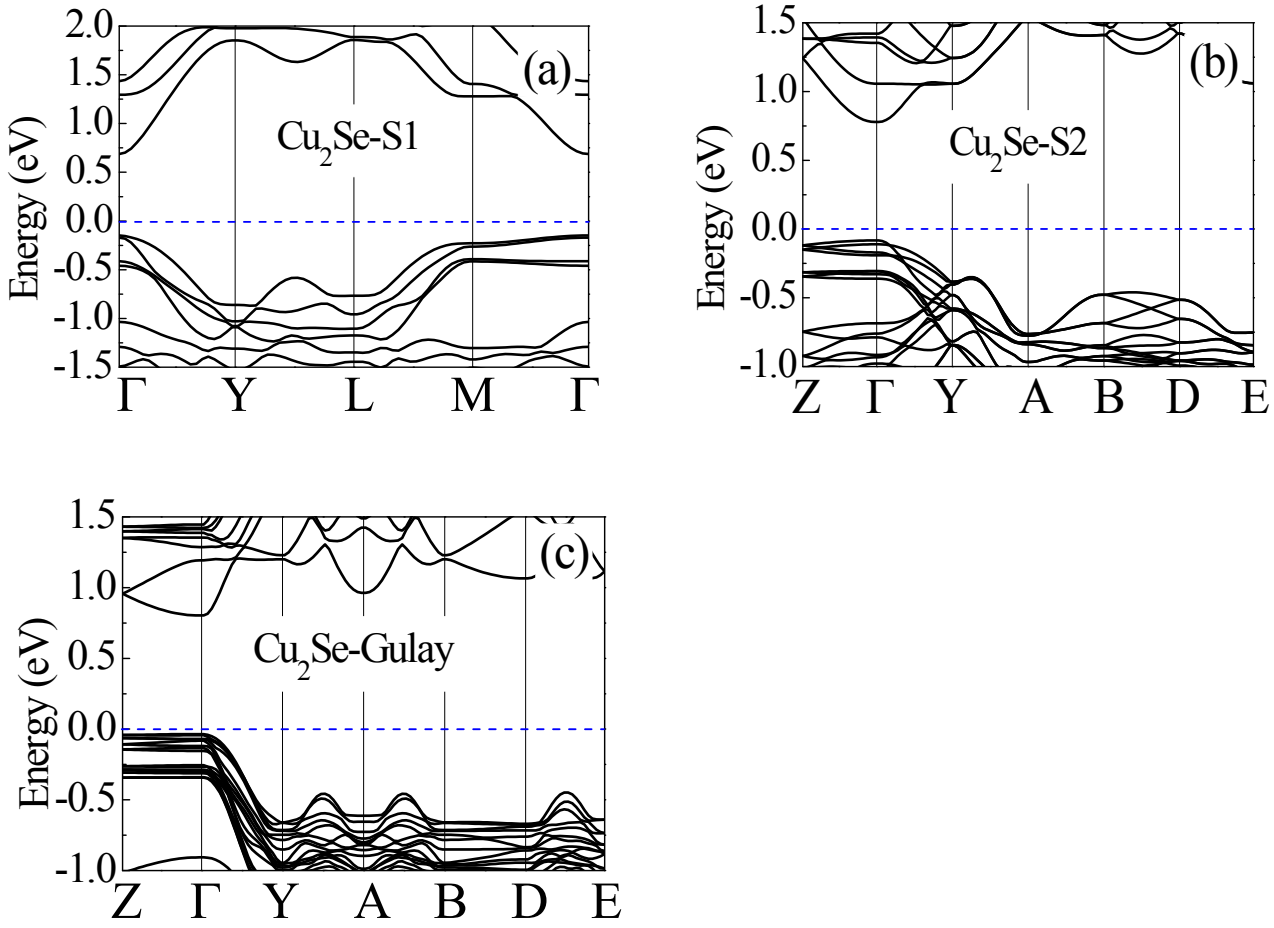

Figure SI1. Electronic band structures for Cu_2Se in the LT (a) S1, (b) S2, and (c) Gulay structures.

