

Effect of localized boron impurities on the line shape of the fundamental band gap transition in photomodulated reflectance spectra of (B,Ga,In)As

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Photomodulated reflectance (PR) spectra of (B,Ga,In)As epilayers reveal unusual changes of the fundamental band gap PR line shape with temperature and hydrostatic pressure. We show that these changes arise because temperature variation or hydrostatic pressure shifts the conduction band edge (CBE) into resonance with boron-related cluster states. The resulting line shape changes are described by a level repulsion model which yields states of mixed character with an exchange of oscillator strengths. This model is corroborated by theoretical calculations which show a finite density of boron cluster states above the CBE at room temperature, with appropriate symmetry to couple to the CBE state.

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I. INTRODUCTION

The incorporation of the isovalent impurity N into the host material GaAs leads to an unconventional semiconductor alloy behavior in the sense that the virtual crystal approximation (VCA) fails to explain the observed characteristics of its electronic structure. For example, Shan *et al.* observed anticrossing effects in the conduction band yielding a strong redshift of the band gap with N concentration and the occurrence of a new E_+ band due to a strong interaction between localized N states and the GaAs host states.¹ The underlying reason is the difference in atomic radii and electronegativity between the N and As atoms. The differences in size and electronegativity between B and Ga are also distinct, though considerably smaller.

(B,Ga)As and (B,Ga,In)As alloys have been studied intensively over the past few years. However, the influence of the isovalent impurity B on the band structure of the GaAs host material is still not completely understood. In particular, the findings related to localized B states are contradictory. On the one hand, photomodulated reflectance (PR) measurements at 295 K of (B,Ga)As alloys by Shan *et al.* show no band anticrossing effects of localized B states and the extended GaAs conduction band edge (CBE) state.² In agreement with other experimental³⁻⁶ and theoretical studies,⁷ Shan *et al.* observed only a small shift of the fundamental band gap with increasing B content compared to the strong redshift measured in Ga(N,As) alloys with increasing N concentration.^{1,4,8} They therefore concluded that the isolated B levels are located far above the CBE of GaAs and hardly interact with the CBE state at Γ . On the other hand, Hofmann *et al.* observed a strong increase of the electron effective mass of 44% in (B,Ga,In)As compared to (Ga,In)As in discrepancy with the effective mass calculated with the VCA approach.⁹ Teubert *et al.* reported electron mobilities of $800 \text{ cm}^2(\text{Vs})^{-1}$ in (B,Ga,In)As which are somewhat between those of conventional alloys and the very low values measured in Ga(N,As) (Ref. 10). Applying pressure decreases the mobility further, and the values become comparable to those observed in Ga(N,As) (Ref. 10). Lindsay *et al.* performed tight-binding calculations followed by an analysis based on the interactions between the CBE state and a realistic distribution of isolated B atoms, B-B pairs, and B clusters.^{11,12} An isolated B atom has no B second neighbors,

while a B-B pair consists of two B atoms which share an As neighbor, with clusters then containing larger numbers of contiguous B atoms. The model predicts highly localized B cluster states close to the CBE of GaAs which weakly interact with the extended CBE state, leading to the large electron effective mass and the comparatively low electron mobilities. The finding of localized B impurity states is experimentally supported by magnetotransport measurements under hydrostatic pressure which allows one to extract an effective density of states by localized B clusters in agreement with tight binding calculations.¹³

In modulation spectroscopy line shapes of measured spectra are typically described by simply modeling the signals with first or third order derivatives of complex Gaussian or Lorentzian oscillators for each transition independently.¹⁴⁻¹⁶ For fitting the energetic position of the transition E_i , width of the peak Γ_i , and the intensity I_i are varied for each signal. The assumption of uncoupled oscillators yields good results for electronic transitions in bulk materials, heterostructure semiconductors, quantum wells, and superlattices among others, see, Ref. 17, for example. Line shape models for coupled oscillators are the exception. So far only in the case of vertical-cavity surface-emitting lasers (VCSEL) a model has been developed for modulation spectroscopy of a coupled cavity mode and one quantum well transition.¹⁸⁻²¹ When studying alloys doped with isovalent impurities via modulation spectroscopy one has to consider how the localized states and host states interact with each other. As mentioned above in Ga(N,As), a strong repulsion of the states leads to the occurrence of the E_- host conduction band-like and the E_+ N-like states which are well separated in energy.¹ Thus in PR individual signals appear which can be fitted with quasi-independent, conventional oscillators as the line width is much smaller than the splitting.

