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Optical anisotropy and spin polarization in ordered GaInP

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Spontaneous CuPt-like ordering of $Ga_xIn_{1-x}P$ causes a splitting at the valence band maximum (VBM) and induces an anisotropy in the intensities of the transitions between these split VBM components and the conduction band minimum. We calculate these intensities as function of ordering parameter η, and show that the transition intensities depend strongly on the light polarization $\hat{e}$ and the degree of long-range order η in the sample. Furthermore, for sufficiently ordered single-subvariant sample, 100% spin polarization of emitted photoelectrons is predicted.

Spontaneous CuPt-like ordering of $Ga_xIn_{1-x}P$ has been widely observed in vapor phase growth on GaAs (001) substrate.[1] The ordered phase consists of alternate cation monolayer planes $Ga_{x+\eta/2}In_{1-x-(\eta/2)}$ and $Ga_{x-\eta/2}In_{1-x+\eta/2}$ stacked along the $[\bar{1}11]$ or the $[1\bar{1}1]$ directions (known as the two $CuPt_B$ subvariants), where $0\leqslant\eta\leqslant 1$ is the long-range order parameter.[2] Perfect ordering ($\eta=1$) corresponds to successive planes of pure Ga followed by pure In, etc. This type of 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 electroreflectance,[4,5] polarized photoluminescence,[6] and polarized piezoreflectance.[7] However, quantitative analysis of these experiments requires the knowledge of *optical transition rates* between the split VBM components and the conduction band minimum (CBM) as a function of the degree η of long-range order. We provide here an easy to use formalism to calculate the intensities at the Γ point as a function of η. We will show that the transition rate depends strongly on the polarization of the light $\hat{e}$ and on the degree of long-range order η. Furthermore, we predict that for a sufficiently ordered single-subvariant sample, 100% spin-polarization of emitted photoelectrons can be obtained.

Neglecting mixing between valence and conduction states, the VBM states for $(\bar{1}11)$ ordering can be described by the 6×6 Hamiltonian:

$$H_v=\frac{1}{3}\begin{pmatrix} 0 & \Delta^O-i\Delta^{SO} & \Delta^O & 0 & 0 & \Delta^{SO} \\ \Delta^O+i\Delta^{SO} & 0 & -\Delta^O & 0 & 0 & -i\Delta^{SO} \\ \Delta^O & -\Delta^O & 0 & -\Delta^{SO} & i\Delta^{SO} & 0 \\ 0 & 0 & -\Delta^{SO} & 0 & \Delta^O+i\Delta^{SO} & \Delta^O \\ 0 & 0 & -i\Delta^{SO} & \Delta^O-i\Delta^{SO} & 0 & -\Delta^O \\ \Delta^{SO} & i\Delta^{SO} & 0 & \Delta^O & -\Delta^O & 0 \end{pmatrix}. \tag{1}$$

In this representation all four 3×3 blocks contain the spin-orbit elements, while the two diagonal 3×3 blocks also contain the elements for $(\bar{1}11)$ ordering. If the film is *not* lattice matched to the substrate, an additional strain term, neglected here, has to be added to the diagonal blocks.[8] Here, $\Delta^O(\eta)=\eta^2\Delta^O(1)$ is the crystal field splitting due to ordering[2] and Δ^{SO} is the spin-orbit splitting. For $Ga_{0.5}In_{0.5}P$, we calculated[2] $\Delta^O(\eta=1)=0.20$ eV and $\Delta^{SO}=0.10$ eV. The eigenvalues and eigenvectors of the valence states can be obtained by solving Eq. (1). The three spin-degenerate energy levels (in decreasing order) $E_1(\Gamma_{4v,5v})$, $E_2(\Gamma_{6v})$, and $E_3(\Gamma_{6v})$ {shifted by $\frac{1}{6}[\Delta^{SO}+\Delta^O(\eta)]$} are

$$\begin{aligned} E_1(\eta)&=\tfrac{1}{2}[\Delta^{SO}+\Delta^O(\eta)], \\ E_2(\eta)&=+\tfrac{1}{2}\sqrt{[\Delta^{SO}+\Delta^O(\eta)]^2-\tfrac{8}{3}\Delta^{SO}\Delta^O(\eta)}, \\ E_3(\eta)&=-\tfrac{1}{2}\sqrt{[\Delta^{SO}+\Delta^O(\eta)]^2-\tfrac{8}{3}\Delta^{SO}\Delta^O(\eta)}. \end{aligned} \tag{2}$$

