Theory of reflectance-difference spectroscopy in ordered III-V semiconductor alloys

Su-Huai Wei and Alex Zunger
National Renewable Energy Laboratory, Golden, Colorado 80401
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Spontaneous CuPt-like ordering in III-V alloys causes an anisotropy in the intensities of the transitions between the split valence-band maximum states and the conduction-band minimum. This optical anisotropy has been detected in ordered III-V alloys using modulated reflectivity, and more recently, using reflectance-difference spectroscopy (RDS). We derive here a general formula relating the ordering-induced bulk RDS intensity with the degree of long-range order. We show that the previously neglected coupling between the spin-orbit split-off band and the crystal-field split-off band is crucial for determining the RDS intensity of the Ga$_x$In$_{1-x}$P alloy.

I. INTRODUCTION

Spontaneous CuPt-like ordering of $A_xB_{1-x}C$ alloys has been widely observed in vapor-phase growth of many III-V systems on (001) substrates. The ordered phase consists of alternate cation monolayer planes $A_x+(y/2)B_{1-x}-(y/2)$ and $A_x-(y/2)B_{1-x}+(y/2)$ stacked along the [111] or [11$ar{1}$] directions, where $0 \leq y \leq 1$ is the long-range order parameter. Perfect ordering ($y=1$) corresponds to successive planes of pure $A$ followed by pure $B$, etc. CuPt-type ordering was predicted$^{2,3}$ to cause a splitting at the valence-band maximum (VBM) and a lowering of the band gap relative to the random alloy. These effects have been observed in electoreflectance,$^{4,5}$ polarized photoluminescence,$^{6}$ and polarized piezoreflectance$^7$ measurements. These experiments$^{4-7}$ have demonstrated that due to the lower symmetry of the ordered bulk alloy, there is a strong anisotropy in the optical responses for light polarized along the $\hat{e}_1=[110]$ and $\hat{e}_2=[110]$ directions. We have previously$^9$ analyzed these experiments, explaining the origin of the polarization anisotropy. Recently, Luo et al.$^9$ measured the ordering-induced reflectance difference for light polarized along $\hat{e}_1$ and $\hat{e}_2$ using reflectance-difference spectroscopy (RDS). RDS was originally proposed by Aspnes and coworkers$^{10}$ to measure surface-induced optical anisotropy in cubic semiconductors for which $R_{\hat{e}_1}=R_{\hat{e}_2}$ in the interior of the sample. Since, as noted above, optical anisotropy also exists in bulk CuPt-ordered alloys,$^{5-8}$ measurements of RDS can shed light on the degree of bulk ordering, if there is no interference from surface effects. In this paper we derive a simple general formula relating the near-band-edge bulk RDS intensity to the degree of long-range order (measured by the ordering parameter $y$).

We find that our calculated near-band-edge peak RDS intensity agrees well with the experimental results of Luo et al.$^9$ for Ga$_0.4$In$_{0.6}$P. We show that the coupling between the spin-orbit split-off band and the crystal-field split-off band is important in determining the RDS intensity for this alloy due to its relatively small spin-orbit splitting and large crystal-field splitting. Previous theory$^9$ using a 4x4 Luttinger model and neglecting coupling with the spin-orbit split-off band is found here to be inadequate for interpreting the experimental results$^9$ for the Ga$_x$In$_{1-x}$P alloy.

II. RDS INTENSITY

RDS is defined as

$$\frac{\Delta R}{R} = 2 \frac{R_{\hat{e}_1} - R_{\hat{e}_2}}{R_{\hat{e}_1} + R_{\hat{e}_2}},$$

(1)

where the reflectance coefficient $R_{\hat{e}}$ for polarization $\hat{e}$ is given by

$$R_{\hat{e}} = \frac{(n_{\hat{e}} - 1)^2 + k_{\hat{e}}^2}{(n_{\hat{e}} + 1)^2 + k_{\hat{e}}^2},$$

(2)

Here $n$ and $k$ are real and imaginary parts of the complex refraction index and are related to the complex dielectric function $\epsilon = \epsilon_1 + i\epsilon_2$ by the relations

$$n^2 = \frac{1}{2} \left[ \epsilon_1 + \sqrt{\epsilon_1^2 + \epsilon_2^2} \right],$$

(3)

and

$$k = \frac{\epsilon_2}{2n}.$$

(4)

Hence, RDS can be obtained from Eqs. (1)–(4) by calculating the complex dielectric function $\epsilon$.