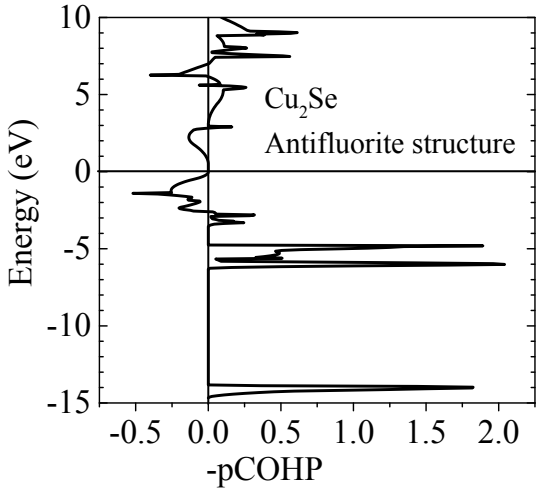

Figure SI2. The pCOHP analysis for the Cu-Se bond in Cu2Se with the antifluorite structure.

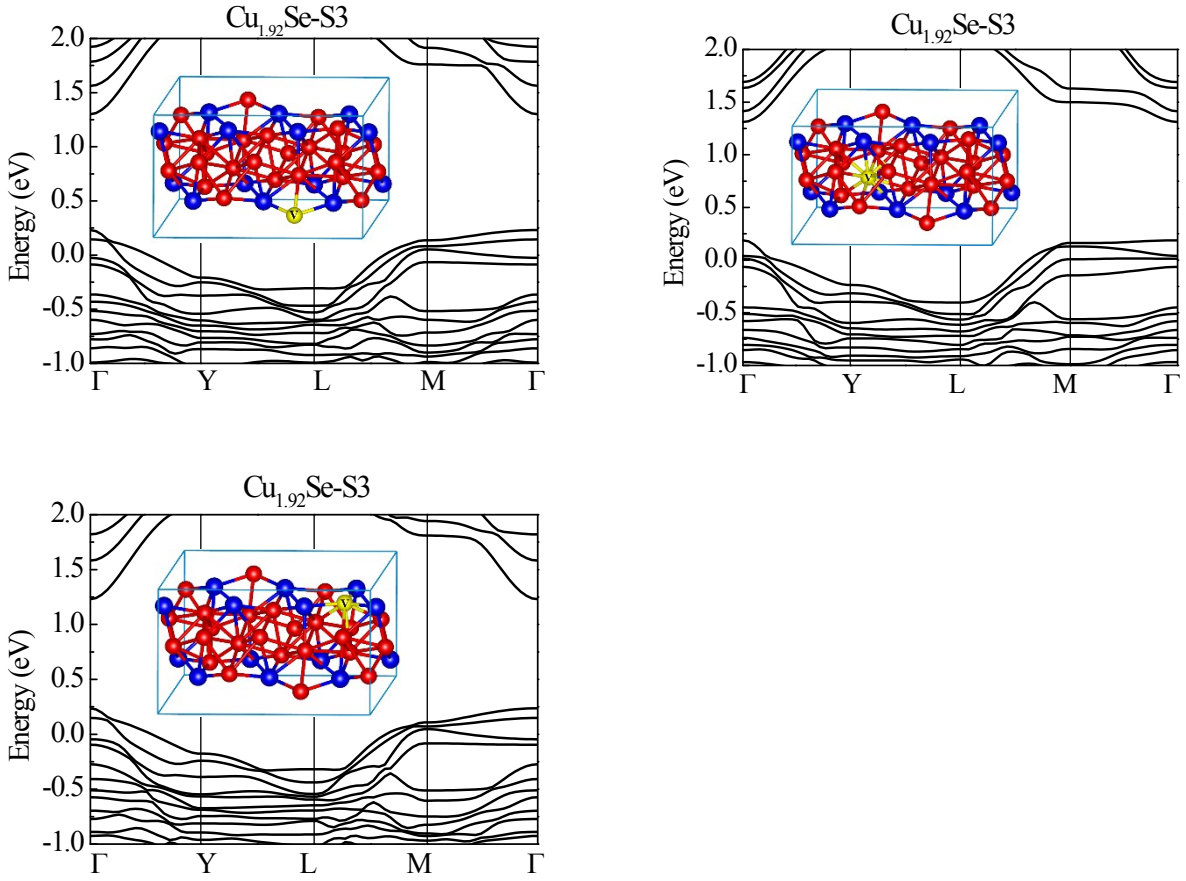

Figure SI3. Electronic band structures of $Cu_{1.92}Se$ in the low temperature S3 structure, with the Cu vacancy (denoted as "V") locating at different Cu sites. The first panel is used in the main text.

