Effect of the reduction of dimensionality on the exchange parameters in semimagnetic semiconductors

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We present experimental results showing a variation of the exchange parameters between carrier spins and Mn spins as a function of quantum-well width in semimagnetic heterostructures. Relative changes of the exchange parameters of about 0.1 are observed by analyzing the Zeeman splittings of the free-exciton states in epitaxially grown $Cd_{1-x}Mn_xTe/Cd_{1-x-y}Mn_xMg_yTe$ quantum wells with no discontinuity of the Mn content at the interfaces. We attribute the well-width dependence of the Zeeman splittings to a **k**-vector dependence of the exchange parameters. [S0163-1829(96)51432-3]

In semimagnetic semiconductors the large exchange interaction between the band states of electrons and holes and the localized *d* electrons of (usually) Mn ions leads to strong magneto-optical effects like Zeeman splittings of the free-exciton states of more than 100 meV. The Zeeman splittings in bulk systems[1] (e.g., $Cd_{1-x}Mn_xTe$) and semimagnetic quantum wells (QW's) such as $CdTe/Cd_{1-x}Mn_xTe$ (Refs. 2 and 3) and $Cd_{1-y}Mn_yTe/Cd_{1-x}Mg_xTe$ (Ref. 4) have been extensively studied. Deviations from the expected behavior in semimagnetic QW's have been attributed to a modification of the magnetic properties at the interface between magnetic and nonmagnetic material. Two interface effects were found: (i) the enhanced paramagnetisms at the interface due to the partial missing of nearest neighbors of Mn ions in the vicinity of Mn ions at the interface,[3] which leads to less antiferromagnetically coupled Mn pairs and to more paramagnetically active single spins; (ii) the diffusion or segregation of Mn atoms into the nonmagnetic well (or barrier).[5] The second effect is especially important in quantum wells with magnetic barriers and nonmagnetic wells, where even a small amount of paramagnetic Mn ions diffused in the well experiences a strong overlap with the excitonic wave function.

Apart from the interface effects, it is unclear yet whether the exchange parameters at the conduction- and valence-band edges (constants α and β at the Γ point) are affected by the reduction of dimensionality. A standard technique to extract the exchange parameters for bulk material is to compare optical measurements and magnetization measurements, but magnetization measurements are extremely difficult for epitaxially grown QW structures due to the limited sample volume. To study the variation of the exchange parameters with well width by optical means only has not been possible up to now, since the influence of the exchange parameters has been screened by the interface related effects mentioned above.

In this paper we study the exchange parameters in semimagnetic QW's using specially designed structures to avoid the interface-related effects. We employ $Cd_{1-x}Mn_xTe/Cd_{1-x-y}Mn_xMg_yTe$ QW's, which fulfill the following requirements necessary for our studies: (i) Our structures have no discontinuity in the Mn content at the interfaces. (ii) Moreover, the exchange interaction, both among the Mn spins and between carriers and Mn ions, exhibits no difference between barrier and well materials.[6] (iii) Since the exchange constant for the valence band is four times stronger than that for the conduction band, it is necessary to have a considerable valence-band offset in order to provide a strong quantization of holes. Our structures have a valence-band offset of about 0.3.[7]

We show experimentally that the exchange parameters are modified by a reduction of dimensionality. We find relative changes of the exchange parameters of about 0.1 with well width in our structures.

