



Strain effects on the spectra of spontaneously ordered Ga x In1-x P

Gi <i U]K Y]UbX`5`Yi `Ni b[Yf`

7]U]h]cb. `5dd`YX`D\ng]Mj`@YHfYg`64ž +) + f% - (7/Xc].`%\$"%\$*` #6%00(\$) +

J]Yk `cb`]bY. `h]d.##Xl "Xc]"cf[#6"%\$*` #6%00(\$) +

J]Yk `HUVY`cZ7 cb]Yb]g. `h]d. #g]V]U]h]cb"U]d"cf[#6%b]Yb]h]U]d#ci fbU`#Ud`# (# 3j Yf1 dXZ]t]

Di V]g\YX`Vmi]h]Y`5`D`Di V]g\]b[

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: cfV]XXYb`f]Ubg]h]cbg`UbX`h]Y`ZYV]W] Y`a`UggYg`cZY`YV]fcbg`UbX`c`Yg]b`b`%`I` ; U] `5g#bD`ei`Ub]h`a`k`Y`g`k`]h`V]t`a`dfYgg] Y`g]f]U]b`

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9j U]i U]h]cb`cZ]h]Y`ZYV]W] Y`c`Y`a`UggYg]b`dgYi`Xca`cfd\]W]t`a`dfYgg] Y`mg]f]U]b]YX` ; U] `b`%`I` `5g#bD`ei`Ub]h`a`k`Y`g`

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b]YfbU`g]f]U]b`UbX`d\c]c`Y`Ug]h]W]ZYV]W]]b` ; U] `5`I` `5g#` U5g`UbX` b`%`I` ; U] `5g`mD`%`m`#bD`W]mg]f]U]g`

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Spontaneous (111) CuPt-like ordering has been widely observed in Ga_xIn_{1-x}P lattice matched ($x=x_0$) to a GaAs(001) substrate. This leads to a band-gap reduction ΔE_g and to a valence-band splitting ΔE_{12} . We explore here the consequence of the coexistence of (001) epitaxial strain (produced by selecting $x \neq x_0$) and (111) chemical ordering. This leads to distinct changes in ΔE_g and ΔE_{12} which could serve as new fingerprints of ordering.

Surface reconstruction-induced ordering¹ of III-V alloys leads to lowering of the band gap¹⁻⁵ and to splitting of the

band is the sixfold degenerate Γ_{15v} state while the direct conduction-band minimum is the Γ_{1c} doublet. The degen-

partially ordered⁷ alloys, and have been seen in electroreflectance,² polarized photoluminescence,³ polarized piezoreflectance⁴ and in spatially resolved photo-

splittings are denoted Δ^{SO} , Δ_{111}^O , and Δ_{001}^S , respectively. We will next describe their effects on the Hamiltonian assuming

the growing Ga_xIn_{1-x}P film was adjusted to the value of the substrate. Consequently, in the absence of strain, both the band-gap reduction $\Delta E_g = E_g(\text{ordered}) - E_g(\text{random})$ and the valence-band splitting $\Delta E_{12} = E_{12} - E_2$ were attributed to the chemical ordering, even independently in different

the six valence states (up, up, up, down, down, down) and ordering effects do not distinguish spin up and spin down, so each is described by two identical 3×3 matrices.

pure misfit strain ($x \neq x_0$) can also lead to valence-band splitting⁸ and to band-gap changes.⁹ In this letter we thus focus on the interesting case of the coexistence of chemical ordering in the direction G_{ord} with epitaxial strain ($x \neq x_0$) in the direction $G_{\text{substrate}}$. This is different from the case of artificially grown strain layer superlattices in which the direction of layer modulation coincides with the direction of strain, so these effects add up colinearly. In contrast, in spontaneously ordered alloys the direction of chemical ordering $G_{\text{ord}} = (111)$ is different from the substrate orientation $G_{\text{substrate}} \cong (001)$. We will show that this noncolinear "vector

for (001) strain the valence (v) Hamiltonian is

$$H_{001,v}^S(\epsilon) = a_v \frac{\Delta V(\epsilon)}{V} + \frac{1}{3} \Delta_{001}^S(\epsilon) \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -2 \end{pmatrix}. \quad (1)$$

Here, a_v is the hydrostatic deformation potential of the valence band, $\Delta V(\epsilon)/V$ is the relative volume change, and $\Delta_{001}^S(\epsilon) = 3b[(C_{11} + 2C_{12})/C_{11}]\epsilon$ is the crystal field splitting, where b is the tetragonal deformation potential and C_{ij} are the elastic constants.

splitting ΔE_{12} , and the functional interrelationship ΔE_g vs ΔE_{12} between them.