In the case of the boron cluster states and the host conduction band edge, the coupling between the states is considerably weaker^{11,12} and the splitting of the resulting mixed states is smaller than their line widths. Furthermore, the uncoupled states are of different symmetry and the mixing of Γ character into the resulting states varies as the states approach each other under applied pressure or as a function of temperature. Thus, new simple line shape models need

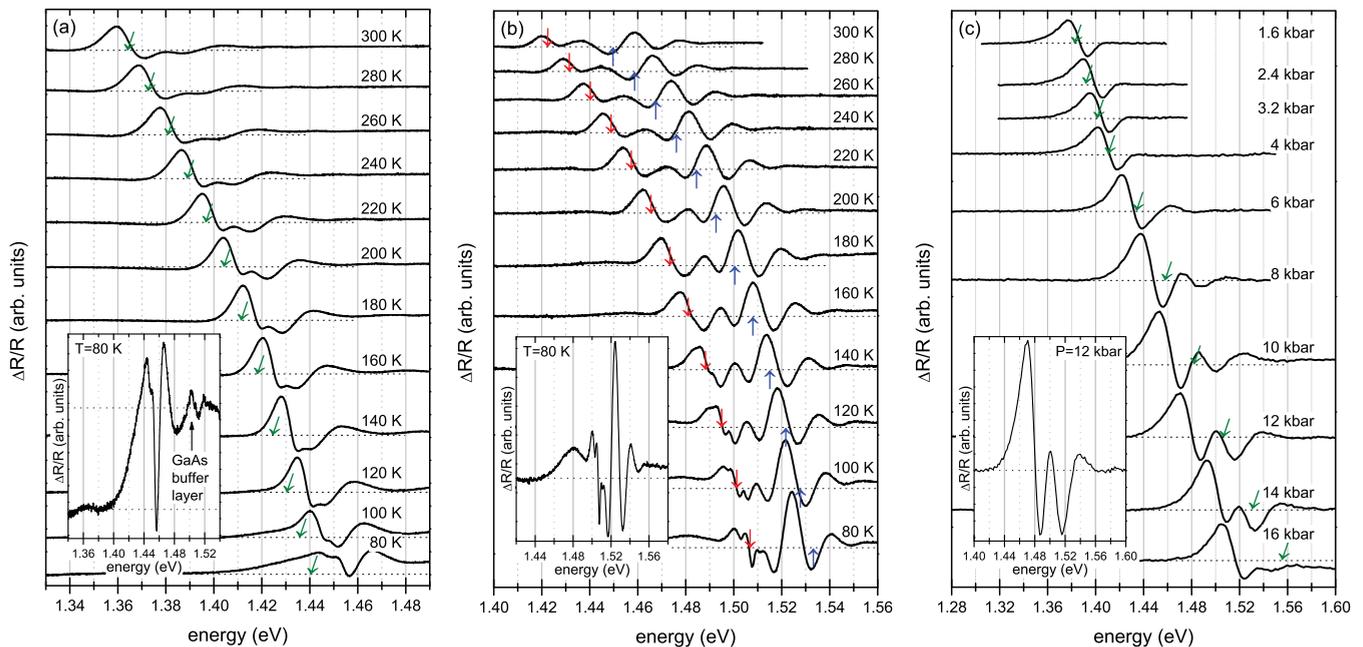


FIG. 1. (Color online) PR spectra at ambient pressure at different temperatures (a) of $B_{0.027}Ga_{0.913}In_{0.06}As$ and (b) of $B_{0.0044}Ga_{0.9956}As$. Symbols indicate the calculated band gap shifts of $Ga_{0.94}In_{0.06}As$ (green, tilted arrows), GaAs (red arrows), and $Al_{0.02}Ga_{0.98}As$ (blue, upside down arrows). (c) PR spectra under hydrostatic pressure at 300 K of $B_{0.027}Ga_{0.913}In_{0.06}As$. The insets show enlargements of the spectra for 80 K in (a) and (b) and for the 12 kbar spectra in (c).

to be developed which empirically account for these effects and qualitatively explain the measured PR line shapes for the lowest band gap transition.

