Supporting Information

Destabilization of ionic compounds under compression: a case of copper halides

Yanlei Geng,[1,2,3] Jianfu Li,[1, a)] Qi Rui,[1] Yong Liu,[1] Jianan Yuan,[1] Jiani Lin,[1] and Xiaoli Wang[1, a)]

[1]*School of Physics and Electronic Information, Yantai University, Yantai 264005, China*

[2]*Center for High Pressure Science and Technology Advanced Research, Beijing 100094, China*

[3]*Synergetic Extreme Condition High-Pressure Science Center, State Key Laboratory of High Pressure and Superhard Materials, College of Physics, Jilin University, Changchun, 130012, China*

[a)] Authors to whom correspondence should be addressed: jianfuli@ytu.edu.cn and xlwang@ytu.edu.cn

Figure

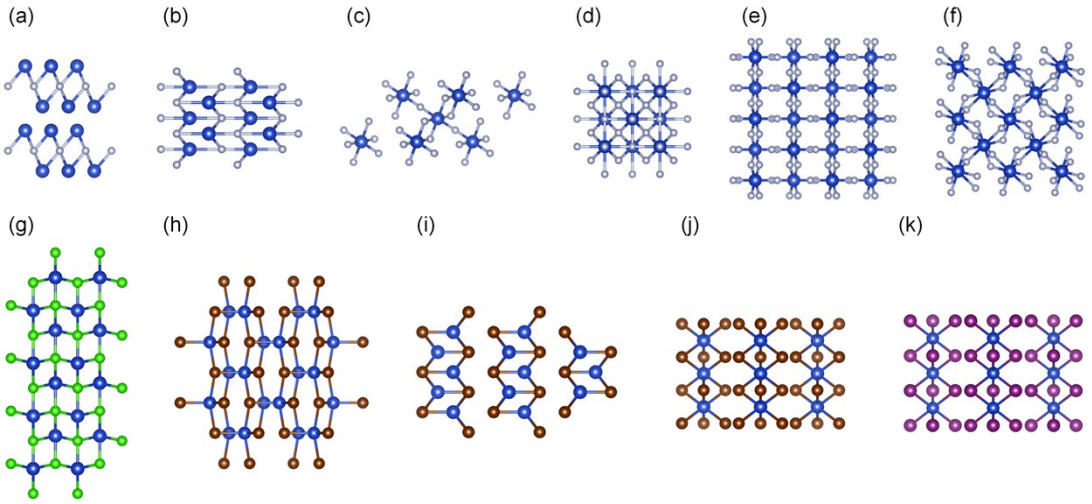

Figure S1. The crystal structures of the stable Cu-X compounds at high pressure. (a) *P*-3*m*1 phase for Cu_2F, (b) *Cmmm* phase for CuF, (c) *R*-3*c* phase for CuF_3, (d) *Fm*-3*m* phase for CuF_3, (e) *Cccm* phase for CuF_4, (f) $P2_1/c$ phase for CuF_4, (g) *Cmcm* phase for CuCl, (h) *Cmcm* phase for CuBr, (i) *P*4/*nmm* phase for CuBr, (j) $P6_3/mcm$ phase for $CuBr_3$, (k) $P6_3/mcm$ phase for CuI_3.