In imperfectly ordered Ga_xIn_{1-x}P alloy, successive (111) cation planes are not pure Ga and pure In, respectively, but degree of CuPt-type order is described by the long-range

$$H_{111,v}^O(\eta) = B_v(\eta) + \frac{1}{3} \Delta_{111}^O(\eta) \begin{pmatrix} 0 & -1 & -1 \\ - & 0 & -1 \end{pmatrix}. \quad (2)$$

to the growth direction) is $\epsilon(x) = [a_s - a_f(x)]/a_f(x)$, where $a_f(x)$ and a_s are the lattice constants of the film and the substrate, respectively. All of our quantities will thus be denoted by the degree of order η and the strain $\epsilon(x)$. The band-gap reduction of the strained and ordered alloy $\Delta E_g(\eta, \epsilon) \equiv E_g(\eta, \epsilon) - E_g(0,0)$ is measured with respect to the unstrained and un-

Here, B_v is the ordering-induced shift of the valence-band energy center while $\Delta_{111}^O(\eta) = \Delta_{111}^O(\eta=1)\eta^2$ are the ordering-induced crystal field splitting.⁷ Placing $H_{001,v}^S$ and $H_{111,v}^O$ on the two diagonal 3×3 blocks and adding the full 6×6 spin-orbit matrix,¹⁰ relative to the energy center of the ordering plus (001) strain are:

$$H_v = \frac{1}{3} \begin{pmatrix} \Delta_{001}^S & -\Delta_{111}^O - i\Delta^{SO} & -\Delta_{111}^O & 0 & 0 & \Delta^{SO} \\ \Delta_{001}^O & \Delta^S & \Delta^O & 0 & 0 & -i\Delta^{SO} \\ 0 & 0 & -\Delta^{SO} & \Delta_{001}^S & -\Delta_{111}^O + i\Delta^{SO} & -\Delta_{111}^O \\ 0 & 0 & -i\Delta^{SO} & -\Delta_{111}^O - i\Delta^{SO} & \Delta_{001}^S & -\Delta_{111}^O \\ \Delta^{SO} & i\Delta^{SO} & 0 & -\Delta_{111}^O & -\Delta_{111}^O & -2\Delta_{001}^S \end{pmatrix} \quad (5)$$

strain ϵ) and degree of ordering η .

The energy for the conduction (c) band minimum is given by

$$E_c(\eta, \epsilon) = E_c(0, 0) + a_c \frac{\Delta V(\epsilon)}{V} + B_c(\eta). \quad (4)$$

Here, $E_c(0, 0)$ is the conduction-band energy of the strain-free random alloy at composition x , a_c is the deformation potential of the conduction band, and B_c is the ordering-induced conduction-band energy shift. Since only relative energy difference between two bands are generally measured, it is convenient to define the center of the three top of valence-band energies as our zero of energy and denote by $a = a_c - a_v$ and $B = B_c - B_v$ as the deformation energies of the average band gap $\bar{E}_g = E_c - \frac{1}{3}(E_1 + E_2 + E_3)$. For (001) strain the relative volume change is given by $\Delta V(\epsilon)/V = 2[(C_{11} - C_{12})/C_{11}]\epsilon$. The ordering induced average band-gap change is given by $B(\eta) = [\Delta E_g(1, 0) + \frac{1}{3}\Delta_{111}^O(1, 0)]\eta^2$, where $\Delta E_g(1, 0)$ is the band-gap reduction of the strain-free and fully order alloy relative to the perfectly random alloy. Hence, the conduction-band energy of Eq. (4) can be written as

$$E_c(\eta, \epsilon) = E_g(0, 0) + \frac{1}{3}\Delta^{SO} + 2a \frac{C_{11} - C_{12}}{C_{11}}\epsilon + \left[\Delta E_g(1, 0) + \frac{1}{3}\Delta_{111}^O(1, 0) \right] \eta^2. \quad (5)$$

