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Structural Origin of Optical Bowing in Semiconductor Alloys

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The principle of conservation and transferability of chemical bonds explains the recent discovery by extended x-ray-absorption fine-structure measurements of two unequal anion-cation bond lengths R_{AC} and R_{BC} in $A_xB_{1-x}C$ zinc-blende semiconductor alloys despite the close adherence of the lattice constant to the average value (Vḗgard rule). This bond alternation, manifested as a structural distortion to a local chalcopyrite coordination around the anions, explains also most of the observed optical bowing in semiconductor alloys.

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The lowest optical band gaps of semiconductor alloys are usually smaller than the concentration (x) weighted average of the band gaps of the constituent binary semiconductors.[1-4] This alloy band-gap reduction ΔE_g is often expressed phenomenologically by $\Delta E_g \equiv bx(x-1)$, where the bowing parameter $b > 0$, reflecting an upward concave nonlinearity, is found to be in the range of $\lesssim 0.9$ eV for III-V alloys[1-3] and $\lesssim 2.4$ eV for II-VI alloys.[4] As with the Mott-Anderson metal-insulator transitions in disordered systems, optical bowing has been ascribed both to intrinsic interelectronic interactions already present in a hypothetically ordered ("virtual") alloy (b_{I}), and to atomic disorder (b_{II}). Previous calculations[5-9] have described b_{I} for $A_xB_{1-x}C$ alloys as the difference $b_{\mathrm{I}} = 4(\overline{E}_g - E_g{}^v)$ between the concentration weighted average band gap $\overline{E}_g$ and the band gap $E_g{}^v$ of a virtual zinc-blende crystal, i.e., using the virtual-crystal approximation (VCA). In the VCA the chemical and structural identities of the individual alloyed elements and bonds are eliminated by assuming: (a) an averaged lattice constant $a_v(x) = xa_{AC} + (1-x)a_{BC}$ (Vḗgard's rule), and (b) the same point group crystal structure as AC and BC, characterized by a single, "average" cation with a corresponding average bond length $\overline{R}(x) = x\boldsymbol{R}_{AC}{}^0 + (1-x)R_{BC}{}^0$ [for zinc-blende crystals, $\overline{R} = (\frac{3}{16})^{1/2}a_v$]. This equal-bond-length VCA has been applied to a range of semiconductors,[5-9] revealing that b_{I} falls considerably short of the experimentally observed bowing $b^{\exp}$ when the cations differ in their characteristic sizes. This created the need for proposing empirical models of disorder[5] for making up the large difference $b^{\exp} - b_{\mathrm{I}}$; however, modern coherent-potential approximation (CPA) calculations[9] do not warrant such large disorder contributions to b. While extensive reparametrization of the tight-binding VCA problem[10] (using 18 parameters) could fit the gap for a 50%–50% composition (at the expense of requiring inexplicably large A-B interactions), the physical origin of optical bowing remains elusive.

Recent experimental findings dramatically contradict the structural model underlying the VCA. First, using extended x-ray-absorption fine-structure (EXAFS) measurements on GaAs-InAs alloys, Mikkelsen and Boyce[11] (MB) have demonstrated that although the lattice parameter $a(x)$ closely follows Vḗgard's rule $a(x) = a_v(x)$ (assumption a), the anion-cation bond lengths $R_{AC}(x)$ and $R_{BC}(x)$ do not average to a single bond $\overline{R}$ but instead remain close, throughout the composition range, to their respective values in the pure binary compounds (invalidating assumption b). Second, Raman scattering experiments[12-13] have often revealed that the $A-C$ and $B-C$ bonds vibrate independently, leading to *two* distinct longitudinal optical modes.

