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[1]The TO phonon frequency at the Γ point is given by [(force constant of the nearest-neighbor atoms)/(reduced mass)]$^{1/2}$. Using 268 and 361 cm^{-1} for the frequencies of TO phonons at the Γ point of GaAs and AlAs, respectively, we find that the force constant of Al-As differs only by 3% from that of Ga-As.

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Spin-Orbit Splitting in Compositionally Disordered Semiconductors

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Because the optical spectra of substitutional semiconductor alloys are so similar to those of the pure compounds, it is widely believed that the virtual-crystal approximation is accurate, i.e., that fluctuations in the crystal potential are negligible. Investigating the effect of alloying on the spin-orbit splitting, we show that this is not true.

Should substitutional semiconductor alloys, such as Si-Ge, Ga-AlAs, or InSb-As, be considered essentially disordered materials? In fact, recent discussions of disordered semiconductors have been restricted to topologically disordered[1] materials, i.e., glasses and amorphous phases. The reason for this is that, in contrast to glasses and amorphous materials, the optical spectra and electronic behavior of these alloys are so similar to those of the ordered, pure parent compounds[2-5] that no effect due to the compositional disorder has been clearly established prior to this Letter. (However, because of the disparity in mass of the substituted elements, the effect of alloying on phonon modes is quite evident.[6])

The usual way to describe an alloy as if it were ordered is to invoke the virtual-crystal approximation[7] (VCA). The VCA assumes a perfect lattice with compositionally averaged atomic potentials at each lattice site. The resulting band structure is exactly analogous to that of the pure compounds forming the alloy because the assumed crystal potential has no disorder. To the authors' knowledge, no explanation why there should be no local fluctuation of the crystal potential has ever been offered. However, it has been widely assumed that if such deviations from the VCA

were important, i.e., if they caused significant mixing of the electronic states found in the ordered crystals, then the band edges and the critical-point features of the optical spectra would be concomitantly broadened. The slight broadening of the critical-point features which is detected in electroreflectance[3,5] may be attributed to macroscopic inhomogeneity in the samples.

Van Vechten and Bergstresser (VV-B) have calculated the variation with alloy composition of the various critical-point features of the optical spectrum for alloys of diamond and zinc-blende semiconductors.[8] That calculation neglected spin-orbit splitting entirely so that comparisons were made with weighted averages of the observed (split) features. It was found that good agreement with experiment could be obtained if it was assumed that the actual variation resulted from two separate effects. First, the variation that would obtain in the VCA was calculated using the dielectric two-band model.[9] Then it was assumed that the actual, spin-orbit–averaged energy of the critical-point feature, $\bar{E}_i(x)$, shifted to lower energy[8,10]—without broadening—by an amount

$$\delta \bar{E}_i(x) = x(1-x)C_{FG}{}^2/A \tag{1}$$

for the alloy $MF_{1-x}G_x$, where x is the mole fraction of compound MG, A is a bandwidth constant ($A = 0.98$ eV), and C_{FG} is the (dielectrically defined) electronegativity difference between elements F and G;

$$C_{FG} = be^2(Z_G/r_G - Z_F/r_F)\exp(-Rk_s),   (2)$$

where b is a constant ($b = 1.5$), Z_G and r_G are the valence and covalent radius of element G, k_s is the linearized Thomas-Fermi screening wave number for the valence electrons, and $R = (r_G + r_F)/2$.

VV-B proposed that, in several cases, a large fraction of the observed nonlinear (concave-up) variation of the direct gap, $\bar{E}_0(x) = \Gamma_1 - \Gamma_{15} = [2E_0(x) + E_0 + \Delta_0(x)]/3$, in these alloys results from the fluctuations, Eq. (2), rather than from the virtual-crystal variation. Despite good agreement with experiment, their argument was not conclusive because, as they noted, a wide range of variations in the VCA can be obtained using the empirical pseudopotential method (EPM) according to the details of the method used to obtain the averaged atomic potential for the sublattice containing the alloyed elements. By prudent choice of averaging procedure, Jones and Lettington[11] and Richardson[12] have obtained reasonable agreement with experiment in several cases without invoking any effect due to deviations from the VCA.

Note that for those EPM calculations[11,12] an explanation of the sharp features of the spectra is provided by the assumption of the VCA. For the VV-B theory, where fluctuations are taken to be important, any explanation must necessarily be more complicated and include the deviations of atomic positions from the sites of a perfect lattice.[13] Phillips[14] and Van Vechten[15] have proposed such arguments based on thermodynamic considerations.

