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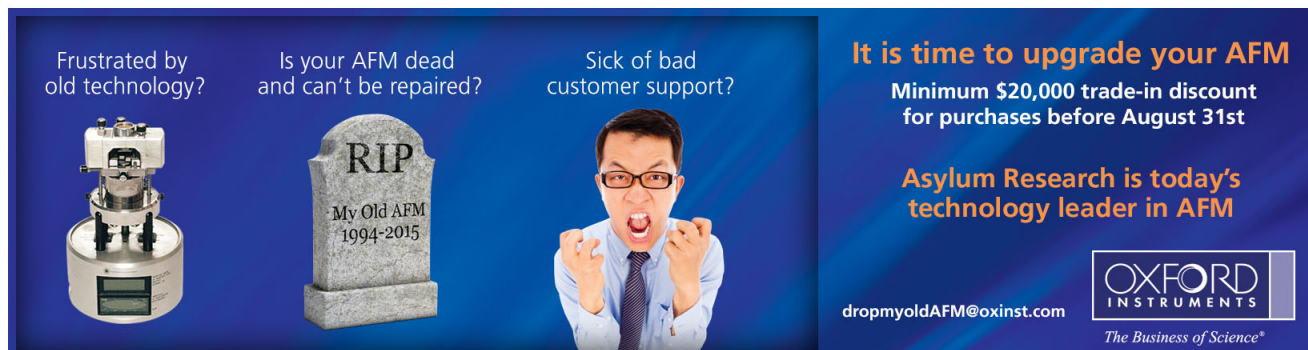
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Pressure dependence of optical transitions in ordered GaP/InP superlattices

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We have calculated the pressure coefficients α of a few optical transitions in (001), (111), (110), and (201) GaP/InP ordered superlattices using *ab initio* methods. The equilibrium atomic geometries under hydrostatic pressure are obtained by direct minimization of the elastic enthalpy. We find that (i) the pressure coefficient of the *lowest* energy transition is uniformly high, due to the Γ_{1c} character of the conduction-band minimum; (ii) the pressure coefficient of the transition to the *second lowest* conduction state at $\bar{\Gamma}$ distinguishes the (111)-oriented (CuPt) superlattice ($\alpha=4.0$ meV/kbar) from the remaining structures ($\alpha\approx-2$ meV/kbar). This is so because in CuPt we have L folding, while in the other structures we have X folding; (iii) the calculated pressures for the $\Gamma\rightarrow X$ crossover are 45, 43, 12, and 16 kbar for the (001), (111), (110), and (201) superlattices, respectively. These trends reflect the zero-pressure $\Gamma_{1c}-X_{1c}$ energy separation and the Γ_{1c} pressure coefficient of these structures. © 1994 American Institute of Physics.

Spontaneous ordering of random alloys into short-period superlattices has now been observed during vapor-phase growth in virtually all III–V semiconductor alloys.¹ As in artificially grown superlattices, Brillouin-zone folding is expected here too.² Table I gives the folding relations of a few states around the band gap for the ordered CuAu, CuPt, Y2, and chalcopyrite structures of GaInP₂. As Table I illustrates, these structures are short-period superlattices with atomic layers oriented along the (001), (111), (110), and (201) directions, respectively. We see that the low-lying $\bar{\Gamma}$ -type conduction states of these superlattices evolve from the Γ_{1c} , X_{1c} , X_{3c} , and L_{1c} states of the parent zinc-blende materials. Since the band-gap pressure coefficients of these *parent* zinc-blende states are rather different (see Table II), one expects that measurements of the band-gap pressure coefficients could aid in the identification of the *superlattice* structures present in a given sample. Furthermore, measurements of the pressure coefficients of a *few* optical transitions in a given superlattice could uncover the extent of the intervalley mixing, e.g., $\Gamma-X$ in the CuAu structure and $\Gamma-L$ in the CuPt structure. A few groups have started experiments in these directions.^{3,4} Here we provide theoretical predictions for the pressure coefficients of a few optical transitions in the main superlattice structures of GaP/InP. While a detailed comparison with the experiment would require knowing whether currently grown samples are substrate-constrained or unconstrained, our results for free-standing superlattices could provide useful guidelines for the interpretation of experimental results.