Here, we show that the B cluster states significantly affect the PR line shape of the band gap transition at Γ in the (B,Ga,In)As alloys under study and a new line shape model is introduced to explain the observed results.

II. EXPERIMENTAL DETAILS

The (B,Ga)As and (B,Ga,In)As epitaxial layers investigated were grown by low-pressure metal-organic vapor-phase epitaxy on (001) GaAs substrates.^{4,5} The boron concentrations were determined by high-resolution x-ray diffraction. Prior to the (B,Ga,In)As growth, a 150 nm thick GaAs buffer layer was deposited. The $B_{0.027}Ga_{0.913}In_{0.06}As$ and $B_{0.0044}Ga_{0.9956}As$ samples have thicknesses of about 1 μm . The latter layer was capped with a thin $Al_{0.02}Ga_{0.98}As$ layer. PR measurements were performed between 77 and 300 K in a cryostat using a halogen lamp as a light source and a 20 mW red diode laser (635 nm) for modulation. In the case of the optical measurements under hydrostatic pressure up to 16 kbar at 300 K, the samples were mounted in a clamp pressure cell and a He-Cd laser (442 nm) was centered on the samples for modulation. Details of the experimental setup are given in Ref. 22.

III. RESULTS AND DISCUSSION

A. Photomodulated reflectance measurements

Recent experimental and theoretical results have demonstrated that weak level repulsion effects occur between the localized boron cluster states and the extended conduction

band state in (B,Ga,In)As.^{11–13} In Fig. 1 we discuss series of spectra obtained from different samples which give concealed evidence that the line shapes of the fundamental transition exhibits unusual behavior which is related to level repulsion effects. For each series we explain how the unusual features may be interpreted in terms of level repulsion.

Figure 1(a) depicts PR spectra taken between 80 and 300 K for the $B_{0.027}Ga_{0.913}In_{0.06}As$ sample. The derivative-like spectral feature at 1.36 eV at 300 K corresponds to the fundamental band gap transition of the quaternary alloy. At 300 K the line shape is typical for a direct band gap and can be well described by an Aspnes bulk-like third-derivative line shape.¹⁵ With decreasing temperature this feature shifts to higher energies as expected. However, its signal strength and shape change dramatically. In particular, below 200 K one observes additional features at higher energy, at about 1.43 eV at 200 K. In the spectrum taken at 80 K (see inset in Fig. 1(a)) it is possible that these features and the band gap signal are exchanging oscillator strengths and a complicated line shape arises which exhibits distinct sharp kinks on top of a broad line. Thus, the line shape at 80 K deviates considerably from Aspnes' third-derivative line shape. This is very unusual: the $B_{0.027}Ga_{0.913}In_{0.06}As$ band gap transition is expected to be the energetically lowest transition between extended states in the sample and the PR line shape of the lowest band gap transition in III-V semiconductors hardly changes in the temperature range considered because excitonic effects are still of minor importance. Also, because the band gap is lower than that of GaAs, the observed effects are not due to a superposition with signals from other layers of the sample: the high energy component of the signal due to the GaAs buffer layer is separately labeled in the inset of

Fig. 1(a). Moreover, the spacing between the lower energy kinks and their sharpness rules out interference effects. These sharp features somewhat resemble those of localized N cluster states in Ga(N,P) observed in electromodulated transmission spectra.²³

