

Trends in band-gap pressure coefficients in chalcopyrite semiconductors

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We present the results of a first-principles calculation of the direct band-gap pressure coefficient a_g for a series of Ga and In semiconductor compounds with both the chalcopyrite (e.g., CuGaSe₂ and CuInSe₂) and the zinc-blende structures (e.g., GaAs and InAs). We found good agreement between the calculated and experimental pressure coefficients. We found that a_g in chalcopyrites are dramatically reduced relative to zinc-blende compounds, and that the Ga/In substitution lowers a_g in chalcopyrites more than in zinc-blende compounds. As a result, the empirical rule suggested for zinc-blende compounds, stating that for a given transition (e.g., $\Gamma_{15v} \rightarrow \Gamma_{1c}$) a_g does not depend on substitutions, has to be modified for chalcopyrites. Based on our results we question the currently accepted experimental value for CuInTe₂ (2.2 meV/kbar); we calculate this value to be close to 5.9 meV/kbar. [S0163-1829(98)51528-7]

The pressure (p) coefficient $a_i^{(p)} \equiv dE_i/dp$ of an inter-band transition i in a semiconductor is an easily measurable quantity that can provide important information on the semiconductor's electronic band structure and optical properties. It is related to the volume (V) deformation potential $dE_i/d\ln V$ via the bulk modulus B through the relation

$$dE$$

To include the effect of changes in the structural parameters (u, η) with V on the band gap we have generalized Eq. (1) to

$$a_g \approx \frac{dE_g}{dp} \approx \left(\frac{1}{B} \right) \frac{dE_g}{d \ln V} + \left(\frac{1}{B} \right) \left[\frac{\partial E_g}{\partial \ln V} + \frac{\partial E_g}{\partial \eta} \frac{\partial \eta}{\partial \ln V} + \frac{\partial E_g}{\partial u} \frac{\partial u}{\partial \ln V} \right]. \quad (3)$$

We have calculated all terms in Eq. (3) using the self-consistent local-density approximation (LDA), as implemented by the relativistic linearized augmented plane wave method.¹⁷ We used the Ceperley-Alder exchange correlation potential¹⁸ as parametrized by Perdew and Zunger.¹⁹ The Ga $3d$ and In $4d$ states are treated on the same footing as the s and p valence states. In calculating the pressure coefficient for the ternary compounds, we first determine the values of $\eta(V)$ and $u(V)$ that minimize the total energy E for a given V . The total energies $E[V]$

found a_g to be twice as large.²¹ The difference is now believed to be attributable to the higher concentration of defects in the earlier samples that dominate the absorption edge. Thus we suggest that the value of a_g in CuInTe_2 should also be reexamined in light of the present calculation. We also note that LDA tends to underestimate a_g , but it at least reproduces the experimental trend quite well.

We see from Table I that the main contribution to a_g of the chalcopyrite compounds comes from the direct volume deformation potential term ($\partial E_g / \partial \ln V$), while the remaining two terms in Eq. (3), associated with the noncubic crystal structure of chalcopyrite, contribute much smaller amounts. This occurs in spite of the rather large value of $\partial E_g / \partial u$ (~ 10 eV), because $\partial u / \partial \ln V$ turns out to be quite small (the positiveness of $\partial u / \partial \ln V$ indicates that the III-VI bond is stronger than the I-VI bond²²). Regarding the contribution from η , we note that both $\partial E_g / \partial \eta$ and $\partial \eta / \partial \ln V$ turn out to be quite small in the chalcopyrites. Our results are consistent with experimental observations²³ that u and η are nearly independent of pressure.

indicate that the currently accepted value⁶ of dE_g/dp is 2.2 meV/kbar for CuInTe₂ is too low.

We summarize our observation in Table III, which explains the observed trends.

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