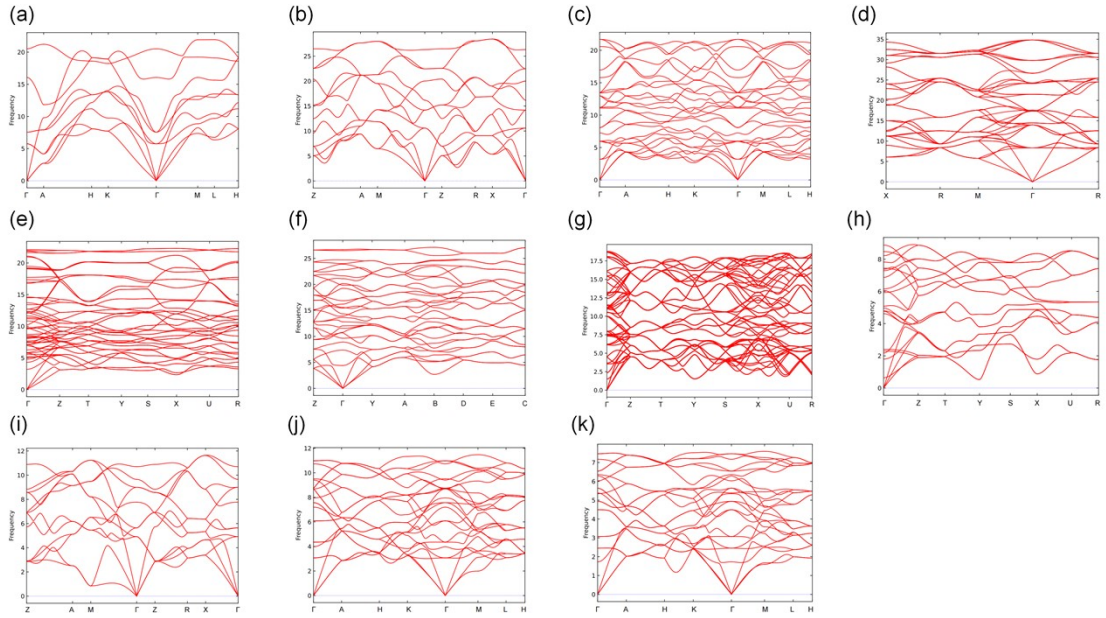

Figure S2. The phonon spectrum at the corresponding pressure. (a) *P*-3*m*1 phase for Cu_2F at 200 GPa, (b) *Cmmm* phase for CuF at 300 GPa, (c) *R*-3*c* phase for CuF_3 at 50 GPa, (d) *Fm*-3*m* phase for CuF_3 at 400 GPa, (e) *Cccm* phase for CuF_4 at 50 GPa, (f) $P2_1/c$ phase for CuF_4 at 150 GPa, (g) *Cmcm* phase for CuCl at 200 GPa, (h) *Cmcm* phase for CuBr at 40 GPa, (i) *P4/nmm* phase for CuBr 100 GPa, (j) $P6_3/mcm$ phase for $CuBr_3$ at 80 GPa, (k) $P6_3/mcm$ phase for CuI_3 at 40 GPa.

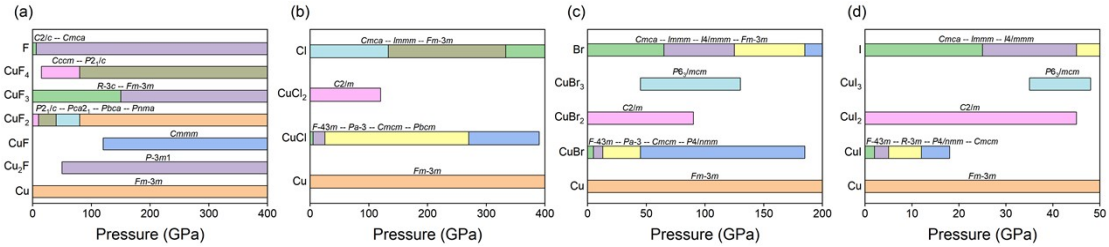

Figure S3. The pressure composition phase diagram of the (a) Cu-F, (b) Cu-Cl, (c) Cu-Br, and (d) Cu-I systems.