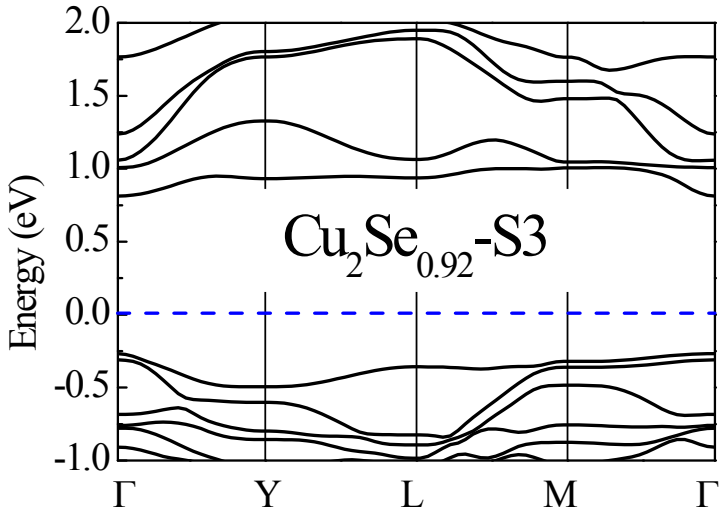

Figure SI4. The band structure of S3 Cu_2Se with Se vacancy.