The temperature dependent PR spectra of the $B_{0.0044}Ga_{0.9956}As$ sample shown in Fig. 1(b) further corroborate this interpretation. At 300 K two features are present. One at about 1.42 eV is assigned to the (B,Ga)As band gap. The second feature at about 1.46 eV is due to an $Al_{0.02}Ga_{0.98}As$ capping layer. The temperature shifts of the band gaps of GaAs and of $Al_{0.02}Ga_{0.98}As$ are shown by arrows as guides to the eye. The spectral feature of (B,Ga)As basically follows the corresponding band gap shift of GaAs, but again the line shape changes considerably with decreasing temperature, in contrast to the (Al,Ga)As signal. In particular, at 80 K, there appears a series of sharp features on the low energy side of the broad signal (see inset in Fig. 1(b)). With decreasing temperature the character of the low energy signal seems to change: the spectral changes do not look like a crossing of signals, but rather as a continuous change from a broad signal to a sharp series of lines with distinct intermediate stages. We attribute this to the mixing and exchange of oscillator strength arising in a level anticrossing with B-related localized states, which show smaller temperature-induced shifts than the host CBE state.

The PR spectra shown in Fig. 1(c) for $B_{0.027}Ga_{0.913}In_{0.06}As$ at different hydrostatic pressures support this attribution. At ambient pressure, the band gap signal of $B_{0.027}Ga_{0.913}In_{0.06}As$ has the typical Aspnes' shape, but with increasing pressure, as it shifts to higher energies, the line shape changes unexpectedly. The pressure-induced band edge shift of $dE_g/dP = 10$ meV/kbar is similar to that of GaAs and (Ga,In)As, in agreement with the findings of Shan *et al.*,² but significant modifications of the PR signal's oscillator strength and line shape occur above 6 kbar. The effect of increasing hydrostatic pressure is similar to decreasing temperature: the CBE at Γ shifts to higher energies at a higher rate than the localized B states.

The observed line shape changes can then be understood by assuming that a level repulsion takes place between the CBE state and B-related localized states which are close by in energy. The histogram in Fig. 2 shows $V_B(E)$, the calculated distribution of B cluster states with energy ϵ_i close to the CBE in $B_{0.027}Ga_{0.973}As$ at 0 K, weighted by the strength of their interaction V_i with the GaAs CBE state, where

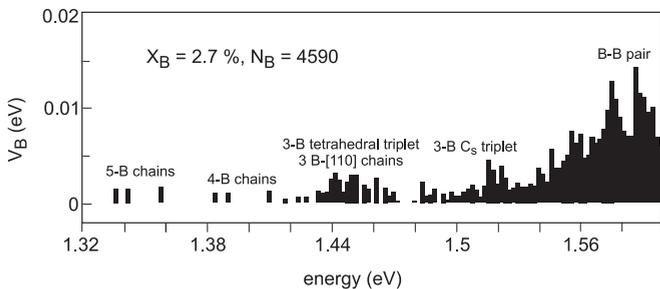


FIG. 2. Calculated distribution of B cluster states weighted by their interaction with the CBE state for $B_{0.027}Ga_{0.973}As$.

$V_B(E) = \sum |V_i|^2 T(E - \epsilon_i)$, and $T(x)$ is a top-hat function of width 2 meV and unit area.²⁴ The interaction of the localized states with the CBE state can mix Γ character into the boron states when the B states and the CBE are almost degenerate in energy, thus making the B states observable in optical experiments. The B state distribution was calculated using the approach described in Refs. 11 and 12. We find a broad distribution of states centered around 1.44 eV at 0 K, associated with a density of about $1 \times 10^{18} \text{ cm}^{-3}$ B three-atom clusters which give states in this energy range. This distribution of states shifts slightly to lower energies with increasing temperature and to higher energies under hydrostatic pressure, in both cases with a smaller rate of shift than that of the CBE of the host. These results strongly support our analysis that the PR line changes shape because of an anticrossing interaction which occurs when the CBE state shift into the distribution of B states, at energies larger than about 1.44 eV.

