Spin Superlattice Formation in $ZnSe/Zn_{1-x}Mn_xSe$ Multilayers

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We present magneto-optical evidence for the formation of a magnetic-field-induced spin superlattice in modulated $ZnSe/Zn_{1-x}Mn_xSe$ structures. In the samples studied, the offsets in both the conduction band and the valence band are very small at zero magnetic field. When a magnetic field is applied, the large Zeeman splitting of the $Zn_{1-x}Mn_xSe$ band edges overcomes the zero-field offsets and results in the formation of a spin superlattice in which spin states of both electrons and holes are spatially and periodically separated.

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The experimental and theoretical study of quantum confinement of carriers in spatially modulated semiconductor structures has been an area of intense activity over the past decade. Magnetic semiconductor quantum wells and superlattices—which are relatively new in this context—have extended this field to include novel *spin-dependent* phenomena [1-3]. A unique property of magnetic semiconductor quantum wells is that the band alignment can be tuned by the application of a magnetic field. An early theoretical study pointed out that—under favorable circumstances—a magnetic field could be used to induce a spin-dependent potential in a magnetic semiconductor superlattice so as to form a "spin superlattice" consisting of spatially separated spin states [4].

The essential idea is explained in Fig. 1. Consider a superlattice formed by alternating layers of a magnetic and a nonmagnetic semiconductor such that the band offsets at zero magnetic field are small. On applying a magnetic field, the band edges in the magnetic semiconductor undergo a huge spin splitting due to the *sp-d* exchange between carriers and localized magnetic ions [5], while the splitting in the nonmagnetic layers is much smaller. When the large Zeeman shift in the magnetic layers overcomes the band offsets in both conduction and valence bands, the magnetic layers act as barriers for electrons and holes in the spin-up state, and as quantum wells for the spin-down state. Hence, spin-up holes and electrons are localized in the nonmagnetic regions of the superlattice, while those of opposite spin are localized in the magnetic layers. The spin states are then spatially modulated with the same period as the structural superlattice, thus forming a spin superlattice. Apart from their novelty, such structures will be crucially important to the understanding of fundamental spin-dependent phenomena of contemporary interest, such as carrier-spin scattering mechanisms in low-dimensional systems [1,2].

Although magnetic-field-induced spatial spin separation for hole states has been demonstrated in $ZnSe/Zn_{0.9}Fe_{0.1}Se$ [3] and $ZnSe/Zn_{0.9}Mn_{0.1}Se$ [6] single quantum wells, the conduction-band offsets were in those cases too large to form a spin superlattice as described above. Further, since single quantum wells were used, only one spin component could be spatially localized. Our approach to the problem is to use $ZnSe/Zn_{1-x}Mn_xSe$ superlattices in which the magnetic alloy composition is judiciously chosen so as to provide small (< 5 meV) band offsets in *both* the conduction and the valence bands. By exploiting the strong bowing of the energy gap of $Zn_{1-x}Mn_xSe$ as a function of the Mn composition when the Mn content is small [5] and by taking into account the effect of strain (the $Zn_{1-x}Mn_xSe$ layers are under compressive biaxial strain in such superlattices), we find that $x=0.05$ provides an ideal alloy composition to suit our purposes. Note that Zeeman shifts are also maximized in the composition range between $x=0.05$ and $x=0.09$ [5].

Several $ZnSe/Zn_{1-x}Mn_xSe$ superlattices were grown by molecular-beam epitaxy (MBE) on (100) GaAs substrates after the deposition of a micron-thick ZnSe buffer layer. The growth temperature for both the buffer layers