For the random alloy ($\eta=0$) E_1 and E_2 are degenerate. Thus ordering splits the Γ_{8v} VBM of the random alloy into the states $|1\rangle=\Gamma_{4v,5v}$ and $|2\rangle\Gamma_{6v}$.

The valence eigenstates Ψ_v of Eq. (1) are linear combination of the six basis functions $\{p_\nu\hat{\sigma}\}$, where $p_\nu=p_x$, p_y, or p_z are the $L=1$ orbital components and $\hat{\sigma}$ are the spinors parallel or antiparallel to the z direction. The conduction states are taken here as $\Psi_c=s\hat{\sigma}$, where s is the $L=0$ orbital component. The transition intensity between Ψ_c and Ψ_v is proportional by the matrix element squared $I_{v,c}=|\langle\bar{\phi}_c|H_{int}|\bar{\phi}_v\rangle|^2\ |\langle\Psi_c|H_{\rm int}|\Psi_v\rangle|^2$, where $H_{\rm int}$ is the interacting Hamiltonian. For *linearly* polarized light along the $[l, m, n]$ direction we have $H_{\rm int}\propto lx+my+nz$, while for *circularly* polarized light $\sigma^{\pm}$ with angular momentum parallel and antiparallel to z' we have[9] $H_{\rm int}\propto x'\pm iy'$. In general, for polarized light $H_{\rm int}$ can be expressed as a linear combination of[10] $x_\mu=x$, y, or z. The transition matrix elements

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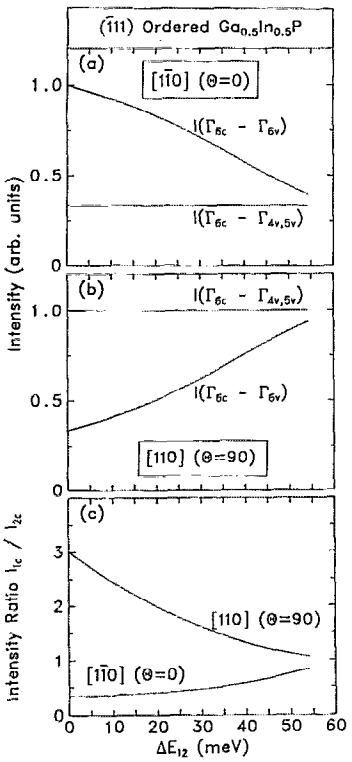

FIG. 1. Calculated transition intensity for $(\bar{1}11)$ordered $Ga_{0.5}In_{0.5}P$ as a function of the valence band splitting ΔE_{12} for (a) light polarized alone $[1\bar{1}0]$ and (b) light polarized alone [110]. Part (c) gives the intensity ratio $I(\Gamma_{6c}-\Gamma_{4v,5v})/I(\Gamma_{6c}-\Gamma_{6v})$.

can be calculated by writing the orbital wave functions and H_{int} in terms of the spherical harmonics Y_{lm} and by noticing that the allowed dipole transitions are for $\Delta m=\pm 1$. This gives the simple selection rule

$$\langle s\hat{\sigma}|x_\mu|p_\nu\hat{\sigma}'\rangle = c\,\delta_{\mu,\nu}\delta_{\sigma,\sigma'}, \tag{3}$$

where c is a normalization parameter.

