Supporting Information for

First-Principles Study of Cu_9S_5: a Novel *p*−Type Conductive Semiconductor

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More details about the calculation method.

It is well known that LDA and GGA cannot reproduce band gaps precisely. The GW method and HSE06 are recognized accurate method to calculate the band gaps. However, due to the larger system of Cu_9S_5 supercell, we only performed a successful GW calculation of Cu_9S_5 when one K-point is used or NBANDS is set to be very small, and the calculation took a long time without convergence when the number of K-points is increased. So the results obtained from GW calculations are unreliable. In this case, Heyd–Scuseria–Ernzerhof (HSE06) is our best choice. In this work, HSE06 is only employed to calculate the band gap along the high-symmetry k-point path K (0,0.5,0)-Γ (0,0,0)-L(0,0,0.5) in the first Brillouin zone for Cu_9S_5 without Cu vacancies to give a benchmark for further GGA+U calculations. However, though it is

capable of predicting the band gap and electronic structure more precisely, they are computationally expensive when used with plane-wave basis sets. Hence, it's hard to apply the HSE06 to all Cu_9S_5 structures to obtain a complete band structure because of the large cost of computational resources. The computationally economical method GGA+U is used to get more details of electronic structures and the best U value is determined by comparing the GGA+U results with HSE06 results.

Table S1. The calculated Cu-S bond length.

	Cu(1)-S	Cu(2)-S	Cu(3)-S
Bond length (Å)	2.407	2.779	2.269

Table S2. The comparison of DFT optimized structural parameters and calculated band gaps with experimental results.

		a=b (Å)	c (Å)	V_0(Å^3)	E_c (eV)	E_v (eV)	E_g (eV)
	exp	3.930	48.140	643.905			1.500
	LDA	3.946 (0.41%)	47.271 (-1.81 %)	637.509 (-0.99%)	0.154	0.152	0.002
	GGA	3.876 (-1.37%)	48.332 (0.40 %)	628.795 (-2.35%)	0.130	0.124	0.006
G	U=3eV	3.890 (-1.02%)	48.207 (0.14 %)	631.580 (-1.91%)	0.106	0.106	0.000
G	U=5eV	3.896 (-0.87%)	48.206 (0.14 %)	633.777 (-1.57%)	0.264	0.093	0.171
A	U=7eV	3.906 (-0.61%)	48.212 (0.15 %)	637.148 (-1.05%)	0.486	0.084	0.402
+	U=9eV	3.912 (-0.46%)	48.249 (0.23 %)	639.429 (-0.70%)	0.715	0.079	0.637
U	U=11eV	3.921 (-0.23%)	48.199 (0.12 %)	641.738 (-0.34%)	0.940	0.062	0.878
	U=13eV	3.926 (-0.10%)	48.246 (0.22 %)	644.010 (0.02%)	1.165	0.070	1.095
	U=15eV	3.931 (0.03%)	48.246 (0.22 %)	645.651 (0.27%)	1.377	0.072	1.305
	HSE						0.610