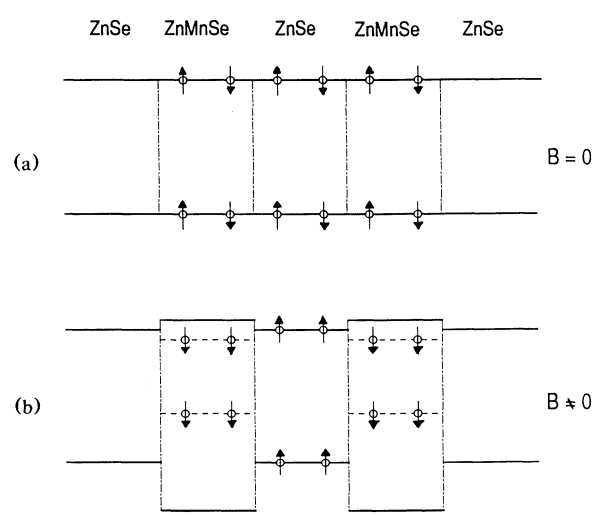

FIG. 1. A schematic diagram of the band structure of a magnetic-field-induced spin superlattice. In the $Zn_{1-x}Mn_xSe$ layers in the lower picture ($B\neq0$), the dotted lines and the solid lines represent, respectively, the spin-down and spin-up states of electrons and heavy holes. The Zeeman splitting in ZnSe layers is negligible. The arrows show where a particular spin state is localized.

and superlattices was 300 °C. The Mn concentration (calibrated using previous growths of thick $Zn_{1-x}Mn_xSe$ epilayers) was varied between $x=0.05$ and $x=0.09$. The superlattices contained ten periods of alternating layers of ZnSe and $Zn_{1-x}Mn_xSe$, each 120 Å thick. The layer thicknesses are wide enough to minimize the effects of wave-function penetration into neighboring layers, while still providing enough confinement to allow ready observation of optical absorption peaks.

Transmission spectra were obtained after removal of the GaAs substrate by mechanical polishing and a subsequent selective etch (1:20 $NH_4OH:H_2O_2$ at room temperature). The absorption experiments were done in the Faraday configuration, with the magnetic field parallel to the wave vector of normally incident light. The experiments were performed in an optical cryostat ($T > 1.5$ K) equipped with a 6-T superconducting magnet. The light source consisted of a halogen lamp with a monochromator. The monochromatic light was circularly polarized to allow the selective identification of transitions between different spin states, following standard selection rules.

The zero-magnetic-field spectra of the superlattices show a strong excitonic absorption peak from the ZnSe buffer, accompanied by an additional strong and well-defined peak. A comparison with the absorption spectrum of a ZnSe epilayer immediately indicates that this additional peak originates from a transition in the superlattice. We identify it as an excitonic transition involving $n=1$ electrons and heavy holes. As pointed out earlier, the formation of a spin superlattice requires small band offsets at zero magnetic field. The sample we will focus on is the one with 5% Mn in which the zero-field absorption from the superlattice is closest to that of ZnSe epilayers, which is a good indication that the zero-field offsets are small. In this sample, the strong peak from the superlattice is 2 meV lower than the position of ZnSe excitonic absorption, indicating that the strained magnetic layers have a band gap slightly smaller than the ZnSe layers. The intensity of the transition suggests that the band alignment is type I, with both holes and electrons confined to the $Zn_{1-x}Mn_xSe$ layers. The behavior of the other superlattices was qualitatively identical, and a detailed comparison will be presented elsewhere.

When a magnetic field is applied, the two spin states in $Zn_{1-x}Mn_xSe$ are Zeeman split, as depicted in Fig. 1. The zero-field transmission spectrum then evolves into a more complicated one, in which the observed transitions have clear polarization dependence. We restrict ourselves here to the strongest observed features which correspond to the exciton transitions associated with $n=1$ heavy-hole and electron subbands. Other transitions involving light holes and higher subbands of the superlattice are also observed but are much weaker and will be discussed in more detail elsewhere. The transmission spectra at $B=5$ T for the two polarizations, σ_L and σ_R, are shown in Fig. 2. Peaks a and d are the Zeeman-split components of the transition described above. Peak c is the excitonic absorption from the ZnSe buffer layer, and peak b is the transition involving $n=2$ excited states.

