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**BAND GAP ANOMALY IN TERNARY CHALCOPYRITES AND OPTICAL
BOWING IN BINARY SEMICONDUCTOR ALLOYS**

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I. Contemporary View of Optical Bowing

The lowest optical band gaps $E(x)$ of semiconductor alloys $A_xB_{1-x}C$ are usually smaller than the concentration (x) weighted average $\bar{E}(x) \equiv xE_{AC} + (1-x)E_{BC}$ of the band gaps E_{AC} and E_{BC} of the end-point AC and BC semiconductors. The upward concave non-linearity in $E(x)$ can be characterized by the bowing parameter b , defined by $E(x) \equiv \bar{E}(x) - bx(1-x)$. Optical bowing has been often analyzed⁴⁻⁶ as arising from a combination of two types of phenomena. Much like in the field of Mott-Anderson metal-nonmetal transition, these are: (i) effects due to electron-electron and electron-core interactions which are already present in a fictitiously ordered ("virtual") crystal, and (ii) effects due to disorder, e.g. compositional disorder (an additional form of disorder can arise from clustering). We refer to these two contributions to the experimental bowing b^{exp} as b_I and b_{II} , respectively. Traditionally, b_I was evaluated⁴⁻⁷ from the Virtual Crystal Approximation (VCA), where it was assumed that the chemical and structural identities of AC and BC are lost in the alloy, and replaced by an average lattice constant $\bar{a}(x)$ with a corresponding (single) average anion-cation bond length $R_{VCA}(x)$. The reason that VCA gives a finite bowing is that most band structure methods show the band energies to be nonlinear functions of the potential parameters. We may express this as $E_{AC} \approx pV_{AC} + qU_{AC}^2 + \dots$, where p and q are coefficients and V_{AC} , and U_{AC} are potential parameters. For example, in the pseudopotential perturbation theory the X gap of a zincblende semiconductor is $E_{AC} \sim 2V_{AC}(220) + a^2/2\pi V_{AC}^2(111)$, and $V_{AC}(hk\ell)$ are potential form factors. In tight-binding (TB)⁷, V_{AC} is the diagonal Hamiltonian element and U_{AC} is a combination of hopping and overlap integrals (as can be verified by a Taylor expansion), etc. This nonlinear form of E_{AC} yields a general result for the bowing parameter, i.e. $b = \beta(\bar{a})[U_{AC}(\bar{a}) - U_{BC}(\bar{a})]^2$, showing that it depends only on the square of the (small) difference between second order terms, interpolated for an intermediate lattice constant \bar{a} . Due to this form of b in VCA, I was able to produce almost any desired value of b , simply by making small adjustments in the difference of the interpolated second order band parameters without spoiling thereby the quality of the band structures of the end-point crystal. Since for a given gap the true informational content of the observed $E(x)$ curve is only one unit (the value of b), I hence find TB-VCA or empirical pseudopotential-VCA methods to be rather uninformative. The situation is somewhat different with the Phillips-Van Vechten dielectric two-band model, where the parameters of the theory are more firmly fixed by fitting to independent data. However, using VCA, Van Vechten and Bergstresser⁴ found that b_I is in general considerably smaller than the observed values b^{exp} , at least for alloys involving chemically very different atoms. For example, for ZnS_xTe_{1-x} they find $b_I = 0.28$ eV, but $b^{exp} \approx 2.1$ eV, and for

ZnSe_xTe_{1-x} they find $b_I = -0.04$ eV, but $b^{exp} = 1.1$ eV. This lead them⁴ and others (e.g. Ref. 1 p. 295) to conclude that disorder effects $b_{II} = b^{exp} - b_I$ are generally dominant. I find this conclusion to be untenable for all isovalent semiconductor alloys except those made of nearly identical species (e.g. Ga_xAl_{1-x}As). The narrow Raman lines¹, the possibility of attaining high mobilities⁸, the sharpness of absorption and reflectance spectra³ (e.g., as opposed to amorphous solids), the smallness of b_{II} as inferred from CPA calculations⁶, and the recent⁹ establishment by EXAFS of the narrow distribution of alloy bond lengths around the values of the pure materials, are few of the reasons for this assertion. Furthermore, the argument⁴ that the existence of bowing of the spin-orbit splitting Δ_{SO} , is conclusive evidence for disorder is objectionable: even an ordered system where not all nearest neighbours to a given atom are identical (e.g. the chalcopyrite structure) will show s-p mixing and hence bowing of Δ_{SO} . I proposed instead to get a handle on b_{II} by doing first a more refined calculation (using nonempirical self-consistent band structure techniques) of b_I and then inspect $b^{exp} - b_I$.

