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Anion displacements and the band-gap anomaly in ternary ABC2 chalcopyrite semiconductors

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Using a first-principles all-electron band-structure approach, we show that the anomalous
(& 50'lo) reduction in the band gaps of the A B"C2 chalcopyrite semiconductors relative to

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TABLE I. Observed lowest band gaps of the Cu-based ternary chalcopyrites (Ref. 1) and the amount hE~ by which they are lowered from the values of the binary analogs (Ref. 6).

Ternary

Band gap
(eV) Binary

Band-gap anomaly
aE (eV)

CuA1S2
CuGaS2
CuInS2
CuA1Se2
CuGaSe2
CuInSe2
CuGa Te2

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0.30 4.0—

0.28

3.5—

30—

g 0.26
2.5—

0.24

I

P 2.0
4lc
UJ

0.22

1.5—

0.22 0.24 0.26 0.28 0.30
Ucalc

FIG. 2. Correlation between the observed (Refs. 1—3)
and calculated (using the CTB model) anion displacement parameters for the ternary chalcopyrites. The uncertain data for the telurides is omitted. Multiple arrows denote various experimental determinations.

1.0—

0.5—

0.0
0.20

I I I I I

0.21 0.22 0.23 0.24 0.25

Anion Displacement u
method is also consistent with the behavior of chal-copyrite lattice constants with alloying; for example, in the system CuInS2~i „~Se2„,if we take

damon =xdsa+ (1 &) ds

then the variations in a i,(x) obtained by the CTB method are within & 0.1% of the observed (Vegard-type) variations. '6
By mapping the all-electron band structure as a function of the structural parameters, we next inves-tigate how atomic radii, encoded in u, g, and a (Figs. 1 and 2) control the electronic properties. '7 We find that whereas variations in the tetragonal strain

parameter rt merely lead to small (=10 t

eV)
changes in the crystal-field splitting and the band gaps, the anion displacement parameter sensitively controls all of the band gaps in the system (Fig. 3). Even a small increase in u from its equilibrium value

of 0 224 (Rcn-sa =2 42 A~ Rin-sa =2 60 A) to its ideal zinc-blende value u =0.25 (Rc„s,=Ri„s,

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is consistent with the controlling role of the anion
displacements: We calculate the same equilibrium u

for CuInSe2 and CuInS2 (u =0.236), but a larger u
value for CuGaSe2 (0.264), leading to

Es(CuGaSe2) —Es(CuInSe2) =)au =0.5 eV as,

aQ

and positive bowing, in good agreement with experi-ment. Our separation of the band-gap anomaly into structural and chemical factors may hence provide in-sight and