To obtain the dielectric function near threshold, we use the one-electron model.$^{11}$ For transition energy $E$ near the band edge this gives

$$\epsilon_2(\hat{e}, \eta, E) \propto \sum_v I_{v,\hat{e}}(\hat{e}, \eta) \frac{\rho_{\hat{e},\eta}(E)}{E^3}.$$

(5)

Here the sum is over the top valence-band states, $I_{v,\hat{e}}(\hat{e}, \eta)$ is proportional to the square of the dipole transition matrix element between valence band $v$ and conduction-band minimum $c$, and $\rho_{\hat{e},\eta}(E)$ is the joint density of states at energy $E$. In Eq. (5) the angular and momentum dependences of the matrix elements $I_{v,\hat{e}}$ in a small energy range (of the order of crystal-field splitting)
are neglected. We also assume that for a small energy interval the joint density of states \( \rho_{c,v}(E) \) can be obtained using the parabolic band model, thus

\[
\rho_{c,v}(E) \propto (2m^*_v)^{3/2} \sqrt{E - E_{\text{min},v}},
\]

where \( m^*_v = (m_m + m_e)/(m_m + m_e) \) is the reduced valence-conduction effective mass, and \( E_{\text{min},v} \) is the minimum transition energy from band \( v \) to the conduction-band minimum. These are good approximations for ordered\(^9\) and disordered\(^11\) alloys. In CuPt-ordered alloys the top of the valence bands (denoted \( \Gamma_6 \) and \( \Gamma_7 \) in the disordered alloy) consists of the three states \( \Gamma_{40,50} \equiv |1\rangle \), \( \Gamma_{60} \equiv |2\rangle \), and \( \Gamma_{60} \equiv |3\rangle \). The transitions \( |1\rangle \rightarrow |c\rangle \), \( |2\rangle \rightarrow |c\rangle \), and \( |3\rangle \rightarrow |c\rangle \) from these valence states to the conduction-band minimum \( |c\rangle \) occur at the energies denoted \( E_{\text{min},c} = E_g, E_g + \Delta E_{12} \), and \( E_g + \Delta E_{13} \), respectively, where \( \Delta E_{12} = E_{12} - E_{13} \). Using Kramers-Kronig relations\(^1\) we can obtain the real part of the dielectric function \( \varepsilon_1 \) from \( \varepsilon_2 \) of Eq. (5). Near the band edge this gives\(^12\)

\[
\varepsilon_1(\varepsilon, E) - \varepsilon_0 \propto \sum_i (2m^*_v)^{3/2} I_{c,v}(\varepsilon, \eta) \sqrt{E_{\text{min},c} - E}/E^2,
\]

where \( \varepsilon_0 \) is the static dielectric constant.

RDS of Eq. (1) can be calculated directly using Eqs. (1)–(7). However, for most III-V alloys, near the band edge \( E - E_{\text{min}} \ll E_g \), \( \Delta E_{12} \ll E_g \) and \( \Delta E_{13} \ll E_g \), and also near the band edge \( \varepsilon_2 \ll \varepsilon_1 \). Hence, to a good approximation (keeping the lowest-order terms of \( \sqrt{E_{\text{min},c} - E} \) in the Taylor expansion), near-band-edge RDS can be expressed as

\[
\frac{\Delta R}{R} = \beta \sum_i (2m^*_v)^{3/2} \Delta I_{c,v}(\varepsilon) \sqrt{E_{\text{min},c} - E},
\]

where the intensity difference at \( \varepsilon_1 \) and \( \varepsilon_2 \) is

\[
\Delta I_{c,v}(\eta) = I_{c,v}(\varepsilon_1, \eta) - I_{c,v}(\varepsilon_2, \eta),
\]

and the coefficient \( \beta \) is

\[
\beta = \frac{2e^2 p_{cv}^2}{\hbar^2 m^*_c n_0 (n_0 - 1)}.
\]

