Fingerprints of CuPt ordering in III-V semiconductor alloys: Valence-band splittings, band-gap reduction, and x-ray structure factors

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Spontaneous CuPt ordering induces a band-gap reduction $\mathrm{D}E_g$ relative to the random alloy, a crystal field splitting D_{CF} at valence-band maximum, as well as an increase of spin-orbit splitting D_{SO}. We calculate these quantities for $\mathrm{Al}_x\mathrm{In}_{12x}\mathrm{P}$, $\mathrm{Al}_x\mathrm{In}_{12x}\mathrm{As}$, $\mathrm{Ga}_x\mathrm{In}_{12x}\mathrm{P}$, and $\mathrm{Ga}_x\mathrm{In}_{12x}\mathrm{As}$ using the local density approximation ~LDA!, as well as the more reliable LDA-corrected formalism. We further provide these values and the valence-band splittings $\mathrm{D}E_{12}$ ~between $\bar{\mathrm{G}}_{4,5v}$ and $\bar{\mathrm{G}}_{6v}^{(1)}$! and $\mathrm{D}E_{13}$ ~between $\bar{\mathrm{G}}_{4,5v}$ and $\bar{\mathrm{G}}_{6v}^{(2)}$! for these materials as a function of the degree h of long range order. In the absence of an independent measurement of h, experiment is currently able to deduce only the ratio $\mathrm{D}E_g/\mathrm{D}_{\mathrm{CF}}$. Our LDA-corrected results for this quantity compare favorably with recent experiments for $\mathrm{Ga}_x\mathrm{In}_{12x}\mathrm{P}$ and $\mathrm{Ga}_x\mathrm{In}_{12x}\mathrm{As}$, but not for $\mathrm{Al}_x\mathrm{In}_{12x}\mathrm{P}$, where our calculation does not support the experimental assignment. The ''optical LRO parameter h'' can be obtained by fitting our calculated $\mathrm{D}E_g(h)$ to the measured $\mathrm{D}E_g(h)$, and by expressing the measured $\mathrm{D}E_{12}(h)$ and $\mathrm{D}E_{13}(h)$ in terms of our calculated $\mathrm{D}_{\mathrm{CF}}(h)$ and $\mathrm{D}_{\mathrm{SO}}(h)$. We also provide the calculated x-ray structure factors for ordered alloys that can be used experimentally to deduce h independently. @S0163-1829~98!01715-9#

I. INTRODUCTION

Spontaneous CuPt-like ordering of isovalent $A_xB_{12x}C$ semiconductor alloys has been widely observed in vapor phase growth of many III-V systems on ~001! substrates.[1] The ordered phase consists of alternate cation monolayer planes $A_{x1h/2}B_{12x2h/2}$ and $A_{x2h/2}B_{12x1h/2}$ stacked along the @111# ~or equivalent! directions, where $0<h<1$ is the long-range order ~LRO! parameter. $h51$ corresponds to the perfectly ordered phase, while $h50$ corresponds to the disordered phase ~Fig. 1!. In *spontaneously* ordered semiconductor alloys, the degree of LRO h is not perfect. The degree of ordering depends on growth temperature, growth rates, III/V ratio, substrate misorientation, and doping.[1]

When the zinc-blende ~ZB! disordered alloy forms the long-range ordered CuPt superlattice, the unit cell is doubled, the Brillouin zone is reduced by half, and the point-group symmetry is changed from T_d to C_{3v}. These lead to a series of predicted and observed changes in material properties,[1–3] including the appearance of pyroelectricity,[4] birefringence,[5,6] modified NMR chemical shifts,[7,8] new effective masses,[9,10] new pressure deformation potentials,[11] polarization of spin,[12] and light,[13–15] new Raman peaks[16,17] and the appearance of a transition to high-energy folded-in states.[18,19] Here, we focus on two other type of changes, namely, ~i! new x-ray diffraction spots that appear at $\$\mathbf{G}_{\mathrm{ZB}}\%1(1/2,1/2,1/2)$, where $\$\mathbf{G}_{\mathrm{ZB}}\%$ are zinc-blende reciprocal lattice vectors, and ~ii! the changes of electronic and optical properties near the band edge. These changes in the ordered alloy are due to the fact that in the ordered phase two zinc-blende **k** points ~and states associated with them! fold into a single **k** point in the CuPt Brillouin zone. Those folded states that have the same superlattice symmetry can couple to each other. This coupling leads to energy-level shifts and to splitting of those states that were degenerate in the random alloy.[14,19]

