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Electronic and structural properties of grain boundaries in $CuInSe_2$

Supplementary Information

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1 Symmetry along the (112) planes

Figure S1(a) shows the first cation-Se layer parallel to the *ab*-plane in our supercell (as viewed from the left in, e.g., Figs. 9 in the main text). Because of periodicity, the atoms on the top and bottom edges are the same (similarly, of course, the atoms on the left edge are the same as the atoms on the right edge). Fig. S1(b) shows the CIS (112) plane corresponding to this layer. The black solid lines depict the projection on the (112) plane of the conventional tetragonal CIS cell. The yellow solid lines give a possible choice of a primitive cell for this plane. The red solid lines delineate what would be the boundaries of our supercell on such a plane plane. This shows that that the supercell does not preserve the periodicity of CIS over the (112) planes in the direction of the *b*-axis. Indeed, the atoms on the lower edges in Figures S1(a) and (b) are not the same. This means that the Se close to the lower edge in Fig. S1(a) are coordinated to a cation antisite, violating the octet rule. On the other hand, the periodicity in the direction of the *a*-axis is preserved.

Note that one can try to preserve the periodicity in both directions by taking a supercell with a much larger cross section on the *ab*-plane. This does not have a too interesting benefit, however, because, as we explain in the main article, the right-hand side of the GB results from a $\sim 60°$ rotation around the *c*-axis, which is not commensurate with the CIS periodicity over the (112) planes. Thus, the left side of the GB would still end up with antisites at the upper and bottom edges, and the computational burden would be much heavier.

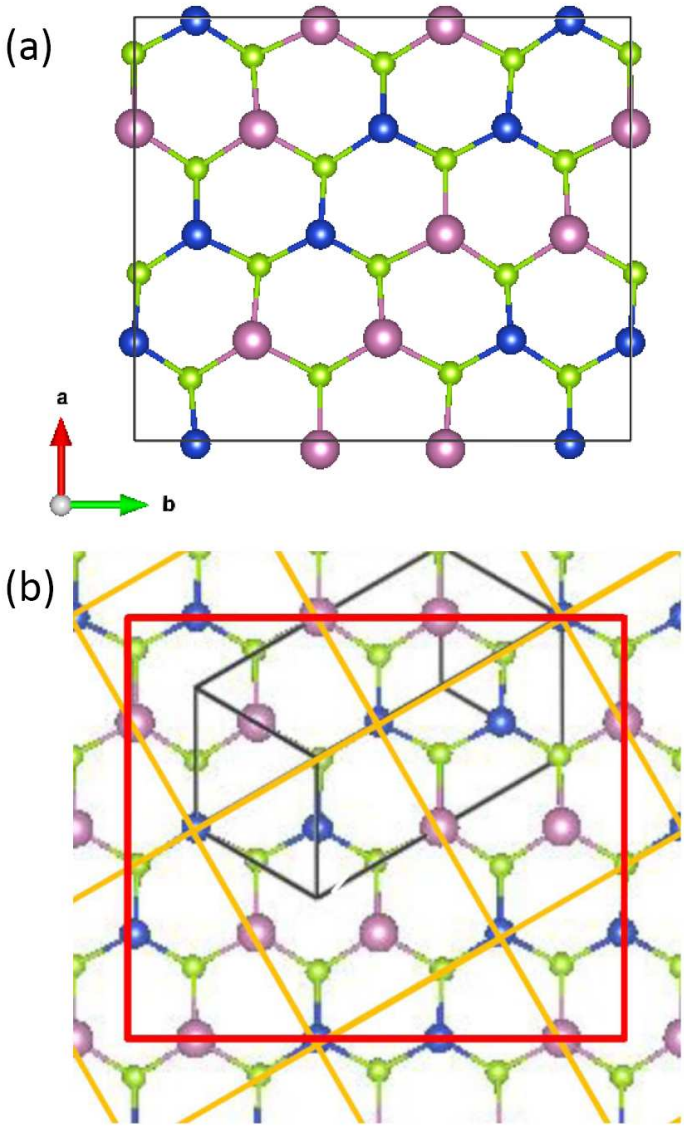

Fig. S1:

2 Grain boundary model

The relaxed atomic positions in our $CuInSe_2$ (CIS) grain boundary (GB) supercell model are given below. The VASP format is used, except that the atom numbers are added for more information. These are the numbers referred to in the main article and in the figures further down.

