EPR and Ferromagnetism in Diluted Magnetic Semiconductor Quantum Wells

Jürgen König[1] and Allan H. MacDonald[2]
[1]*Institut für Theoretische Festkörperphysik, Universität Karlsruhe, 76128 Karlsruhe, Germany*
[2]*Department of Physics, University of Texas at Austin, Austin, Texas 78712, USA*
(Received 3 October 2002; published 11 August 2003)

Motivated by recent measurements of electron paramagnetic resonance spectra in modulation-doped CdMnTe quantum wells [F. J. Teran *et al.*, Phys. Rev. Lett. **91**, 077201 (2003)], we develop a theory of collective spin excitations in quasi-two-dimensional diluted magnetic semiconductors. Our theory explains the anomalously large Knight shift found in these experiments as a consequence of collective coupling between Mn-ion local moments and itinerant-electron spins. We use this theory to discuss the physics of ferromagnetism in (II,Mn)VI quantum wells and to speculate on the temperature at which it is likely to be observed in *n*-type modulation-doped systems.

DOI: 10.1103/PhysRevLett.91.077202 PACS numbers: 75.50.Pp, 73.43.–f, 75.30.Ds

Substitution of transition metal elements in a semiconductor lattice often adds local moments [1] to the system's low-energy degrees of freedom and can lead to qualitatively new physics. Important progress [2] has recently been achieved in understanding the materials science and physics of (II,Mn)VI and (III,Mn)V ternary compound semiconductors in which Mn has been substituted on a relatively small fraction of the cation sites. When these systems are doped *p*-type, the Mn ions spontaneously align at low temperatures in both bulk and quantum-well systems with typical ferromagnetic transition temperatures $\sim$1 K in the quantum-well case and $\sim$100 K in the bulk. Although there is broad agreement that ferromagnetism in these systems is due to carrier-mediated interactions between Mn local moments, consensus [3] on the details of this picture is still building as the body of experimental studies on well characterized samples grows. In this connection it is intriguing that ferromagnetism has *never* been observed when these semiconductors are *n*-doped [4]. Recent inelastic Raman and resistively detected electron paramagnetic resonance (EPR) studies of *n*-doped (Cd,Mn)Te quantum wells by Teran *et al.* [5] provide important information about the role played by quantum-well electrons in correlating Mn-ion local-moment-spin orientations. In particular, these authors have discovered an avoided crossing between well-defined electron spin and Mn-ion spin-resonance modes, an effect which demonstrates that the two subsystems can couple collectively.

Quantum-well diluted magnetic semiconductor (DMS) systems are unusual in that they consist of a quasi-3D Mn-ion system coupled to quantum-well electrons that have only two-dimensional (2D) translational degrees of freedom. In this Letter, we present a theoretical analysis which completely accounts for the observations of Teran *et al.,* including the size of the avoided crossing gap they see. The theory sheds light on the physics that controls ferromagnetism in DMS quantum wells and on the essential differences between electron- and hole-doped cases. It follows from our theory that the gap discovered experimentally occurs because quantum-well electrons and Mn-ion spins are coupled ferromagnetically in *n*-doped systems. According to our theory the ferromagnetic transition temperature is controlled by spin-orbit coupling strength, a quantity that can be adjusted *in situ* by biasing the quantum well [6] and is much larger in *p*-doped systems. We conclude that ferromagnetism *will* occur in *n*-doped quantum wells, but only at temperatures well below those predicted by mean-field theory and below those which have been studied experimentally. In the following, we first describe our theory of collective excitations of the coupled local-moment and quantum-well-electron spin subsystems and then discuss ferromagnetism in *n*-doped (Cd,Mn)Te systems.