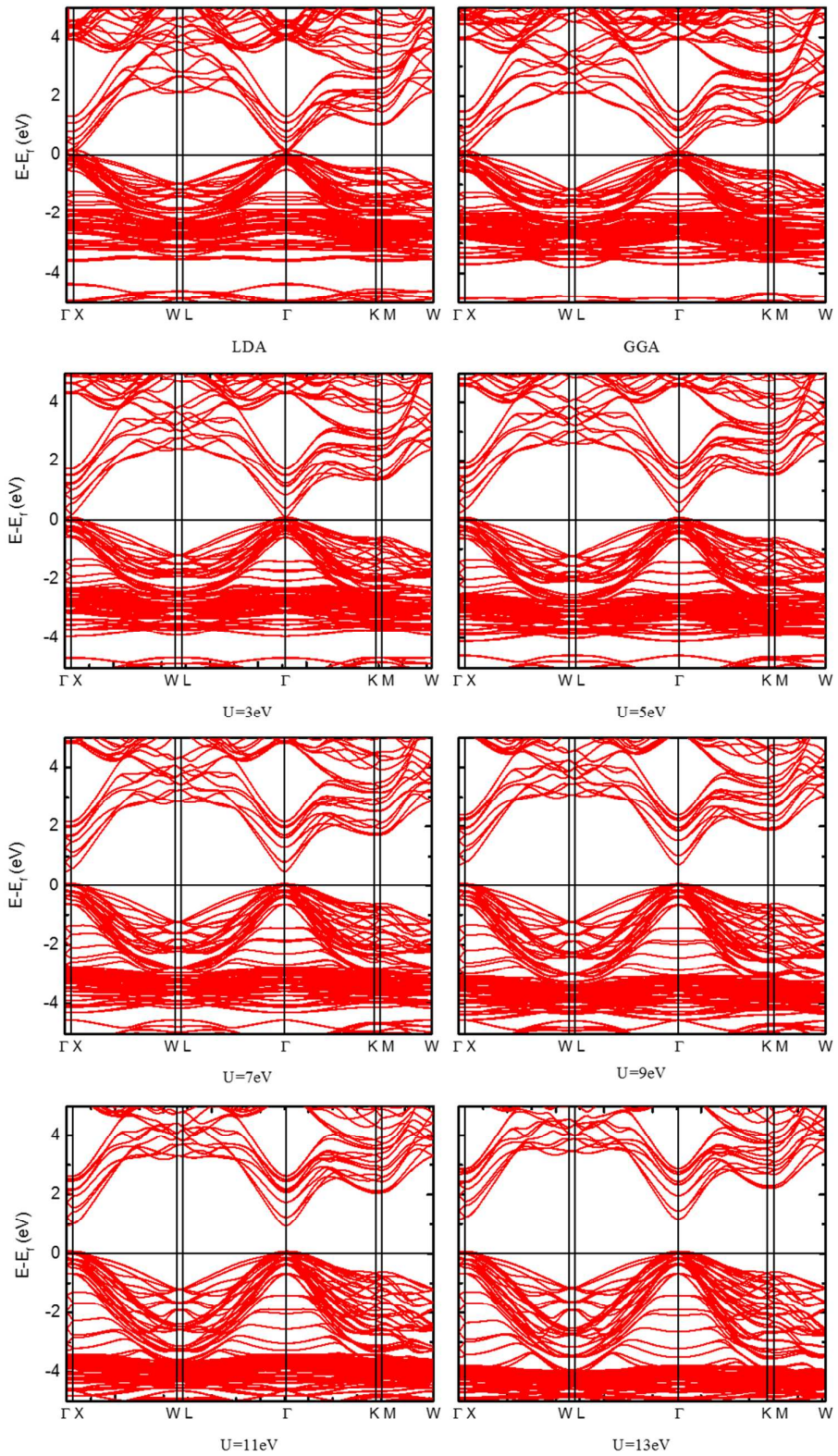

Figure S1. Band structures of Cu_9S_5 using LDA, GGA, and GGA+U with different U

values.

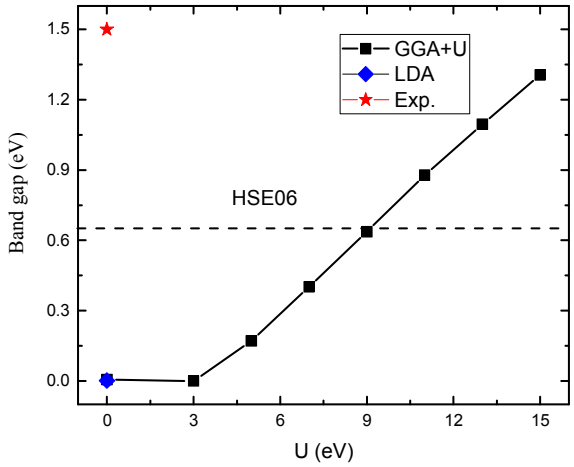

Figure S2. Calculated GGA+U band gap for Cu_9S_5 as a function of the U parameter. The stars and the diamond correspond to the experimental value and the LDA value, respectively. The dash line represents the HSE06 value of 0.623 eV.