We have calculated the transition intensities $I_{v,c}$between the valences $|1\rangle$ and $|2\rangle$ and the conduction state in $(\bar{1}11)$ ordered $Ga_{0.5}In_{0.5}P$ as a function of $\Delta E_{12}(\eta)=E_1(\eta)-E_2(\eta)$. We consider linearly polarized light with polarization $\hat{e}\|[1\bar{1}0]$ (defined as $\Theta=0$); $\hat{e}\|[110]$ (defined as $\Theta=90°$) and in between. Figure 1 shows the calculated intensities for the transitions $\Gamma_{4v,5v}-\Gamma_{6c}$ and $\Gamma_{6v}-\Gamma_{6c}$ as function of ΔE_{12} for polarization $\hat{e}\|[1\bar{1}0]$ (part a) and $\hat{e}\|[110]$ (part b). Measured intensities include, in addition to $I_{v,c}$, line broadening, joint density of states, and the Boltzmann population factors. We see from Figs. 1(a) and 1(b) that the intensity $I(\Gamma_{6c}-\Gamma_{4v,5v})$ does not depend on ΔE_{12}, thus on degree of ordering. This is so since there is no coupling between $\Gamma_{4v,5v}$ and the other two Γ_{6v} valence states. In contrast, the intensity $I(\Gamma_{6c}-\Gamma_{6v})$ depends strongly on ΔE_{12}, because the coupling between the two Γ_{6v} states depends on the degree of ordering, thus on ΔE_{12}.

We will distinguish in what follows two limits of coupling: The quasicubic limit when $\Delta^O \ll \Delta^{SO}$ and the trigonal limit when $\Delta^O \gg \Delta^{SO}$. In the quasicubic regime (small η) we have [Eq. (2)] $\Delta E_{12}\approx 0$. In this limit the polarization ratio is

$$\frac{I(\Gamma_{6c}-\Gamma_{4v,5v})}{I(\Gamma_{6c}-\Gamma_{6v})}=\begin{cases}1/3; & \hat{e}\|[1\bar{1}0]\\ 3; & \hat{e}\|[110]\end{cases}. \tag{4}$$

Since in this "weak ordering" regime, $\Gamma_{4v,5v}$ and Γ_{6v} are nearly degenerate, only the combined intensity $I(\Gamma_{6c}-\Gamma_{4v,5v})+I(\Gamma_{6c}-\Gamma_{6v})$ can be measured. For $\Delta E_{12}=0$ this combined intensity is the same for the [110] or the $[1\bar{1}0]$ polarization [Figs. 1(a) and 1(b)], as appropriate for a cubic system. Thus no polarization dependence should be detected if the two transitions are not resolved. As the degree of order (thus, ΔE_{12}) increase, the intensity ratios $I(\Gamma_{6c}-\Gamma_{4v,5v})/I(\Gamma_{6c}-\Gamma_{6v})$ approaches unity for both polarization directions. In the extreme trigonal limit [Fig. 1(c)]

$$\frac{I(\Gamma_{6c}-\Gamma_{4v,5v})}{I(\Gamma_{6c}-\Gamma_{6v})}=\begin{cases}1; & \hat{e}\|[1\bar{1}0]\\ 1; & \hat{e}\|[110]\end{cases} \tag{5}$$

and the polarization dependence for both transitions $I(\Gamma_{6c}-\Gamma_{4v,5v})$ and $I(\Gamma_{6c}-\Gamma_{6v})$ are given by [Figs. 1(a) and 1(b)]

$$\frac{I_{110}}{I_{1\bar{1}0}}=3. \tag{6}$$

Figure 2 depicts the calculated normalized intensities as function of the polarization angle Θ. We find that in this case the intensity can be described by