We consider an *n*-type quantum well with width d (in the $\hat{z}$ direction) and one occupied subband. The quantum-well geometry makes it convenient to split the three-dimensional spatial coordinates into $(\mathbf{r}, z)$, where $\mathbf{r}$ is the x-y-plane projection. When subband mixing is neglected [7] the electron wave function separates, $\Psi(\mathbf{r}, z) = \psi(\mathbf{r})\chi(z)$, where $\chi(z)$ can be chosen to be real. We take advantage of the large ratio between the Mn density and the electron density in the samples studied by Teran *et al.* and in typical [8] modulation-doped (II,Mn)VI quantum-well systems, replacing the random distribution of Mn local moments by a continuum density $N_{\mathrm{Mn}}(z)$. We are interested in the collective excitations in the presence of an external magnetic field $\mathbf{B} = (0, 0, B)$. The Hamiltonian $H = H_{\mathrm{kin}} + H_{\mathrm{Zeeman}} + H_{\mathrm{sd}}$ is the sum of three terms. The kinetic energy of the electrons is described by

$$H_{\mathrm{kin}} = \int d^2r \int_0^d dz \chi^2(z) \times \sum_\sigma \hat{\psi}_\sigma^\dagger(\mathbf{r}) \left(\frac{(-i\hbar\boldsymbol{\nabla} + e\mathbf{A}/c)^2}{2m^*} - \mu \right) \hat{\psi}_\sigma(\mathbf{r}), \quad (1)$$

where $\mathbf{A}$ is the vector potential. The Zeeman term reads

$$H_{\mathrm{Zeeman}} = \mu_B \mathbf{B} \cdot \int d^2r \int_0^d dz [g_e \hat{\mathbf{s}}(\mathbf{r}, z) + g_{\mathrm{Mn}} \mathbf{S}(\mathbf{r}, z)], \quad (2)$$

where $\mu_B > 0$ is the electron Bohr magneton. Here

$$\hat{\mathbf{s}}(\mathbf{r}, z) = \frac{1}{2}\chi^2(z)\sum_{\sigma\sigma'}\hat{\psi}^\dagger_\sigma(\mathbf{r})\boldsymbol{\tau}_{\sigma\sigma'}\hat{\psi}_{\sigma'}(\mathbf{r}) \tag{3}$$

is the electron spin density, $\boldsymbol{\tau}_{\sigma\sigma'}$ is the vector of Pauli matrices, and $\mathbf{S}(\mathbf{r}, z)$ is the spin density of the Mn system. The ferromagnetic ($J_{\rm sd} < 0$) coupling between the electron and local-moment [2] spins is described by

$$H_{\rm sd} = J_{\rm sd}\int d^2r\int_0^d dz\mathbf{S}(\mathbf{r}, z)\cdot\hat{\mathbf{s}}(\mathbf{r}, z). \tag{4}$$

As in our earlier work [9] on bulk DMS ferromagnets, we develop our theory of elementary spin excitations in a language where the conduction-band degrees of freedom are integrated out. The local moments with spin $S = 5/2$ are represented by Holstein-Primakoff (HP) bosons with retarded conduction-band mediated interactions. Because $g_{\rm Mn} > 0$, the external magnetic field tends to align the Mn spins along the negative $\hat{z}$ direction. For small fluctuations around this state we can approximate the spin fields in a coherent-state functional-integral representation of the HP-boson partition function by $S^+ \approx \bar{w}\sqrt{2N_{\rm Mn}(z)S}$, $S^- \approx w\sqrt{2N_{\rm Mn}(z)S}$, and $S^z = -N_{\rm Mn}(z)S + \bar{w}w$, where the complex variables $\bar{w}, w$ label boson coherent states. The partition function is formally expressed as $Z = \int\mathcal{D}(\bar{w}w)\exp(-S_{\rm eff}[\bar{w}w])$ with the effective action

$$S_{\rm eff}[\bar{w}w] = \int_0^\beta d\tau\int d^2r\int_0^d dz[\bar{w}\partial_\tau w + g_{\rm Mn}\mu_B BS^z] - {\rm lndet}G^{-1}(\bar{w}w). \tag{5}$$

The electron Green's function in this equation may be partitioned into mean-field and fluctuating terms, $G^{-1}(\bar{w}w) = (G^{\rm MF})^{-1} + \delta G^{-1}(\bar{w}w)$, where

$$(G^{\rm MF})^{-1} = \left(\partial_\tau - \frac{\hbar^2\tilde{\boldsymbol{\nabla}}^2}{2m^*} - \mu\right) + \frac{\Delta + g_e\mu_B B}{2}\tau^z, \tag{6}$$

with $\tilde{\boldsymbol{\nabla}} = \boldsymbol{\nabla} + (ie/\hbar c)\mathbf{A}$, and the fluctuating part is

$$\delta G^{-1}(\bar{w}w) = -\frac{|J_{\rm sd}|}{2}\int_0^d dz\chi^2(z)[\sqrt{2N_{\rm Mn}(z)S}(\bar{w}\tau^- + w\tau^+) + \bar{w}w\tau^z]. \tag{7}$$