The needed input data for evaluating Eqs. (3) and (5) are (i) the concentration dependent properties: $E_g(x)$, $\epsilon(x)$, $\Delta^{SO}(x)$, $C_{ij}(x)$, $a(x)$, and $b(x)$ of the random alloy ($\eta=0$) and (ii) the ordering dependent properties: $\Delta_{111}^O(1, 0)$ and

assuming the usual quadratic bowing form

$$P(x) = xP(\text{GaP}) + (1-x)P(\text{InP}) - b_P x(1-x), \quad (6)$$

where b_P is the bowing parameters for property P . For the spin-orbit splitting we use the bowing⁷ $b_{\Delta^{SO}} = -0.02$ eV,

and deformation potentials. These input values for $\text{Ga}_x\text{In}_{1-x}\text{P}$ are given in Table I. For the second category of quantities, we use our previously calculated band structure values⁷ $\Delta_{111}^O(1, 0) = 0.20$ eV and $\Delta E_g(1, 0) = -0.32$ eV.

Using these input data we solve Eqs. (3) and (5), obtaining (a) the band-gap reduction $\Delta E_g[\eta, \epsilon(x)]$ and (b) the valence-band splitting $\Delta E_{12}[\eta, \epsilon(x)] = E_1[\eta, \epsilon(x)] - E_2[\eta, \epsilon(x)]$. Figure 1 depicts these quantities as a function of the film composition x , while Fig. 2 shows them as a function of the degree η of long range order. The following are the important features:

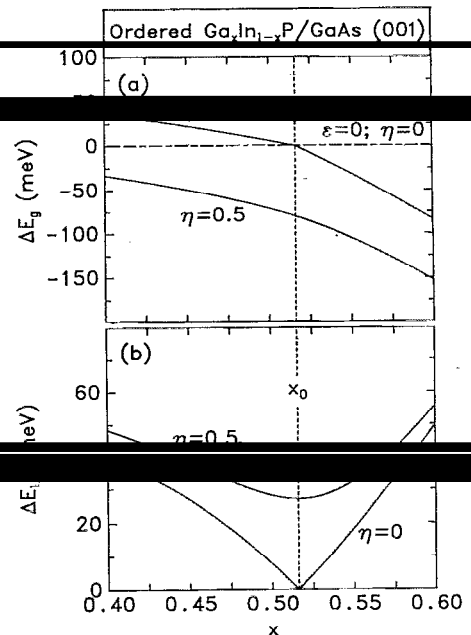


FIG. 1. (a) The band-gap reduction $\Delta E_g(\eta, \epsilon) \equiv E_g[\eta, \epsilon(x)] - E_g[0, 0]$ as a function of composition x at $\eta=0$ and $\eta=0.5$. The dashed horizontal line is valence-band splitting ΔE_{12} of the strained alloy with ordering as function of composition x at $\eta=0$ and $\eta=0.5$.

TABLE I. Room-temperature experimental parameters (from 12) used to calculate band-edge energy levels of $\text{Ga}_x\text{In}_{1-x}\text{P}$ as function of strain and ordering.

Properties	GaP	InP
a_0 (Å)	5.4512	5.8687
E_g (eV)	2.78	1.35
Δ^{SO} (eV)	0.08	0.11
C_{11} (Gpa)	141	102
C_{12} (Gpa)	62	58
b (eV)	-1.8	-1.6

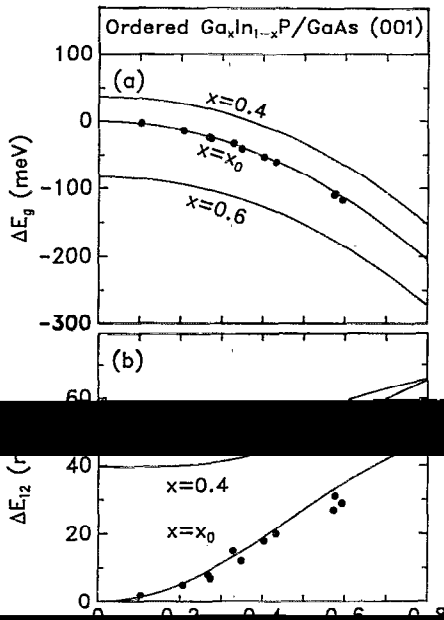


FIG. 2. Same as Fig. 1, but plotted as function of x at composition x_0 .