In this Letter we demonstrate that (i) application of Bragg's[14] classical principle of conservation of tetrahedral bonds (CTB) shows that when the atomic size mismatch $\delta \equiv \alpha/\beta = (R_{AC}{}^2 - R_{BC}{}^2)/(R_{AC}{}^2 + R_{BC}{}^2)$ is large, the system will adopt a new local arrangement which preserves the identity of the individual bonds by creating bond alternation $\alpha \neq 0$. In tetrahedrally bonded semiconductors the relaxed structure corresponds to the local chalcopyrite arrangement[15] proposed by MB,[11] where the anions C are displaced from their ideal zinc-blende sites by $u - \frac{1}{4} = \alpha/a^2$ ($\alpha = 0$, or $u = \frac{1}{4}$ in VCA). (ii) In contrast to VCA,[5-9] the averaging of bond lengths ($\alpha = 0$, in assumption b) does not follow from the experimentally established averaging of the lattice constants (assumption a), but instead both the existence of a bimodal distribution $\alpha \neq 0$ and Vḗgard's rule $a(x) \cong a_v(x)$ follow simultaneously from the CTB. (iii) a, α, and u can be calculated solely from the classical atomic radii,[16] or alternatively from the quantum mechanical orbital radii[17] in agreement with EXAFS data when available (as shown in Ref. 11), and provides predictions when it is not. (iv) The first application of a self-consistent band-structure technique to the semiconductor alloy problem (equimolar InP-GaP in the $InGaP_2$ chalcopyrite arrangement) demonstrates that bond alternation accounts for most of the observed optical bowing, hence b_{II} is smaller than hitherto accepted in empirical models of disorder.[5]

Structure model.—We suggest that, to zero order, a tetrahedrally bonded *AC*-*BC* crystal will attain values of anion displacement u, lattice parameter a, and tetragonal strain parameter $\eta = c/2a$ such that the difference between each bond length and the sum of the tetrahedral radii of its constituent atoms $R_{ij} - d_i - d_j$ will be minimized simultaneously for all bonds. Here the d_i are Pauling's tetrahedral covalent radii[16] or the orbital radii that scale linearly with them.[17] Applying the CTB model to the chalcopyrite structure[15] where $R_{AC} = [u^2 + (1+\eta^2)/16]^{1/2} a$, $R_{BC} = [(u - \frac{1}{2})^2 + (1+\eta^2)/16]^{1/2} a$, one finds for constant[18] η the equilibrium values

$$a_{\mathrm{eq}}^2 = 4\alpha^2/\{\beta - [\beta^2 - (2+\eta^2)\alpha^2]^{1/2}\},$$
$$u_{\mathrm{eq}} = \tfrac{1}{4} + \alpha/a_{\mathrm{eq}}^2. \tag{1}$$

TABLE I. Calculated crystal parameters for III-III-V compounds.

Compound	a_v (Å)	a_{eq} (Å)	u_{eq}
$GaAlP_2$	5.450	5.450	0.250
$GaAlAs_2$	5.635	5.635	0.250
$GaAlSb_2$	6.051	6.051	0.250
$InGaP_2$	5.658	5.650	0.278
$InGaAs_2$	5.843	5.835	0.277
$InGaSb_2$	6.258	6.251	0.275