Here \( \hbar \omega_k = E_g, m_0 \) is the free-electron mass, \( n_0 \) is the refraction index in the absence of ordering, and \( P_{cv} = \langle x, P_x, y \rangle \) is the Kane matrix element.\(^11,13\) Equation (8) indicates that RDS can be calculated readily once the normalized dipole matrix elements \( \Delta I_{c,v}(\eta) \) [Eq. (9)] and the transition energies \( E_{\text{min},c}(\eta) \) are known. In Sec. III we will show how these quantities can be calculated.

### III. Matrix Elements and Transition Energies

To calculate \( I_{c,v}(\varepsilon, \eta) \) and \( E_{\text{min},c}(\eta) \), we follow our method given in Ref. 8 in which the spin-up and spin-down states for \( p_x, p_y, \) and \( p_z \) orbitals are allowed to couple by ordering and by spin-orbit interactions. This neglects \( s \) and \( d \) character at top of the valence bands. Under this assumption, the \( \Gamma_{40,50}, \Gamma_{60} \), and \( \Gamma_{60} \) valence states for \( \{111\} \) ordering can be described by the \( 6 \times 6 \) Hamiltonian:\(^8\)

\[
H_\eta(\eta) = \frac{1}{3} \left[
\begin{array}{ccccccc}
0 & \Delta^0 - i \Delta^\text{SO} & \Delta^0 & 0 & 0 & \Delta^\text{SO} \\
\Delta^0 + i \Delta^\text{SO} & 0 & -\Delta^0 & 0 & 0 & -i \Delta^\text{SO} \\
\Delta^0 & -\Delta^0 & 0 & -\Delta^\text{SO} & 0 & 0 \\
0 & 0 & -\Delta^\text{SO} & 0 & 0 & 0 \\
\Delta^\text{SO} & i \Delta^\text{SO} & 0 & \Delta^0 & 0 & \Delta^0 \\
0 & i \Delta^\text{SO} & -\Delta^0 & 0 & 0 & 0
\end{array}
\right].
\]

Here \( \Delta^0(\eta) \) is the crystal-field splitting due to ordering and \( \Delta^\text{SO}(\eta) \) is the spin-orbit splitting. We have previously shown\(^2\) that these can be expressed in terms of the values for completely ordered (\( \eta = 1 \)) and perfectly random (\( \eta = 0 \)) alloys as

\[
\Delta^0(\eta) = \Delta^0(0) + \eta^2 [\Delta^0(1) - \Delta^0(0)],
\]

\[
\Delta^\text{SO}(\eta) = \Delta^\text{SO}(0) + \eta^2 [\Delta^\text{SO}(1) - \Delta^\text{SO}(0)].
\]

The end-point parameters \( \Delta^0(0), \Delta^0(1), \Delta^\text{SO}(0), \) and \( \Delta^\text{SO}(1) \) are obtained from first-principles band theory.\(^14\) If the film is not lattice matched to the substrate, an additional strain term, neglected here, has to be added to the diagonal blocks of Eq. (11).\(^8\)