$$I(\Theta)=I_{110}\sin^2\Theta+I_{1\bar{1}0}\cos^2\Theta. \tag{7}$$

For the $\Gamma_{6c}-\Gamma_{4v,5v}$ transition [Fig. 2(a)] the intensity is independent of η. For the $\Gamma_{6c}-\Gamma_{6v}$ transition, however, we see a strong dependence on the ordering parameter η. $I(\Theta)$ can be either an increasing function (at large η) or a decreasing function (at small η) of the polarization angle Θ. Figure 2 compares our calculated results (lines) with the recent polarized electroreflectance data of Kanata *et al.*[5] (solid dots). We find that the best fit to the measured intensities is obtained using $\eta=0.58$. Inserting this value into Eq. (2) gives a valence band splitting of $\Delta E_{12}=34$ meV. The directly measured[5] valence band splitting of this sample is $\Delta E_{12}=34\pm 4$ meV, in excellent agreement with the above value. Thus our intensity analysis is consistent with the energetic analysis. The analysis of Ref. 5 of the same data neglected polarization cross-terms[10] and is thus incomplete.

Our model has an interesting conclusion on $I_{v,c}$ vs η: in most previous analyses of experimental data,[6,7,5,11] the intensity ratio of the quasicubic limit [Eq. (4)] was applied to *all* degrees of ordering η. The ordering dependence of the intensity ratio was thus missed. As we see in Figs. 1(c) and 2(b) this assumption could introduce large errors.

We have also studied the ordering-induced changes in *spin polarization of emitted photoelectrons*. We use for this purpose circularly polarized light[9,12] $\sigma^{\pm}$ with its angular momentum along the ordering direction $z'=[\bar{1}11]$. We thus have $H_{\text{int}}\propto x'\pm iy'$, where $x'=1/\sqrt{2}(x+y)$ and $y'=1/\sqrt{6}\,(-x+y-2z)$. The spinors parallel and antiparallel to the $[\bar{1}11]$ ordering direction are given by

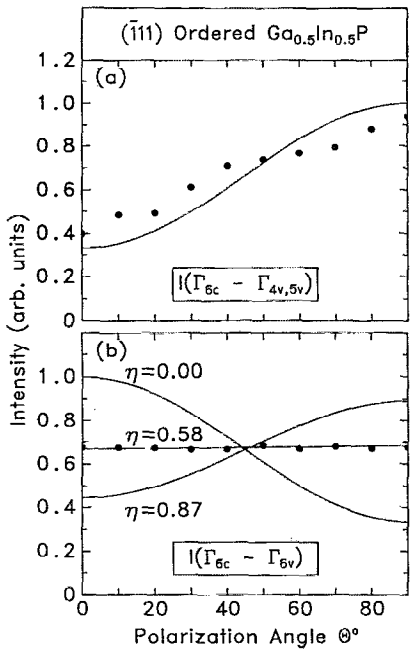

FIG. 2. Calculated transition intensity of $(\bar{1}11)$ ordered $Ga_{0.5}In_{0.5}P$ as a function of polarization angle Θ. Here, $\Theta=0$ denotes light polarized along $[1\bar{1}0]$, while $\Theta=90$ denotes light polarized along [110]. (a) The $\Gamma_{4c}-\Gamma_{4v,5v}$ transition. The intensity is independent of η. (b) The $\Gamma_{6c}-\Gamma_{6v}$ transition at $\eta=0$, 0.58, and 0.87. The corresponding ΔE_{12} are 0, 34, and 50 meV, respectively. The solid dots in (a) and (b) are the experimental data of Kanata *et al.* (Ref. 5).

$$\uparrow' = \cos\frac{\theta}{2}e^{-i(\varphi/2)}\uparrow + \sin\frac{\theta}{2}e^{i(\varphi/2)}\downarrow,$$

$$\downarrow' = -\sin\frac{\theta}{2}e^{-i(\varphi/2)}\uparrow + \cos\frac{\theta}{2}e^{i(\varphi/2)}\downarrow, \tag{8}$$

where the angles θ and φ are determined by the equation $[\sin\theta\cos\varphi, \sin\theta\sin\varphi, \cos\theta]=1/\sqrt{3}[\bar{1},1,1]$. The $\uparrow$ and $\downarrow$ are the spinors parallel and antiparallel to the [001] direction, respectively. The electron spin polarization P is defined as[9,12]