The positions of the ground-state absorption peak in each polarization are plotted in Fig. 3 as a function of the applied magnetic field. The solid lines in this figure are calculated results which will be discussed later. In Fig. 4 we also show the intensities I_R and I_L of the spin-up and spin-down transitions, respectively, as a function of magnetic field [7]. We now argue that the data in Figs. 3 and

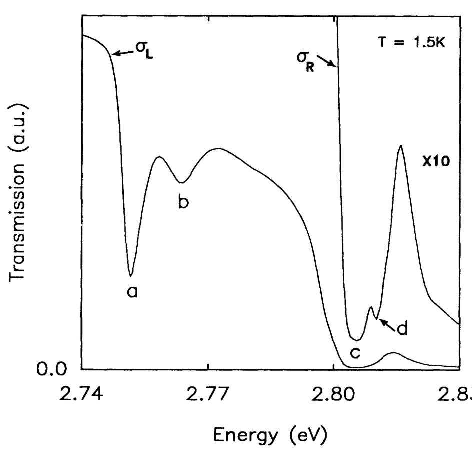

FIG. 2. Magnetotransmission spectra at $B=5$ T for the two polarizations σ_L and σ_R. The drop in transmission near 2.8 eV represents the absorption by the ZnSe buffer layer. The transitions marked in the figure are identified as, peak a, spin-down transition with $n=1$; b, $n=2$ spin-down transition; c, exciton absorption from the ZnSe buffer; and d, spin-up transition with $n=1$.

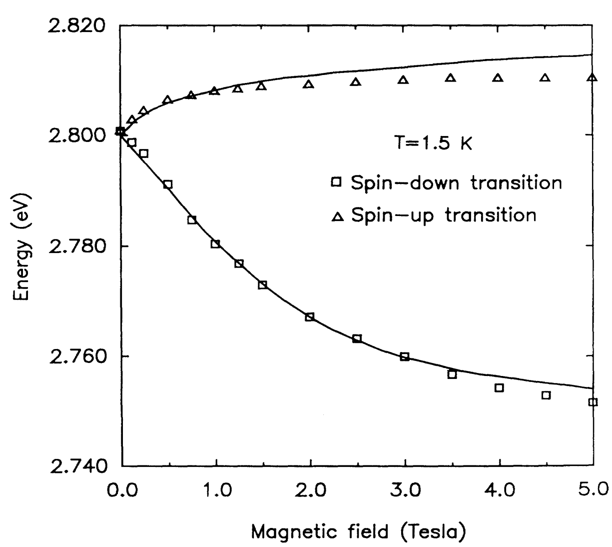

FIG. 3. Transition energies of the Zeeman-split excitonic transitions from $n=1$ heavy-hole to $n=1$ conduction band. The solid lines are calculated results.

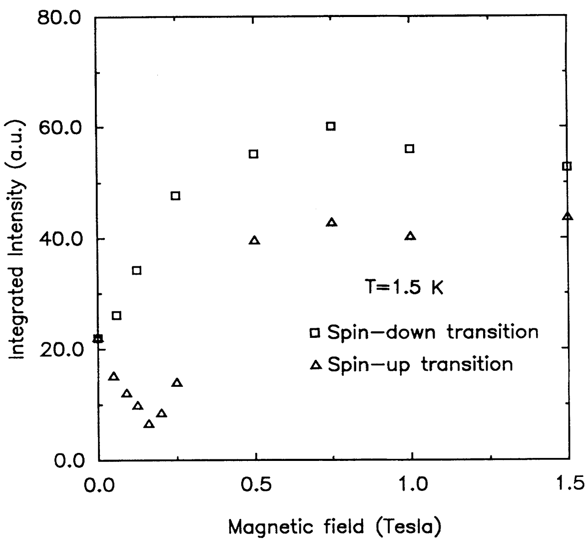

FIG. 4. Integrated intensities of the Zeeman-split excitonic transitions as a function of the magnetic field. The squares and triangles represent the spin-down and spin-up transitions, respectively.

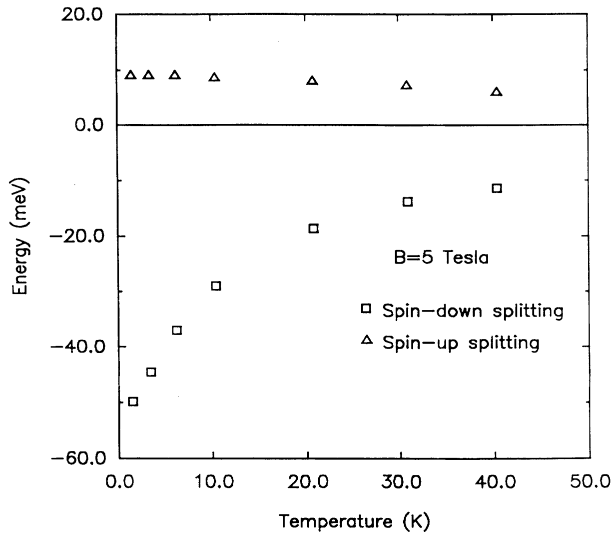

FIG. 5. Temperature dependence of the Zeeman shifts observed in both circular polarizations. The spin-up and the spin-down transitions are respectively represented by the triangles and the squares.