The experiments were performed on samples grown by molecular-beam epitaxy (MBE). $Cd_{0.96}Zn_{0.04}Te$ serves as substrate, which, for example, is lattice-matched to $Cd_{0.60}Mg_{0.40}Te$ or $Cd_{0.90}Mn_{0.10}Te$.[8] Both these compounds have valence-band offsets of 0.3 with respect to CdTe or to each other.[7] Due to the similar variation of the band gap with composition, $Cd_{1-x}Mn_xTe$, $Cd_{1-x}Mg_xTe$, and $Cd_{1-x-y}Mn_xMg_yTe$ have similar photoluminescence (PL) halfwidths as a function of $x+y$.[6] In $Cd_{1-x-y}Mn_xMg_yTe$ magnetic and nonmagnetic properties can be tailored nearly independently. We study $Cd_{1-x}Mn_xTe/Cd_{1-x-y}Mn_xMg_yTe$ QW's with Mn contents $0.04 \leqslant x \leqslant 0.11$ and Mg contents $0.20 \leqslant y \leqslant 0.25$. Therefore, our structures are closely lattice matched to the $Cd_{0.96}Zn_{0.04}Te$ substrate. The carrier confinement conditions determined by the Mg content are very similar for all QW's studied. The structure of our samples is schematically shown in the inset of Fig. 1. After a $Cd_{1-x-y}Mn_xMg_yTe$ buffer of about 2000 Å there are several $Cd_{1-x}Mn_xTe$ QW's separated by 500-Å-thick barrier layers of $Cd_{1-x-y}Mn_xMg_yTe$. The well widths are typically 300, 80, 45, and 18 Å. Finally, a 5000-Å-thick cap layer of $Cd_{1-x-y}Mn_xMg_yTe$ was grown. During the growth of the ternary quantum wells the Mg cell was closed, and for the growth of the quaternary layer both fluxes of Mn and Mg were offered simultaneously. In the MBE process the sticking coefficients of both Mn and Mg on Te are considerably larger than the competing Cd. Under the growth conditions applied for the fabrication of the quaternary layers Mn and Mg are built in at the expense of Cd and the growth of $Cd_{1-x-y}Mn_xMg_yTe$ on $Cd_{1-x}Mn_xTe$ by additional Mg

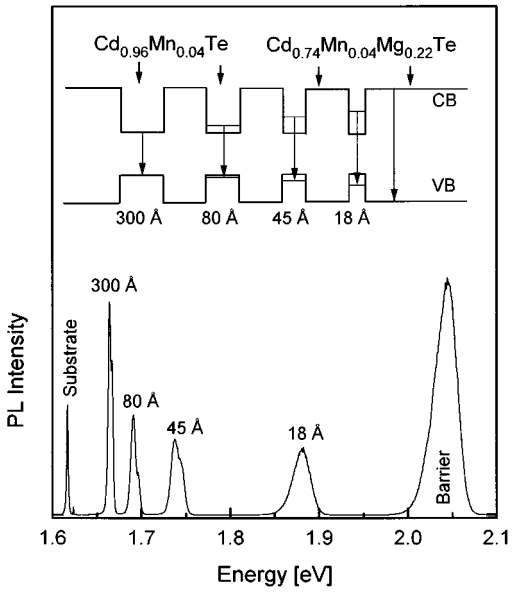

FIG. 1. Photoluminescence of a $Cd_{0.96}Mn_{0.04}Te/Cd_{0.74}Mn_{0.04}Mg_{0.22}Te$ quantum-well structure on $Cd_{0.96}Zn_{0.04}Te$ substrate and well width of 18, 45, 80, and 300 Å taken at $T=1.8$ K. The photoluminescence spectrum is excited at $\hbar\omega_{exc}=2.4$ eV. The sample structure is schematically illustrated in the inset (CB =conduction band, VB=valence band).

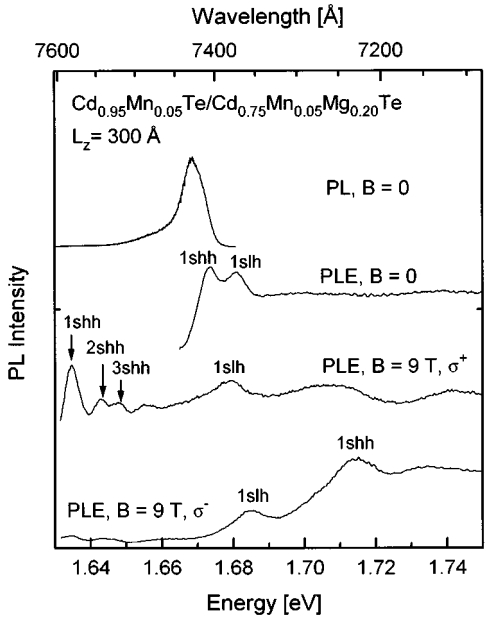

FIG. 2. Photoluminescence and photoluminescence excitation spectra of a 300-Å-wide $Cd_{0.95}Mn_{0.05}Te/Cd_{0.75}Mn_{0.05}Mg_{0.20}Te$ quantum well at $B=0$ (top) and at $B=9$ T (applied parallel to the structure growth axis) under σ^+- and σ^--polarized excitation (bottom); $T=1.8$ K.

offer does not change the Mn content.[6] The samples were mounted in the Faraday configuration in the bore of a superconducting split-coil magnet (fields up to $B=9.5$ T), immersed in superfluid helium at 1.8 K. PL was excited by the 514-nm line of an argon-ion laser. PL excitation spectra were carried out using tunable Pyridine 2, DCM, Rhodamine 6G, and Rhodamine 110 dye lasers. The spectral resolution is 0.1 meV.