```
CIS Sigma3 GB
   1.09258752770000
    13.0480191422999994    0.0000000000000000    0.0000000000000000
     0.0000000000000000   15.2747494542000002    0.0000000000000000
     0.0000000000000000    0.0000000000000000   28.1584973418999986
   Cu   In   Se
    72    72   144
Direct
1   0.0346836624988010  0.7376059778573421  0.2544830819078172
2   0.5371112248188264  0.5005311692626460  0.2503603493392129
3   0.2324810746437489  0.9989927389307922  0.0261724534601507
4   0.1813504867156549  0.5005871571682941  0.3617215841389924
5   0.6852078723256433  0.2509062724059622  0.3626025965493214
6   0.7387063842234076  0.7505940884329214  0.0273093822972586
7   0.3416313417431075  0.2532477657103684  0.4728100317733705
8   0.3859795233104777  0.7509760429898313  0.1391869947409385
9   0.8362595673632931  0.9915880096771018  0.4733641535878145
10  0.8894643076241352  0.5014977817587166  0.1423141080850751
11  0.0324313429360660  0.5091282505780669  0.2495922461158638
12  0.5376991185843598  0.2519520625241663  0.2499865666769778
13  0.1891781298941631  0.2609836790183064  0.3598163417408589
14  0.2386024451020164  0.7595071442862061  0.0244069943590501
15  0.6837364740431938 -0.0001000253534953  0.3614414731563043
16  0.7373715918712950  0.5012109937475413  0.0275988210430308
17  0.3412121404746883  0.0017022068322234  0.4712983661576537
18  0.3871061799239967  0.5007521400137829  0.1390928999878255
19  0.8905180251185525  0.2518728196860124  0.1395939501578795
20  0.8382778309403563  0.7480005250068312  0.4724663397043516
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22  0.7851979988930882  0.8731788960207929  0.2512645085621235
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24  0.4361025409113139  0.8734368530374900  0.3607067697715391
25  0.1316671545139281  0.3740485177198789  0.1451598798057872
26  0.0860297712497824  0.8682682707904839  0.4761986908367519
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28  0.9421996913515953  0.6249433324472922  0.3562737257118754
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82	0.2518859387077385	0.2377540152059664	0.9417492918162758
83	0.3111928541601851	0.7409500033631632	0.6144464775605191
84	0.2597127232748525	0.7630982964690458	0.9460396911038551
85	0.1355007797534356	0.0103495527723357	0.7199762705280218
86	0.1231816236984393	0.4895988200144689	0.7243808383701600
87	0.9361459847452770	0.2570289870675828	0.8310616945916749
88	0.9504836413070961	0.7389523309296011	0.8360351068700549
89	0.8082645178368483	0.9905694266542265	0.6147824623486865
90	0.7618317949428945	0.0087526254177811	0.9417008543345187
91	0.8236670258998466	0.5083858958885245	0.6086639763590059
92	0.7479436485701242	0.4937332198912786	0.9473892599603122
93	0.6378609490135267	0.2580306120399231	0.7193197456643315
94	0.6239416912136797	0.7415621311624335	0.7261122848209436
95	0.4485561315359762	0.0066506211495496	0.8308845247533420
96	0.4382097742604747	0.4923401692576508	0.8357264634509708
97	0.0671160328839478	0.3760124783818607	0.6112929112031723
98	0.0014587605613534	0.3741987238579831	0.9437835881572623
99	0.0653437249382671	0.8726661809852746	0.6109572637874319
100	0.0051395443859645	0.8736995995482029	0.9436017377023570
101	0.5526255420923041	0.1259202200377905	0.6080682315255642
102	0.5159135254294837	0.1232627780719194	0.9481556005992701
103	0.5787757529166968	0.6236750482553578	0.6152352273021423
104	0.4910937521175054	0.6266388725544395	0.9402808284729813
105	0.3902187616327181	0.3748314216330336	0.7255745100114976