In the absence of spin-orbit coupling, the valence-band maximum ~VBM! of the *random* alloy has G_{15v} symmetry and the conduction-band minimum ~CBM! has G_{1c} symmetry. In the *ordered* material, the G_{15v} state splits into $\bar{\mathrm{G}}_{3v}(\mathrm{G}_{15v})$ and $\bar{\mathrm{G}}_{1v}(\mathrm{G}_{15v})$ ~we denote ordered states with an overbar and indicate the zinc-blende parentage in parentheses! while the two lowest conduction states at $\bar{\mathrm{G}}$ are $\bar{\mathrm{G}}_{1c}(\mathrm{G}_{1c})$ and $\bar{\mathrm{G}}_{1c}(L_{1c})$.

$$\Delta E_{12}(\eta) = \frac{1}{2}\left[\Delta_{SO}(\eta) + \Delta_{CF}(\eta)\right] - \frac{1}{2}\left\{\left[\Delta_{SO}(\eta) + \Delta_{CF}(\eta)\right]^2 - \frac{8}{3}\Delta_{SO}(\eta)\Delta_{CF}(\eta)\right\}^{1/2},$$

$$\Delta E_{13}(\eta) = \frac{1}{2}\left[\Delta_{SO}(\eta) + \Delta_{CF}(\eta)\right] + \frac{1}{2}\left\{\left[\Delta_{SO}(\eta) + \Delta_{CF}(\eta)\right]^2 - \frac{8}{3}\Delta_{SO}(\eta)\Delta_{CF}(\eta)\right\}^{1/2}, \quad (4)$$

where $\Delta_{SO}(\eta)$ is the spin-orbit splitting and $\Delta_{CF}(\eta) = \bar{\Gamma}_{3v}$
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thus, there is a larger perturbation in the valence band of $Al_{0.5}In_{0.5}X$ than in $Ga_{0.5}In_{0.5}X$.

(iii) The band-gap reduction $\Delta E_g(1)$ is smaller in $Al_{0.5}In_{0.5}X$ than in $Ga_{0.5}In_{0.5}X$. This can be understood by noticing that (1) the LDA atomic s orbital energies of Al, Ga, and In are nonmonotonic, namely, -7.9, -9.3, and -8.6 eV, respectively, and (2) atomic relaxation in lattice mismatch common-anion alloys tends to shift the charge from the long bond (In-X) to the short bonds (Ga-X in $Ga_{0.5}In_{0.5}X$ and Al-X in $Al_{0.5}In_{0.5}X$).[32] Consequently, the band-gap reduction due to atomic relaxation is larger in $Ga_{0.5}In_{0.5}X$ (since Ga receives charge, and its s is deeper in energy than In), but smaller in $Al_{0.5}In_{0.5}X$ (since Al receives charge, and its s is shallower in energy than In).

(iv) Relative to the random alloy, the VBM wave function of the ordered compounds is more localized on the cation having larger atomic number.[33] Thus, $[\Delta_{SO}(1)-\Delta_{SO}(0)] > 0$. However, for common-anion systems Δ_{SO} of the two binary constituents are similar, thus the ordering-induced increase $[\Delta_{SO}(1)-\Delta_{SO}(0)]$ is rather small (0.00–0.02 eV). The increase is slightly greater for $Al_{0.5}In_{0.5}X$ than for $Ga_{0.5}In_{0.5}X$, because of the larger atomic number difference between Al and In.

III. LDA CORRECTIONS

It is well known[24] that the LDA underestimates the band gap. This is seen in Table II and Table III where our LDA gaps of binary zinc-blende compounds are compared with experiment.[27] Since the level repulsion between the states depends on the energy separations, these LDA errors will affect the calculated crystal-field splitting Δ_{CF} and the band-gap reduction ΔE_g (the effect on Δ_{SO} is, however, negligible).

Several methods have been proposed to correct these LDA errors, e.g., calculating the quasiparticle (QP) energies.[26] In this study, we use the fact that the LDA errors $\epsilon_{n,k}^{LDA}-\epsilon_{n,k}^{expt}$ for band n and wave vector k are known for the binary constituents (Table II and Table III). We thus design a cure for LDA that reproduce, via a fit, the state-dependent errors in the *zinc-blende binaries*, and then use this approach for the pseudobinary alloys $A_{1-x}B_xC$, assuming that the LDA error does not change with alloying. Instead of shifting energy bands rigidly, we use a self-consistent approach with *atom-dependent LDA corrections*. Specifically, we add to the LDA calculations external potentials[34] inside the muffin-tin

