# Mn ion clustering in II-VI semimagnetic semiconductor heterostructures

S. J. Weston,* M. O'Neill, J. E. Nicholls, J. Miao, W. E. Hagston, and T. Stirner†
*Department of Physics, University of Hull, Hull HU6 7RX, United Kingdom*
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The results of photoluminescence excitation experiments in $Cd_{1-x}Mn_xTe$ and $Zn_{1-x}Mn_xSe$ diluted magnetic semiconductor quantum-well structures are shown to be consistent with the occurrence of a clustering of the magnetic Mn ions. Possible clustering mechanisms are discussed briefly together with alternative explanations of the data. [S0163-1829(98)09835-X]

## I. INTRODUCTION

The large magneto-optical effects in diluted magnetic semiconductors (DMS) have been of great interest for many years.[1] A significant body of work has been concerned with the incorporation of the paramagnetic manganese ($Mn^{2+}$) ion into the crystal lattice of, e.g., $Cd_{1-x}Mn_xTe$. Since nearest-neighbor Mn ions form antiferromagnetic spin pairs, a knowledge of the distribution of the Mn ions in the crystal is relevant to an understanding of experiments involving Zeeman splittings. The paramagnetic response of the Mn ions in bulk material has been parametrized empirically[2] by the two semiphenomenological parameters $S_{\rm eff}$, the effective spin, and $T_{\rm eff}$, the effective temperature. The former has been calculated theoretically[3] and can be described equivalently by introducing an effective Mn ion concentration $\overline{x}$ via the relation $xS_{\rm eff}=5/2\overline{x}$. On the other hand, the effective temperature is related to a sum over the exchange integrals $J_{ij}$ between the Mn ion $i$ and its neighboring ions $j$.[4] It can be written as the sum of the sample temperature $T_{\rm s}$ and an empirical parameter $T_0$, i.e. $T_{\rm eff}(x)=T_{\rm s}+T_0(x)$.

The question of whether the distribution of magnetic ions in DMS's is random or not, has been addressed by several authors.[5–7] In the case of bulk DMS, for example, by analyzing the experimentally measured magnetization steps, Shapira found strong indications for a random distribution of the magnetic ions.[8] To date most investigations of the Zeeman splitting in DMS quantum-well structures have also assumed a completely random distribution of the Mn ions in the crystal. However, recently we have pointed out some of the possible consequences of a nonrandom distribution of the magnetic ions.[3,9] In particular, we have shown that alloy clustering can give rise to one of several effects which are dependent on the nominal concentration $x$ of the Mn ions. This arises from the fact that, relative to a random distribution, the effect of clustering is to give rise to regions in which $x$ is increased and to other regions where $x$ is decreased. Consequently, alloy clustering can give rise to the following scenarios: (i) a reduction in $\overline{x}$ (or equivalently $S_{\rm eff}$) but virtually no change in $T_0$, (ii) an increase in $T_0$ (or equivalently $T_{\rm eff}$) but virtually no change in $\overline{x}$, or (iii) both a reduction in $\overline{x}$ and an increase in $T_0$. It is important to note that a nonrandom distribution of the Mn ions can give rise to effects which resemble the ''enhanced paramagnetism'' at quantum-well interfaces.[3,10,11] The difference being that clustering, in general, reduces the paramagnetism as a result of a local accumulation of the magnetic ions. An enhancement in $S_{\rm eff}$ and a reduction in $T_0$ (which could be viewed, in effect, as due to a local variation in $x$) have already been observed at the $CdTe/Cd_{1-x}Mn_xTe$ interface.[12] Bulk magnetization measurements are, in general, too insensitive a probe for detecting clustering effects on the scale of only a few crystal units. However, the highly localized carrier wave functions that occur in quantum wells, for example, enable one to investigate much smaller volumes of the crystal. Any clustering effects on this scale could, e.g., be reflected in the magnitude of the Zeeman splitting. The present paper describes the results of Zeeman splitting measurements which are consistent with the occurrence of a clustering of Mn ions in DMS quantum-well structures.

The paper is structured as follows. Section II reviews briefly the theoretical formalism utilized to evaluate Zeeman splittings in an external magnetic field. In Sec. III A experimental results obtained for quantum wells in the $Cd_{1-x}Mn_xTe$ materials system are presented and analyzed. The experimental results are shown to be consistent with the presence of a Mn ion clustering of the type (ii) described above. Section III B examines magneto-optical studies in the $Zn_{1-x}Mn_xSe$ system. Here the experimental results are found to be consistent with a Mn ion distribution giving rise to clustering of type (i) described above. Finally, in Sec. IV the results are summarized and possible alternative explanations described.