The exchange contribution to the conduction-band spin splitting that appears in $G^{\rm MF}$ is given by $\Delta = |J_{\rm sd}|\bar{N}_{\rm Mn}S$, where $\bar{N}_{\rm Mn} = \int_0^d dz\chi^2(z)N_{\rm Mn}(z)$. Expanding to second order in the boson fields and Fourier transforming, we can write the quadratic part of the spin-wave action as

$$S_{\rm eff}[\bar{w}w] = \frac{1}{\beta}\sum_m\int\frac{d^2k}{(2\pi)^2}\int_0^d dz\int_0^d dz'\bar{w}(\mathbf{k}, z, \nu_m)D^{-1}(\mathbf{k}, z', z, \nu_m)w(\mathbf{k}, z', \nu_m), \tag{8}$$

where ν_m are the bosonic Matsubara frequencies. The kernel $D^{-1}(\mathbf{k}, z', z, \nu_m)$ in Eq. (8) is obtained from a straightforward calculation which leads to a fermion loop diagram specified by an unwieldy expression that we do not reproduce here. Instead, we specialize to the case of $\mathbf{k} = 0$ probed by the EPR and Raman experiments of Teran *et al.* In this limit the kernel is given by the physically transparent expression:

$$D^{-1}(\mathbf{k} = 0, z', z, \nu_m) = \left[-i\nu_m + g_{\rm Mn}\mu_B B + \frac{|J_{\rm sd}|}{2}(n_\downarrow - n_\uparrow)\chi^2(z)\right]\delta(z - z') + \frac{SJ^2_{\rm sd}\chi^2(z)\chi^2(z')\sqrt{N_{\rm Mn}(z)N_{\rm Mn}(z')}}{2}\frac{n_\downarrow - n_\uparrow}{i\nu_m - \Delta - g_e\mu_B B}, \tag{9}$$

where n_σ is the (2D) mean-field conduction-electron spin density for spin σ. At $\mathbf{k} = 0$ this expression is valid at any Landau level filling factor. The first term on the right-hand side of Eq. (9) represents the energy cost of flipping an individual Mn spin and includes the *Knight shift K* contribution (see below) due to exchange coupling with band electrons whose spin density depends on the position of a Mn-ion within the quantum well. The second term is the correction to the energy cost (at $\mathbf{k} = 0$) which occurs because the quantum-well electron system responds to Mn-spin reorientations. Collective excitations are determined by locating zeroes of the kernel determinant. Since uniform spin orientation fluctuations correspond in our continuum theory to $w_0(z) \propto \sqrt{N_{\rm Mn}(z)}$, the energies $E = \hbar\Omega$ of the collective excitations we seek [10] are obtained by solving

$$\int_0^d dz\int_0^d dz' w_0(z)D^{-1}(0, z', z, i\nu_m = \Omega)w_0(z') = 0, \tag{10}$$

which implies collective excitations at

$$E = \frac{E_{\rm Mn} + E_e}{2} \pm \sqrt{\frac{(E_{\rm Mn} - E_e)^2}{4} + K\Delta}. \tag{11}$$

The quantities in Eq. (11) all have simple physical interpretations. The expressions $E_{\rm Mn}$ and E_e denote mean-field transition energies in which the magnetic quantum number is increased by one for Mn and electron spins, respectively. Each mean-field excitation energy has two contributions, the Zeeman energy and the exchange energy due to coupling between the two spin subsystems. For the Mn spin, $E_{\rm Mn} = E^Z_{\rm Mn} + K$, where the Zeeman term is $E^Z_{\rm Mn} = g_{\rm Mn}\mu_B B$ and the *Knight shift* is

$$K = \frac{|J_{\rm sd}|(n_\downarrow - n_\uparrow)}{2}\frac{\bar{N}_{\rm Mn}}{N_{\rm Mn}d}. \tag{12}$$

$K/(g_{\rm Mn}\mu_B)$ is the mean exchange field experienced by the local moments because of the electron spin polarization.