In Fig. 1 a typical PL spectrum of a $Cd_{0.90}Mn_{0.10}Te/Cd_{0.75}Mn_{0.10}Mg_{0.15}Te$ structure with several QW's is shown. The spectrum consists of well-resolved lines from the barrier layer, the QW's and from the $Cd_{0.96}Zn_{0.04}Te$ substrate. The x and y contents of the quaternary layers were determined from the energy of the exciton recombinations in the 300-Å-wide $Cd_{1-x}Mn_xTe$ well and the quaternary barrier layer. More details about the determination of x and y contents have been described in Ref. 6.

The magnetic properties of the semimagnetic QW's are studied by analyzing the Zeeman splittings of the free-exciton states via PL excitation (PLE) spectroscopy. PLE spectra at field strengths $B=0$ and 9 T together with a PL spectrum at $B=0$ T of a 300-Å-wide $Cd_{0.95}Mn_{0.05}Te/Cd_{0.75}Mn_{0.05}Mg_{0.20}Te$ QW are shown in Fig. 2. The PLE spectra are detected on the low-energy side of the PL line. In magnetic fields the PLE spectra are taken under right- and left-circularly polarized excitation. The observation of $2s$- and $3s$-exciton states at magnetic fields demonstrates the high quality of the studied samples. The large Zeeman splitting of the $1s$ hh state of, e.g., 80 meV at $B=9$ T is caused by the sp-d exchange interaction between the heavy-hole exciton states and the magnetic moments of the Mn ions and is proportional to the magnetization of the Mn-ion system. It has been shown for $Cd_{1-x}Mn_xTe$ that the Zeeman splitting (ΔE_{hh}) is well described by a modified Brillouin function $B_{5/2}$. For heavy-hole excitons it has the following form:[1]

$$\Delta E_{hh}=f(\alpha-\beta)N_0xS_{eff}B_{5/2}\left(\frac{\frac{5}{2}g\mu B}{k(T+T_0)}\right), \qquad (1)$$

where α and β are the exchange constants at the Γ point for the conduction and valence band,[9] respectively, N_0 is the number of unit cells per unit volume, $g=2$, μ is the Bohr magneton, S_{eff} is the effective spin, and T is the lattice temperature. The parameters S_{eff} and T_0 characterize the magnetic properties of the Mn-ion system, which are determined by the antiferromagnetic interaction of neighboring Mn ions. The effective spin decreases and T_0 increases with increasing x content.[1,3] The exchange constants α and β characterize the exchange interaction of the band states with the magnetic moments of the Mn ions. $N_0\alpha=0.22$ eV and $N_0\beta=-0.88$ eV have been determined for $Cd_{1-x}Mn_xTe$ (Ref. 1) at the Γ point and we have shown in our previous work that they could also be applied to $Cd_{1-x-y}Mn_xMg_yTe$.[6] We have introduced in Eq. (1) an additional factor f to account for changes in the exchange parameters with well width. Since changes in the exchange parameters are contributed by changes in the valence band (factor f^v) and in the conduction band (factor f^c), f is defined as $f\equiv(f^c\alpha-f^v\beta)/(\alpha-\beta)$. We can use $f=1$ for thick $Cd_{1-x}Mn_xTe$ and $Cd_{1-x-y}Mn_xMg_yTe$ layers. Note that Eq. (1) also applies to QW's since in contrast to all previously studied QW's in magnetic fields the band edges of the well and barrier layers shift by the same values leading to symmetrical Zeeman splittings for wells. Diamagnetic shifts of the exciton states are negligible in the range of magnetic fields studied here.

