Supplementary Materials for "Prediction of new ZnS-CaS alloys with anomalous electronic properties"

Jie Gao,[1] Yifeng Duan,[1, a)] Changming Zhao,[1] Wenjie Liu,[1] Haiming Dong,[1, b)] Dekun Zhang,[2, c)] and Huafeng Dong[3, d)]

[1)] *School of Physics, China University of Mining and Technology, Xuzhou 221116, China.*

[2)] *School of Materials Science and Engineering, China University of Mining and Technology, Xuzhou, 221116, China*

[3)] *School of Physics and Optoelectronic Engineering, Guangdong University of Technology, Guangzhou, 510006, China.*

(Dated: 9 January 2019)

[a)]Electronic mail: yifeng@cumt.edu.cn

[b)]Electronic mail: hmdong@cumt.edu.cn

[c)]Electronic mail: dkzhang@cumt.edu.cn

[d)]Electronic mail: hfdong@gdut.edu.cn

TABLE S1. Bulk modulus B (GPa), shear modulus G (GPa), Young's modulus E (GPa), Poisson's ratio v and Vickers hardness H_v (GPa) for possible ZnS, CaS and ZnS-CaS alloys at ambient pressure.

Phase	B	G	E	v	Hv
ZB-ZnS	70	34	87	0.293	3.62
RS-ZnS	86	46	117	0.274	5.95
Cmcm-ZnS	87	46	118	0.274	5.98
RS-CaS	56	40	96	0.216	8.33
$Pm\bar{3}m$-CaS	62	18	50	0.365	-0.35
$I4/$mcm-$CaZnS_2$	60	32	82	0.273	4.30
$R\bar{3}$-Ca_2ZnS_3	51	20	52	0.329	0.75
$R\bar{3}$-$Ca_7Zn_2S_9$	40	18	48	0.303	1.34

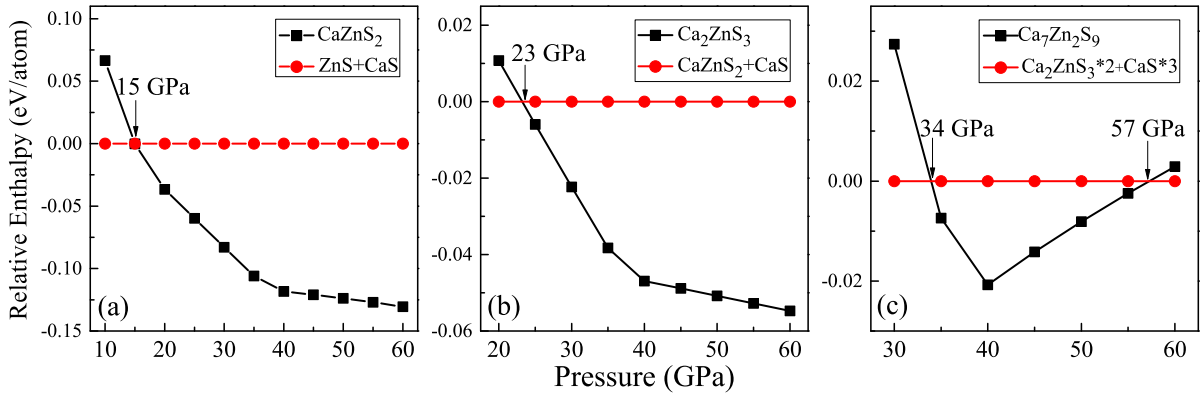

Fig. S1. Formation enthalpy of ZnS-CaS alloys with respect to decomposition into (a) ZnS and CaS, (b) $CaZnS_2$ and CaS, and (c) Ca_2ZnS_3 and CaS, where the stable phases with the lowest energy are chosen for special pressures.

