PHYSICAL REVIEW B VOLUME 58, NUMBER 4 15 JULY 1998-II

Trends in band-gap pressure coefficients in chalcopyrite semiconductors

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(Received 22 April 1998)

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., $CuGaSe_2$ and $CuInSe_2$) 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 $CuInTe_2$ (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 $a_i^{(p)}=dE_i/dp$ of an interband 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

$$\frac{dE_i}{dp}=-\left(\frac{1}{B}\right)\frac{dE_i}{d\ln V}. \tag{1}$$

For semiconductors with the diamond and zinc-blende structures, an ''empirical rule''[1] was formulated by Paul for the pressure coefficients of various band gaps ranging from the direct band gap at zone center Γ (denoted as a_g) to the indirect gaps involving zone-edge conduction-band valleys at the L and X points. According to this rule $a_i^{(p)}$ depends mainly on the symmetry (e.g., Γ_{15v} to Γ_{1c}, L_{1c}, X_{1c}, etc.) of the transition i. For transition involving the same symmetry points, $a_i^{(p)}$ is nearly the same for different semiconductors in the family of tetrahedrally coordinated systems. While the foundation of the rule has never been examined rigorously (this is the subject of a future publication[2]), the rule has been used extensively in the past to identify the symmetry of optical transitions[3] and to determine the band offset at zinc-blende semiconductor interfaces.[4] The applicability of the rule to other tetrahedrally coordinated semiconductors has also never been investigated to the best of our knowledge. In this paper, we examine the applicability of such a rule to chalcopyrite compounds[5] ABC_2 using the latest experimental values[6–10] of a_g (last column of Table I).[6–8] We see from the data that (i) a_g in chalcopyrite is fairly constant when the group-I transition metal A is varied, but (ii) when the group-III cation B is changed from Ga to In, a_g can decrease by as much as 40%. (iii) Comparing with experimental data[11–14] for zinc-blende GaX and InX ($X=$As and Sb, last column of Table II), we found that a_g for chalcopyrites are much smaller than in the corresponding III-V compounds. (iv) In III-V compounds, a_g increases significantly as the anion atomic number increases.[11–16]

We have investigated a_g theoretically in these materials and found good agreement between theoretical and experimental values[6–10] (except for $CuInTe_2$, which we expect to have the value of ~5.9 meV/kbar, rather than the much smaller known experimental value of 2.2 meV/kbar). We explain why a_g is smaller and more cation dependent in chalcopyrites than in III-V's and why a_g increases with anion atomic number. Based on the theoretical calculation we show that the ''empirical rule''[1] has to be modified.

To understand the difference in the behavior of a_g between chalcopyrite and zinc-blende semiconductors, we note that the chalcopyrite has a tetragonal symmetry rather than the cubic zinc-blende symmetry. The chalcopyrite structure can be considered as being derived from the zinc-blende structure by doubling the conventional unit cell along the c axis. In most chalcopyrite systems, the ratio $\eta=c/2a$ of the lattice constant along the c axis (denoted by c) to twice the lattice constant perpendicular to the c axis (denoted by a) is not equal to 1. In addition, chalcopyrite compounds have two kinds of cations and hence two bond lengths: R_{A-C} and R_{B-C}. The difference between R_{A-C} and R_{B-C} can be expressed in terms of a dimensionless, cell-internal coordinate u:

$$u=\frac{1}{4}+\frac{R_{A-C}^2-R_{B-C}^2}{a^2}. \tag{2}$$

TABLE I. Calculated pressure coefficients of the direct band gap of six chalcopyrite semiconductors. The results are given for the transition from the *highest* of the three crystal-field split valence-band states. For $(dE_g/dp)|_{\text{calc.}}$ we also give the value in parenthesis representing an average over the three crystal-field split states. Individual contributions, [Eq. (3)] to the pressure coefficients are also given.