106	0.3688060873488094	0.8747699502479176	0.7185107170647321
107	0.2039062400681205	0.1239335880885969	0.8381424459786021
108	0.1815329701346172	0.6233908708744871	0.8282807837985977
109	0.8793435902949872	0.1254150647499546	0.7156033272775730
110	0.8806421271288691	0.6238501625487728	0.7290741570869509
111	0.7044581737819703	0.3753879205035262	0.8369875276695149
112	0.6809495121413719	0.8757373402650976	0.8302545978616882
113	0.3275263711518859	0.0010415559648639	0.6166705928183553
114	0.2408076283876439	0.9978341024061068	0.9463575698218276
115	0.3039763153374221	0.4976007850779438	0.6064242420675513
116	0.2686910827115240	0.5040231809354038	0.9419962638192722
117	0.1171428134951188	0.2541093923538931	0.7165337880823295
118	0.1420131923993529	0.7483397090755688	0.7276750354063846
119	0.9429399465387291	0.0003907738953321	0.8415979322879933
120	0.9432774694835706	0.4965383543380192	0.8260126042826234
121	0.8279762526100800	0.2509205795795222	0.6166034441828853
122	0.7402737977722692	0.2526432818286750	0.9408116990347476
123	0.8019071387913540	0.7494822779240267	0.6062680431238582
124	0.7668767509302056	0.7502944573149884	0.9479884985643868
125	0.6393997076307020	0.0000452519478929	0.7263911671775505
126	0.6190290984950405	0.5002581457819718	0.7185415135308324
127	0.4327604650114113	0.2497971567714158	0.8294951589790407
128	0.4533354482798541	0.7499818519301397	0.8370379276636953
129	0.0626318838717530	0.1342973338482605	0.6158711572160565

130	0.0123293382145341	0.1133675325308280	0.9481056309980674
131	0.0711295417177743	0.6149112752063073	0.6073091755734858
132	0.9978781771022092	0.6359982015847113	0.9422601936333420
133	0.5601397020119725	0.3674457154835624	0.6151516568853993
134	0.5107830286952739	0.3832767220513466	0.9467340473779035
135	0.5724649506247256	0.8821426026737961	0.6084956057765177
136	0.4980201186772412	0.8688815631870196	0.9429805969894818
137	0.3745265051306321	0.1193423370649639	0.7261800619205016
138	0.3848490253501889	0.6315916542038317	0.7186923047450866
139	0.1978985426496152	0.3829665288660613	0.8281492080795494
140	0.1886193426402956	0.8660311839112742	0.8389990442933568
141	0.8875963314060527	0.3662686697482634	0.7238157808852294
142	0.8723315009996592	0.8830903673245776	0.7222270059095610
143	0.6886917305644024	0.1187574838104325	0.8364765244723741
144	0.6987929260548500	0.6320636338991302	0.8310761084969481

3 Defects in the supercell

In Figs. S2 we show the $\Sigma 3$ GB model with the different defects we consider. Specifically, V_{Cu}, In_{Cu}, Cu_{In}, Na_{Cu} and $2V_{Cu}$-In_{Cu} are shown in Figs. 2(a), (b), (c), (d), and (e), respectively. All these show the relaxed structures. In the case of the point defects, the defect is at the location that minimizes the total energy. For V_{Cu} and Na_{Cu}, the numbers of the Se atoms surrounding the defect are also given.

The Cu and In chemical potentials used in the calculations in the main article are the following (the Se chemical potential plays no role in the energetics of the defects we consider). In-rich conditions: $\Delta\mu_{Cu} = -0.2$ eV, $\Delta\mu_{In} = -0.15$ eV; In-poor conditions: $\Delta\mu_{Cu} = -0.5$ eV, $\Delta\mu_{In} = -2.5$ eV.

The charge transition levels in Fig. 8 for the defects in the $\Sigma 3$ GB are give by (values above the VBM; recall that the gap in CIS is ~ 1 eV):

- V_{Cu}: $\epsilon(0|-) = 115$ meV.
- In_{Cu}: $\epsilon(+2|+) = 127$ meV; $\epsilon(+|0) = 585$ meV.
- Cu_{In}: $\epsilon(0|-) = 35$ meV; $\epsilon(-|-2) = 377$ meV.