B. Line shape model

In the following, we will describe an empirical model of the PR line shape based on level anticrossing to explain the unusual features of the PR spectra. For simplicity, we consider two states only, namely the extended CBE state and a second, B-related state. When we include an anticrossing interaction M between these two states, the Hamiltonian of this system then has the form

$$\mathcal{H} = \begin{pmatrix} E_c & M \\ M & E_b \end{pmatrix}, \quad (1)$$

where E_c and E_b are the energies of the unperturbed host CBE and of the localized B state, respectively. We assume that the unperturbed host CBE E_c shifts in energy and crosses the B state energy level E_b , which we assume for this model to be at a constant energy. The two eigenvalues E_i ($i = 1, 2$) of \mathcal{H} correspond to the energy levels of the new states $\Psi^{(i)}$ formed through the anticrossing interaction. The corresponding wave functions $\Psi^{(i)}$ are linear combinations of the two unperturbed wave functions ϕ_c and ϕ_b where the eigenvectors of \mathcal{H} yield the corresponding coefficients $\alpha_c^{(i)}$ and $\alpha_b^{(i)}$, which describe the mixing of the two unperturbed wave functions.

In the electric dipole approximation, the probability of a transition at the Γ point between a valence band edge (VBE) state $|\phi_{VBE}\rangle$ to a CBE state $|\phi_{CBE}\rangle$ is proportional to the square of the matrix element

$$|\langle \phi_{CBE} | e\vec{r} | \phi_{VBE} \rangle|^2, \quad (2)$$

where $e\vec{r}$ is the electric dipole operator. The electric dipole transition across the band gap for the Ga(In)As host state ϕ_c is allowed whereas that to an unperturbed localized B state ϕ_b , due to a lack of Γ character, is forbidden

$$|\langle \phi_c | e\vec{r} | \phi_{VBE} \rangle|^2 \neq 0, \quad |\langle \phi_b | e\vec{r} | \phi_{VBE} \rangle|^2 = 0. \quad (3)$$

Thus, one obtains for the new conduction band states $\Psi^{(i)} = \alpha_c^{(i)}\phi_c + \alpha_b^{(i)}\phi_b$ arising due to the level repulsion

$$|\langle \Psi^{(i)} | e\vec{r} | \phi_{VBE} \rangle|^2 = |\alpha_c^{(i)}|^2 |\langle \phi_c | e\vec{r} | \phi_{VBE} \rangle|^2. \quad (4)$$

The transition probabilities between the valence band state and the two new conduction band states depend on the degree of mixing between the host conduction band state

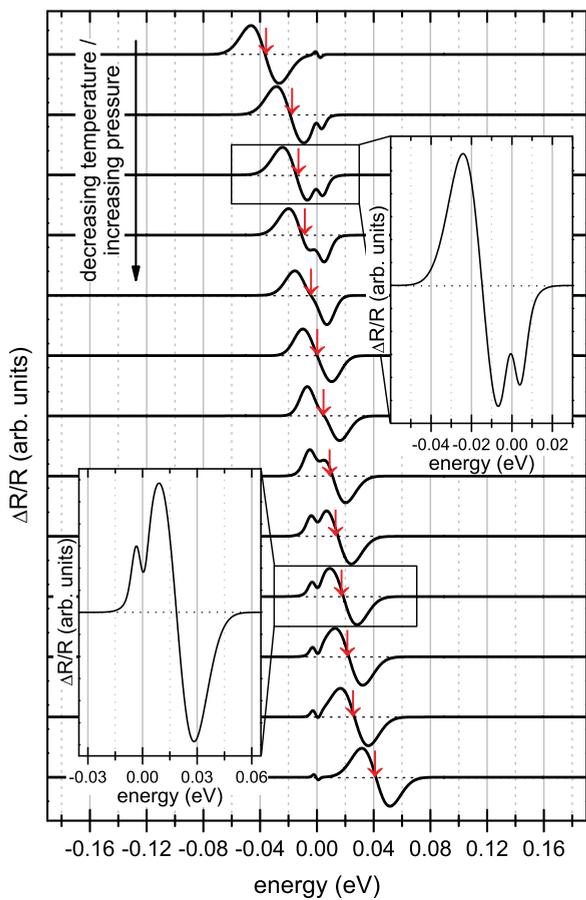


FIG. 3. (Color online) Line shape modeling on the basis of an anticrossing behavior between an extended band state and a localized boron state. The latter state was chosen to be at 0 eV while the extended band state shifts with temperature like the band gap in GaAs (red arrows). The insets show enlargements of the marked spectra.

and the localized B state (i.e., they depend on the fractional Γ character, $|\alpha_c^{(i)}|^2$ of the new conduction band states). In particular, in the vicinity of the resonance, both transitions will become allowed and thus be observable in the PR spectra.