The eigenvalues and eigenvectors of the valence states are obtained by diagonalizing Eq. (11). The energies of the three spin-degenerate levels \( E_1, E_2, \) and \( E_3 \) (for \( \Gamma_{40,50}, \Gamma_{60}^{(1)} \) and \( \Gamma_{60}^{(2)} \) states, respectively, in decreasing order) are

\[
E_1(\eta) = \frac{1}{2} [\Delta^\text{SO} + \Delta^0],
\]

\[
E_2(\eta) = -\frac{1}{3} [\Delta^\text{SO} + \Delta^0] + \frac{1}{2} \sqrt{[\Delta^\text{SO} + \Delta^0]^2 - \frac{8}{3} \Delta^\text{SO} \Delta^0},
\]

\[
E_3(\eta) = -\frac{1}{3} [\Delta^\text{SO} + \Delta^0] - \frac{1}{2} \sqrt{[\Delta^\text{SO} + \Delta^0]^2 - \frac{8}{3} \Delta^\text{SO} \Delta^0}.\]  

(13)
where $\Delta^{SO} = \Delta^{SO}(\eta)$ and $\Delta^{O} = \Delta^{O}(\eta)$ are given by Eq. (12). For the random alloy $E_1$ and $E_2$ are degenerate, since $\Delta^{O}(\eta = 0) = 0$. Notice that we apply the $\eta^2$ rule to $\Delta^{O}$ and $\Delta^{SO}$ [Eq. (12), not to $E(\eta)$], thus, due to the coupling between the crystal-field and spin-orbit splittings, $E_1$ and $E_2$ in Eq. (13) have more complicated functional forms than the $\eta^2$ dependence.

We assume that the lowest conduction state $\Gamma_{6c}$ consists of pure spin-up and spin-down $s$ orbitals. Hence the conduction-band Hamiltonian can be represented by a $2 \times 2$ diagonal matrix with

$$E_c(\eta) = E_g(0) + \Delta E_g(1)\eta^2 + \frac{1}{2} [\Delta^{SO}(\eta) + \Delta^{O}(\eta)].$$  \hspace{1cm} (14)

Here $E_g(0)$ is the band gap of random alloy and $\Delta E_g(1) = E_g(1) - E_g(0)$ is the band-gap reduction of the fully ordered alloy. By definition, $E_{min,c}(\eta) = E_c(\eta) - E_g(0)$ in Eqs. (7) and (8).

The valence eigenstates $\Psi_e$ of Eq. (11) are linear combinations of the six basis functions $\{p, \tilde{\sigma}\}$, where $\tilde{\sigma}$ are the spinors parallel or antiparallel to the $z$ direction. The conduction states are $\Psi_c = s \tilde{\sigma}$. The transition intensity between $\Psi_e$ and $\Psi_c$ is proportional to the matrix element squared $I_{c,e}(\tilde{\sigma}, \tilde{\sigma}) = |\langle \Psi_c | H_{int} | \Psi_e \rangle |^2$, where $H_{int} \propto \delta$ is the interaction Hamiltonian. For linearly polarized light along the $\tilde{\sigma} = [l,m,n]$ direction we have $H_{int} \propto lx + my + nz$. We chose the normalization constant $\alpha$ such that $I_{c,e}$ is a dimensionless quantity and $\sum_0 = -1, 2, 3 |I_{c,e}|^2 = 2$. This specifies the parameter $\beta$ given in Eq. (10). The transition matrix elements can now be calculated by writing the orbital wave functions and $H_{int}$ in terms of the spherical harmonics $Y_{l,m}$ and by noticing that for allowed dipole transition $\Delta M = \pm 1$. This gives the simple selection rule

$$\langle s \tilde{\sigma} | x_\mu \tilde{\sigma} \rangle = \Delta_{\mu} \delta_{\mu,0}.$$  \hspace{1cm} (15)