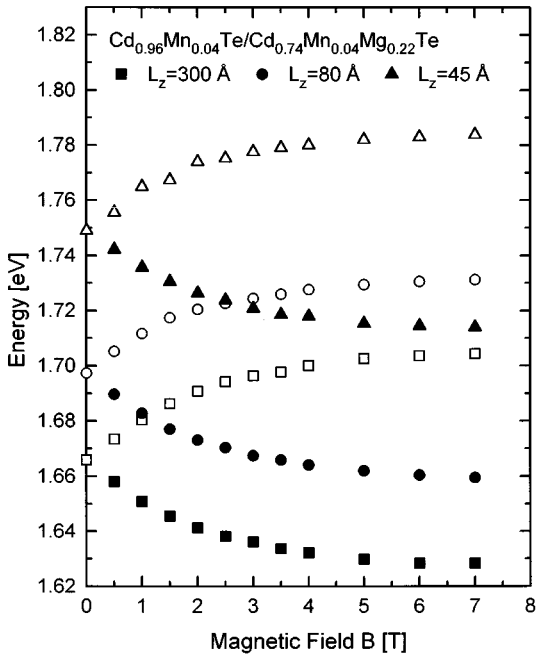

FIG. 3. Zeeman splittings of heavy-hole excitons of $Cd_{0.96}Mn_{0.04}Te/Cd_{0.74}Mn_{0.04}Mg_{0.22}Te$ quantum wells determined by photoluminescence excitation spectra in magnetic fields applied parallel to the structure growth axis; $T=1.8$ K. The upper branches (σ^-) are shown by open symbols, lower branches (σ^+) are shown by filled symbols.

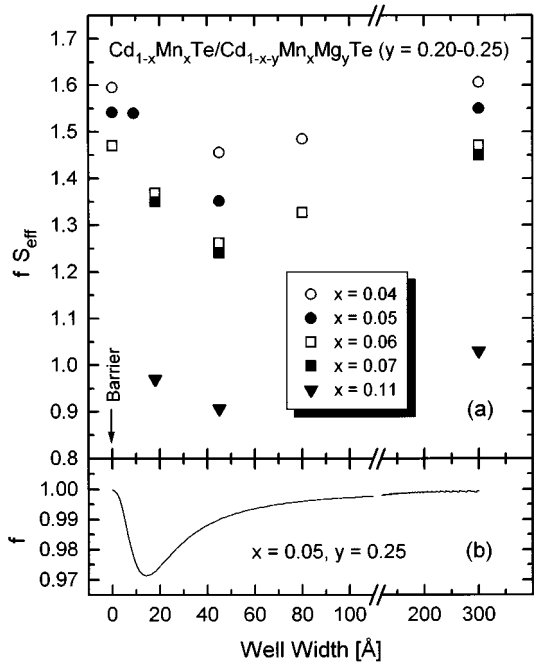

FIG. 4. (a) $fS_{\rm eff}$ fitted with Eq. (1) as a function of well width for different Mn contents in $Cd_{1-x}Mn_xTe/Cd_{1-x-y}Mn_xMg_yTe$ quantum wells at $T=1.8$ K. (b) Reduction factor f [see Eq. (2)] for the exchange constants as a function of well width for $x=0.05$, $y=0.25$.

Figure 3 shows the Zeeman pattern of the heavy-hole excitons for three different QW's of the $Cd_{0.96}Mn_{0.04}Te/Cd_{0.74}Mn_{0.04}Mg_{0.22}Te$ structure. σ^+ branches are denoted by filled symbols, σ^- branches are denoted by open symbols. At first sight, the Zeeman splittings are practically identical, only the lines of the smaller wells are blueshifted due to the higher subband energy. The Zeeman splittings were fitted varying the quantities T_0 and $fS_{\rm eff}$ in Eq. (1). For the 300-Å-thick $Cd_{1-x}Mn_xTe$ wells and the quaternary layers (where we take $f=1$) the values for T_0 and $S_{\rm eff}$ agree well with the values measured in bulk $Cd_{1-x}Mn_xTe$ (Ref. 1) and in $Cd_{1-x}Mn_xTe$ MBE-grown epilayers[3] within the error bars of our measurements (± 0.5 K for T_0 and ± 0.1 for $S_{\rm eff}$). We now study how $fS_{\rm eff}$ behaves in QW's.

In Fig. 4(a) we show $fS_{\rm eff}$ as a function of well width. Values for one Mn concentration are always determined from one sample only. Qualitatively we find the same behavior for all samples studied so far. While for $L_z\rightarrow\infty$ and $L_z\rightarrow 0$ the bulk values of T_0 and $S_{\rm eff}$ are reproduced, $fS_{\rm eff}$ has a minimum in all of our structures at the well width of $L_z=45$ Å, which does not necessarily agree with the real minimum in the well width dependence. This real minimum is difficult to determine since only a limited number of measurable wells can be incorporated into one structure. The relative variation of $fS_{\rm eff}$ with well width is about 0.1. We note that we find that same relative variation also in $Cd_{1-x}Mn_xTe/Cd_{1-y}Mg_yTe$ QW's for $x=0.10$ and 0.18 and well widths between 40 and 300 Å (smaller wells cannot be evaluated in this case due to dominating interface effects). We attribute the changes in $fS_{\rm eff}$ with well width to changes in f for the following reasons: (i) $S_{\rm eff}$ is not modified in the quaternary material in comparison to $Cd_{1-x}Mn_xTe$, and (ii) if $S_{\rm eff}$ were the responsible factor, the observed effect should be a function of Mn content, which is obviously not the case for the range of studied contents $0.04\leqslant x\leqslant 0.18$. Therefore, we now propose a model explaining why f could be a function of the well width. As background information we first mention some results on studies of the exchange constants at the critical L point.