Based on these considerations, the PR spectra of the $B_x\text{Ga}_{1-x-y}\text{In}_y\text{As}$ samples can be modeled as follows. We assume that the two transitions from the VBE to the unperturbed states ϕ_c and ϕ_b are broadened in energy and can be described by Gaussian oscillators centered at E_c and E_b with line width σ_c and σ_b , respectively. A broad Gaussian $g_c(E - E_c)$ represents the fundamental allowed transition between the VBE and CBE and a narrower Gaussian $g_b(E - E_b)$ describes the forbidden transition between the VBE and B state. The mixing of the conduction band state due to the level repulsion leads to the new conduction band states $\Psi^{(i)}$ and the corresponding transition from the VBE can also be described by Gaussian oscillators $g^{(i)}(E - E_i)$ centered at E_i ($i = 1, 2$). We assume that the line widths of these new Gaussians are determined by the degree of mixing between the unperturbed states

$$\sigma_i^2 = |\alpha_c^{(i)}|^2 \sigma_c^2 + |\alpha_b^{(i)}|^2 \sigma_b^2, \quad (5)$$

whereas the oscillator strength observed in an optical transition $G^{(i)}$ will be proportional to the fraction of the Γ character of the new conduction band states

$$G^{(i)}(E - E_i) = |\alpha_c^{(i)}|^2 g^{(i)}(E - E_i). \quad (6)$$

The PR line shapes of the two transitions of mixed character are then modeled simply by taking the derivatives of the corresponding new oscillators $G^{(i)}(E - E_i)$ with respect to energy. To illustrate the model, we have plotted the corresponding PR line shapes in Fig. 3. The transition of the unperturbed localized B state is centered at $E_b = 0$ eV whereas that of the unperturbed CBE state shifts from $E_c = -35$ meV (top of the figure) to 40 meV (bottom of the figure). The line width and interaction parameters assumed are $\sigma_c = 0.01$ eV, $\sigma_b = 0.001$ eV, and $M = 0.005$ eV. It can be clearly seen that, as the separation between the localized B state and the extended CBE state decreases, the interaction between them leads to significant mixing of Γ character into the localized level. This mixing modifies the signal strength and shape of the two corresponding PR signals even when they are still