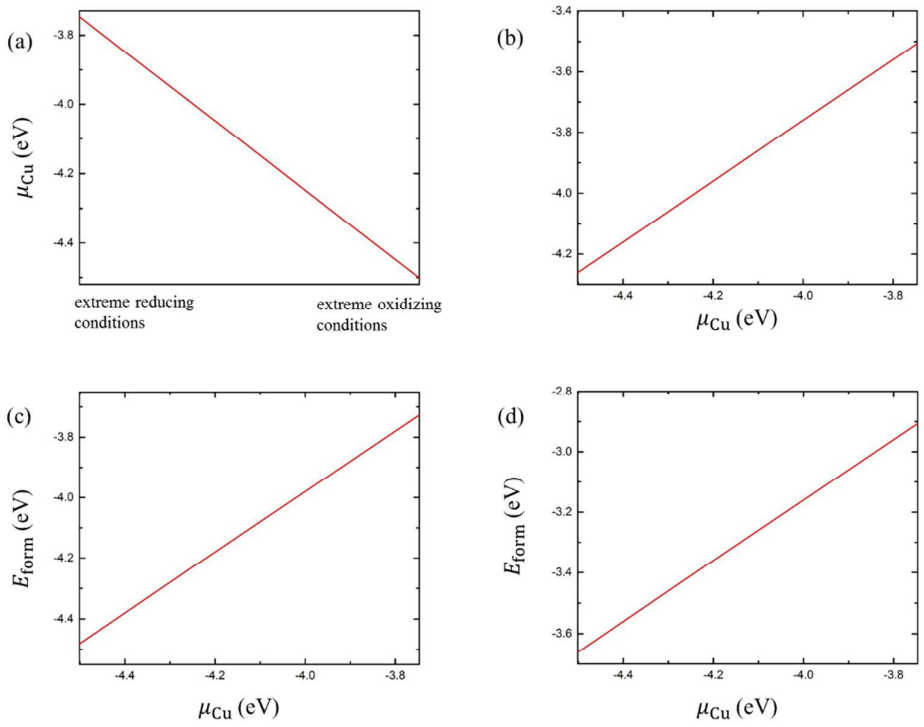

Figure S3. (a) Chemical potential of Cu atoms, (b) the formation energy of Cu(1) (tetrahedral central Cu) vacancy, (c) the formation energy of Cu(2) (octahedral central Cu) vacancy, and (d) the formation energy of Cu(3) (trigonal central Cu) vacancy.

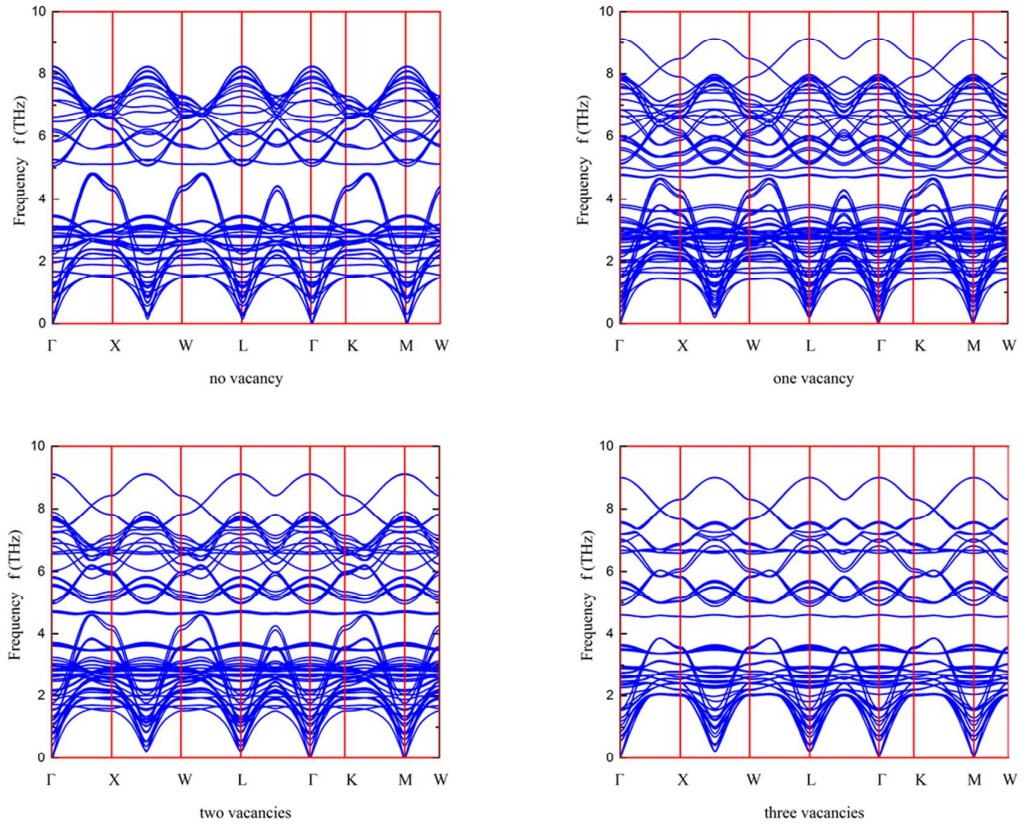

Figure S4. Phonon dispersion band structure of Cu_9S_5 with no vacancy, one vacancy, two vacancies, and three vacancies along the high-symmetry k-point path in the first Brillouin zone.

