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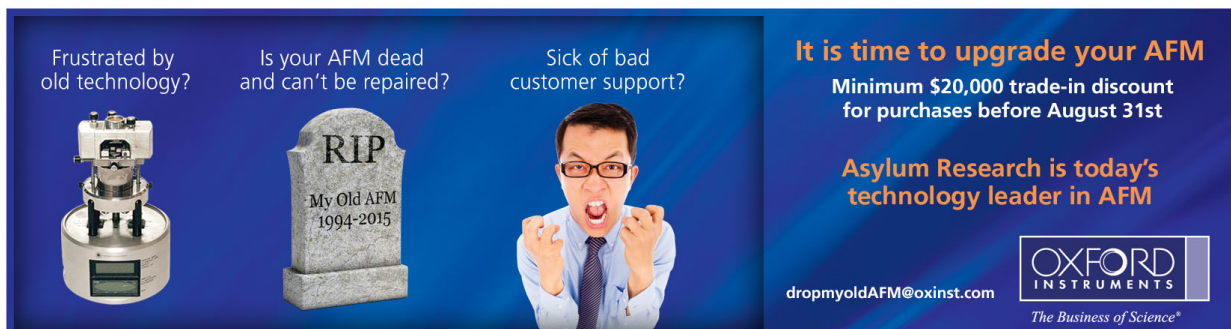
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# Strain effects on the spectra of spontaneously ordered $\text{Ga}_x\text{In}_{1-x}\text{P}$

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Spontaneous (111) CuPt-like ordering has been widely observed in  $\text{Ga}_x\text{In}_{1-x}\text{P}$  lattice matched ( $x=x_0$ ) to a GaAs(001) substrate. This leads to a band-gap reduction  $\Delta E_g$  and to a valence-band splitting  $\Delta E_{12}$ . 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  $\Delta E_g$  and  $\Delta E_{12}$  which could serve as new fingerprints of ordering.

Surface reconstruction-induced ordering<sup>1</sup> of III-V alloys leads to lowering of the band gap<sup>1-5</sup> and to splitting of the valence-band maximum (VBM).<sup>1,3,4</sup> These effects have been predicted theoretically for perfectly ordered<sup>6</sup> as well as for partially ordered<sup>7</sup> alloys, and have been seen in electroreflectance,<sup>2</sup> polarized photoluminescence,<sup>3</sup> polarized piezoreflectance,<sup>4</sup> and in spatially resolved cathodoluminescence.<sup>5</sup> In these experiments, the composition  $x$  of the growing  $\text{Ga}_x\text{In}_{1-x}\text{P}$  film was adjusted to the value ( $x=x_0$ ) which gives lattice matching to the GaAs(001) 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  $\Delta E_{12} = E_1 - E_2$  were attributed to the chemical ordering seen independently in diffraction experiments.<sup>1</sup> However, even in the absence of ordering, pure misfit strain ( $x \neq x_0$ ) can also lead to valence-band splitting<sup>8</sup> and to band-gap changes.<sup>9</sup> In this letter we thus focus on the interesting case of the coexistence of chemical ordering in the direction  $G_{\text{ord}}$  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 addition" of ordering and strain effects can lead to interesting changes in the band-gap reduction  $\Delta E_g$ , valence-band splitting  $\Delta E_{12}$ , and the functional interrelationship  $\Delta E_g$  vs  $\Delta E_{12}$  between them.

In imperfectly ordered  $\text{Ga}_x\text{In}_{1-x}\text{P}$  alloy, successive (111) cation planes are not pure Ga and pure In, respectively, but  $\text{Ga}_{x+\eta/2}\text{In}_{1-x-\eta/2}$  and  $\text{Ga}_{x-\eta/2}\text{In}_{1-x+\eta/2}$ , respectively. The degree of CuPt-type order is described by the long-range order parameter<sup>7</sup>  $0 \leq \eta \leq 1$ . The epitaxial strain (perpendicular 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  $\eta$  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 gap of the random, strain-free alloy  $E_g(0, 0)$  at the same composition. In this reference system, the top of the valence

band is the sixfold degenerate  $\Gamma_{15v}$  state while the direct conduction-band minimum is the  $\Gamma_{1c}$  doublet. The degeneracy at the top of valence band is lifted by spin-orbit (SO) coupling, ordering ( $O$ ) and strain ( $S$ ). The corresponding splittings are denoted  $\Delta^{SO}$ ,  $\Delta_{111}^O$ , and  $\Delta_{001}^S$ , respectively. We will next describe their effects on the Hamiltonian assuming *small deviations* of  $x$  from  $x_0$  (i.e., a linear theory).