4 provide direct evidence for the formation of a magnetic-field-induced spin superlattice. We first focus on the transition involving spin-down electrons and holes, which are localized in the $Zn_{1-x}Mn_xSe$ layers.

Since both electrons and holes are localized in the $Zn_{1-x}Mn_xSe$ layers at zero field, the application of a magnetic field merely increases this type-I confinement for the spin-down components (as depicted in Fig. 1). The spin-down transition hence shows a large redshift with increasing magnetic field, corresponding to the redshift of the "effective" band gap of the $Zn_{1-x}Mn_xSe$ quantum wells (Fig. 3). In addition, the increased confinement enhances the intensity of the transition with increasing magnetic field (Fig. 4). Because of the large effective masses of electrons and holes in wide-gap $Zn_{1-x}Mn_xSe$ (and ZnSe), and the relatively large well width, the increase of the transition intensity saturates quickly with increasing barrier height (and therefore the magnetic field).

The situation is somewhat more complicated for the spin-up transition. As we increase the magnetic field from zero, the magnetic-field-induced shifts of the spin-up states in the $Zn_{1-x}Mn_xSe$ layers will eventually overcome the small band offsets and the $Zn_{1-x}Mn_xSe$ layers will act as barriers for the spin-up electron and heavy-hole states. It is well known that in diluted-magnetic-semiconductor (DMS) materials, the Zeeman splitting for heavy holes is much larger than for electrons [5]. At the same time, it has been shown that the valence-band offset is much less than the conduction-band offset in $Zn_{1-x}Mn_xSe$ [8]. This implies that the heavy-hole Zeeman shift will overcome the band offset before the electron Zeeman shift. As soon as the spin-up holes and electrons are localized in the nonmagnetic layers, the Zeeman shift of the spin-up transition no longer has a strong dependence on magnetic field. Unlike the spin-down case, the magnetic field now merely raises the barrier height of the confining potential. This has some effect while the barrier is shallow (at low fields), but becomes less effective as the barrier height increases. This results in the observed asymmetry between the Zeeman shift of spin-up transitions and that of spin-down transitions (Fig. 3).

Since the spin-up holes will be localized in ZnSe layers before the electrons as we raise the magnetic field, it is then expected that in a certain range of magnetic field spin-up holes are localized in the ZnSe layers while the spin-up electrons are still localized in the $Zn_{1-x}Mn_xSe$ layers. This forms a type-II band alignment for this spin state, and is indeed evidenced in the intensity of the spin-up transition as a function of the magnetic field, as shown in Fig. 4. Here the triangles represent the integrated absorption for the spin-up-state transition. It is clear that as the magnetic field is raised from zero, the intensity of the spin-up transition first decreases, indicating the initial decrease of the barrier height in the type-I case, and then a type I to type II conversion. When the Zeeman shift for the spin-up electrons overcomes the conduction-band offset, both spin-up electrons and holes become localized in the ZnSe quantum wells. The band alignment for spin-up electrons and holes is once again type I, with an accompanying increase in the absorption intensity. Beyond this magnetic field, a spin superlattice is now in existence. The difference in the saturated (high-field) transition intensities for the two spin states is merely the result of the difference in level mixing for the Landau levels involved. This also occurs in the bulk and has no direct relation with the superlattice structure.

Another confirmation of spin superlattice formation comes from the temperature dependence of the Zeeman splitting. The Zeeman splitting in a DMS is typically very sensitive to the temperature, especially for low-Mn concentrations. In the discussed spin superlattice, only the spin-down state is in the DMS layers, while the spin-up state is localized in the ZnSe layers. Thus the temperature dependence of the spin-down transition should be much larger compared to the spin-up transition. Figure 5 shows the temperature dependence of the Zeeman splitting as a function of temperature. The energy is measured as the difference between the transition energies at 5 T and the zero-field transition energy. The expected difference in the temperature behavior between the spin-down transition (squares) and the spin-up transition (triangles) is clearly evident.