Compound	$-\frac{\partial E_g}{\partial \ln V}$ (eV)	$-\frac{\partial E_g}{\partial \eta}$ (eV)	$\frac{\partial \eta}{\partial \ln V}$	Product (eV)	$-\frac{\partial E_g}{\partial u}$ (ev)	$\frac{\partial u}{\partial \ln V}$	Product (ev)	$-\frac{dE_g}{d\ln V}$ (eV)	$\frac{1}{B}$ (Mbar^{-1})	$\left.\frac{dE_g}{dp}\right\|_{\text{calc.}}$ (meV/kbar)	$\left.\frac{dE_g}{dp}\right\|_{\text{exp}}$ (meV/kbar)
$CuGaSe_2$	4.17	−1.24	−0.08	0.10	−11.6	0.012	−0.14	4.13	1.24	5.1 (4.9)	5.0[a]
$CuInSe_2$	2.49	1.01	0.12	0.12	−12.5	0.023	−0.29	2.32	1.41	3.3 (3.1)	3.0[a]
$CuGaTe_2$	4.70	−1.70	−0.04	0.07	−11.6	0.004	−0.05	4.72	1.63	7.7 (7.5)	
$CuInTe_2$	3.50	1.27	−0.05	−0.06	−12.4	0.015	−0.19	3.25	1.76	5.7 (5.9)	2.2[a]
$AgGaSe_2$	3.17	−0.41	0.23	−0.09	−16.8	0.018	−0.30	2.78	1.56	4.3 (5.0)	5.1[b]
$AgInSe_2$	1.68	−1.25	0.14	−0.18	−14.7	0.032	−0.47	1.03	1.71	1.8 (2.4)	2.7[c]

[a] Reference 6.
[b] Reference 7.
[c] Reference 8.

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

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

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 potential[18] 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 $E[V]$ are then fitted to the equation of states of Murnaghan[20] to obtain V_{eq}, η_{eq}, and u_{eq} and the bulk modulus. The partial derivatives in Eq. (3) are obtained near the calculated equilibrium positions. Table I lists the resultant values for the chalcopyrites, while in Table II we compare the chalcopyrite pressure coefficients with those of the corresponding III-V compounds (the two partially derivative $\partial\eta/\partial\ln V$ and $\partial u/\partial \ln V$ are, of course, both zero in the zinc-blende compounds).

In general, we find quite good agreement between the experimental[6–8,11–14] and calculated band-gap pressure coefficients in the zinc-blende and chalcopyrite compounds. The only exception for the chalcopyrites is $CuInTe_2$ where the experimental value[6] (2.2 meV/kbar) is much smaller than our theoretical value of 5.9 meV/kbar. We will explain below why our calculated value fits the chemical trend that heavier anions, such as Te should have a larger a_g. We also note that the experimental a_g in chalcopyrite compounds such as $AgGaS_2$ was first measured by optical absorption to be as small as 2 meV/kbar,[8] but more recent measurements based on photoluminescence and two-photon absorption have

TABLE II. Comparison of calculated deformation potentials and bulk moduli of the chalcopyrite compounds with the corresponding III–V compounds. For the chalcopyrite compounds, results are averaged over the crystal-field splitting.

Compound	$-\frac{dE_g}{d\ln V}$ (eV)	$\frac{1}{B}$ (Mbar^{-1})	$\left.\frac{dE_g}{dp}\right\|_{\text{calc.}}$ (meV/kbar)	$\left.\frac{dE_g}{dp}\right\|_{\text{exp}}$ (meV/kbar)
$CuGaSe_2$	3.92	1.24	4.9	5.0[a]
$CuInSe_2$	2.23	1.41	3.1	3.0[a]
GaAs	7.25	1.35	9.8	10.8[b]
InAs	4.88	1.66	8.1	9.6–10.8[c]
$CuGaTe_2$	4.61	1.63	7.5	
$CuInTe_2$	3.36	1.76	5.9	2.2[a]
GaSb	7.01	1.81	12.7	14.0[d]
InSb	5.54	2.16	11.9	14.0[e]

[a] Reference 6.
[b] Reference 11.
[c] Reference 12.
[d] Reference 13.
[e] Reference 14.

TABLE III. Observed chemical trend for the change of inverse of the bulk modulus, the volume deformation potential, and the pressure coefficient of the direct band gap.

Change	$\frac{1}{B}$	$-\frac{dE_g}{d\ln V}$	$\frac{dE_g}{dp}=-\frac{1}{B}\frac{dE_g}{d\ln V}$
III-V→I-III-VI$_2$	Decreases	Decreases	Strong decreases
Ga→In (in III-V)	Increases	Decreases	Nearly unchanged
Ga→In (in I-III-VI$_2$)	Small increases	Decreases	Decreases
As→Sb or Se→Te	Increases	Nearly unchanged	Strong increases

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 bond[22]). 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 observations[23] that u and η are nearly independent of pressure.

In the following, we will explain the observed chemical trends in a_g for chalcopyrites and the corresponding III-V compounds. We raise and address three questions, (a)–(c) below.