The charge transition levels for the defects in bulk CIS are (values also with respect to the VBM):

- V_{Cu}: $\epsilon(0|-) = 15$ meV;
- Cu_{In}: $\epsilon(0|-) = 190$ meV; $\epsilon(-|-2) = 585$ meV.
- V_{In}: $\epsilon(0|-) = 56$ meV; $\epsilon(-|-2) = 444$ meV; $\epsilon(-2|-3) = 765$ meV.

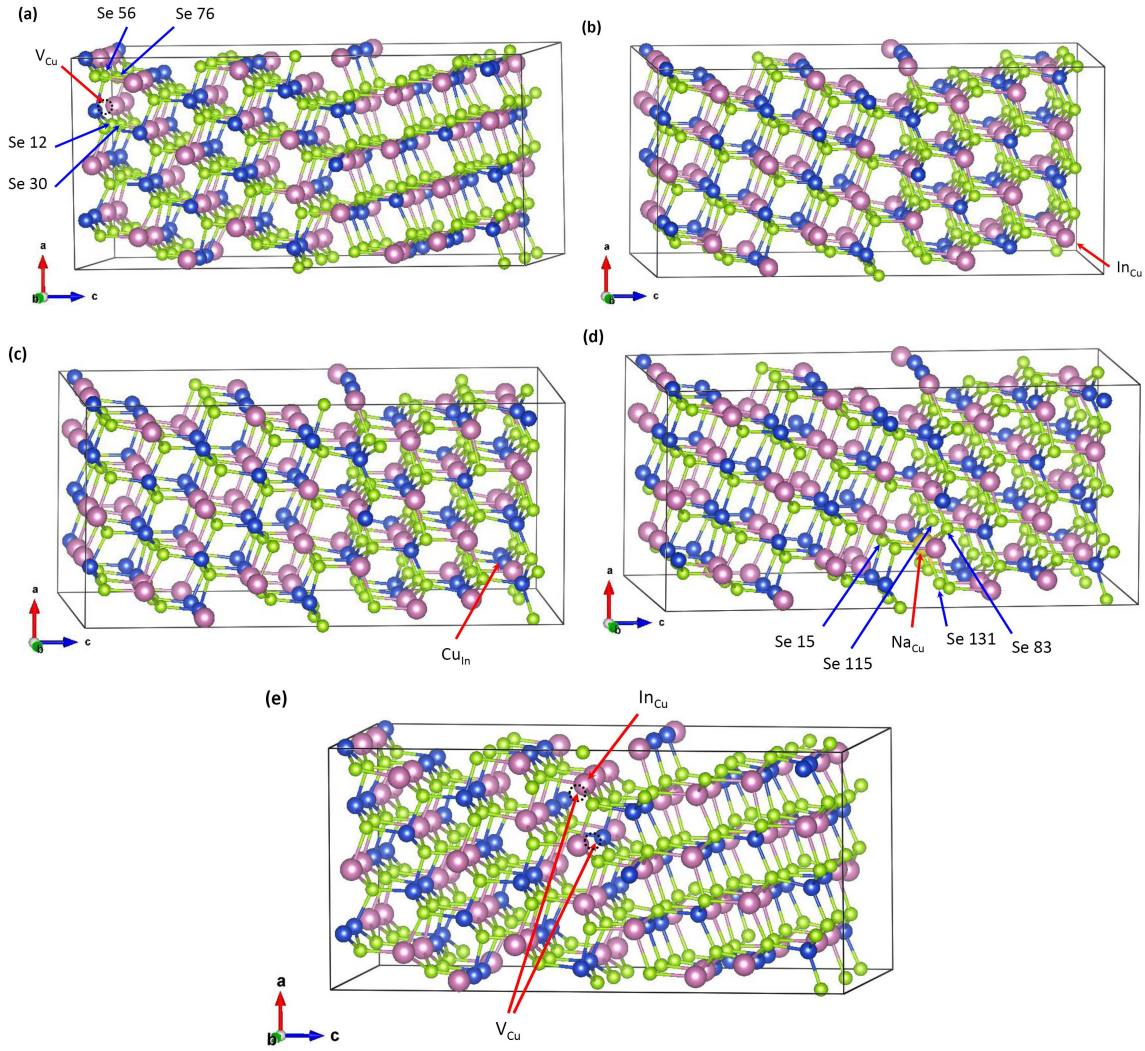
(a)
Se 56
Se 76
V_{Cu}
Se 12
Se 30
(b)
In_{Cu}
(c)
Cu_{In}
(d)
Se 15
Se 115
Na_{Cu}
Se 131
Se 83
(e)
In_{Cu}
V_{Cu}
a
c

Fig. S2:

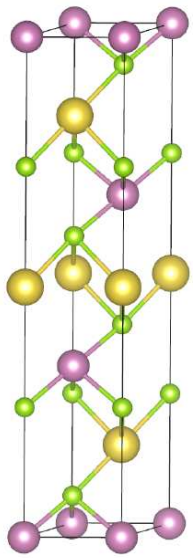

Fig. S3:

4 $NaInSe_2$ hole barrier

We consider here the possibility that $NaInSe_2$ (NIS) forms a hole barrier. The idea, advanced by Persson and Zunger [1], is that if $NaInSe_2$ forms at a GB, the lack of *p*-*d* repulsion in this compound will cause a lowering of the VBM at the GB with respect to the grain interior. To try to verify this, we study the band alignment between $CuInSe_2$ and $NaInSe_2$. This is determined by the bulk properties of these compounds, so it is an analysis that can be considered to be complementary to our findings in the main article. We include it in this supplementary material for completeness.

The space group of NIS in Hermann-Mauguin notation is $R\bar{3}m$, No. 166. The unit cell of is shown in Fig. S3. The HSE06 calculated lattice parameters and band gap are given in Table 1. The hypothesis that formation of NIS at the GB results in a hole barrier can be tested by aligning the band structures of NIS and CIS. We find that NIS has a considerably larger band gap of 2.26 eV, compared to CIS. We align NIS and CIS by calculating the branch-point energy (BPE) by a weighed average over the BZ of the bulk band structures