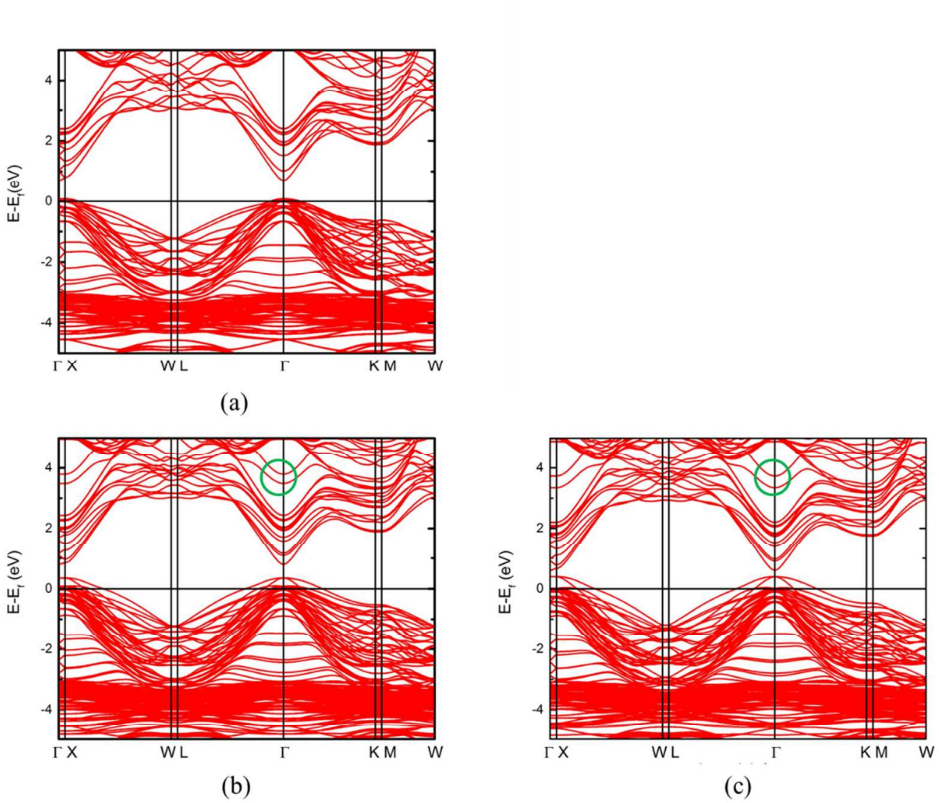

Figure S5. Calculated band structures of (a) Cu_9S_5, (b) Cu_9S_5 with one neutral defect, and (c) Cu_9S_5 with one charged defect.