Figure 1 shows our calculated difference in matrix element squared $I_{c,e}(\tilde{\sigma}_{110}, \eta) - I_{c,e}(\tilde{\sigma}_{110}, 0)$ for the three transitions $\nu = 1, 2$, and 3 in $Ga_0.5In_0.5P$ [Fig. 1(a)] and $Ga_0.3In_0.7As$ [Fig. 1(b)] as a function of ordering parameter $\eta$. Diagonalization of Eq. (11) requires $\Delta^{O}$ and $\Delta^{SO}$. For $Ga_0.5In_0.5P$, we calculated $\Delta^{O}(\eta = 1) = 0.20$ eV and $\Delta^{SO}(\eta = 1) = 0.10$ eV. For $Ga_0.3In_0.7As$, the calculated values are $\Delta^{O}(\eta = 1) = 0.10$ eV and $\Delta^{SO}(\eta = 1) = 0.35$ eV. We see from Fig. 1 that for the $\Gamma_{6c} \rightarrow \Gamma_{6c}$ transition the intensity difference $\Delta I_{c,1}$ does not depend on the degree of long-range order $\eta$. This is so since there is no coupling between the $\Gamma_{4c,5c}$ state and the two $\Gamma_{6c}$ states. In contrast, the intensity differences $\Delta I_{c,2}$ and $\Delta I_{c,3}$ (for the $\Gamma_{6c} \rightarrow \Gamma_{6c}$ and $\Gamma_{6c} \rightarrow \Gamma_{6c}$ transitions, respectively) depend on $\eta$, because the two valence states have the same $\Gamma_{6c}$ symmetry, hence they can couple to each other. The coupling mixes the wave function of these states, and thus changes the intensity differences $\Delta I$. The coupling strength depends

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**FIG. 1.** Calculated normalized transition intensity difference $I_{c,e}(\tilde{\sigma}_{110}, \eta) - I_{c,e}(\tilde{\sigma}_{110}, 0)$ for (111) ordering as a function of the ordering parameter $\eta$. $\Delta I_{c,1}$, $\Delta I_{c,2}$, and $\Delta I_{c,3}$ are for the transitions between the states $\Gamma_{6c} \rightarrow \Gamma_{4c,5c}$, $\Gamma_{6c} \rightarrow \Gamma_{6c}$, and $\Gamma_{6c} \rightarrow \Gamma_{6c}$, respectively. (a) $Ga_0.5In_0.5P$. (b) $Ga_0.3In_0.7As$. Note the deviations of $\Delta I_{c,2}$ and $\Delta I_{c,3}$ from the simple approximation of constants [Eq. (15) and Ref. 9].

**FIG. 2.** Calculated peak RDS intensity at $E_0$ for (111) ordering (a) $Ga_0.5In_0.5P$. The solid dots are the experimental data of Luo et al. (Ref. 9). Solid lines are calculated using the present theoretical model [Eq. (17)] using $A = -0.0395$ (eV$^{-1/2}$). The dashed line is calculated using Eq. (21), where coupling between crystal-field and spin-orbit splittings are neglected. (b) $Ga_0.3In_0.7As$. Solid lines are calculated using present theoretical model [Eq. (17)] using $A = -0.070$ (eV$^{-1/2}$). The dashed line is calculated using Eq. (21).
on the ratio between the crystal-field splitting $\Delta^0(\eta)$ and the spin-orbit splitting $\Delta^{SO}(\eta)$ and increases with $\eta$. For Ga$_{0.5}$In$_{0.5}$P with its small $\Delta^{SO}$ and large $\Delta^0$ (Ref. 2), the effect of coupling is very large [Fig. 1(a)]. On the other hand, for Ga$_{0.5}$In$_{0.5}$As, having a larger $\Delta^{SO}$ and a smaller $\Delta^0$ (Ref. 2), the effect is somewhat smaller [Fig. 1(b)].

When $\Delta^0=0$ (the cubic regime), states $|1\rangle$ and $|2\rangle$ are degenerate [see Eq. (13)]. In this limit the combined intensity difference $\Delta I_{c,1} + \Delta I_{c,2} = - \Delta I_{c,3} = 0$, hence there is no optical anisotropy (as appropriate for a cubic system).