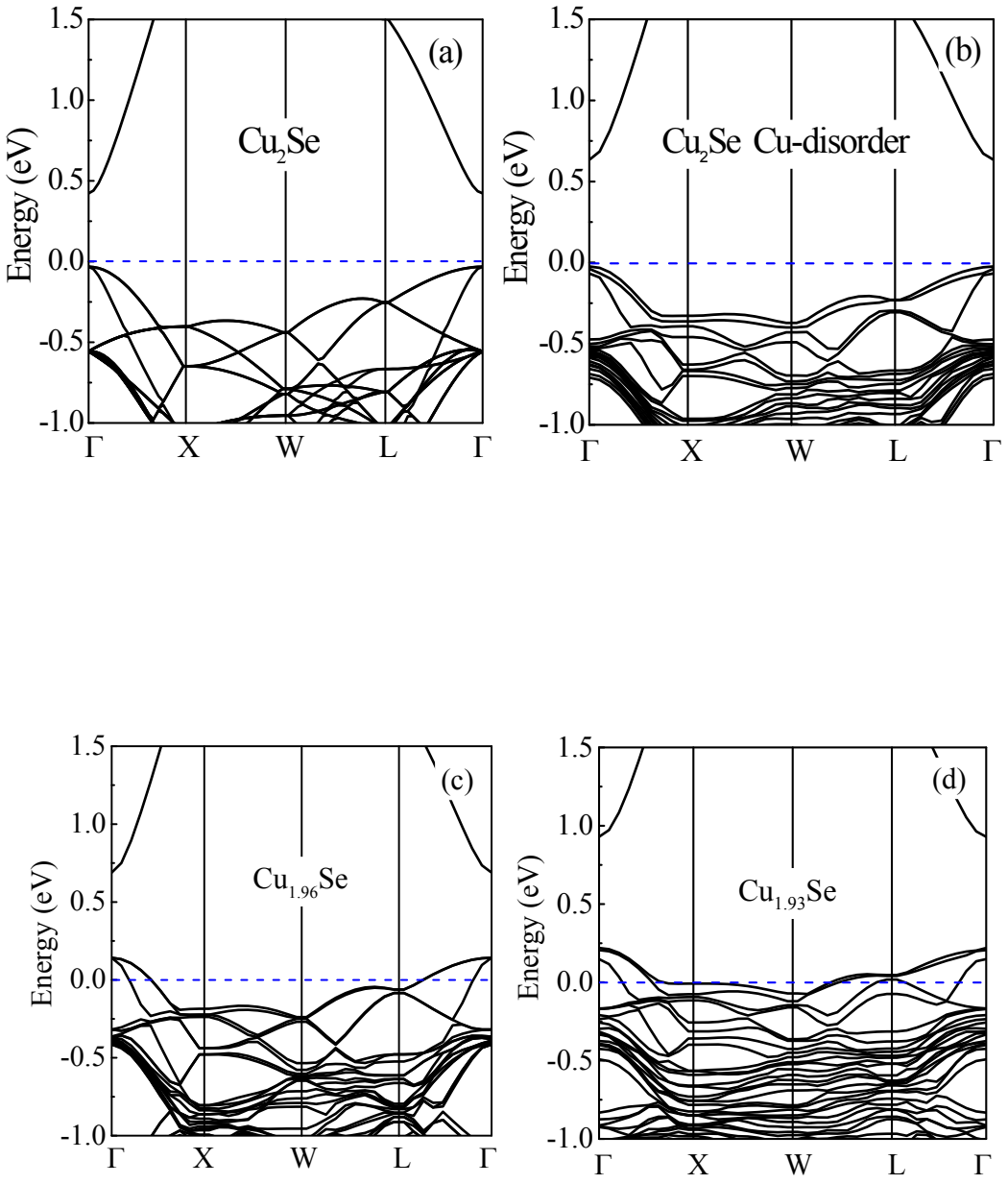

Figure SI5. Electronic band structures of (a) Cu_2Se, (b) Cu_2Se with all Cu ions disordered, (c) $Cu_{1.96}Se$ and (d) $Cu_{1.93}Se$. All the calculated structures are based on the high temperature antifluorite structure ($Cu_{54}Se_{27}$). Dotted lines denote the respective Fermi-levels.

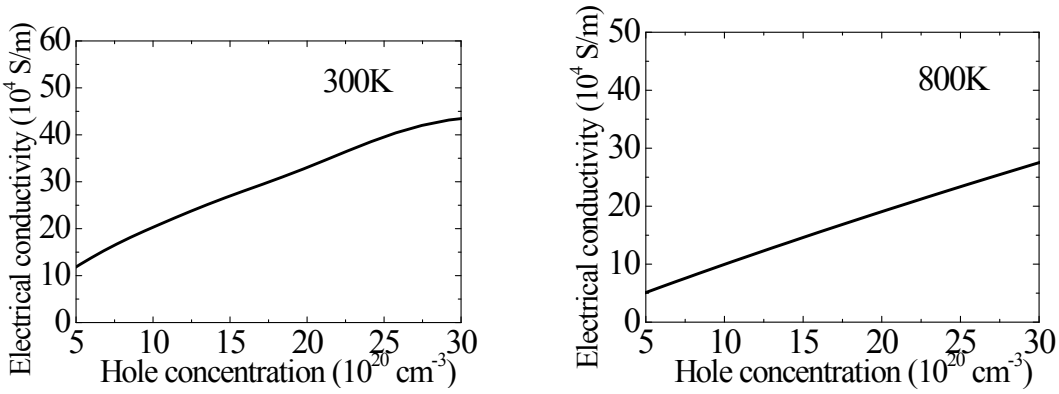

Figure SI6. The theoretical absolute electrical conductivities as a function of hole concentrations at 300K and 800K.