To follow the evolution of the band structure with pressure, one must first calculate the change in the unit-cell vectors and the cell-internal atomic positions induced by external hydrostatic pressure. For simple *zinc-blende* structures, there is but a single structural parameter, i.e., the cubic lattice constant a . To linear order in the external pressure P , its pressure dependence is given by $a(P)=a_0(1-P/3B_0)$, where a_0 is the equilibrium zero-pressure lattice constant and B_0 is the bulk modulus. The dependence of the structural parameters of a *superlattice* on the external pressure is more complicated. We can determine the atomic geometry at pres-

sure P by minimizing the zero-temperature enthalpy $H=E+PV$, where E is the internal energy and V is the volume of the system. In a periodic solid H is a function of the strain components $\{\epsilon_{\alpha\beta}\}$ and of the cell-internal atomic positions $\{\tau_{s,\alpha}\}$. By minimizing H with respect to these variables, one obtains the equilibrium atomic geometry of the system. We will refer to this approach as the “direct minimization method.” While, in principle, the internal energy E can be computed by *ab initio* local-density-approximation (LDA) methods,⁵ here we approximate E using the Keating’s valence-force-field (VFF) method,⁶ where all the bond-bending force constants involved in the ternary compounds (e.g., Ga–P–In, ...) have been fitted to the LDA total energies of 25 ordered Ga_{*m*}In_{*n*}P_{*m+n*} compounds.⁷ A conjugate-gradient minimization of the enthalpy then yields, for each external pressure P , the values of $\{\epsilon_{\alpha\beta}, \tau_{s,\alpha}\}$. As an example, the lattice constants a and c of a tetragonal, free-standing (GaP)₁/(InP)₁ (001) superlattice (CuAu structure) are shown as a function of the external pressure P in Fig. 1. We use the VFF method only to determine the structural parameters of the superlattice; the pressure coefficients are calculated by applying first-principles methods to these structures.

It is interesting to compare this direct minimization method with the conventional continuum elasticity approximation (CEA),⁸ in which the internal energy E is expanded to second order in strain around the equilibrium zero-pressure geometry. Neglecting terms of order $P\epsilon_{\alpha\beta}^2$ and higher, the enthalpy reads:

$$H = E_0 + \frac{1}{2} V_0 \sum_{\alpha\beta\gamma\eta} \epsilon_{\alpha\beta} c_{\alpha\beta\gamma\eta} \epsilon_{\gamma\eta} + P V_0 \left(1 + \sum_{\alpha} \epsilon_{\alpha\alpha} \right), \quad (1)$$

where $c_{\alpha\beta\gamma\eta}$ are the elastic constants:

$$c_{\alpha\beta\gamma\eta} = \frac{1}{V_0} \frac{\partial^2 E}{\partial \epsilon_{\alpha\beta} \partial \epsilon_{\gamma\eta}}, \quad (2)$$

and V_0 is the zero-pressure unit-cell volume. For every value of $\{\epsilon_{\alpha\beta}\}$ in this expansion we assume that the internal degrees

TABLE I. Folding relations between zinc-blende states (in parenthesis) and superlattice $\bar{\Gamma}$ states for four different GaP/InP ordered structures defined in the heading. The LDA-calculated energy differences $\Delta\epsilon_{\text{LDA}}$ (in eV, with reference to the VBM and the CBM), and the calculated pressure coefficients α (in meV/kbar, with reference to the VBM) are given for the $\bar{\Gamma}$ states of the completely ordered superlattices. The label CBM+ i denotes the i th level above the CBM, while VBM- i denotes the i th level below the VBM.