$$P=\frac{I_- - I_+}{I_- + I_+}, \tag{9}$$

where I_- and I_+ are the transition intensities for $\downarrow'$ spin and $\uparrow'$ spin, respectively. In Fig. 3 we show the calculated spin intensities $(I_- - I_+)_{1c}$ and $(I_- - I_+)_{2c}$ for ordered $Ga_{0.5}In_{0.5}P$ alloys. For the random alloy ($\Delta E_{12}=0$) the states $|1\rangle$ and $|2\rangle$ (both Γ_{8v}) are degenerate. In this case, we find that optical pumping from both states leads to a $P=50\%$ electron spin polarization.[9] For ordered alloy ($\eta\neq 0$), the $|1\rangle=\Gamma_{4v,5v}$ and $|2\rangle=\Gamma_{6v}$ states split. We find that photoelectrons generated from the $\Gamma_{4v,5v}$ and the Γ_{6v} states are both fully polarized $P=\pm 100\%$. Hence, if the splitting ΔE_{12} is large enough to allow optical pumping only from the highest $\Gamma_{4v,5v}$ state, the generated photoelectrons can be 100% spin polarized. A theoretical 100% spin polarization of electron can also be achieved by using (001) ordered material [e.g., $Al_{0.5}Ga_{0.5}As$ (Ref. 13)], as proposed by Ciccacci *et al.*[12] However, since $(\bar{1}11)$ ordered material has much larger valence band splitting than (001) ordered samples,[3,14] we suggest that $(\bar{1}11)$ ordered III-V alloys (e.g., $Ga_{0.5}In_{0.5}P$) could be a better candidate of spin polarized photoelectron source.

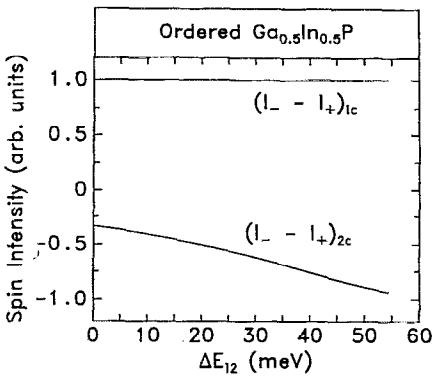

FIG. 3. Calculated spin intensity $(I_- - I_+)_{1c}$ and $(I_- - I_+)_{2c}$ (in arbitrary units) of ordered $Ga_{0.5}In_{0.5}P$ as a function of the valence band splitting ΔE_{12}. The angular momentum of the circularly polarized light is in the same direction as the ordering vector. The generated photoelectron from each band is fully polarized.

Note that despite the identical optical response with respect to the linearly polarized light along [110] and $[1\bar{1}0]$ of the two $CuPt_B$ $[(1\bar{1}1)$ and $(\bar{1}11)]$ subvariants, their response to the circularly polarized light is predicted to be different. Using the σ^+ light noted above but for $(1\bar{1}1)$ ordering, we find that the spin polarization P for the transition from the top $\Gamma_{4v,5v}$ state is only 20% and the total intensity $I_- + I_+$ is reduced to 55.56% of the intensity for $(\bar{1}11)$ ordering. This difference can be used to distinguish $(1\bar{1}1)$ ordering from $(\bar{1}11)$ ordering, which is not possible using the linearly polarized light. This also indicates that in order to obtain the highest efficiency in generating spin polarized electrons, single variant crystals are required.

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[10] Note that due to phase correlation, the transition intensity for coherent, linearly polarized light, e.g., $H_{\rm int}=x+y$ is different from the sum of the intensities of the two incoherent polarized light $H_{\rm int}=x$ and $H_{\rm int}=y$. Reference 5 has incorrectly assumed in their intensity analysis that $|\langle\Psi_c|x+y|\Psi_v\rangle|^2=|\langle\Psi_c|x|\Psi_v\rangle|^2+|\langle\Psi_c|y|\Psi_v\rangle|^2$.
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