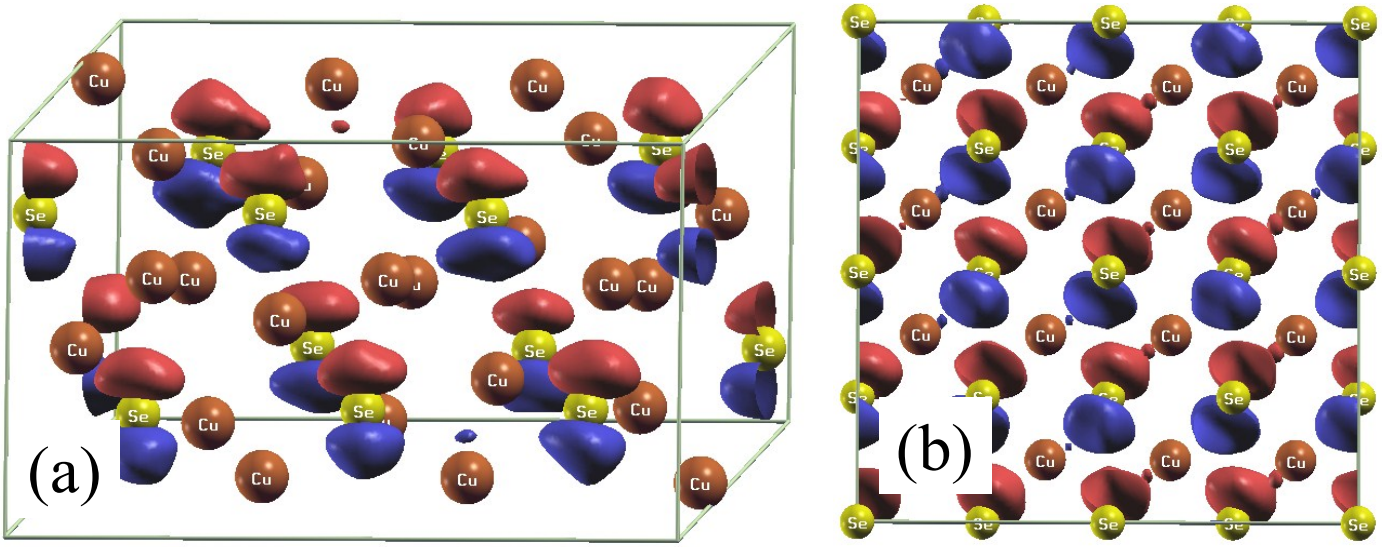

Figure SI7. The electron wave functions at the valence band maxima for (a) the low temperature phase (S3 structure) and (b) the high temperature phase. The colors indicate the signs of the wave functions.

Table SI1. Structural parameters and atomic coordinates for S1, S2, S3, and Gulay structures.

Structure	Space group	Lattice parameters					
		a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)
S1	P-1 (2)	7.101	7.122	7.407	81.227	80.503	119.878
S2	C2/c (15)	7.120	12.333	14.364	90.000	100.333	90.000
S3	P-1 (2)	7.078	12.434	7.428	90.236	108.736	90.038
Gulay	C2/c (15)	7.092	12.331	29.418	90.000	106.969	90.000

Structure	atom	*x*/a	*y*/b	*z*/c	Structure	atom	*x*/a	*y*/b	*z*/c
S1	Cu1	0.3881	0.6669	0.6818	Gulay	Cu1	0.2991	0.4477	0.3299
	Cu2	0.0590	0.9998	0.6862		Cu2	0.9849	0.8059	0.4211
	Cu3	0.7674	0.3325	0.8149		Cu3	0.6352	0.1202	0.3308
	Cu4	0.0543	0.6948	0.4336		Cu4	0.3284	0.4829	0.4515
	Cu5	0.5997	0.9200	0.4397		Cu5	0.0216	0.4301	0.3898
	Cu6	0.2823	0.3842	0.4348		Cu6	0.6546	0.1430	0.4236
	Se7	0.5800	0.6645	0.2203		Cu7	0.7179	0.5154	0.3589
	Se8	0.2420	0.0038	0.2172		Cu8	0.9625	0.7834	0.2935
	Se9	0.9008	0.3264	0.2111		Cu9	0.2478	0.8189	0.3582
S2	Cu1	0.7804	0.9174	0.5853		Cu10	0.5642	0.7583	0.3897
	Cu2	0.2861	0.7493	0.5937		Cu11	0.9461	0.0442	0.3587
	Cu3	0.3064	0.0829	0.6492		Cu12	0.3451	0.2074	0.3914
	Cu4	0.0164	0.9036	0.4674		Se13	0.9894	0.1423	0.4450
	Cu5	0.5779	0.7834	0.4669		Se14	0.6242	0.7801	0.3046
	Cu6	0.6178	0.0638	0.4676		Se15	0.9628	0.4451	0.3048
	Se7	0.3572	0.9171	0.3566		Se16	0.3244	0.8181	0.4448
	Se8	0.3650	0.2473	0.3604		Se17	0.6648	0.4802	0.4475
	Se9	0.8675	0.0858	0.3607		Se18	0.3059	0.1211	0.3024
S3	Cu1	0.5426	0.8375	0.6577					
	Cu2	0.5604	0.5133	0.6880					
	Cu3	0.5823	0.1735	0.7514					
	Cu4	0.1653	0.8502	0.4367					
	Cu5	0.1269	0.4631	0.4277					
	Cu6	0.1156	0.2062	0.4231					
	Cu7	0.0527	0.9828	0.6906					
	Cu8	0.1064	0.6594	0.8356					
	Cu9	0.0606	0.3295	0.6835					
	Cu10	0.6569	0.9694	0.4458					
	Cu11	0.5834	0.6694	0.4526					
	Cu12	0.7224	0.3400	0.4252					
	Se13	0.7604	0.8424	0.2349					

Se14	0.7425	0.5066	0.2227
Se15	0.7339	0.1729	0.2094
Se16	0.2486	0.9968	0.2164
Se17	0.2438	0.6554	0.2172
Se18	0.2444	0.3240	0.2049