A correct theoretical fit to the observed data requires a calculation that evaluates the complete band structure and includes a variational approach to account for electron-hole correlation effects [9]. Such a full-scale calculation will be given elsewhere, with a detailed fit to the experimental results. At this point, we believe that the essential mechanism for the formation of the spin superlattice can be understood reasonably well using an accurate band-structure calculation in the $\mathbf{k}\cdot\mathbf{p}$ approximation [10], without including a variational binding-energy calculation. In our calculation, we include the conduction band and the p-like valence bands, and employ the following parameters: the layer thicknesses, the sp-d exchange interaction constants, and the bulk band parameters for ZnSe and $Zn_{0.95}Mn_{0.05}Se$. The unstrained, zero-field valence-band offset is assumed to be negligibly small on the basis of previous studies of $ZnSe/Zn_{1-x}Mn_xSe$ [8]. The effect of strain moves up the heavy-hole state in $Zn_{1-x}Mn_xSe$ to create a weak type-I band alignment, in which both electrons and heavy holes are confined in the $Zn_{1-x}Mn_xSe$ layer, as observed in the experiments. The theory readily reproduces the qualitative aspects of our experimental observations, clearly showing the magnetic-field-induced transformation from a type-I to a type-II superlattice, and then the subsequent transformation to a type-I spin superlattice. Quantitative comparison between theory and experiment is obtained by subtracting the bulk exciton binding energy from the calculated results. As shown in Fig. 3, the agreement is surprisingly good, given the fact that electron-hole correlation is neglected. We note also that the disagreement between theory and experiment at high magnetic fields is to be expected since the barriers are then high enough to affect the exciton binding energy due to carrier confinement (which is not taken into account in the calculation).

Finally, we comment that we have also observed transitions involving subbands other than the lowest heavy-hole and conduction subbands described above. In fact, even subbands above the barriers (with the subband quantum number n up to 4) can be clearly resolved—despite the weak transition probabilities—indicating the exceptional quality of the superlattice. Such transitions will be important for a complete numerical fitting.

In conclusion, we have presented experimental evidence for the formation of a spin superlattice in $ZnSe/Zn_{1-x}Mn_xSe$ through a careful choice of alloy composition, strain configuration, and layer thickness. Further theoretical and experimental studies of such spin-selective confinement in modulated structures can be expected to provide fundamentally new insights into the properties of low-dimensional quantum systems.

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We note that a similar effect has recently been observed at SUNY Buffalo in $ZnSe/Zn_{0.99}Fe_{0.01}Se$ [11].

[1] D. D. Awschalom, M. Freeman, N. Samarth, H. Luo, and J. K. Furdyna, Phys. Rev. Lett. **66**, 1212 (1991).
[2] M. Freeman, D. D. Awschalom, J. M. Hong, and L. L. Chang, Phys. Rev. Lett. **64**, 2430 (1990).
[3] X. Liu, A. Petrou, J. Warnock, B. T. Jonker, G. A. Prinz, and J. J. Krebs, Phys. Rev. Lett. **63**, 2280 (1989).
[4] M. von Ortenberg, Phys. Rev. Lett. **49**, 1041 (1982).
[5] J. K. Furdyna, J. Appl. Phys. **64**, R29 (1988).
[6] B. T. Jonker, X. Liu, W. C. Chou, and A. Petrou, J. Appl. Phys. **69**, 6097 (1991).
[7] In calculating the integrated absorption for specific lines, we have carefully taken into account the ZnSe absorption background.
[8] R. L. Gunshor, L. A. Kolodziejski, A. V. Nurmikko, and N. Otsuka, Annu. Rev. Mater. Sci. **18**, 325 (1988).
[9] G. Bastard, *Wave Mechanics in Quantum Well Structures* (Les Editions de Physique, Paris, 1988).
[10] L. R. Ram-Mohan, K. H. Yoo, and R. L. Aggarwal, Phys. Rev. B **38**, 6151 (1988).
[11] A. Petrou (private communication); W. C. Chou *et al.*, preceding Letter, Phys. Rev. Lett. **67**, 3820 (1991).