Table 1: Structural parameters and band gap of $NaInSe_2$

	a (Å)	c (Å)	z	E_g (eV)
Experiment [4]	3.972	20.890	0.260	N/A
This work	3.981	20.894	0.260	2.26

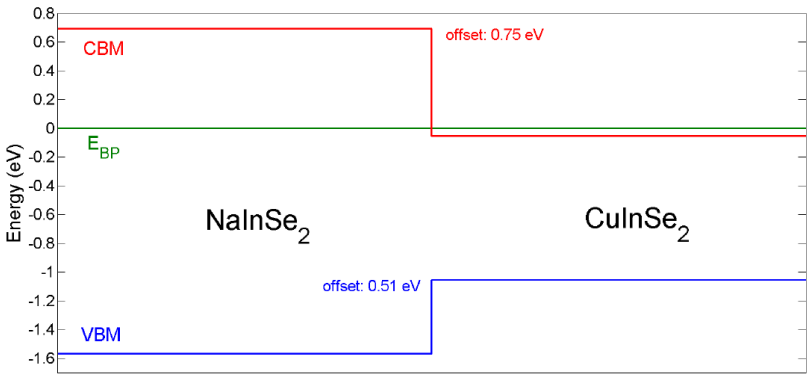

Fig. S4:

[2]. The number of bands used in the average is chosen following the latter reference. Consequently, we use 12 valence bands and 6 conduction bands for the BPE of NIS and 16 valence bands and 8 conduction bands for CIS. The alignment is shown in Fig. S4. It is straddling (type-I) [3], i.e., the VBM of NIS is below the VBM of CIS, and the CBM of NIS is above the CBM of CIS, with an offset of 0.51 eV between VBMs and 0.75 eV between the CBMs. Thus, the absence of the *p-d* repulsion in NIS indeed leads to a lowering of its VBM compared to CIS. Yet, due to the larger band gap of NIS, the alignment is not staggered (type-II) [3]. The latter would indeed separate electrons and holes in opposite directions. The straddling alignment, however, does not lead to an effective hole barrier. Both electrons and holes are confined to the grain interior. There is no reduced recombination of electrons and holes resulting from this scenario and moreover electrical conductivity across the GBs is strongly suppressed. This leads to the conclusion that phase segregation of NIS at the grain boundary is very unlikely to result in the expected hole barrier.

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