Spin-orbit coupling is zero for the  $s$ -like  $\Gamma_{1c}$  state, while the six valence states ( $x\uparrow, y\uparrow, z\uparrow, x\downarrow, y\downarrow, z\downarrow$ ) are coupled by the  $6 \times 6$  spin-orbit Hamiltonian given in Ref. 10. Both strain and ordering effects do not distinguish spin up and spin down, so each is described by two identical  $3 \times 3$  matrices.

For (001) strain the valence ( $v$ ) Hamiltonian is<sup>8,11</sup>

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

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.

For pure (111) chemical ordering the valence Hamiltonian is<sup>11</sup>

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

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.<sup>7</sup> Placing  $H_{001,v}^S$  and  $H_{111,v}^O$  on the two diagonal  $3 \times 3$  blocks and adding the full  $6 \times 6$  spin-orbit matrix,<sup>10</sup> relative to the energy center of the top of valence band, the total valence Hamiltonian of (111) ordering plus (001) strain are:

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

Solving Eq. (3) gives the valence-band levels (in decreasing order)  $E_1$ ,  $E_2$ , and  $E_3$  as a function of composition  $x$  (or strain  $\epsilon$ ) and degree of ordering  $\eta$ .

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

TABLE I. Room-temperature experimental parameters (Ref. 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
$\Delta^{SO}$ (eV)	0.08	0.11
$C_{11}$ (Gpa)	141	102
$C_{12}$ (Gpa)	62	58
$a$ (eV)	-9.9	-6.4
$b$ (eV)	-1.8	-1.6

$\Delta E_g(1, 0)$  of the fully ordered alloy. The first category of quantities are obtained for the random  $\text{Ga}_x\text{In}_{1-x}\text{P}$  alloy by 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 bowing<sup>7</sup>  $b_{\Delta^{SO}} = -0.02$  eV, while for the direct gap the bowing is<sup>12</sup>  $b_{E_g} = 0.76$  eV. We assume zero bowing for lattice constant, elastic constants, 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 values<sup>7</sup>  $\Delta_{111}^O(1, 0) = 0.20$  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  $\eta$  of long range order. The following are the important features:

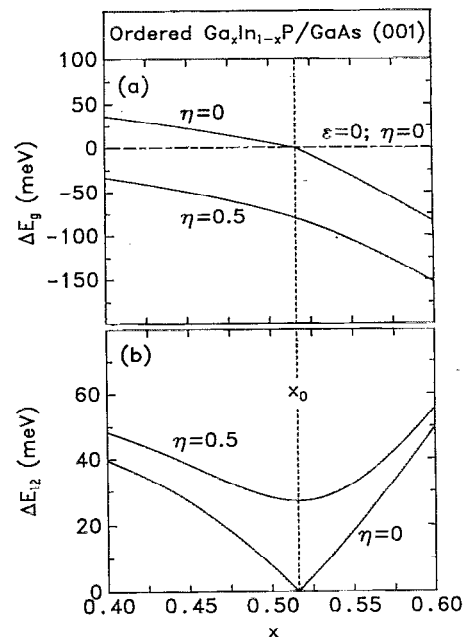


FIG. 1. (a) The band-gap reduction  $\Delta E_g(\eta, \epsilon) \equiv E_g[\eta, \epsilon(x)] - E_g[0, 0]$  as a function of composition  $x$  at  $\eta=0$  and  $\eta=0.5$ . The dashed horizontal line denotes  $\Delta E_g(0, 0)$ .  $x_0 = 0.516$  is the lattice-matched composition. (b) The valence-band splitting  $\Delta E_{12}$  of the strained alloy with ordering as function of composition  $x$  at  $\eta=0$  and  $\eta=0.5$ .

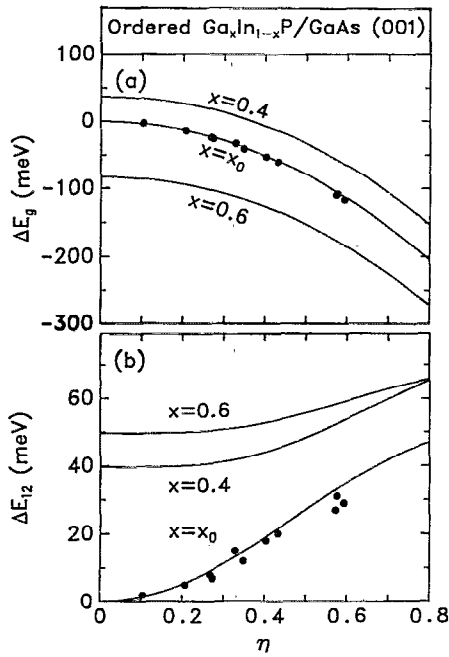


FIG. 2. Same as Fig. 1, but plotted as function of  $\eta$  at compositions  $x=x_0$ ,  $x=0.4$  and  $x=0.6$ . Solid circles indicate our fit to the data of Ref. 4.