(a) Why are a_g in III-V compounds much larger than the a_g in the corresponding chalcopyrites?

(i) The larger a_g in III-V compounds relative to chalcopyrites is mainly due to the larger $dE_g/d\ln V=-[dE_{\rm cbm}-dE_{\rm vbm}]/d\ln V$ in III-V's. This reflects two effects.[2] First, III-V compounds are more covalent than chalcopyrites, thus the cation s-anion s coupling is larger in III-V's than in chalcopyrites. When pressure is applied (and bond length decreases), the energy $E_{\rm cbm}$ of the antibonding conduction-band minimum (cbm) in III-V's moves upwards faster than in chalcopyrites. Second, the anion p-cation d coupling is weaker in III-V's than in chalcopyrites (since the latter have high lying Cu 3d state). Thus, when pressure is applied, the *upward* shift[2] of the valence-band maximum (vbm) energy $E_{\rm vbm}$ is smaller in III-V's than in chalcopyrites.

(ii) Due to the strong III-VI bond in chalcopyrite compounds,[22] the bulk modulus B in chalcopyrite is larger than the corresponding III-V compounds.

Thus, the product $a_g=-(1/B)(dE_g/d\ln V)$ for III-V compounds is much larger than the corresponding product in chalcopyrite compounds.

(b) Why do Ga→In replacements have a larger effect in chalcopyrites than in III-V compounds?

(i) For both the chalcopyrites and III-V compounds, $-dE_g/d\ln V$ decreases when Ga is replaced by In, largely as a result of the effect on the conduction band: the Ga 4s orbital is about 0.7 eV lower than the In 5s orbital, and the Ga-anion bond length is shorter than the In-anion bond length. Thus, the cation-anion s-s coupling in Ga compounds is stronger than in In compounds, so under compression, $E_{\rm cbm}$ moves up faster in Ga compounds than in In compounds. This effect in chalcopyrite compounds is smaller than the corresponding effect in the III-V compounds, because the conduction-band minimum in chalcopyrite compounds is only partially localized on the column III cation atom.

(ii) However, since in semiconductor compounds, the bulk modulus B is proportional[24] to l^{-m}, where l is the bond length and $m\sim3.5$, the smaller atomic size of Ga causes B to be larger in the Ga compounds than in the In compounds.

Thus, for $a_g=-(1/B)(dE_g d\ln V)$, the reduction in $-dE_g/d\ln V$ when Ga is replaced by In in chalcopyrite and zinc-blende semiconductor compounds is partially offset by the increase in $1/B$. For zinc-blende semiconductors, this cancellation of the two effects is nearly complete, so a_g is nearly independent of the cation. However, in chalcopyrite compounds the group-III cations account for only half of the cation sites, so the increase of B is not as large as in the III-V's, thus the cancellation effect is less complete in chalcopyrite than in the corresponding III-V compounds.

(c) Why does a_g increase with the anion atomic number?

(i) $-dE_g/d\ln V$ changes little when the anion atomic number increases (see second column in Table II) unlike the case of the cations. This is because the anion-cation s-s coupling does not change much when the anion atomic number increases. This constancy reflects again a cancellation of two effects: on one hand, changing Se→Te or As→Sb raises the anion s orbital energy (by 2.1 and 1.6 eV, respectively), thus increase the coupling with the cation s orbital. On the other hand, heavier anions mean a longer anion-cation bond, which acts to reduce the anion-cation coupling.

(ii) However, since the bond length increases significantly as the anion gets heavier the bulk moduli decrease significantly.[24] This effect is similar to the one caused by replacement of Ga by the heavier In.

The net result is that the product $dE_g/dp=-(1/B)\times(dE_g/d\ln V)$ increases significantly when Se→Te or As→Sb. The large dependence of a_g on anion suggests that the ''empirical rule of pressure deformation potential''[1] does not apply in this case.[2] Our analysis and calculated value also indicate that the currently accepted value[6] of $dE_g/dp = 2.2$ meV/kbar for $CuInTe_2$ is too low.

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

The work at NREL was supported by the U.S. Department of Energy under Contract No. DE-AC36-83-CH10093. The work at Berkeley was supported by the Director, Office of Energy Research, Office of Basic Energy Science, Materials Science Division, the U.S. Department of Energy, under Contract No. DE-AC03-76-SF00098. The part of this work carried out in Korea was supported by the Korea Science and Engineering Foundation (KOSEF 981-0208-033-2).

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