Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information for

Mercurial Possibilities: Determining Site Distributions in Cu_2HgSnS_4 Using $^{63/65}Cu$, ^{119}Sn, and ^{199}Hg Solid-state NMR Spectroscopy

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Table S1. EDX analyses (mol %) for Cu_2MSnS_4 (M = Zn, Cd, Hg).

	Cu_2***Zn***SnS_4	Cu_2***Cd***SnS_4	Cu_2***Hg***SnS_4	expected
Cu	24	24	25	25
M	12	13	11	12
Sn	13	12	11	13
S	51	51	53	50

Table S2. Tetragonal cell parameters for Cu_2MSnS_4 (M = Zn, Cd, Hg). [a]

	a (Å)	c (Å)	$c/2a$ ratio	V (Å^3)	Reference
Cu_2ZnSnS_4	5.436	10.85	0.998	320.6	Hahn1965
	5.4356(1)	10.8352(2)	0.997	320.13(1)	**This work**
Cu_2CdSnS_4	5.582	10.86	0.973	338.4	Hahn1965
	5.5920(1)	10.8399(2)	0.969	338.97(1)	Rosmus2014
	5.583	10.824	0.969	337.4	Olekseyuk2019
	5.5829(5)	10.8245(10)	0.969	337.39(5)	Bhattacharya2021
	5.5930(1)	10.8441(2)	0.969	339.22(1)	**This work**
Cu_2HgSnS_4	5.566	10.88	0.977	337.1	Hahn1965
	5.542(3)	10.908(7)	0.984	335.0(2)	Kaplunnik1977
	5.555	10.911	0.982	336.7	Gruzdev1988
	5.577(1)	10.898(2)	0.977	339.0(1)	Himmrich1991
	5.5749(6)	10.882(1)	0.976	338.21(4)	Kabalov1998
	5.580(2)	10.895(3)	0.976	339.2(2)	Vu2019
	5.5819(1)	10.8925(2)	0.976	339.38(1)	**This work**

[a] Standard uncertainties, where reported, are shown in parentheses. The list for Cu_2ZnSnS_4 is not comprehensive, because there are hundreds of previous reports of this compound.

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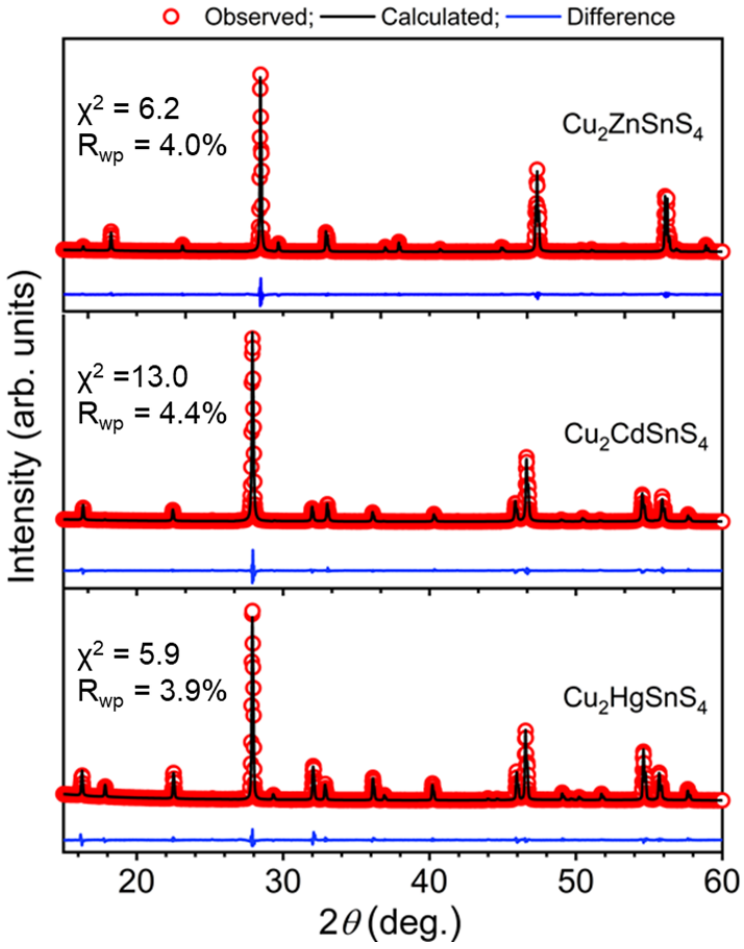

Figure S1. The Le Bail fittings of powder XRD patterns for Cu_2ZnSnS_4, Cu_2CdSnS_4, and Cu_2HgSnS_4.