Name Superlattice Unit cell	CuAu (GaP) ₁ /(InP) ₁ (001) Tetragonal			CuPt (GaP) ₁ /(InP) ₁ (111) Trigonal			Y2 (GaP) ₂ /(InP) ₂ (110) Orthorhombic			Chalcopyrite (GaP) ₂ /(InP) ₂ (201) Tetragonal		
	Folding	$\Delta\epsilon_{\text{LDA}}$	α	Folding	$\Delta\epsilon_{\text{LDA}}$	α	Folding	$\Delta\epsilon_{\text{LDA}}$	α	Folding	$\Delta\epsilon_{\text{LDA}}$	α
	CBM+2	$\bar{\Gamma}_{1c}(X_{3c})$	1.21	0.3	$\bar{\Gamma}_{1c}(\Gamma_{15c})$	3.16	-0.5	$\bar{\Gamma}_{3c}(X_{3c})$	0.88	-0.8	$\bar{\Gamma}_{3c}(X_{3c})$	0.86
CBM+1	$\bar{\Gamma}_{4c}(X_{1c})$	0.85	-1.6	$\bar{\Gamma}_{1c}(L_{1c})$	1.07	4.0	$\bar{\Gamma}_{3c}(X_{1c})$	0.52	-2.2	$\bar{\Gamma}_{2c}(X_{1c})$	0.56	-2.3
CBM	$\bar{\Gamma}_{1c}(\Gamma_{1c})$	0.00	7.3	$\bar{\Gamma}_{1c}(\Gamma_{1c})$	0.00	6.4	$\bar{\Gamma}_{1c}(\Gamma_{1c})$	0.00	7.6	$\bar{\Gamma}_{1c}(\Gamma_{1c})$	0.00	8.1
VBM	$\bar{\Gamma}_{5v}(\Gamma_{15v})$	0.00	0.0	$\bar{\Gamma}_{3v}(\Gamma_{15v})$	0.00	0.0	$\bar{\Gamma}_{4v}(\Gamma_{15v})$	0.00	0.0	$\bar{\Gamma}_{4v}(\Gamma_{15v})$	0.00	0.0
VBM-1	$\bar{\Gamma}_{4v}(\Gamma_{15v})$	-0.23	-0.7	$\bar{\Gamma}_{1v}(\Gamma_{15v})$	-0.31	-0.7	$\bar{\Gamma}_{3v}(\Gamma_{15v})$	-0.13	-0.4	$\bar{\Gamma}_{5v}(\Gamma_{15v})$	-0.04	-0.2
VBM-2	$\bar{\Gamma}_{5v}(X_{5v})$	-2.53	-3.9	$\bar{\Gamma}_{3v}(L_{3v})$	-1.27	-2.3	$\bar{\Gamma}_{1v}(\Gamma_{15v})$	-0.15	-0.4	$\bar{\Gamma}_{5v}(X_{5v})$	-2.41	-4.0

of freedom $\{\tau_{s,\alpha}\}$ are relaxed to the minimum-energy configuration. Minimizing the enthalpy with respect to strain, we obtain:

$$\sum_{\gamma\eta} c_{\alpha\beta\gamma\eta}\epsilon_{\gamma\eta} = -P\delta_{\alpha,\beta}. \quad (3)$$

The solution of this linear system gives the strain components $\epsilon_{\alpha\beta}$ as a function of the external pressure P . When dealing with superlattice structures, however, one often resorts to the cubic approximation to continuum elasticity (CCEA), where (i) the elastic matrix is assumed to have the same form as in cubic materials, so that only the lattice constant can change with pressure, and (ii) in ternary systems the cubic elastic constants c_{11} and c_{12} are taken as the average of the elastic constants of the binary constituents. In Fig. 2 we compare the ratio c/a between the lattice constants of a tetragonal (GaP)₁/(InP)₁ (001) superlattice obtained by the CCEA method with that resulting from the direct minimization of the VFF enthalpy. While c/a is constant in the CCEA approximation, it increases almost linearly with pressure in

the VFF method, suggesting that the CCEA elastic constants are somewhat different from the more accurate VFF ones. In the following we will use therefore the VFF direct minimization approach to determine the atomic geometry of GaP/InP superlattices under hydrostatic pressure.