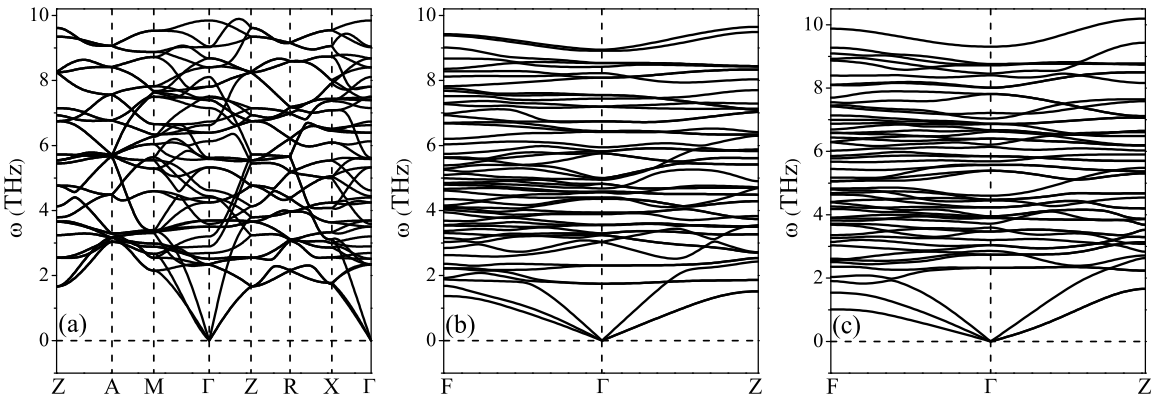

Fig. S2. The phonon spectrums of predicted (a) $I4/mcm$-$CaZnS_2$, (b) $R\bar{3}$-Ca_2ZnS_3 and (c) $R\bar{3}$-$Ca_7Zn_2S_9$ at 0 GPa.

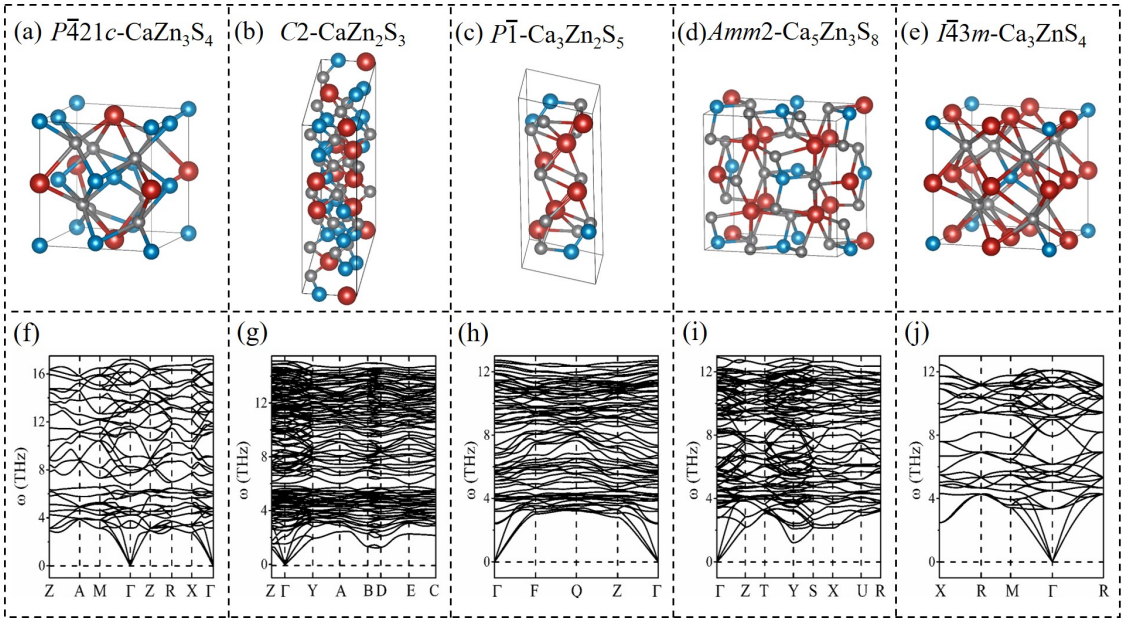

Fig. S3. The upper panels show the crystal structures of the predicted thermodynamically metastable ZnS-CaS alloys at special pressures, whose phonon spectrums are listed correspondingly in the bottom panels.

TABLE S2. Structural parameters and atomic coordinates for metastable ZnS-CaS alloys at different pressures.