### IV. RESULTS

Ordering-induced RDS [Eq. (8)] has a peak ($p$) intensity at the energy $E = E_g$. The RDS value at that energy is

$$\left[ \frac{\Delta R}{R} \right]_p = \beta \sum_{\nu=2,3} (2m^*_\nu)^{3/2} \times \Delta I_{c,\nu}(\eta) \sqrt{E_{\text{min},\nu}(\eta) - E_g(\eta)} .$$

Equation (16) shows that the RDS peak intensity at $E = E_g$ can be calculated.

Figure 2 shows our calculated RDS intensity at $E_g$ for Ga$_{0.5}$In$_{0.5}$P [Fig. 2(a)] and Ga$_{0.5}$In$_{0.5}$P [Fig. 2(b)] as a function of the square root of band-gap reduction $-\Delta E_g(\eta)^{1/2} = \left[ -\Delta E_g(1)^{1/2} \right]_{\eta}$, where $\Delta E_g(1)$ is the band-gap reduction of the fully ordered alloy. For Ga$_{0.5}$In$_{0.5}$P we calculated $\Delta E_g(1) = -0.32$ eV, while for Ga$_{0.5}$In$_{0.5}$As we have $\Delta E_g(1) = -0.30$ eV. In what follows we assume that the reduced effective masses are the same for both materials.

This leads to

$$\left[ \frac{\Delta R}{R} \right]_p = A \left( \Delta I_{c,1}(\eta) \sqrt{\Delta E_{12}(\eta)} + \Delta I_{c,2}(\eta) \sqrt{\Delta E_{13}(\eta)} \right) .$$

where $A = \beta (2m^*)^{3/2}$. Our results are compared in Fig. 2(a) with the experimental data of Luo et al. for Ga$_{0.5}$In$_{0.5}$P. We find that the best fit can be obtained by using $A = -0.0395$ (eV$^{-1/2}$). Using $m^* = 0.06m_0$, $n_0 = 3.3$, $E_g = 1.92$ eV, and $2P_{5/2}^2/m_0 = 21$ eV, we estimate that $A = -0.0378$ (eV$^{-1/2}$), which is very close to the fitted value. From Fig. 2(a) we conclude that Eq. (17) can be used along with our previously calculated $\Delta I_{c,\nu}(\eta)$ and $E_{\text{min},\nu}(\eta)$ to predict the ordering-induced bulk RDS intensity at threshold. Equating the measured and calculated RDS intensity can then be used to deduce the degree of ordering in a given sample.

For Ga$_{0.5}$In$_{0.5}$As we use the values $m^* = 0.03m_0$, $n_0 = 3.7$, $E_g = 0.75$ eV, and $2P_{5/2}^2/m_0 = 24$ eV. This gives $A = -0.070$ (eV$^{-1/2}$). This value is larger than the one for Ga$_{0.5}$In$_{0.5}$P, mainly because Ga$_{0.5}$In$_{0.5}$As has a much smaller band gap. No experimental RDS results are yet available for Ga$_{0.5}$In$_{0.5}$As.

### V. TESTING APPROXIMATIONS

We next explore approximations to our general result of Eq. (17) which will shed light on the recent calculation by Luo et al. for Ga$_{0.5}$In$_{0.5}$P.

When $\Delta^0 \ll \Delta^{SO}$ (the quasicubic regime) the coupling between the crystal-field-split $\Gamma_{6e}^{(1)}$ state and the spin-orbit-split $\Gamma_{6o}^{(2)}$ state is weak. Taylor expansion of Eq. (13) shows that in this limit one can approximate

$$\Delta E_{12}(\eta) \approx \frac{3}{2} \Delta^0(\eta) = \frac{3}{2} \Delta^0(\eta = 1) \eta^2 .$$

Furthermore, in this limit one can also approximate the dipole matrix elements squared using its value at $\eta = 0$, which yields (see Fig. 1)

$$\Delta I_{c,1} = \frac{3}{2} ,$$

$$\Delta I_{c,2} = -\frac{3}{2} ,$$

$$\Delta I_{c,3} = 0 .$$

Using these values in Eq. (8) leads to

$$\frac{\Delta R}{R} = \frac{3}{2} A \left[ \sqrt{E_g(\eta) - E} - \sqrt{E_g(\eta) + \Delta E_{12}(\eta)} - E \right] .$$