The band structure at the atomic configuration corresponding to a given external pressure is calculated using the LDA⁵ as implemented by the linearized augmented plane wave method (LAPW).⁹ The calculation is semirelativistic for the valence states; spin-orbit coupling is thus neglected. The pressure coefficients relative to the valence-band maximum (VBM) are displayed in Tables I and II. From these results we can conclude that:

(i) In all four superlattices the lowest-energy optical transition evolves from a Γ_{1c} -folding state, so its pressure coefficient is rather high. However, mixing with off- Γ states (e.g., X_{3c} in CuAu, L_{1c} in CuPt) lowers the pressure coefficient with respect to the average of the Γ_{1c} values of the binaries (8.2 meV/kbar). The extent of this lowering effect depends on the pressure coefficients of the folded zinc-blende states (Table II) and on the strength of the intervalley mixing. Note that in the chalcopyrite structure, where the

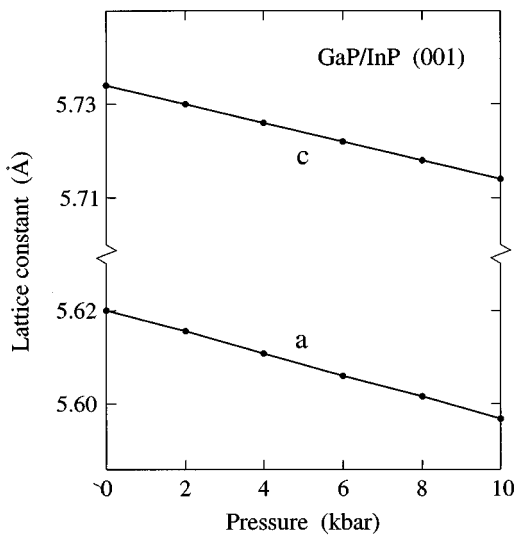


FIG. 1. Pressure dependence of the lattice constants a and c of a free-standing (GaP)₁/(InP)₁ (001) superlattice (CuAu structure), as obtained from the VFF direct minimization method.

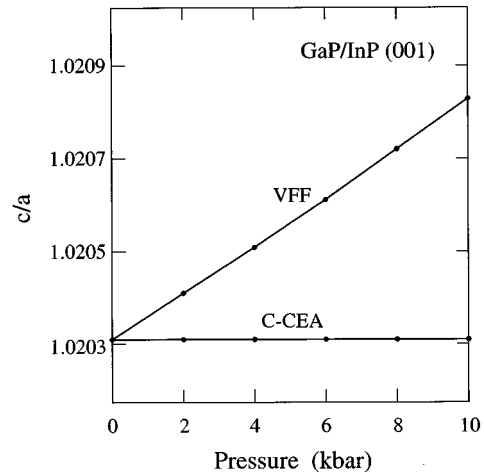


FIG. 2. Pressure dependence of the c/a lattice-constant ratio for the CuAu structure, as obtained from the cubic approximation to continuum elasticity (CCEA) and from the VFF direct minimization method (VFF).

TABLE II. LDA-calculated pressure coefficients in meV/kbar (with respect to the VBM) of bulk GaP and InP.

	Γ_{1c}	X_{1c}	X_{3c}	L_{1c}
GaP	9.0	-2.0	-0.9	3.3
InP	7.4	-1.9	0.2	3.4

mixing with off- Γ states is rather weak, the pressure coefficient is very close to the binary average.