	Structure	Parameters(Å,°)	Atom	x	y	z	P(GPa)
$CaZn_3S_4$	$P\bar{4}21c$	a=b=5.62	Ca(2b)	0.00	0.00	0.50	70
		c=6.02	Zn(4d)	0.00	0.50	0.04	
		$\alpha = \beta = \gamma$=90	Zn(2a)	0.00	0.00	0.00	
			S(8e)	0.25	0.20	0.19	
$CaZn_2S_3$	$C2$	a=8.45	Ca(4c)	1.00	0.26	0.67	50
		b=5.85	Ca(2b)	0.00	0.28	0.50	
		c=17.38	Ca(2a)	0.00	0.82	0.00	
		$\alpha = \gamma$=90	Zn(4c)	0.00	0.76	0.67	
		β=133.49	Zn(4c)	0.52	0.29	0.85	
			Zn(4c)	0.04	0.29	0.19	
			Zn(2a)	0.00	0.31	0.00	
			Zn(2b)	0.50	0.26	0.50	
			S(4c)	0.19	0.97	0.64	
			S(4c)	0.32	0.04	0.85	
			S(4c)	0.69	0.04	0.82	
			S(4c)	0.81	0.97	0.69	
			S(4c)	0.68	0.60	0.97	
			S(4c)	0.70	0.07	0.48	
$Ca_3Zn_2S_5$	$P\bar{1}$	a=11.47	Ca(2i)	0.29	0.52	0.41	30
		b=5.32	Ca(2i)	0.52	0.77	0.25	
		c=5.34	Ca(2i)	0.09	0.85	0.14	
		α=107.80	Zn(2i)	0.90	0.66	0.36	
		β=99.34	Zn(2i)	0.30	0.01	0.92	
		γ=78.00	S(2i)	0.31	0.00	0.34	
			S(2i)	0.07	0.38	0.22	
			S(2i)	0.88	0.08	0.33	
			S(2i)	0.53	0.26	0.25	
			S(2i)	0.27	0.45	0.90	
$Ca_5Zn_3S_8$	$Amm2$	a=8.95	Ca(8f)	0.26	0.75	0.57	30
		b=8.82	Ca(2a)	0.00	0.50	0.55	
		c=6.11	Zn(2a)	0.00	0.00	0.55	
		$\alpha = \beta = \gamma$=90	Zn(2b)	0.50	0.00	0.08	
			Zn(2b)	0.50	0.00	0.57	
			S(4c)	0.69	0.00	0.83	
			S(4c)	0.21	0.00	0.33	
			S(4d)	0.00	0.21	0.76	
			S(4e)	0.50	0.81	0.32	
Ca_3ZnS_4	$I\bar{4}3m$	a=b=c=6.27	Ca(6b)	0.50	0.00	0.00	30
		$\alpha = \beta = \gamma$=90	Zn(8c)	0.00	0.00	0.00	
			S(2a)	0.71	0.29	0.29	

TABLE S3. Elastic constants tensors of predicted ZnS-CaS alloys.