To determine the extent of disorder-induced mixing, we examine the spin-orbit splittings[16,17] Δ_0 and Δ_1 in the spectra of these alloys[5,18-21] (see Fig. 1 and Table I). In contrast to experiment, the variation of Δ_0 and Δ_1 with composition predicted using the VCA is essentially linear.[5,19,20] Although nonlinearities in Δ_1 have previously been observed,[5,18,19] interpretation has been unclear because the failure of the $\Delta_1 = 2\Delta_0/3$ rule[17] even in pure compounds (e.g., GaP) suggested that the critical points for the two components are not at the same point on the Λ axis of the Brillouin zone. Thus, variation of this separation with composition might explain the Δ_1 non-
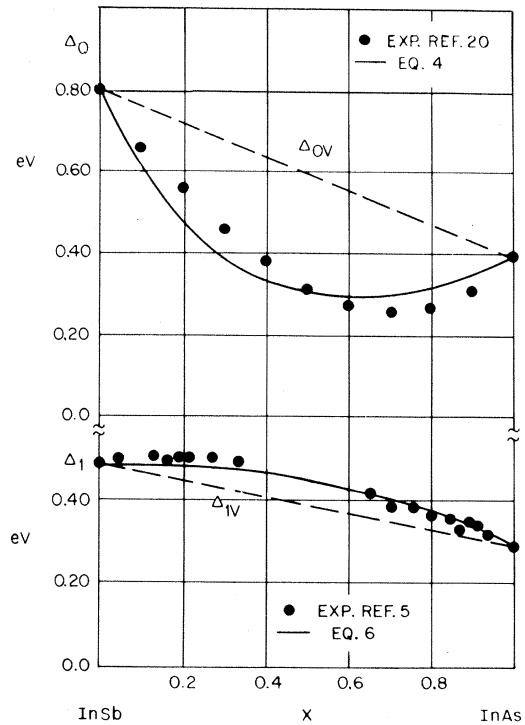

FIG. 1. Variation of spin-orbit splitting with alloy composition in the InAs-Sb system. Values of Δ_0 and Δ_1 measured by room-temperature electroreflectance (Refs. 5 and 20) are shown. The dashed lines labeled Δ_{0v} and Δ_{1v} indicate the linear variation that would be expected in the virtual crystal approximation.

linearity in the VCA.[19] We feel the present observation of large nonlinearities in Δ_0 and the quantitative analysis of Δ_1 given below exclude all VCA explanations.

A rigorous derivation (without the VCA) of $\Delta(x)$ from standard impurity band theory[22] will be extremely difficult because (a) in cases where the data on the deviation from linearity are most reliable, e.g., InAs-Sb, the effects are so large that use of perturbation theory is not justified; (b) the readjustment of bond lengths and bond angles required to achieve thermodynamic stability and to sharpen the band edges[14,15] severely complicates such an analysis.

Therefore, a somewhat heuristic analysis proceeds as follows. One might expect intraband scattering to predominate over interband scattering[10,23] because the corresponding energy denominator would usually be much less. To explain the observed decrease in $\Delta_0(x)$ below the VCA prediction, one must argue[23] that the state corresponding to the split-off Γ_7 state is pushed up in energy more than the light- and heavy-hole states,

TABLE I. Calculated and observed deviations from linearity for several 50%-50% alloys. Estimates of experimental uncertainty are made by the present authors.

| Alloy | $\Delta_{0v} - \Delta_0$ | | $\Delta_1 - \Delta_{1v}$ | | Ref. |
	Calc (meV)	Expt (meV)	Calc (meV)	Expt (meV)	
InAs–Sb	295	285 ± 10	58	58 ± 5	5, 20
Ga–InSb	92	$\cdots$	17	13 ± 5	5
Ga–InAs	29	37 ± 10	38	18 ± 5	5, 20
InAs–P	4	20 ± 10	11	32 ± 10	5
GaAs–P	3	5 ± 10	18	32 ± 10	5, 20
Ga–InP	4	0 ± 10	92	70 ± 20	19
Ga–AlAs	1	5 ± 10	4	8 ± 5	20
Si–Ge	1	7 ± 10	19	$\cdots$	21

Γ_8. In second-order perturbation theory the Γ_8 states are pushed up by interaction with all other valence-band states, while Γ_7 is pushed both up and down by states respectively below and above it. Therefore, Δ_0 is either increased or decreased by such interactions depending on the distribution of valence-band density of states relative to Γ_7 and Γ_8 and of the strength of the corresponding matrix elements. This would suggest a formula like

$$\Delta_{0v}(x) - \Delta_0(x) = \frac{x(1 - x)C_{FG}^2}{A' - \Delta_{0v}(x)}, \tag{3}$$

where Δ_{0v} is the linear interpolation of Δ_0 (VCA result) and A' is a bandwidth parameter, which in general would vary with the band structure of the parent compounds.