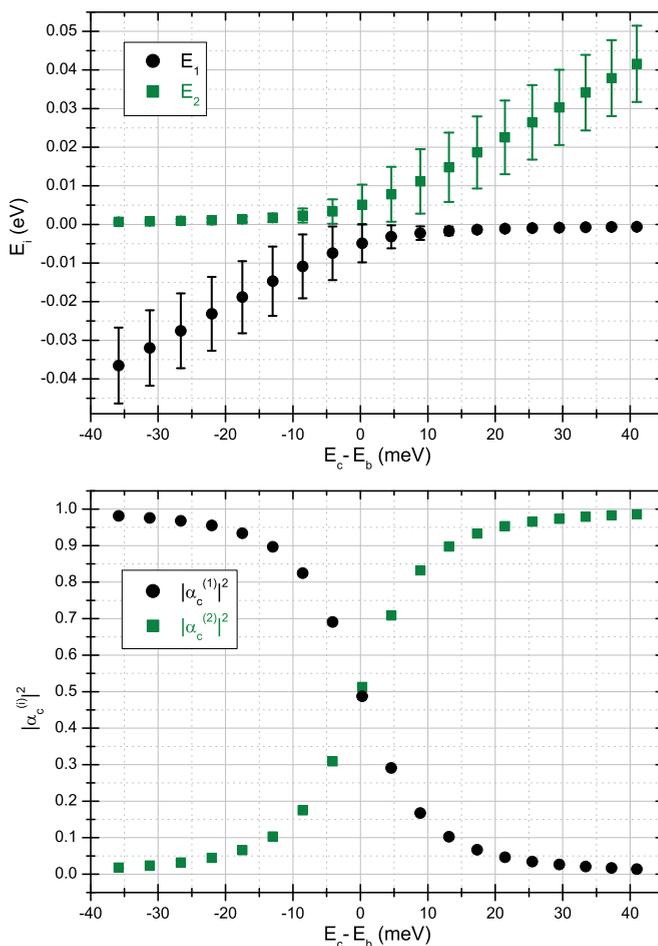


FIG. 4. (Color online) Top: Evolution of the energies and line widths (magnified by a factor of 100) of the new conduction band states at $\Psi^{(1)}$ and $\Psi^{(2)}$ as a function of the energy separation between the unperturbed boron state ϕ_b and the host CBE state ϕ_c . Bottom: Evolution of the host-like contribution of $\Psi^{(1)}$ and $\Psi^{(2)}$ as a function of the energy separation between the unperturbed states ϕ_b and ϕ_c .

clearly separated. Hence, the B-related state becomes visible in the spectrum when the CBE and B state are close in energy.

Figure 4 further illustrates the features of the model. The top graph shows the evolution of the energies and line widths of the new conduction band states $\Psi^{(1)}$ and $\Psi^{(2)}$ as a function of the energy separation between the unperturbed B state ϕ_b and the host CBE state ϕ_c . The bottom graph shows the corresponding plot of the host CBE-like contribution to the new states, which provides a measure for their PR signal strengths. For $E_c - E_b < 0$ (i.e., when the host conduction band state is lower in energy than the unperturbed B state) the lower new conduction band state $\Psi^{(1)}$ is host-like, basically possessing the same energy shift $E_1 \approx E_c$, the same line width $\sigma_1 \approx \sigma_c$, and the same symmetry character $|\alpha_c^{(1)}|^2 \approx 1$ as the host CBE state. The corresponding feature in the PR spectrum resembles that of a typical direct band gap transition. The state $\Psi^{(2)}$ is B-like and hardly visible in the modeled PR spectrum as $|\alpha_c^{(2)}|^2 \approx 0$. As expected, the situation changes close to resonance, where both states $\Psi^{(1)}$ and $\Psi^{(2)}$ become visible in the modeled PR spectra. They both shift in energy and their line widths change (i.e., σ_1 decreases and σ_2 increases). At resonance, both signals are of the same oscillator strength and line width as $|\alpha_c^{(1)}|^2 = |\alpha_c^{(2)}|^2 = 0.5$. Due to the level repulsion, the energy deviation from the energy positions of the unperturbed states is largest. However, the repulsion is too small to separate the two signals and a complicated signal form arises due to the overlap. After the resonance, with increasing $(E_c - E_b) > 0$, the character of the states is further reversed (i.e., $\Psi^{(1)}$ becomes B-like and vanishes in the PR spectra whereas $\Psi^{(2)}$ becomes host CBE-like and resembles the PR feature of a typical direct band gap transition). According to the model, the unusual PR line shapes found in the experiment occur close to resonance, where both transitions involving the new conduction band states are visible in the PR spectrum. The character of the two states is reversed leading to the line width

changes and the unusual dependence of the corresponding transition energies as a function of energy separation between the unperturbed states (i.e., as a function of temperature or pressure in the experiment). Even considering one B state only, the model is in qualitative agreement with experiment.

It should be noted that the CBE state in reality crosses a distribution of B states which all may couple to a certain degree with the host CBE state. This implies that many more oscillators may somewhat contribute to the PR line widths, as can be seen in the experimental spectrum shown in the inset of Fig. 1(b). Therefore, a quantitative fitting of the PR line shapes of the $B_xGa_{1-x-y}In_yAs$ samples on this empirical basis is hardly possible and beyond the scope of this paper.

IV. SUMMARY

We conclude that the changes in PR line shape observed experimentally are consistent with a model assuming level repulsion between a CBE state and a distribution of localized B states which initially lie above the CBE at room temperature and ambient pressure. This level ordering leads to a normal fundamental band gap line shape at room temperature, which evolves to an anomalous line shape with several additional features as hydrostatic pressure is applied or the sample temperature is lowered. Our results and analysis therefore both explain the evolution of the PR line shape of the fundamental band gap transition and give further evidence of the existence of localized B cluster states in the vicinity of the CBE in (B,Ga)As and (B,Ga,In)As alloys.

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