Phase	Elastic constant tensor C_{ij} (GPa)
$I4$/mcm-$CaZnS_2$	$\begin{pmatrix} 99 & 56 & 17 & 0 & 0 & 0 \\ & 99 & 17 & 0 & 0 & 0 \\ & & 162 & 0 & 0 & 0 \\ & & & 26 & 0 & 0 \\ & & & & 26 & 0 \\ & & & & & 31 \end{pmatrix}$
$R\bar{3}$-Ca_2ZnS_3	$\begin{pmatrix} 72 & 42 & 32 & -3 & -6 & 0 \\ & 72 & 32 & 3 & 6 & 0 \\ & & 97 & 0 & 0 & 0 \\ & & & 23 & 0 & 6 \\ & & & & 23 & -3 \\ & & & & & 15 \end{pmatrix}$
$R\bar{3}$-$Ca_7Zn_2S_9$	$\begin{pmatrix} 68 & 39 & 21 & -5 & 2 & 0 \\ & 68 & 21 & 5 & -2 & 0 \\ & & 66 & 0 & 0 & 0 \\ & & & 21 & 0 & -2 \\ & & & & 21 & -5 \\ & & & & & 14 \end{pmatrix}$
$C2$-$CaZn_2S_3$	$\begin{pmatrix} 43 & 24 & 28 & 0 & -15 & 0 \\ & 91 & 36 & 0 & -4 & 0 \\ & & 88 & 0 & -22 & 0 \\ & & & 9 & 0 & 4 \\ & & & & 33 & 0 \\ & & & & & 8 \end{pmatrix}$
$Amm2$-$Ca_5Zn_3S_8$	$\begin{pmatrix} 92 & 45 & 7 & 0 & 0 & 0 \\ & 82 & 23 & 0 & 0 & 0 \\ & & 141 & 0 & 0 & 0 \\ & & & 16 & 0 & 0 \\ & & & & -15 & 0 \\ & & & & & 10 \end{pmatrix}$
$P\bar{1}$-$Ca_3Zn_2S_5$	$\begin{pmatrix} 83 & 31 & 31 & 3 & 9 & 1 \\ & 86 & 44 & -5 & 9 & -2 \\ & & 78 & 5 & -2 & -8 \\ & & & 30 & -20 & 17 \\ & & & & 17 & -7 \\ & & & & & 35 \end{pmatrix}$
$P\bar{4}21c$-$CaZn_3S_4$	$\begin{pmatrix} 114 & 30 & 33 & 0 & 0 & 0 \\ & 114 & 33 & 0 & 0 & 0 \\ & & 98 & 0 & 0 & 0 \\ & & & -13 & 0 & 0 \\ & & & & -13 & 0 \\ & & & & & -2 \end{pmatrix}$
$I\bar{4}3m$-Ca_3ZnS_4	$\begin{pmatrix} 121 & 22 & 22 & 0 & 0 & 0 \\ & 121 & 22 & 0 & 0 & 0 \\ & & 121 & 0 & 0 & 0 \\ & & & -11 & 0 & 0 \\ & & & & -11 & 0 \\ & & & & & -11 \end{pmatrix}$