It is analogous to the Knight shift experienced by nuclei in a spin-polarized electron gas in NMR experiments. The average Mn density in this expression, $N_{\rm Mn}$, defined by $N_{\rm Mn}d = \int_0^d dz N_{\rm Mn}(z)$, is not equal to the quantity $\bar{N}_{\rm Mn}$ which appeared previously in the mean-field quantum-well electron spin gap; the effective 3D electron density that appears in Eq. (12) involves the quantum-well width and the Mn distribution within the quantum well in a nonobvious way that follows from our detailed analysis.

For the quantum-well electrons, $E_e = E_e^Z + \Delta$, the Zeeman term is $E_e^Z = g_e \mu_B B$. Following the NMR analogy, the mean-field electron spin splitting $\Delta = |J_{\rm sd}| \bar{N}_{\rm Mn} S$ corresponds to the nuclear-polarization induced Overhauser shift in electron spin-resonance frequencies. Because $g_{\rm Mn} > 0$, and therefore $E_{\rm Mn}^Z > 0$, the mean-field Mn-spin configuration points in the negative $\hat{z}$ direction. For the conduction-band electrons, there is a competition between the Overhauser energy $\Delta > 0$ and the Zeeman term $E_e^Z < 0$ ($g_e < 0$). The Overhauser shift dominates except at very strong magnetic fields, i.e., the mean-field electron spin polarization is along the negative z axis.

Equation (11) is able to account quantitatively for the experiments of Teran *et al.* In their sample the avoided crossing is seen in a strong magnetic field near Landau level filling factor $\nu = 3$, where the electronic state has two occupied majority-spin Landau levels and one minority spin, i.e., $n_\downarrow - n_\uparrow = n/3 \approx 2 \times 10^{11}$ cm^{-2}. For a Mn fraction that is constant across the quantum well we obtain $N_{\rm Mn} = \bar{N}_{\rm Mn} \approx 4.4 \times 10^{19}$ cm^{-3} for the studied sample [5]. The width of the quantum well is $d \approx 10$ nm. At low temperatures, the Mn spins are fully polarized by the external magnetic field. Using the experimental [5] low-temperature value for $\Delta \approx 1.65$ meV, we conclude that $|J_{\rm sd}|$ in (Cd,Mn)Te is 0.015 eV nm^3, in agreement with Ref. [11]. Using these values we conclude that $K \approx 1.5$ μeV and hence the avoided crossing gap $\sqrt{K\Delta} \approx 0.05$ meV, in close agreement with the experimental estimate ≈ 0.03 meV. In the quantum Hall regime, the gap's temperature dependence may be attributed to the temperature-dependent Mn spin polarization and the consequent temperature dependence of Δ (see Fig. 1). At these strong fields the Mn spins polarization is described by the Brillouin function so that $\Delta(T)/\Delta(0) = B_{5/2}(5 g_{\rm Mn}\mu_B B/2k_B(T + T_{\rm AF}))$ where the phenomenological parameter $T_{\rm AF} = 0.18$ K accounts for the direct antiferromagnetic Mn-Mn coupling [5].

The close agreement between experimentally observed and calculated anticrossing gaps supports our effective model for DMSs in which the low-energy degrees of freedom are local $S = 5/2$ Mn spins that are exchange coupled to band-electron spins. The avoided crossing establishes that both Mn and band spins behave collectively and that they are coupled, conditions under which ferromagnetism is expected. The ferromagnetic transition temperature of this quantum-well system can be estimated by applying the mean-field approach that appears to be generally successful when applied [12] to bulk (III,Mn)V materials. Assuming uniform Mn-doping and particle-in-a-box subband wave functions, the mean-field critical temperature for quantum wells [13] can be written as

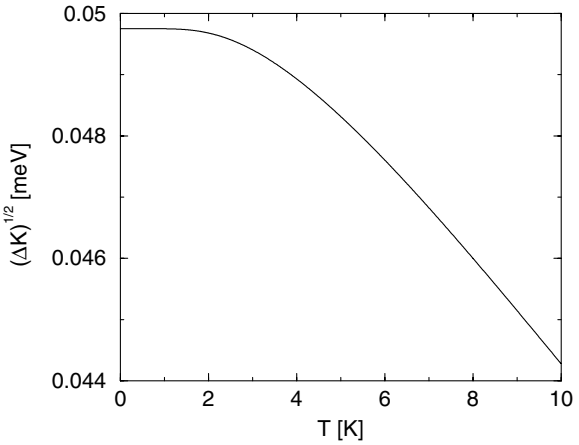

FIG. 1. Temperature dependence of the gap $\sqrt{\Delta K}$.