(ii) The pressure coefficients given in Table I correspond to *perfect* long-range order (LRO parameter $\eta=1$), where the admixture with off- Γ states is maximal. The pressure coefficients for lower degrees of order ($0 < \eta < 1$) can be derived from:¹⁰

$$\alpha(\eta) = \alpha(0) + \eta^2[\alpha(1) - \alpha(0)]. \quad (4)$$

Approximating the pressure coefficient $\alpha(0)$ of the random alloy with the average of the binaries (Table II), we obtain $\alpha_{\Gamma}(0)=8.2$ meV/kbar and $\alpha_X(0)=-2.0$ meV/kbar. This compares well with the previously measured pressure coefficients of the disordered $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$ alloy: $\alpha_{\Gamma}(0)=8.8$,³ 8.6 ± 0.6 ,¹¹ and 8.4 ± 0.2 (Ref. 12) meV/kbar, and $\alpha_X(0)=-2.0 \pm 0.2$ meV/kbar.¹² In all the four structures considered here we have $\alpha_{\Gamma}(1) < \alpha_{\Gamma}(0)$, so from Eq. (4) it follows that the pressure coefficient of the conduction-band minimum (CBM) *decreases* with increasing ordering.

(iii) The VBM \rightarrow CBM+1 transition distinguishes the L_{1c} -folding CuPt structure ($\alpha=4.0$ meV/kbar) from the remaining X_{1c} -folding superlattice structures ($\alpha \approx -2$ meV/kbar).

(iv) Since the Γ_{1c} -folding states have large, *positive* pressure coefficients, while the X_{1c} -folding states have *negative* pressure coefficients, one expects that above a critical pressure P_c the X_{1c} -folding states will become lower in energy than the Γ_{1c} -folding states. This $\Gamma \rightarrow X$ crossover has been observed both in *disordered* and in *ordered* $\text{Ga}_x\text{In}_{1-x}\text{P}$ alloys.^{3,11,13,14} In pure InP we find that the $\Gamma \rightarrow X$ crossover occurs at 103 kbar, in good agreement with the extrapolated value of 104 kbar obtained by Müller *et al.*¹⁵ from photoluminescence measurements. When GaP is added to InP to form the $\text{Ga}_x\text{In}_{1-x}\text{P}$ alloy, the X -like conduction band is lowered in energy with respect to the CBM (it becomes the CBM for $x \geq 0.7$ at zero pressure¹⁴). Thus, the $\Gamma \rightarrow X$ transition pressure is expected to decrease as GaP is added. Using the LDA-corrected $\Gamma_{1c}-X_{1c}$ gaps at zero pressure and our calculated pressure coefficients we estimate P_c to be 45 kbar in CuAu, 43 kbar in CuPt, 12 kbar in Y2 and 16 kbar in chalcopyrite. Note that the values of P_c are larger in the

CuAu and CuPt structures than in the Y2 and chalcopyrite structures, because in the former case the $\Gamma_{1c}-X_{1c}$ energy separation is larger and the Γ_{1c} pressure coefficient is smaller.

(v) For the disordered $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$ alloy we can estimate P_c using our approximated values for $\alpha_{\Gamma}(0)$ and $\alpha_X(0)$ and the zero-pressure $\Gamma_{1c}-X_{1c}$ energy separation of 0.29 eV.¹² This gives $P_c=28$ kbar. Thus, we predict a *lower* transition pressure in the disordered alloy than in the CuAu and CuPt ordered structures. However, the Y2 structure, if present in the sample, will show a $\Gamma \rightarrow X$ crossover at a lower pressure than the disordered phase.

(vi) Uchida *et al.*³ identified an emission with *negative* pressure coefficient $\alpha = -0.5$ meV/kbar from a state located ~ 0.28 eV above the direct gap at zero pressure. They suggested that this could come from the *second* (X -folded) $\bar{\Gamma}$ conduction state of the Y2 structure. However, the *first* (Γ -folded) conduction state of the Y2 structure is expected to be higher in energy (with respect to the VBM) than the CBM of the CuPt structure (our calculated energy difference is ~ 0.2 eV). Hence, an emission from the Y2 CBM should have been observed if sufficiently large domains of Y2 were present in the sample.

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