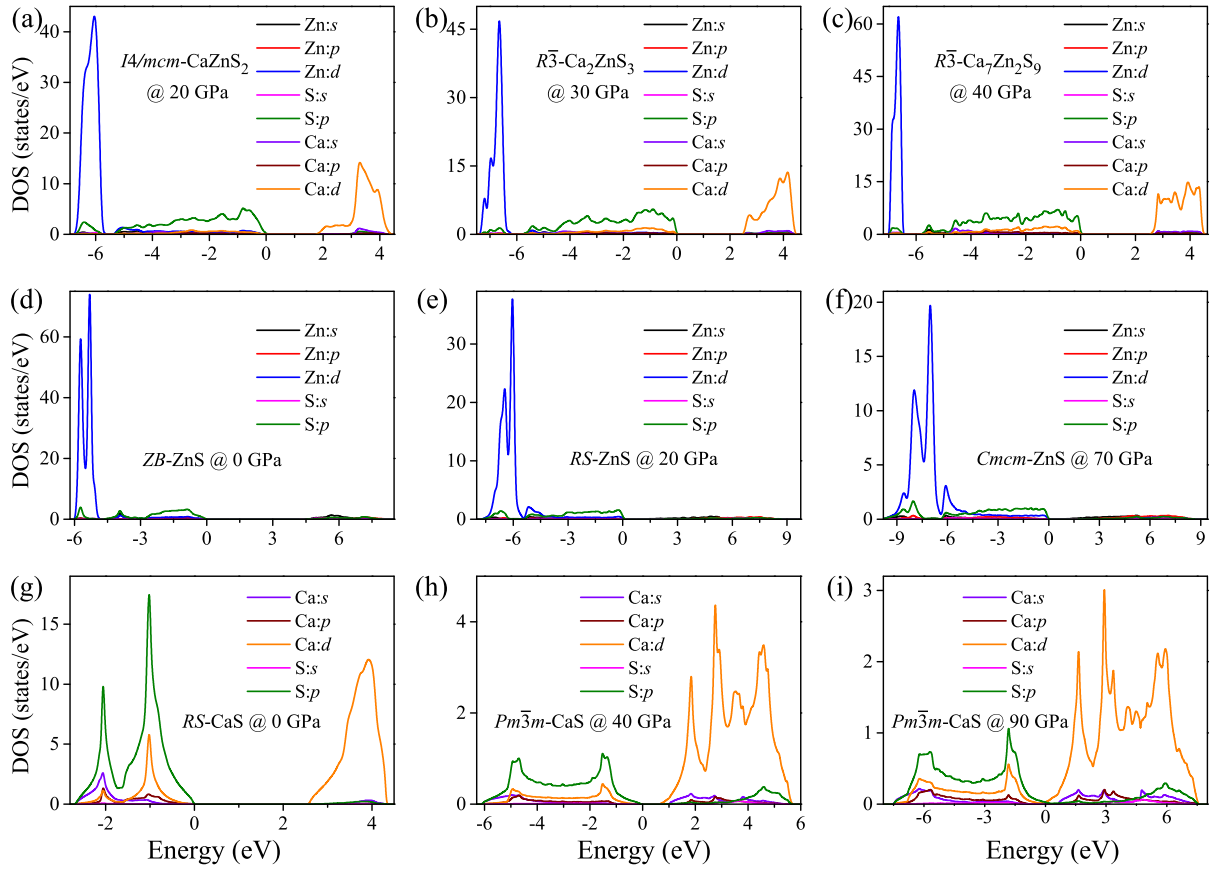

Fig. S4. Full DOS of ZnS, CaS and their alloys at different pressures based on TB-mBJ functional. ZnS-CaS alloys: (a) $I4/mcm$-$CaZnS_2$ at 20 GPa, (b) $R\bar{3}$-Ca_2ZnS_3 at 30 GPa, (c) $R\bar{3}$-$Ca_7Zn_2S_9$ at 40 GPa; ZnS: (d) ZB at 0 GPa, (e) RS at 20 GPa, (f) $Cmcm$ at 70 GPa; and CaS: (g) RS at 0 GPa, (h) $Pm\bar{3}m$ at 40 GPa, (i) $Pm\bar{3}m$ at 90 GPa. The VBM is set to zero in each panel.

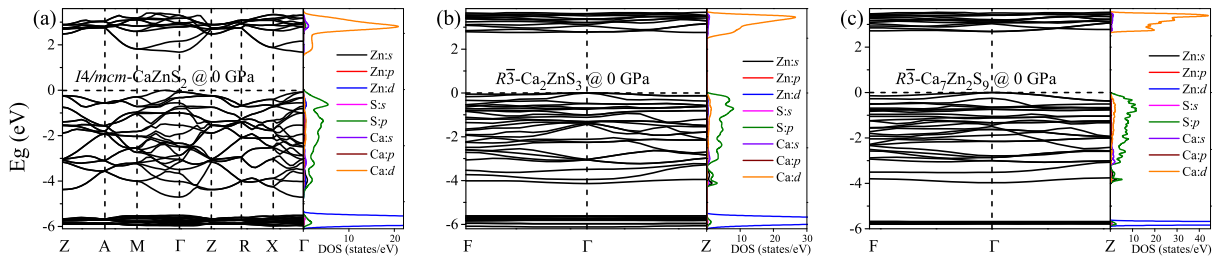

Fig. S5. Band structures and DOS of ZnS-CaS alloys based on TB-mBJ functional.

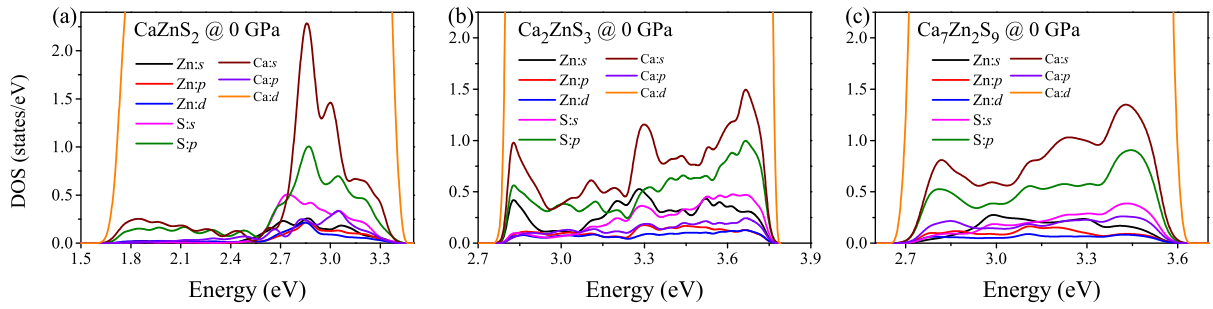

Fig. S6. Projected DOS above the Fermi level of stable ZnS-CaS alloys based on TB-mBJ functional.