The calculated values of a and u with[11,18] $\eta = 1$ and Pauling's tetrahedral radii[16] are given in Table I for all III-III-V compounds (the values of $InAlX_2$ are identical to those of $InGaX_2$ since[16] $d_{\mathrm{Ga}} = d_{\mathrm{Al}}$). For comparison, we give the Vêgard values a_v, computed for consistency with the same binary lattice parameters used by Pauling. Table I shows that the single assumption of conservation of tetrahedral radii explains the main observation of MB[11]: that $a \simeq a_v$ despite the fact that, in contrast to the VCA, cation-anion bonds can show a bimodal distribution with a separation $\alpha = a^2(u - \frac{1}{4})$. This can be seen analytically by expanding Eq. (1) in the size mismatch parameter $\delta \equiv \alpha/\beta$ (0.07 for $InGaAs_2$), indicating that the leading terms in a and u are the Vêgard-VCA values, but that the correction to u is *first* order, while the correction to a is only *second* order. The values of a and u obtained for equimolar GaAs-InAs from Eq. (1) (unlike Ref. 11, with no experimental input on the ternaries) are within 1% of the data of MB.[11] The remaining values, as well as those that can be calculated simply from Eq. (1) for all II-II-VI compounds, constitute predictions useful for future improved VCA calculations based on the chalcopyrite structure. For a system with a small size mismatch δ (e.g., GaAs-AlAs) the solutions of Eq. (1) approach the zinc-blende limit ($u = \frac{1}{4}$, $\eta = 1$, $a = a_v$) for which existing calculations show[9] that $b_{\mathrm{I}} \simeq 0$ and the bowing is disorder induced. This suggests that δ is the relevant structural measure delineating the predominance of ordered local bonding effects ($|\delta| > 0$) over disorder effects ($\delta \simeq 0$). Note further that most of the 36 real chalcopyrite crystals[15] (e.g. $ZnSiP_2$) exhibit bond alternation $u \neq \frac{1}{4}$ and that Eq. (1) explains[19] the observed values of a and u of all ternary chalcopyrites. Hence, the observation of the breakdown of the equal-bond VCA in alloys[11] is a particular case of a broader phenomenon in ternary compounds. (It is therefore not impossible that under controlled conditions, some equimolar alloys with sufficient *A*-*B* electronegativity difference and large δ will form oriented chalcopyrite domains.)

Electronic structure.—We propose that the structurally induced bowing b_{I} is controlled by bond alternation and that the disorder contribution b_{II} results from compositional disorder around C and from the existence of a distribution of α (or u) around α_{eq} (or u_{eq}), i.e., a finite width of the bimodal distribution.[11] We calculate the first contribution by applying the all-electron first-principles mixed-basis band-structure method[20] to study self-consistently the electronic structure of equimolar InP-GaP in the $InGaP_2$ chalcopyrite structure as a function of α. We use a basis set of 94 compressed atom orbitals[20] plus 350 plane waves, an exchange coefficient of 0.9 (to fit the gaps of the pure binaries) and iterate the potential to self-consistency within a tolerance of 1 mRy. To identify the physical factors controlling b_{I} we separate it into a cation electronegativity component $b_{\mathrm{I}}^{\mathrm{CE}} = 4[\bar{E}_g - E_g(ABC_2; u = \frac{1}{4})]$ and a structural component $b_{\mathrm{I}}^{\mathrm{S}} = 4[E_g(ABC_2, u = \frac{1}{4}) - E_g(ABC_2, u = u_{\mathrm{eq}})]$. The first contribution, as in the VCA[5-10] assumes an equal-bond arrangement $R_{AC} = R_{BC}$, but in contrast to VCA it permits the existence of the two distinct cations $A \neq B$ and hence allows for a different self-consistent charge separation in the $A-C$ and $B-C$ (as well as in the $A-A, B-B$ and $A-B$) bonds. The second contribution measures the bowing due to the relaxation of the bond lengths to their equilibrium (unequal bond) configuration characterized by $u_{\rm eq}$ (Table I). We find for the fundamental $\Gamma_{15v} \to \Gamma_{1c}$ band gap $b_{\rm I}^{\rm CE} = 0.25$ eV and $b_{\rm I}^{S} = 0.17$ eV, or a total of $b_{\rm I} = 0.42$ eV, which together with the recently calculated[9] CPA value for the disorder contribution $b_{\rm II} = 0.08$ eV, produces a total bowing $b = 0.50$ eV, very close to the recent experimental value[1] of 0.50 ± 0.04 eV. Previously,[5] a disorder contribution $b_{\rm II}$ that is four times larger than the actual CPA value was necessary to explain the experimental bowing. For the indirect gap to X_{1c} we find $b_{\rm I} = 0.10$ eV, which together with the disorder-induced component $b_{\rm II} = 0.09$ eV, produces a bowing $b = 0.19$ eV, close to the observed value[1] $b = 0.16 \pm 0.03$ eV. This suggests that the proper composition dependence could be obtained by applying the VCA to the chalcopyrite structure, rather than to the zinc-blende structure.[5-10]