Unfortunately, we have not been able to find any prescription which can bring formulas of the form of Eq. (3) into reasonable agreement with our data. The difficulties lie both with the trend from one system to another and with the calculated and experimental asymmetries of $\Delta_{0v}(x)$ $- \Delta_0(x)$ as a function of x. We conclude that, at least for systems where E_0 is small,[24] interband mixing and effects beyond second-order perturbation theory, particularly those connected with the deviations from a perfect lattice,[14,15] dominate the effect on Δ_0. This might occur because (a) the potential fluctuations might be thought of as a collection of extended electric dipoles between say As and Sb sites in InAs-Sb, so matrix elements between states of opposite parity, e.g., p-like valence and s-like conduction states, should be much greater than between similar components; (b) as Γ_7 is pushed both up and down, the net effect may be small.

However, we find that the following simple description of Δ_0 does achieve agreement with experiment. We denote by $y(x)$ the fraction of conduction band, antibonding-s character mixed into the valence-band maximum by the disorder. We presume that $y(x)$ equals $\delta \overline{E}_0(x)$ divided by an averaged E_0 gap, and so by Eq. (1)

$$y(x) = x(1 - x)C_{FG}^2 / A\widetilde{E}_{0v}(x), \tag{4}$$

where

$$3/\widetilde{E}_{0v}(x) = 2/E_{0v}(x) + 1/[E_0 + \Delta_{0v}(x)],$$

and $E_{0v}(x)$ is the value of $E_0(x)$ calculated in the VCA.[8] As the s-like (conduction-band) component makes zero contribution to Δ_0, we have

$$\Delta_0(x) = [1 - y(x)]\Delta_{0v}(x). \tag{5}$$

In the case of the E_1 and $E_1 + \Delta_1$ features, which in the compounds and in the VCA result from a critical point on the Λ axis, second-order perturbation theory should be more accurate. These features are less sensitive to strain and so ought to be less affected by the deviations from the perfect lattice. Also, E_1 is never less than 1.5 eV so that interband mixing should be negligible. We find that an acceptable fit to experiment can be had if we assume the analog of Eq. (3) with $A' = 0$. Thus we propose

$$\Delta_1(x) - \Delta_{1v}(x) = x(1 - x)KC_{FG}^2 / \Delta_{1v}(x), \tag{6}$$

where K is taken to be a constant and fitted to the InAs-Sb data; $K = 0.14$. (The magnitude of K may indicate the strength of our proposed selection rule for the fluctuating potential.)

The calculated values of Δ_0 and Δ_1 are compared with experiment in Table I for seven cases at $x = 0.5$ and in Fig. 1 for InAs-Sb as a function

of x. Note that the values of C_{FG} given in Ref. 8 were calculated for $x = 0.5$. The variation of the dielectric screening term be^{-Rk_s} in Eq. (2) across the composition range causes some variation in C_{FG}. Thus $C_{As,Sb}$ is 16% larger when evaluated for nearly pure InAs than for nearly pure InSb.

We conclude that the VCA is not adequate to describe the optical properties of substitutional semiconductor alloys, and that our heuristic analysis is probably correct. It will be interesting to obtain data for In-GaSb, InSb-Bi, and Hg-CdTe so that Eq. (5) can be given a severe test at compositions where E_0 nears zero.

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Lifetime Effects in $(p, 2p)$ Reactions

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Deep-hole excitations formed in knockout reactions decay rapidly by the ejection of additional nucleons. Other coherent processes that lead to the same final states are discussed. These may be important in some circumstances.

Quasifree scattering processes are generally believed to be useful probes of inner-shell structure in nuclei.[1] In particular $(p, 2p)$ and $(e, e'p)$ reactions carried out at high bombarding energies exhibit peaks in the missing-energy spectrum that are interpreted in terms of the ejection of protons from deeply bound orbitals. In this Letter we discuss aspects of the mechanism by which these reactions take place.

As an example we consider the reaction ^{12}C$(p,$ $2p)^{11}$B, studied by Tyrén et al.[2] with 460-MeV incident protons in a coplanar symmetric geometry. We consider the well-resolved peak of width 10 MeV, centered at a missing energy of 36 MeV, that is attributed to the knockout of an $s_{1/2}$ proton from ^{12}C. The great width of this peak indicates the rapid decay of the $s_{1/2}$ hole ($\sim 10^{-22}$ sec) as it breaks down into more complex configurations.

A missing energy of the same order required for $s_{1/2}$ ejection can also be supplied to the nu-