Coquillat *et al.*[10] carried out most of the few magneto-optical experiments studies of the interband transitions away from the center of the Brillouin zone at the L point (0.5,0.5,0.5). They found a reduction factor of $\Delta E_L/\Delta E_\Gamma=\frac{1}{16}$ for the Zeeman splittings, independent of Mn concentration. A theoretical tight-binding analysis of the exchange constants at the L point by Bhattacharjee[11] came to the conclusion that the dominating part of the **k**-vector dependence of the exchange parameters has to be attributed (i) for the conduction band, to the projection of the conduction-band wave function on the cation s-orbital Bloch sum and (ii) for the valence band, to the hopping interference factor

$$f(\mathbf{k})\equiv\left|\sum_{\boldsymbol{\delta}_1} e^{i\mathbf{k}\cdot\boldsymbol{\delta}_1}+0.1\sum_{\boldsymbol{\delta}_2} e^{i\mathbf{k}\cdot\boldsymbol{\delta}_2}\right|^2$$

between the Mn-d orbitals and the first- and second-neighbor anion p orbitals, where $\boldsymbol{\delta}_1,\boldsymbol{\delta}_2$ denote the coordinates of the first- and second-neighbor anion p orbitals. Since the model of Ref. 11 is only satisfactory for the valence-band contribution, we neglect the conduction-band contribution for an estimation. This, together with $\beta/\alpha\approx 4$, leads to a reduction factor for the exchange integral of

$$f = 0.2 + 0.8\frac{F(\mathbf{k})}{F(0)}. \quad (2)$$

This $\mathbf{k}$ dependence can also be applied to QW's, where the wave vector $\mathbf{k}_z$ is nonzero due to the confinement along the growth axis z. For well and barrier $\mathbf{k}_z$ is given by

$$\mathbf{k}_z^w = \frac{1}{\hbar}\sqrt{2m_{\mathrm{hh}}E} \quad \text{and} \quad \mathbf{k}_z^b = \frac{1}{\hbar}\sqrt{2m_{\mathrm{hh}}(V-E)}, \quad (3)$$

where E is the energy of the first subband in the valence band and V is the valence-band offset. In Fig. 4(b) we plot for illustration the reduction factor from Eq. (2) for $Cd_{0.95}Mn_{0.05}Te/Cd_{0.70}Mn_{0.05}Mg_{0.25}Te$ as a function of well width, while only taking the variation due to $\mathbf{k}_z$ into account with $\mathbf{k}_x = \mathbf{k}_y = \mathbf{k}_\parallel = 0$. We use $m_{\mathrm{hh}} = 0.485$ (Ref. 12) and a valence-band offset V of 100 meV.[7] The comparison of Figs. 4(a) and 4(b) shows a qualitative agreement. The variation of f is about a factor of 2–3 smaller than that found experimentally. Although the well width where the minimum of the exchange parameter occurs is difficult to evaluate from Fig. 4(a), there seems to be a disagreement in this well width between experiment and estimation. But, two significant contributions are not considered now. (i) The conduction-band contribution to f is neglected in our description. In the frame of the model of Ref. 11 this contribution is strongly underestimated. The data from Ref. 10 together with the model from Ref. 11 show that the $\mathbf{k}$-vector dependence of the conduction-band exchange parameters could give a contribution which is, for small $\mathbf{k}$, as important as the valence-band contribution. Including the variation of the conduction-band parameters means that the minimum of f is shifted to larger well widths, as it is found in our experiments. (ii) Solving the exciton problem variationally with appropriate parameters, we find that for our structures the values of $\mathbf{k}_\parallel$ are smaller than the values of $\mathbf{k}_z$ by about a factor of 4 and could not affect the minimum value of f strongly, but could shift the minimum of f to larger well widths, too.

