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Strain effects on the spectra of spontaneously ordered $Ga_xIn_{1-x}P$

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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 ordering[1] of III-V alloys leads to lowering of the band gap[1–5] and to splitting of the

partially ordered[7] alloys, and have been seen in electroreflectance,[2] polarized photoluminescence,[3] polarized

pure misfit strain ($x\neq x_0$) can also lead to valence-band splitting[8] 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

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

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

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

and ordering effects do not distinguish spin up and spin

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

$$H^S_{001,v}(\epsilon)=a_v\frac{\Delta V(\epsilon)}{V}+\frac{1}{3}\Delta^S_{001}(\epsilon)\begin{pmatrix}1&0&0\\0&1&0\\0&0&-2\end{pmatrix}. \tag{1}$$

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

$$H^O_{111,v}(\eta)=B_v(\eta)+\frac{1}{3}\Delta^O_{111}(\eta)\begin{pmatrix}0&-1&-1\\-&0&-1\\-&-&0\end{pmatrix}. \tag{2}$$

Here, B_v is the ordering-induced shift of the valence-band energy center while $\Delta^O_{111}(\eta)=\Delta^O_{111}(\eta=1)\eta^2$ are the ordering-induced crystal filed splitting.[7] Placing $H^S_{001,v}$ and $H^O_{111,v}$ on the two diagonal 3×3 blocks and adding the full 6×6 spin-orbit matrix,[10] relative to the energy center of the top of valence band, the total valence Hamiltonian of (111) ordering plus (001) strain are:

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$$
\begin{pmatrix}
\Delta^S_{001} & -\Delta^O_{111}-i\Delta^{SO} & -\Delta^O_{111} & 0 & 0 & \Delta^{SO} \\
\Delta^O_{111}+i\Delta^{SO} & \Delta^S & -\Delta^O & 0 & 0 & -i\Delta^{SO} \\
0 & 0 & -\Delta^{SO} & \Delta^S_{001} & -\Delta^O_{111}+i\Delta^{SO} & -\Delta^O_{111} \\
0 & 0 & -i\Delta^{SO} & -\Delta^O_{111}-i\Delta^{SO} & \Delta^S_{001} & -\Delta^O_{111} \\
\Delta^{SO} & i\Delta^{SO} & 0 & -\Delta^O_{111} & -\Delta^O_{111} & -2\Delta^S_{001}
\end{pmatrix}. \tag{3}
$$

strain ϵ) and degree of ordering η.

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

$$E_c(\eta,\epsilon)=E_c(0,0)+a_c\frac{\Delta V(\epsilon)}{V_0}+B_c(\eta). \tag{4}$$

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 $B(\eta)=[\Delta E_g(1,0)+\frac{1}{3}\Delta^O_{111}(1,0)]\eta^2$, 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

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

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: $\Delta^O_{111}(1,0)$ and

TABLE I. Room-temperature experimental parameters (Ref. 12) used to calculate band-edge energy levels of $Ga_xIn_{1-x}P$ 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

assuming the usual quadratic bowing form

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

where b_P is the bowing parameters for property P. For the spin-orbit splitting we use the bowing[7] $b_{\Delta^{SO}}=-0.02$ eV,

and deformation potentials. These input values for $Ga_xIn_{1-x}P$ are given in Table I. For the second category of quantities, we use our previously calculated band structure values[7] $\Delta^O_{111}(1,0)=0.20$ 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:

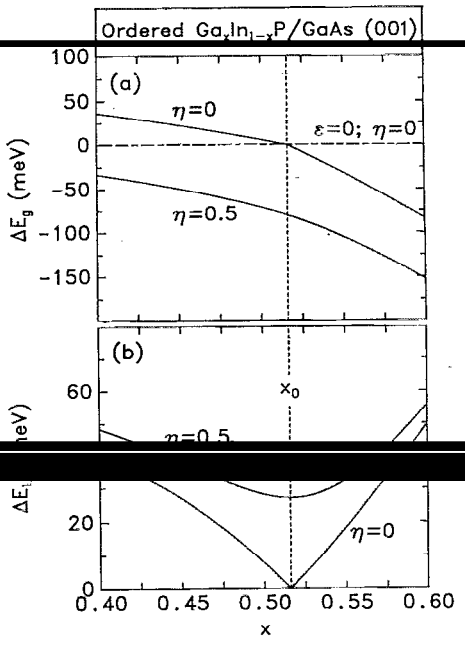
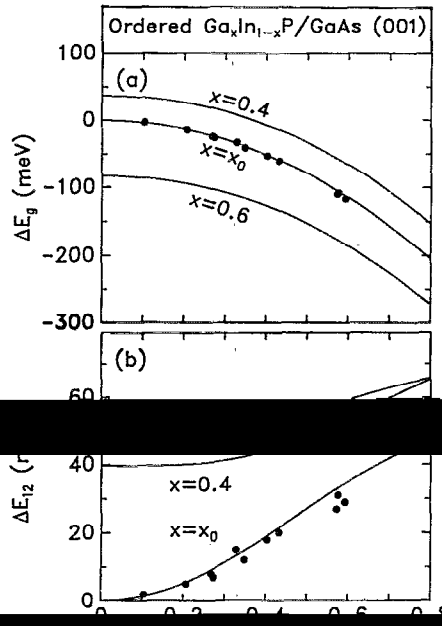


FIG. 1. (a) The band-gap reduction $\Delta E_g(\eta,\epsilon)\equiv E_g[\eta,\epsilon(x)]-E_g[0,0]$ as a function of composition x at $\eta=0$ and $\eta=0.5$. The dashed horizontal line

valence-band splitting ΔE_{12} of the strained alloy with ordering as function of composition x at $\eta=0$ and $\eta=0.5$.



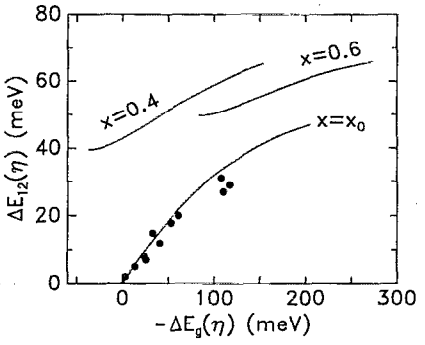


FIG. 3. The correlation between ΔE_g and ΔE_{12} as function of η at compo-

FIG. 2. Same as Fig. 1 but plotted as function of η at compositions $x=$

(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

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 GaInP[9] and GaInAs.[9]

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

circles 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-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*

($x \neq x_0$) 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 vise versa [Figs. 1(b) and 2(b)].

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

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