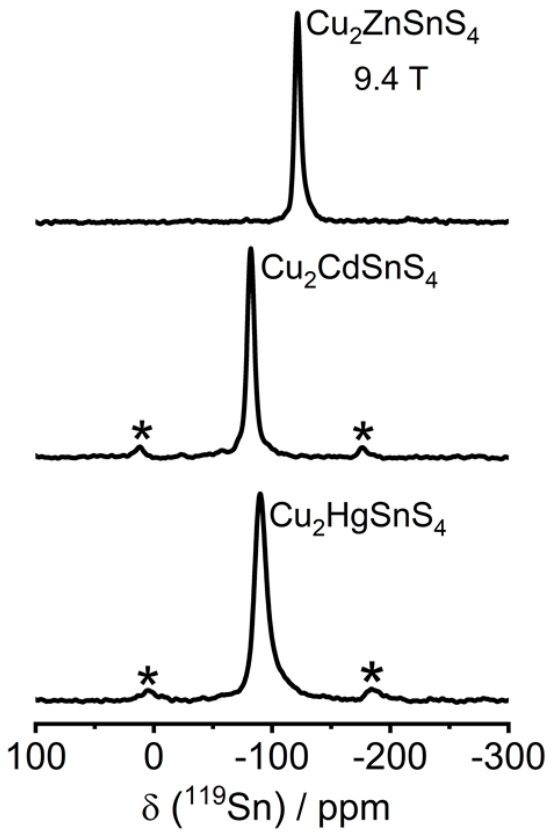

Figure S2. Experimental ^{119}Sn MAS NMR spectra for Cu_2ZnSnS_4, Cu_2CdSnS_4, and Cu_2HgSnS_4. The asterisks (*) mark spinning sidebands due to a small CSA.

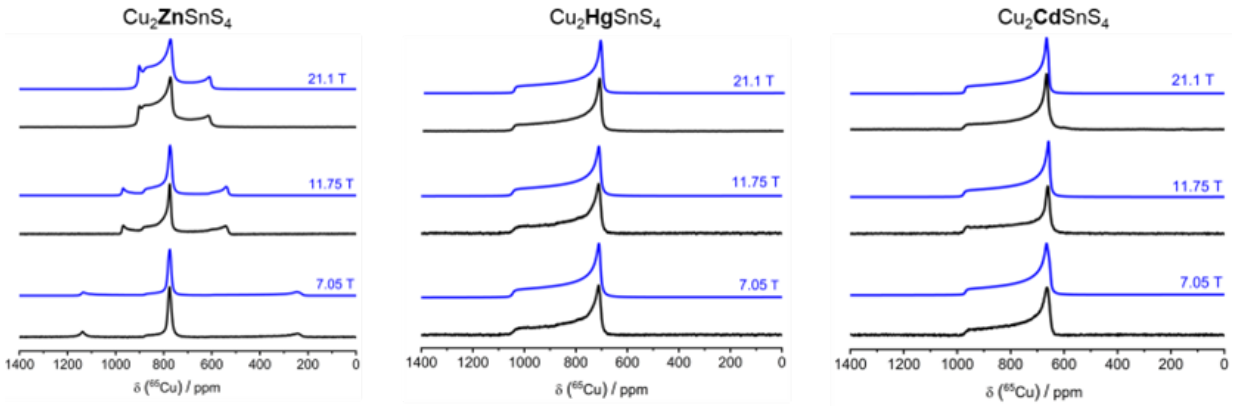

Figure S3. Experimental (black, ppm scale) and spectral simulations (blue) for non-spinning ^{65}Cu NMR spectra at 7.05, 11.75 and 21.1 T for Cu_2ZnSnS_4, Cu_2HgSnS_4, and Cu_2CdSnS_4. The NMR spectral simulations were performed using the Dmfit software.

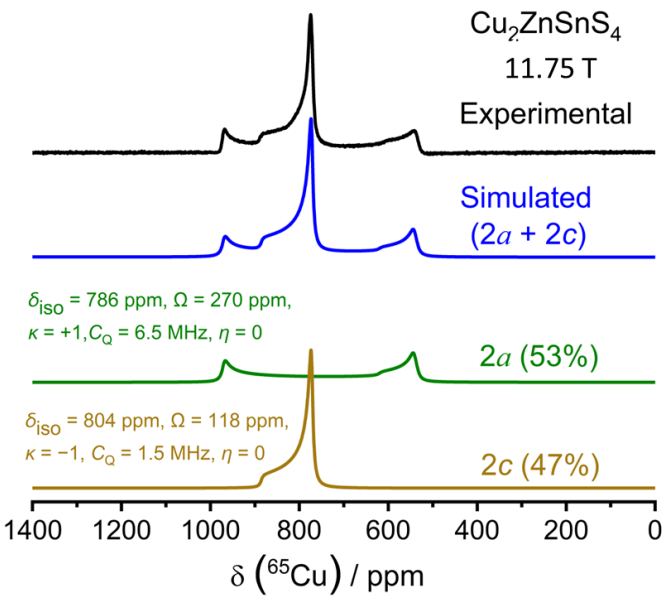

Figure S4. Deconvolution of the non-spinning ^{65}Cu NMR spectrum for Cu_2ZnSnS_4.