$$k_B T_c^{\rm MF} = \frac{S+1}{4} \frac{K^{\rm max}\Delta}{\epsilon_{\rm F}}, \tag{13}$$

where $K^{\rm max} = n|J_{\rm sd}|/(2d)$ is the value of the Knight shift when the quantum-well electrons are completely spin polarized and $\epsilon_{\rm F}$ is the paramagnetic 2D electron gas Fermi energy. Using experimental values for $\Delta \approx 1.65$ meV, $K^{\rm max} \approx 4.5$ μeV, and the effective mass $m^* = 0.107 m_e$ we find that $T_c^{\rm MF} \approx 5.6$ mK.

In three-dimensional DMS ferromagnets, we expect [14] mean-field theory to be reliable when the carrier density is smaller than the Mn density and $\Delta < \epsilon_{\rm F}$. These conditions are both satisfied here. In the quasi-2D case, however, long-wavelength collective excitations have a significant negative impact on tendencies toward long-range magnetic order. In fact, for the model studied here which has no spin-orbit interactions, continuous spin-rotational invariance implies that long-range magnetic order is impossible at finite temperatures in 2D [15]. Thermal and quantum fluctuations at low temperatures in these quasi-2D ferromagnets are even more important than usual because 2D electron gas properties lead to vanishing spin stiffness [10,16]. Long-range magnetic order is possible in (II,Mn)VI quantum wells only because spin-orbit coupling favors magnetization orientations perpendicular to the quantum wells.

In symmetric quantum wells spin-orbit interactions are described by the Dresselhaus Hamiltonian, $H_D = \gamma(-\sigma_x k_x + \sigma_y k_y)\langle k_z^2 \rangle$. Evaluating the magnetization-orientation dependence of the energy correction due to this term by second-order perturbation theory we find that the easy axis is perpendicular to the quantum well. The collective-excitation energy gap is twice the anisotropy energy per Mn spin. We find that

$$E_{\rm so} = \frac{\gamma^2 \langle k_z^2 \rangle^2 k_{\rm F}^2 n}{S N_{\rm Mn} d \max\{\Delta, 2\epsilon_{\rm F}\}}, \quad (14)$$

taking $\langle k_z^2 \rangle = (\pi/d)^2$ for the lowest quantum-well subband, and $k_{\rm F}^2 = 2m^*\epsilon_{\rm F}/\hbar^2$. When $E_{\rm so}$ is small the Curie temperature will be limited by collective fluctuations [14]. Taking account of the expected dispersionless 2D spin-wave bands and estimating the Curie temperature as the temperature at which S magnons per Mn spin are thermally excited, we predict that $k_B T_c^{\rm coll} \approx (S + 1/2) E_{\rm so}$. Plugging in $\gamma \approx 12\,{\rm meV\,nm^3}$ for the Dresselhaus coefficient in the CdTe conduction band [17], this implies that $T_c^{\rm coll} \approx 0.4$ mK in the sample studied by Teran *et al.,* considerably smaller than the mean-field estimate. It is interesting to note that with increasing Mn-doping concentration $N_{\rm Mn}$ the mean-field Curie temperature increases [Eq. (13)] while collective-fluctuation energy decreases [Eq. (14)]. For asymmetric quantum wells the spin-orbit interactions are dominated by Rashba coupling, and, depending on the degree of asymmetry, the collective-excitation energy gap will become larger until, eventually, the system can again reach the mean-field regime. Stronger spin-orbit interactions in the valence band [18] may explain the apparent success of mean-field theory in predicting ferromagnetic transition temperatures there. The strong antiferromagnetic interactions that occur between neighboring Mn ions will reduce [2,18] the number of Mn spins that can be spontaneously aligned by the relatively weak but longer ranged carrier-mediated interactions, but should not preclude ferromagnetism when the Mn mole fraction is low.

In conclusion, we presented a theory of collective spin excitations in DMS quantum wells which explains the anomalously large Knight shift observed in recent experiments. We use our theory to discuss the physics of ferromagnetism in n-type DMS quantum-well systems, which has not yet been observed. We point out that spin-orbit interactions are necessary to support ferromagnetism, predict ferromagnetic transition temperatures in symmetric quantum wells that can be well below those implied by mean-field theory, and suggest that a crossover between collective-fluctuation-limited and mean-field-interaction-limited ferromagnetism can be observed in these systems by using a bias voltage to adjust the spin-orbit interaction strength.