We note that the influence of the dimensionality on the exchange parameters should be taken into account while studying semimagnetic interface effects in quantum wells. Moreover, the modification of the exchange parameters becomes increasingly important when the dimensionality of the system is further reduced. The strongest reduction of dimensionality is realized in quantum dots. Recently, magnetoabsorption data have been published for $Cd_{1-x}Mn_xSe$ nanocrystals.[13] A relatively small redshift of the absorption edge is observed in magnetic fields. An exact analysis of the data with respect to our question is complicated by uncertainties in the Mn content, the distribution of dot sizes and surface effects on the magnetic properties, which should be stronger than the interface effects in QW's due to the large surface to volume ratio. However, a modification of the exchange parameters due to the low dimensionality could explain the experimental results.

In conclusion, we have studied the Zeeman splittings of the semimagnetic heterostructures $Cd_{1-x}Mn_xTe/Cd_{1-x-y}Mn_xMg_yTe$ that allow us to vary independently magnetic and nonmagnetic properties and have no discontinuity of the Mn concentration at the interfaces between quantum wells and barriers. We have shown that the reduction of dimensionality affects the exchange parameters in semimagnetic semiconductors considerably. We attribute the observed effect to a $\mathbf{k}$-vector dependence of the respective exchange parameters. This effect is strong enough that it should be taken into account in the evaluation of interface related effects in heterostructures with a discontinuity in the Mn content at the interfaces, where the exchange parameter effect is usually screened. Moreover, a further reduction of dimensionality to one- and zero-dimensional systems should lead to even stronger effects. We hope that our experiments will stimulate more detailed tight-binding band-structure calculations. This is essential for further studies of semimagnetic structures of low dimensionality.

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[1] J. A. Gaj, R. Planel, and G. Fishman, Solid State Commun. **29**, 435 (1979).
[2] B. Kuhn-Heinrich, M. Popp, W. Ossau, E. Bangert, A. Waag, and G. Landwehr, Semicond. Sci. Technol. **8**, 1239 (1993), and references therein.
[3] W. J. Ossau and B. Kuhn-Heinrich, Physica B **184**, 422 (1993).
[4] B. Kuhn-Heinrich, W. Ossau, E. Bangert, A. Waag, and G. Landwehr, Solid State Commun. **91**, 413 (1994).
[5] J. A. Gaj, W. Grieshaber, C. Bodin-Deshayes, J. Cibert, G. Feuillet, Y. Merle d'Aubigné, and A. Wasiela, Phys. Rev. B **50**, 5512 (1994).
[6] G. Mackh, M. Hilpert, D. R. Yakovlev, W. Ossau, H. Heinke, T. Litz, F. Fischer, A. Waag, G. Landwehr, R. Hellmann, and E. O. Göbel, Phys. Rev. B **50**, 14 069 (1994).
[7] B. Kuhn-Heinrich, W. Ossau, T. Litz, A. Waag, and G. Landwehr, J. Appl. Phys. **75**, 8046 (1994); B. Kuhn-Heinrich, W. Ossau, H. Heinke, F. Fischer, T. Litz, A. Waag, and G. Landwehr, Appl. Phys. Lett. **63**, 2932 (1993).
[8] W. Ossau, U. Zehnder, B. Kuhn-Heinrich, A. Waag, T. Litz, and G. Landwehr, Superlattices Microstruct. **16,** 5 (1994).
[9] J. Ginter, J. A. Gaj, and Le Si Dang, Solid State Commun. **48,** 849 (1983).
[10] D. Coquillat, J. P. Lascaray, M. C. Desjardins-Deruelle, J. A. Gaj, and R. Triboulet, Solid State Commun. **59,** 25 (1986); D. Coquillat, J. P. Lascaray, J. A. Gaj, J. Deportes, and J. K. Furdyna, Phys. Rev. B **39,** 10 088 (1989).
[11] A. K. Bhattacharjee, Phys. Rev. B **41,** 5696 (1990); *Proceedings of the XX International Conference on the Physics of Semiconductors, Thessaloniki, 1990*, edited by E. M. Anastassakis and J. D. Joannopoulos (World Scientific, Singapore, 1990), p. 763.
[12] M. Said and M. A. Kanehisa, Phys. Status Solidi B **157,** 311 (1990).
[13] K. Yanata, K. Suzuki, and Y. Oka, J. Appl. Phys. **73,** 4595 (1993).