II. A New View of Optical Bowing

Our previous studies^{10,11} of the electronic structure of chalcopyrite ABC₂ semiconductors (e.g. A = Cu; B = Al, Ga, In; C = S, Se, or A = Cd, Zn; B = Si, Ge, Sn; and C = P, As, Sb) have shown that their band gaps are substantially smaller than those of their binary analogues (e.g. ZnSe is the binary analogue of CuGaSe₂) much like the band gaps of the A_xB_{1-x}C alloy are smaller than the average gap of their binary analogs. We further find that a large part of this anomaly results from the existence of generally unequal bond lengths $R_{AC} \neq R_{BC}$. We can measure this difference ("bond alternation") by the dimensionless "anion displacement parameter" $u = 1/4 + (R_{AC}^2 - R_{BC}^2)/a^2$, where if $u = 1/4$ the system degenerates into an equal bond structure (e.g. as in VCA). Using a chalcopyrite ABC₂ model for the 50%-50% A_xB_{1-x}C alloy, and performing band structure calculations self-consistently as a function of u , we can determine the gap variation $\partial E(ABC_2)/\partial u$. We find that this mechanism of reduction of band gaps in response to the internal stress exerted by the unequal bond lengths is common to real chalcopyrites (e.g. CuInSe₂) and to pseudo chalcopyrite models (e.g. In_{0.5}Ga_{0.5}P = InGaP₂). The difference is largely quantitative: $\partial E(ABC_2)/\partial u$ is $\sim 18-21$ eV for I-III-V₂ chalcopyrites, 10-15 eV for II-IV-VI₂ pnictides, and 1-3 eV for the III-III-V pseudo chalcopyrites. One can express this structural (s) contribution to the lowering $E - \bar{E}$ of the band gap as $\Delta E^S = a|_{A-B}|(u - 1/4) + c|_{A+B}|(u - 1/4)^2 + \dots$. Clearly, $a = 0$ when $A=B$, since then the transformation $(u - 1/4) \rightarrow (1/4 - u)$ carries the lattice into itself, hence $a|_{A-B}|$ must depend on the difference between A and B. But even for AAC₂ (or BBC₂), ΔE^S can differ from zero if $u \neq 1/4$, hence we have the second order term $c|_{A+B}|$ that depends on the "average" of A and B. To evaluate ΔE^S we need to know u at equilibrium (u_{eq}). A simple model of "conservation of tetrahedral bonds"¹⁰ is then used to predict the equilibrium u values. The results agree very well with experiment when data are available.¹⁰

In addition to this structural contribution ΔE^S to $E - \bar{E}$, we find a chemical (chem) contribution ΔE^{chem} . It results from the fact that even if $u = 1/4$ (i.e. when $R_{AC} = R_{BC}$), the electronic charge density can distribute itself differently on the A-C

and the B-C bonds, reflecting their relative electronegativities. Again, this contribution is calculated from self-consistent band theory.^{10,11} Clearly, it depends on the difference between A and B. We can hence write the total band gap reduction $\Delta E_I = \Delta E^S + \Delta E^{\text{chem}}$ due to (deterministic) order effects as $\Delta E_I = a|_{A-B}|(u - 1/4) + c|_{A+B}|(u - 1/4)^2 + \Delta E|_{A-B}^{\text{chem}}$. For a 50%-50% alloy, $b_I = 4\Delta E_I$.

This analysis shows that: (i) the fact that b^{exp} scales with the $|A-B|$ electronegativity difference $\Delta\chi_{AB}$ is not a manifestation of disorder, as previously assumed (e.g. Ref. 1 p. 295, Ref. 4), since this scaling already exists in the ordered model, both due to structural and chemical effects, (ii) ΔE_I is decided both by a chemical mismatch $\Delta\chi_{AB}$, and by a structural mismatch $\Delta u = (u - 1/4)$. We can have systems in which both factors are small (e.g. $\text{Ga}_x \text{Al}_{1-x} \text{As}$), systems with large Δu but small $\Delta\chi$ (e.g. $\text{ZnS}_x \text{Se}_{1-x}$), etc. (iii) quantitative evaluations of ΔE_I for $\text{In}_x \text{Ga}_{1-x} \text{P}$, $\text{ZnS}_x \text{Se}_{1-x}$ and $\text{ZnSe}_x \text{Te}_{1-x}$ show the "order contribution" b_I to account for about 80%-90% of the observed bowing, hence disorder effects are far smaller than hitherto accepted. (iv) When both the chemical and the structural mismatch are small (e.g. $\text{Al}_x \text{Ga}_{1-x} \text{As}$), disorder is the prevailing phenomena. As the dissimilarity in the alloyed atoms (both $\Delta\chi$ and Δu) becomes larger, there is a tendency for prevalence of local atomic order, and bond lengths are organized deterministically around the anions, as observed⁹ in EXAFS for $\text{In}_x \text{Ga}_{1-x} \text{As}$. When the dissimilarity is even larger, the system will order crystallographically, as is the case in real chalcopyrites. However, as the temperature is raised¹¹, chalcopyrites undergo a disorder transition, where the A and B cations randomize to form a zincblende lattice, reflecting the prevalence of the entropy term over the enthalpy term. This suggests that for sufficiently low temperatures and sufficiently dissimilar elements A and B, ordered alloys could be grown. Finally, when the dissimilarity is too large, the solubility becomes limited, defect levels can appear in the band gap (e.g. GaP-GaN, GaP-GaSb), and clustering and spinodal decomposition can occur. (v) Interestingly, the normal mode that carries a zincblende lattice into a chalcopyrite structure is the W_1 phonon mode. This suggests that its softening (evolution) would signal transition into disorder (local order).