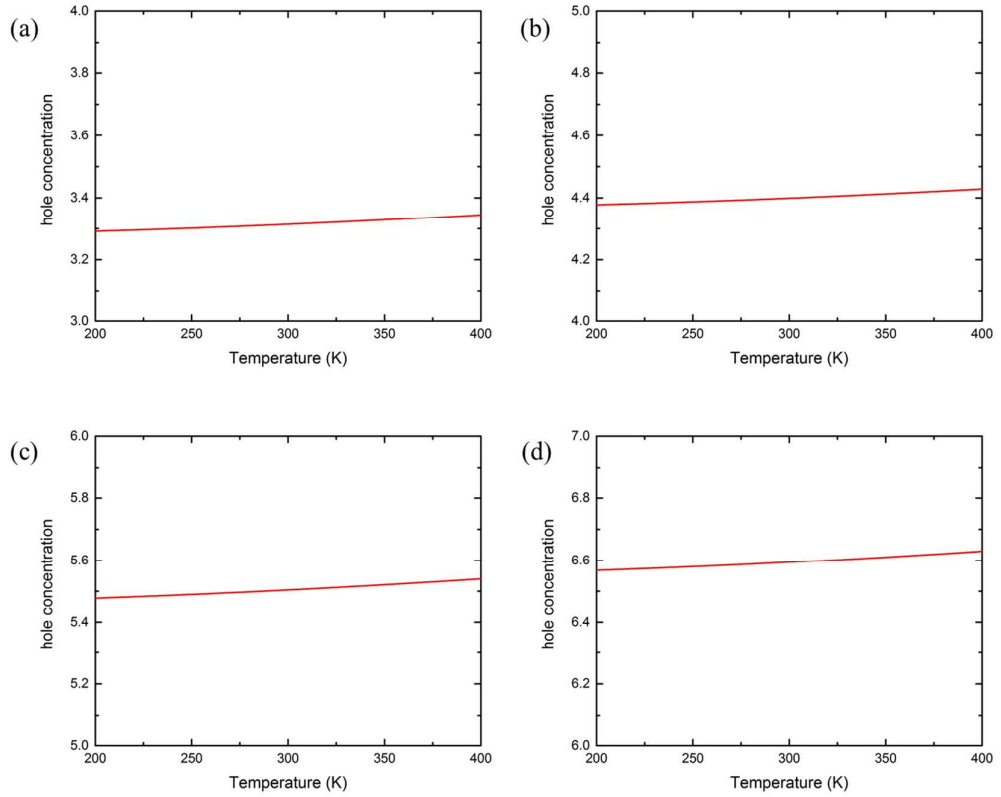

Figure S6. Calculated hole concentration as function of temperature: (a) Cu_9S_5, (b) Cu_9S_5 with one Cu vacancy, (c) Cu_9S_5 with two Cu vacancies, and (d) Cu_9S_5 with three Cu vacancies.

Table S3. The lattice parameters of Cu_9S_5 without vacancy, with one vacancy, two vacancies and three vacancies.

	no vacancy	one vacancy	two vacancies	three vacancies
$a = b$ (Å)	3.91	3.90	3.89	3.87
c (Å)	48.24	48.08	47.95	47.78

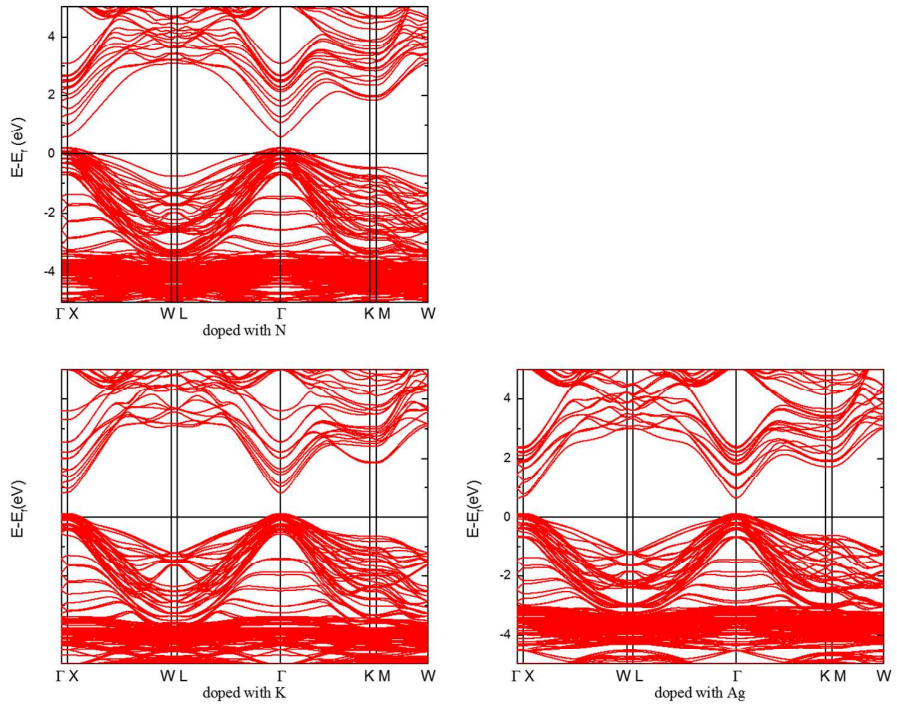

Figure S7. Band structure of Cu_9S_5 with N-doping, K-doping, and Ag-doping.

Table S4. The comparison of lattice parameters of Cu_9S_5 without doping, with one Cu vacancy, Ag, K, and N doping.

	Pure	Cu vacancy	Ag	K	N
$a = b$ (Å)	3.91	3.90	3.92	3.89	3.85
c (Å)	48.24	48.08	48.62	49.71	47.81