We acknowledge helpful discussions with T. Dietl, D. Frustaglia, and M. Governale and thank F. J. Teran and M. Potemski for showing us their results prior to publication. This work was supported by the Deutsche Forschungsgemeinschaft under the Center for Functional Nanostructures and the Emmy-Noether program, by the Department of Energy under Grant No. DE-FG03-02ER45958, and by the Welch Foundation.

[1] A. Zunger, in *Solid State Physics*, edited by H. Ehrenreich and D. Turnbull (Academic Press, Orlando, 1986), Vol. 38, p. 276.
[2] For recent reviews of bulk and quantum-well cases, respectively, see T. Dietl, Semicond. Sci. Technol. **17**, 377 (2002) and Byounghak Lee, T. Jungwirth, and A. H. MacDonald, Semicond. Sci. Technol. **17**, 393 (2002).
[3] For a discussion of the issues, see J. König, J. Schliemann, T. Jungwirth, and A. H. MacDonald, in "Electronic Structure and Magnetism of Complex Materials", edited by D. J. Singh and D. A. Papaconstantopoulos, Springer Series in Material Sciences Vol. 54 (Springer, New York, 2003), pp. 163–211.
[4] Since Mn is an acceptor in (III,V) semiconductors, n-doping is possible only in (II,VI) semiconductors.
[5] F. J. Teran *et al.*, preceding Letter, Phys. Rev. Lett. **91**, 077201 (2003).
[6] E. I. Rashba, Sov. Phys. Solid State **2**, 1109 (1960).
[7] In wider quantum wells the interplay between magnetic order and quantum-well subband mixing becomes important: B. H. Lee *et al.*, Phys. Rev. B **65**, 193311 (2002).
[8] T. Dietl, in *Diluted Magnetic Semiconductors*, Handbook of Semiconductors Vol. 3B (North-Holland, New York, 1994).
[9] J. König, H. H. Lin, and A. H. MacDonald, Phys. Rev. Lett. **84**, 5628 (2000); J. König, T. Jungwirth, and A. H. MacDonald, Phys. Rev. B **64**, 184423 (2001).
[10] In the continuum approximation, the collective-excitation spectrum consists of a number of 2D branches [D. Frustaglia, J. König, and A. H. MacDonald (unpublished)]. When most Mn ions are strongly coupled to the quantum-well electrons, the coherent motion ansatz employed here, $w_0 \propto \sqrt{N_{\rm Mn}(z)}$, is accurate. Using a Debye-like approximation we estimate that in the sample of Teran *et al.* approximately half of the collective excitations are in this lowest-energy branch.
[11] J. Furdyna, J. Appl. Phys. **64**, R29 (1988).
[12] T. Dietl *et al.*, Science **287**, 1019 (2000); T. Jungwirth *et al.*, Phys. Rev. B **59**, 9818 (1999).
[13] A. Haury *et al.*, Phys. Rev. Lett. **79**, 511 (1997); B. H. Lee, T. Jungwirth, and A. H. MacDonald, Phys. Rev. B **61**, 15 606 (2000).
[14] J. Schliemann, J. König, H. H. Lin, and A. H. MacDonald, Appl. Phys. Lett. **78**, 1550 (2001); J. Schliemann, J. König, and A. H. MacDonald, Phys. Rev. B **64**, 165201 (2001).
[15] N. D. Mermin and H. Wagner, Phys. Rev. Lett. **17**, 1133 (1966).
[16] P. Kossacki *et al.*, Physica (Amsterdam) **6E**, 709 (2000).
[17] M. Cardona, N. E. Christensen, and G. Fasol, Phys. Rev. B **38**, 1806 (1988); see also M. Braun and U. Rössler, J. Phys. C **18**, 3365 (1985).
[18] P. Kossaki *et al.*, Physica (Amsterdam) **12E**, 344 (2002); H. Boukari *et al.*, Phys. Rev. Lett. **88**, 207204 (2002); J. Cibert *et al.*, J. Cryst. Growth **201–202**, 670 (1999).