The peak RDS is then

$$\frac{\Delta R}{R} = -\frac{3}{2} A \sqrt{\Delta E_{12}(\eta)} .$$

Equation (21) indicates that when band coupling is neglected, the peak RDS intensity is a linear function of $\sqrt{-\Delta E_g(\eta)} \ll \eta$. Equations (20) and (21) were derived (using a different approach) in Ref. 9, and were used there to fit their experimental data for Ga$_{0.5}$In$_{0.5}$P. We show Eq. (21) as dashed lines in Fig. 2, using our best-fit value $A = -0.0395$ (eV$^{-1/2}$) for Ga$_{0.5}$In$_{0.5}$P and $A = -0.070$ (eV$^{-1/2}$) for Ga$_{0.5}$In$_{0.5}$As. Figure 2(a) compares this result with the experimental data (solid dots) and with our more complete theoretical results (solid lines). We see that the approximated result of Eq. (21) agrees with the more complete result of Eq. (17) only for a small range of $-\Delta E_g \ll \eta$.

To see why this is so, Fig. 1 tests approximation (19) while Fig. 3 tests approximation (18). As we can see,
these approximations hold for Ga$_{0.5}$In$_{0.5}$As up to \((-\Delta E_g)^{1/2} \leq 0.2 \text{ eV}^{1/2}\), while for Ga$_{0.5}$In$_{0.5}$P the applicability of Eqs. (20) and (21) is restricted to \((-\Delta E_g)^{1/2} \leq 0.1 \text{ eV}^{1/2}\). In general, however, the coupling between the crystal-field splitting and the spin-orbit splitting causes $\Delta I_{c,2}$, $\Delta I_{c,3}$, and $\Delta E_{12}/\Delta \theta$ to vary with $\eta$, unlike what simplifications (18) and (19) suggest. We further see that all experimental data points shown in Fig. 2(a) exceed the \([-\Delta E_g]^{1/2} \ll \eta\) region where Eqs. (20) and (21) are applicable. Consequently, by fitting experimental data to Eqs. (20) and (21), the valence-band splitting $\Delta E_{12}$ is overestimated. Furthermore, a large value of the parameter $A = -0.068 \text{ (eV}^{-1/2}\text{)}$ was needed in Ref. 9 to fit Eq. (21) to the experimental data for Ga$_{0.5}$In$_{0.5}$P. This number, however, is about 80% too large relative to our theoretical estimate $A = -0.038 \text{ (eV}^{-1/2}\text{)}$.

VI. SUMMARY

We have derived a general formula for ordering-induced bulk RDS intensity near the band edge as a function of ordering parameter $\eta$. Our results do not include the surface contribution to RDS, which could be important. We find that our calculated peak RDS intensity at $E_g$ agrees well with the experimental results. We show that coupling between the spin-orbit split-off band and the crystal-field split-off band is important in determining the RDS intensity for the Ga$_{x}$In$_{1-x}$P alloy due to its relatively small spin-orbit splitting and large crystal-field splitting. Previous theory, which neglects coupling between the crystal-field split states and the spin-orbit split state, is not applicable to the full range of ordering parameters covered by current samples.

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13In this paper we use the convention that the argument in the square root is positive; otherwise the square root function is zero.
17In Ref. 9, Luo et al. assume $m^* = \frac{1}{2}m_e$, i.e., $m_s = m_e$. This underestimates $m^*$ since in actuality $m_s \ll m_e$. Furthermore, they quoted $2P_{e}^{1}/m_0 = 80 \text{ eV}$, which is too large by about a factor of 4 relative to the value of 21 eV given in Ref. 13. The value calculated from first-principles pseudopotential band theory is $\sim 16 \text{ eV}$ [K. Mader (private communication)].