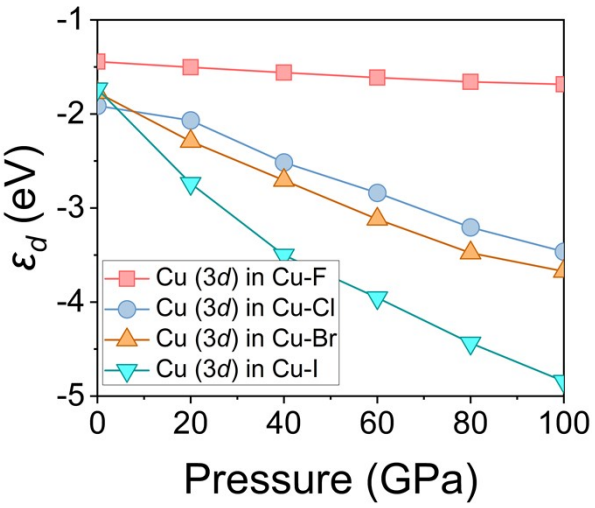

Figure S4. Pressure-driven shift of Cu-3*d* band centers (ε_d) in Cu-X systems. Evolution of ε_d with increasing pressure for Cu-F, Cu-Cl, Cu-Br, and Cu-I systems, illustrating the progressive downshift in *d*-orbital band centers under compression.

Table

Table S1. The parameters of the predicted structures for Cu-X compounds.

Space group	Pressure (GPa)	Lattice parameter (Å)		Atom	site	Wyckoff position		
Cu_2F (P-3m1)	200	a = 2.214 b = 2.214 c = 4.765	α = 90.000 β = 90.000 γ = 120.000	Cu1 F1	2d 1b	0.333 0.000	0.667 0.000	0.814 0.500
CuF ($Cmmm$)	300	a = 2.269 b = 2.269 c = 4.436	α = 90.000 β = 90.000 γ = 90.000	Cu1 F1	2c 2c	0.000 0.000	0.500 0.500	0.342 0.870
CuF_3 (R-3c)	50	a = 4.301 b = 4.301 c = 12.325	α = 90.000 β = 90.000 γ = 120.000	Cu1 F1	6b 18e	0.000 -0.333	0.000 -0.359	0.000 0.583
CuF_3 (Fm-3m)	400	a = 4.229 b = 4.229 c = 4.229	α = 90.000 β = 90.000 γ = 90.000	Cu1 F1 F2	4a 4b 8c	0.000 0.000 0.750	0.000 0.000 0.250	0.000 0.500 0.250
CuF_4 ($Cccm$)	50	a = 5.448 b = 5.991 c = 4.776	α = 90.000 β = 90.000 γ = 90.000	Cu1 F1 F2	4e 8l 8h	0.750 0.805 0.500	0.750 0.965 0.197	1.000 0.500 0.750
CuF_4 ($P2_1/c$)	150	a = 3.691 b = 4.056 c = 4.106	α = 90.000 β = 96.785 γ = 90.000	Cu1 F1 F2	2c 4e 4e	0.000 0.793 0.646	0.500 0.632 0.339	1.000 0.594 1.178
CuCl ($Cmcm$)	150	a = 2.699 b = 8.085 c = 3.360	α = 90.000 β = 90.000 γ = 90.000	Cu1 Cl1	4c 4c	0.000 -0.500	0.905 0.141	1.250 1.250
CuBr ($Cmcm$)	40	a = 4.789 b = 5.493 c = 4.278	α = 90.000 β = 90.000 γ = 90.000	Cu1 Br1	4c 4c	-0.500 -0.500	0.111 0.685	0.750 0.750
$CuBr_3$ ($P6_3/mcm$)	80	a = 4.985 b = 4.985 c = 5.035	α = 90.000 β = 90.000 γ = 120.000	Cu1 Br1	2b 6g	0.000 0.000	0.000 0.382	0.500 0.750

CuBr (*P*4/*nmm*)	100	*a* = 2.949 *b* = 2.949 *c* = 5.248	*α* = 90.000 *β* = 90.000 *γ* = 90.000	Cu1 Br1	2c 2c	0.000 0.000	0.500 0.500	0.108 0.676
CuI_3 ($P6_3/mcm$)	40	*a* = 5.641 *b* = 5.641 c = 5.626	α = 90.000 *β* = 90.000 *γ* = 120.000	Cu1 I1	2b 6g	0.000 0.372	0.000 0.000	1.000 0.750