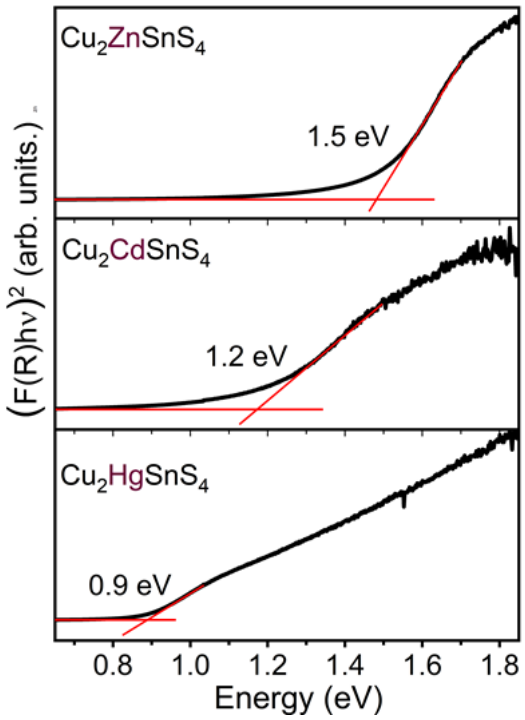

Figure S5. Optical diffuse reflectance spectra for Cu_2ZnSnS_4, Cu_2CdSnS_4, and Cu_2HgSnS_4, with fittings made on the assumption of direct band gaps.

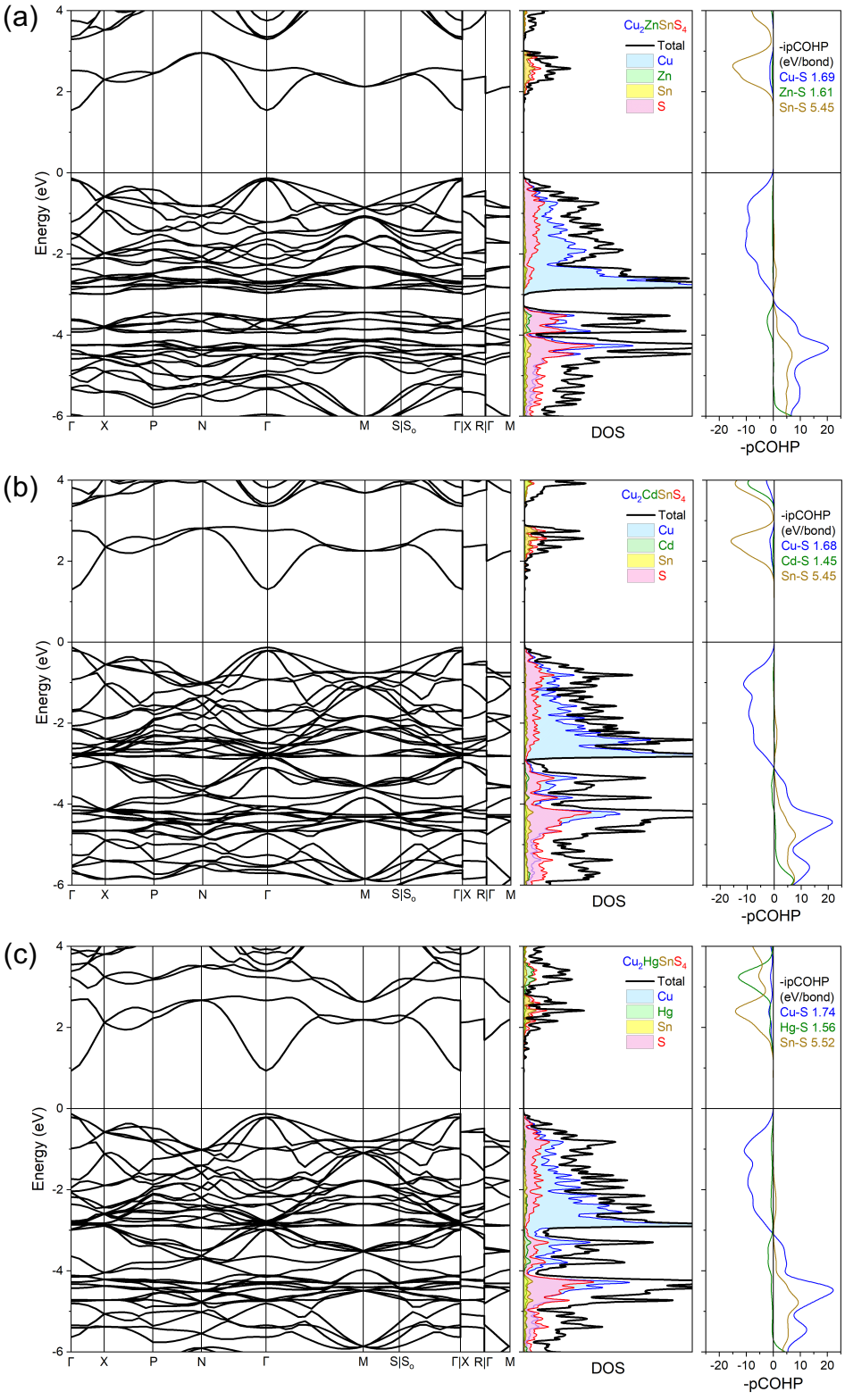

Figure S6. Electronic band structure, DOS, and –pCOHP curves for Cu_2ZnSnS_4, Cu_2CdSnS_4, and Cu_2HgSnS_4 compounds.