The cation electronegativity and the structural components of the chemical bowing $b_{\rm I}$ have simple physical origins. $b_{\rm I}^{\rm CE}$ reflects the lowering of the conduction band (and, to a smaller extent, the raising of the valence band) due to a charge separation on the two cation sublattices. $b_{\rm I}^{S}$ reflects the further lowering of the conduction band due to the stretching of the bond with the less tightly bound valence orbitals (In-P) in going from $u = \frac{1}{4}$ to $u > \frac{1}{4}$; it hence represents the change in the gap due to the *internal* pressure exerted by bond alternation. This lowering is consistent with the known variation of the direct gaps in binary semiconductors with pressure. (Weighting the deformation potentials[21] of pure AX and BX by the squares of the wave-function amplitudes at the A and B sites in the valence- and conduction-band edges in the alloy predicts $b_{\rm I}^{S}$ within 10% of our value.) Figure 1 shows the calculated electronic charge densities at the conduction-band minimum for $u = \frac{1}{4}$ (solid line) and $u_{\rm eq} = 0.278$ (dashed line, origin at P). The shaded areas denote the increase (decrease) in the In-P (Ga-P) bond charge density as the system undergoes a transition from equal to alternating bonds. As $u = \frac{1}{4} \to u > \frac{1}{4}$, charge is shifted from the In site to the bond, lowering thereby the energy of this state. We note that much of the band-gap anomaly of real ternary chalcopyrites is due to a $u = \frac{1}{4} \to u \neq \frac{1}{4}$ structural relaxation[19]; hence, this anomaly and optical bowing in size mismatched III-V alloys share a common structural origin.

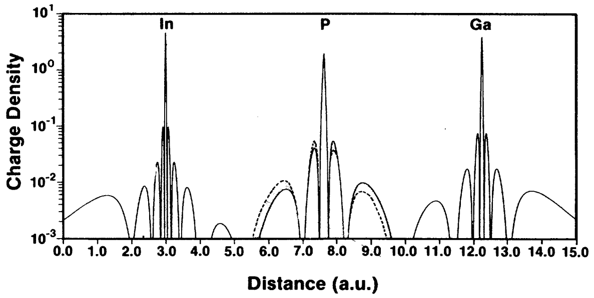

FIG. 1. The electronic charge density at the conduction-band minimum of $\rm InGaP_2$ for $u = 0.25$ (solid line) and $u_{\rm eq} = 0.278$ (dashed line, origin at P).

Implications for phonons.—Compared with the single infrared-active mode of the binaries, a local chalcopyrite coordination has nine allowed optical modes, four of which are expected to be strong, each corresponding to antiphase vibrations in the A-C and B-C bonds.[22] The highest-frequency chalcopyrite LO mode is nearly indistinguishable from the corresponding zinc-blende mode.[22] However, the remaining modes that appear between the highest LO and lowest TO modes are characteristic of chalcopyrite ordering. Raman scattering on $A_xB_{1-x}C$ alloys has revealed hitherto unexplained *sharp* modes between the TO and LO modes of the light-mass binary. The possibility that the new band is an impurity state was ruled out by Hirlimann, Besserman, and Balkanski,[12] by comparing InGaP with GaAsP. Pearsall, Carles, and Portal[23] have recently shown that the polarization dependence of the unexplained InGaAs bands below the highest LO mode is inconsistent with zinc-blende modes. Similarly, Kakimoto and Katoda[24] have observed an unexplained optical mode in InGaAs near the equimolar composition. We suggest that, unlike broad disorder-induced modes, these sharp modes arise from local chalcopyrite coordination. A reexamination of the Raman data is called for.

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[18] Similar predictions are obtained for a if instead of using $\eta = 1$ we fix η by the constraint that the angle around the B atom remains tetrahedral. $\eta \equiv 1$ is the preferred choice since the alloy does not have a preferred direction (no birefringence); the predicted orientation-averaged crystal-field splitting is hence vanishingly small.

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