(i) *Pure strain with no ordering* ( $x \neq x_0$ ;  $\eta=0$ , see Fig. 1): (a) Here, any nonzero strain leads to a splitting of the VBM [Fig. 1(b)], but only tensile strain ( $\epsilon > 0, x > x_0$ ) leads to a band-gap reduction, while compressive strain ( $\epsilon < 0, x < x_0$ ) leads to a band-gap increase [Figs. 1(a) and 2(a)]. (b) The  $\Delta E_{12}$  vs  $x$  and the  $\Delta E_g$  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  $\alpha$  for the light-hole gap  $E_g$  vs  $x$  is much smaller than the slope  $\beta$  for the heavy-hole gap. These features have been observed in strained random alloys of GaInP<sup>9</sup> and GaInAs.<sup>9</sup>

(ii) *Pure chemical ordering with no strain* ( $x=x_0$ ;  $\eta \neq 0$ , see Fig. 2): (a) This leads universally to a valence-band splitting and to a band-gap reduction for any  $\eta > 0$ . The solid circles in Fig. 2 show the recent piezomodulated reflectivity data of Alonso *et al.*<sup>4</sup> We find that the  $\eta$  which fits the theoretical  $\Delta E_g$  also fits the theoretical  $\Delta E_{12}$  of the same samples. This then gives a “self-consistent” way of deducing  $\eta$  from optical measurements.<sup>7</sup> (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.<sup>11,9,13</sup> This ordering-induced reduction of the in-plan 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 strain*: (a) The coexistence of ordering ( $\eta \neq 0$ ) with strain ( $x \neq x_0$ ) is predicted to remove the cusp in the  $\Delta E_g$  vs  $x$  and  $\Delta E_{12}$  vs  $x$  curves (Fig. 1). (b) Chemical ordering is also predicted to reduce the dependence of  $\Delta E_{12}$  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)]. This reflects the fact that the ordering-induced  $\Delta_{111}^O$  and the strain-induced  $\Delta_{001}^S$  crystal field splittings are complemen-

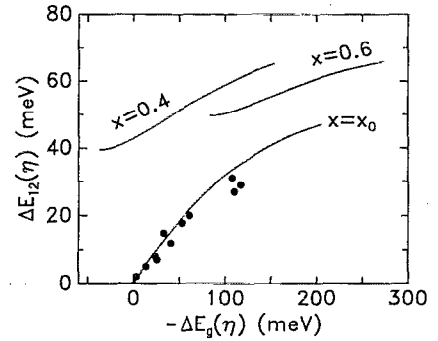


FIG. 3. The correlation between  $\Delta E_{12}$  and  $\Delta E_g$  as function of  $\eta$  at compositions  $x=x_0$ ,  $x=0.4$  and  $x=0.6$ . Solid circles indicate our fit to the data of Ref. 4.

tary, so the combined effect is larger than the individual one. (d) It is useful to plot the measured  $\Delta E_g$  vs  $\Delta E_{12}$  (Fig. 3). There are three domains in this plane: If the measured data fall on the  $x=x_0$  line one can conclude that *chemical ordering* is the cause of both  $\Delta E_g$  and  $\Delta E_{12}$ . If data fall *above* the calculated  $x=x_0$  line, *epitaxial strain* is the logical cause as well, as seen in Fig. 3 for the  $x=0.4$  and  $x=0.6$  lines. If the 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 splitting. A possible cause is *clustering of like atoms* (the initial stage of phase separation). Thus, a  $\Delta E_g$  vs  $\Delta E_{12}$  plot of measured points could be used as a guide for the relative importance of ordering, strain, and clustering/phase separation.

In summary, we have shown that measurements of  $\Delta E_g$  and  $\Delta E_{12}$  of Ga<sub>x</sub>In<sub>1-x</sub>P films *mismatched* with the GaAs(001) can be used to observe new fingerprints of ordering. This includes the “rounding of the cusp” of  $\Delta E_{12}$  vs  $x$ , flattening of the  $\Delta E_{12}$  vs  $x$  curve, and the shifts in the  $\Delta E_g$  vs  $\Delta E_{12}$  curve. These predictions await experimental testing.

<sup>1</sup>For 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).

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