~i! $D_{CF}(1)$ is reduced for $Al_{0.5}In_{0.5}P$, $Al_{0.5}In_{0.5}As$, and $Ga_{0.5}In_{0.5}P$, but increased for $Ga_{0.5}In_{0.5}As$. This can be understood by noticing that the LDA correction shifts the $\bar{G}_{1c}(G_{1c})$ upwards. For $Al_{0.5}In_{0.5}P$, $Al_{0.5}In_{0.5}As$, and $Ga_{0.5}In_{0.5}P$ alloys, where LDA calculations already give positive band gaps, the upward shift of $\bar{G}_{1c}(G_{1c})$ reduces the repulsion between the $\bar{G}_{1c}(G_{1c})$ and $\bar{G}_{1v}(G_{15v})$, thus reducing the crystal-field splitting. On the other hand, LDA calculation gives a negative band gap for $Ga_{0.5}In_{0.5}As$, i.e., $\bar{G}_{1c}^{LDA}(G_{1c})$ is below $\bar{G}_{1v}^{LDA}$

gree of ordering, we have calculated the static x-ray structure factors $\rho(\mathbf{G})$ of the fully ordered $AlInP_2$, $AlInAs_2$, $GaInP_2$, and $GaInAs_2$. The structure factors $\rho(\mathbf{G})$ are the Fourier transform of the electron charge density $\rho(\mathbf{r})$, i.e.,

$$\rho(\mathbf{G}) = \frac{1}{V}\int_V \rho(\mathbf{r}) e^{i\mathbf{G}\cdot\mathbf{r}} d\mathbf{r}. \tag{9}$$

Here $\mathbf{G}$ is the reciprocal lattice vector and V is the unit cell volume. The diffraction intensity I is proportional to $|\rho(\mathbf{G})|^2$.

Our calculated results are shown in Table V. We find that (i) the structure factors for the ordered alloy taken at the ZB allowed $\{\mathbf{G}_{ZB}\}$ are very similar to those of the random alloys (not shown), except for some small splittings due to the lower symmetry of the ordered alloy. However, (ii) new structure factors appear at $\{\mathbf{G}_{ZB}\}+(1/2,1/2,1/2)$ in the ordered alloy that do not exist in the perfectly random alloy. Observation of $\rho(\mathbf{G})$ at these superstructure spots (marked with an asterisk in Table V) would be one of the strongest indications of the existence of the ordered phase. Since $\rho(\mathbf{G})$ for these new structure factors is proportional to η^2, accurate measurement of the intensity of the diffraction spectrum $I(\mathbf{G},\eta)$ can, in principle, be used to derive the degree of order η by comparing it with the calculated values for perfectly ordered systems (Table V).

In an actual experimental measurement at finite temperature, the measured intensity is reduced by the thermal vibration of the lattice. The dynamic (temperature) effect is often approximated by the Debye-Waller factors.[38] In this approximation the relation between the measured dynamic structure factor $\rho_{expt}(\mathbf{G},\eta)$ and the calculated static structure factor $\rho_{calc}(\mathbf{G},\eta)$ is

$$\rho_{expt}(\mathbf{G},\eta) = \rho_{calc}(\mathbf{G},\eta) e^{-B(T)G^2}, \tag{10}$$

where $B(T)$ is a temperature-dependent constant. Since $\rho(\mathbf{G}_{ZB},\eta)$ is essentially ordering independent for the zinc-blende allowed $\mathbf{G}_{ZB}$ vectors, measuring $\rho_{expt}(\mathbf{G}_{ZB})$ can be used to derive the value B from Eq. (10) and Table V. This B can in turn be used in Eq. (10) to calculate $\rho_{calc}(\mathbf{G},\eta)$ from measured $\rho_{expt}(\mathbf{G})$ for the superstructure sports. Finally, the obtained $\rho_{calc}(\mathbf{G},\eta)$ can be used to derive the ordering parameters η using Eq. (5) and the values given in Table V. Experimental testing of our predictions are called for.

VI. SUMMARY

We have calculated the ordering-induced changes in the crystal-field splitting, spin-orbit splitting, and band gap relative to the random alloy for $Al_{0.5}In_{0.5}P$, $Al_{0.5}In_{0.5}As$, $Ga_{0.5}In_{0.5}P$, and $Ga_{0.5}In_{0.5}As$ alloy using the local density approximation, as well as the more reliable LDA-corrected formalism. We provide these values for these materials as a function of the degree η of long-range order. Our LDA-corrected results compare favorably with recent experiments for $Ga_xIn_{1-x}P$ and $Ga_xIn_{1-x}As$, but not for $Al_xIn_{1-x}P$, where our calculation does not support the experimental assignment. We also calculated x-ray structure factors for these ordered alloys, which can be used experimentally to deduce the ordering parameter η.

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