Two recent developments pertaining to the structural model of alloys, are worth mentioning. First¹², a simple valence force field idea has been recently used to predict for more than 60 semiconductor systems the BC bond length $R_{BC}[\underline{AC:B}]$ around an isovalent impurity atom B in an AC crystal (Fig. 1). This theory shows that the amount of bond relaxation relative to the host, $\Delta = R_{BC}[\underline{AC:B}] - R_{AC}^0$ is given simply by $\Delta = (R_{BC}^0 - R_{AC}^0) / [1 + \alpha_{AC} / 6\alpha_{BC} (1 + 10\beta_{AC} / \beta_{BC})]$, where α and β are stretching and bending (Keating) force constants of the pure materials, and R_{BC}^0 , R_{AC}^0 are the B-C and A-C bond lengths of the pure materials, respectively. The predictions of this theory differ significantly from VCA that would give $\Delta = 0$ (i.e., no bond relaxation). The significance in this development is: (i) the bond length $R_{BC}(x)$ in an alloy can be obtained from this data by interpolating linearly between the bond length R_{BC}^0 of the pure BC crystal and the calculated $R_{BC}[\underline{AC:B}]$. This provides structural information for most conceivable isovalent alloys at all concentrations. (ii) The enthalpy of mixing ΔH_m can be calculated from the knowledge of these bond lengths, simply by assuming ΔH_m to arise primarily from the elastic stress due to bond deformation. The results¹² for ΔH_m agree well with experiment even though no adjustable parameters are used, and

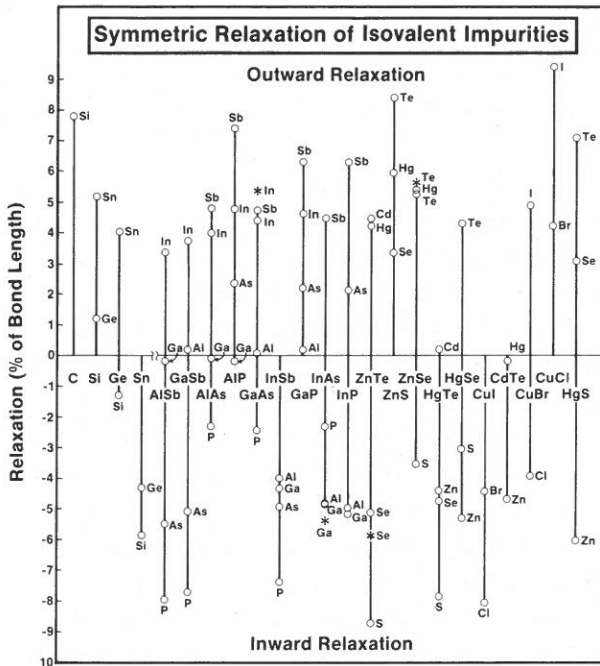


Fig. 1: Calculated¹² bond relaxation (open circles) for isovalent impurities in semiconductors (abscissa). Asterisks denote experimental EXAFS values.

from one another ($u_{eq} = 0.27$). Furthermore, the chalcopyrite arrangement was found to be substantially stabler than the zincblende arrangement, i.e. the total energy (E_t) difference $E_t(\text{InGaP}_2) - 1/2E_t(\text{GaGaP}_2) - 1/2E_t(\text{InInP}_2)$, is negative. Hence, alloys with large chalcopyrite domains could perhaps be made.

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suggest that ΔH_m , much like optical bowing, is decided largely by the response of the alloy to internal strains produced by packing of dissimilar species. The second development¹³ has been the first prediction of the structural parameters of an ordered alloy (GaP-InP in chalcopyrite model) from a self-consistent total energy minimization method. Using a self-consistent pseudopotential band structure approach to InGaP₂, and minimizing the total energy as a function of both the lattice parameter a and the anion displacement parameter u , it was found that although a is very close to the average of InP and GaP (Vegards rule), the bond lengths $R_{\text{Ga-P}}$ and $R_{\text{In-P}}$ are substantially different from