(i) Pure strain with no ordering ($x \neq x_0$; $\eta = 0$) see Fig. 1). (c) Here, any nonzero strain leads to a splitting of the

ΔE_{12} vs x and the ΔE_g vs x (or E_g vs x) curves have a cusp at $x = x_0$, reflecting the change of the VBM from light hole when $x < x_0$ to heavy hole when $x > x_0$. (c) The slope α for the light-hole gap E_g vs x is much smaller than the slope β for the heavy-hole gap. These features have been observed in strained random alloys of GaInP⁹ and GaInAs.⁹

(ii) Pure chemical ordering with no strain ($x = x_0$; $\eta \neq 0$,

curves in Fig. 2 show the recent piezomodulated reflectivity data of Alonso *et al.*⁴ We find that the η which fits the theoretical ΔE_g also fits the theoretical ΔE_{12} of the same samples. This then gives a "self-consistent" way of deducing η from optical measurements.⁷ (b) For the valence-band splitting, chemical ordering is analogous to compressive strain in that both yield a light-hole state at the top of the valence band.^{11,9,13} This ordering-induced reduction of the in-plane effective mass at the valence-band top (relative to the random alloy) would lead to larger exciton radii.

(iii) Coexistence of chemical ordering with epitaxial

($x \neq x_0$) is predicted to remove the cusp in the ΔE_g vs x and

predicted to reduce the dependence of ΔE_{12} on x , as illustrated by the flattening of the $\eta = 0.5$ curve near $x = x_0$ in Fig. 1(b). (c) (001) strain increases the valence-band splitting produced by pure ordering, and vice versa [Figs. 1(b) and 2(b)].

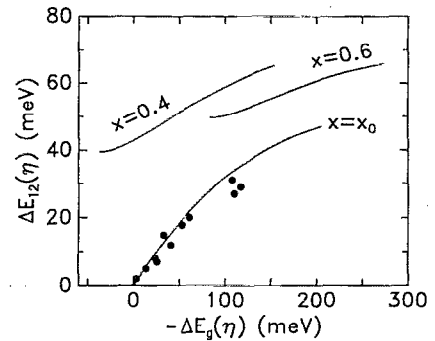


FIG. 3. The correlation between ΔE_g and ΔE_{12} as function of η at composition

tary, so the combined effect is larger than the individual one. (d) It is useful to plot the measured ΔE_g vs ΔE_{12} (Fig. 3). There are three domains in this plane: If the measured data

calculated $x = x_0$ line, epitaxial strain is the logical cause as

data fall below the line (as is the case for the high $|\Delta E_g|$ samples of Fig. 3), we have an effect that produce a lowering in the band gap without a concomitantly large valence-band

tion.

In summary, we have shown that measurements of ΔE_g and ΔE_{12} of Ga_xIn_{1-x}P films mismatched with the GaAs(001) can be used to observe new fingerprints of ordering. This includes the "rounding of the cusp" of ΔE_{12} vs x , flattening of the ΔE_{12} vs x curve, and the shifts in the ΔE_g vs ΔE_{12} curve. These predictions await experimental testing

¹For a recent review on spontaneous ordering, see A. Zunger and S. Mahajan in *Handbook of Semiconductors*, Vol. 3, 2nd ed. (Elsevier, Amsterdam) and references therein (in press).

²T. Nishino, *J. Cryst. Growth* **98**, 44 (1989).

³T. Kanata, M. Nishimoto, H. Nakayama, and T. Nishino, *Phys. Rev. B* **45**, 6637 (1992).

⁴R. G. Alonso, A. Mascarenhas, G. S. Horner, K. A. Bertness, S. R. Kurtz, and J. M. Olson, *Phys. Rev. B* **48**, 11833 (1993).

⁵L. C. Su, S. T. Pu, G. B. Stringfellow, J. Christen, H. Selber, and D. Bimberg, *Appl. Phys. Lett.* **62**, 3496 (1993).

⁶S. H. Wei and A. Zunger, *Phys. Rev. B* **39**, 2272 (1989); *J. Appl. Phys.* **66**, 602 (1989).

⁷S.-H. Wei, D. B. Laks, and A. Zunger, *Appl. Phys. Lett.* **62**, 1937 (1993).
⁸S. H. Wei, D. B. Laks, and A. Zunger, *Phys. Rev. B* **47**, 236 (1993).

⁹C. T. Kuo, S. K. Yung, R. M. Conell, and G. B. Stringfellow, *J. Appl. Phys.* **57**, 5428 (1985).

¹⁰D. J. Chadi, *Phys. Rev. B* **16**, 790 (1977).

¹¹S.-H. Wei and A. Zunger (unpublished).

¹²Landolt-Bornstein, *Numerical Data and Functional Relationships in Science and Technology*, edited by O. Madelung, M. Schulz, and H. Weiss