## II. THEORY

As the $Mn^{2+}$ ions are paramagnetic, the band gap of, e.g., $Cd_{1-x}Mn_xTe$ can be either increased or decreased in response to an external magnetic field depending on whether the $\sigma^-$ or $\sigma^+$ optically polarized transitions are observed.[1] The conduction-band edge changes by an amount $3A$ and the heavy-hole valence-band edge by an amount $3B$ where

$$A=-\frac{1}{6}xN_0\alpha S_{\rm eff}(x)B_J[\mathbf{B},x,T_{\rm eff}(x)]$$

and

$$B=-\frac{1}{6}xN_0\beta S_{\rm eff}(x)B_J[\mathbf{B},x,T_{\rm eff}(x)].$$

$N_0\alpha$ and $N_0\beta$ are the magnetic exchange constants for the electron and the heavy hole, respectively. $B_J$ represents the

 

modified Brillouin function[2] which depends on the external magnetic field **B**, the manganese concentration $x$, and the effective temperature $T_{\rm eff}$. The electronic transitions associated with the $\sigma^-$ polarization observe a band-gap increase of $|3A|+|3B|$, whereas transitions associated with the $\sigma^+$ polarization observe a band-gap decrease of $|3A|+|3B|$. The changes in the conduction- and valence-band potential are nonlinear functions of the magnetic field.

The difference between the calculations presented below and conventional theories is that we have abandoned the mean-field type approach and instead made the substitutions

$$S_{\rm eff}(x)\rightarrow S_{\rm eff}(x,z)$$

and

$$T_{\rm eff}(x)\rightarrow T_{\rm eff}(x,z),$$

where $x$ is the Mn ion concentration and the growth direction is along the $z$ coordinate.

In order to determine the excitonic transition energies and exchange shifts in a magnetic field, the one-particle energies of the electron and the hole were calculated by solving the Schrödinger equation numerically.[13] The exciton binding energies were evaluated utilizing the variational technique developed by Hilton *et al.*[14]

## III. RESULTS

### A. The $Cd_{1-x}Mn_xTe$ system

A series of $Cd_{1-x}Mn_xTe/Cd_{1-y}Mn_yTe$ samples with $x>y$ have been investigated. The samples were grown by molecular-beam epitaxy on (001) InSb substrates followed by a 0.1-$\mu$m buffer layer of CdTe.[15] Photoluminescence excitation measurements were performed at various external magnetic fields. Details of the sample preparation and the photoluminescence excitation experiments are discussed elsewhere.[16,17] In the following we concentrate on the results of two samples which are typical of this series of experiments. Sample 1 contains a 150 Å $Cd_{1-y}Mn_yTe$ ($y=0.036$) well layer sandwiched between two $Cd_{1-x}Mn_xTe$ ($x=0.094$) barrier layers. Sample 2 is basically identical to sample 1, except for the central well layer which has a width of only 75 Å. The observed $k$ dependence of the exchange parameters[18] together with interface effects[2,11,19–21] can be neglected in these samples since the well widths are relatively large and both well and barrier layers are magnetic. The values of the well width, for both quantum wells, were determined independently via double-crystal x-ray diffraction measurements. For the barrier layers the value of the Mn ion concentration $x$ was determined from the zero-field energy position of the excitons observed in these regions (a value which was also confirmed from the observed saturation splittings of these excitons in a magnetic field). Given the above data, it was found that the zero-field energy positions of the excitons in the two different well regions could be fitted with the same choice of $x$ for both samples. Confirmation of this choice of $x$ was again provided by the agreement with the observed saturated field splittings of these two excitons. The only disagreement with the observed data occurred (at intermediate fields) for the exchange shift (i.e., the energy shift of the $\sigma^+$ Zeeman component of the heavy-hole exciton ground state). In this connection it is interesting to note that the photoluminescence excitation experiments show the Zeeman splitting to be essentially symmetric. A valence-band offset of 40% has been employed in the calculations.[22,23]

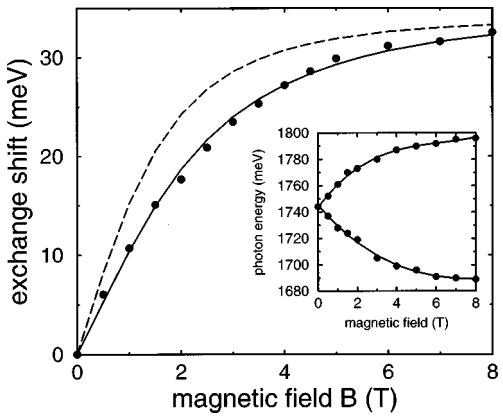


FIG. 1. Exchange shift of sample 1 at $T=1.6$ K. The experimental results are indicated by full circles. The full (dashed) line represents the theoretical calculations including (ignoring) alloy clustering effects. (The Zeeman splitting of the barrier transition for this sample is shown in the inset together with a fit to a modified Brillouin function corresponding to ''random'' $Cd_{0.906}Mn_{0.094}Te$ bulk material.)

The measured exchange shift for sample 1 as a function of the applied magnetic field is shown by the full circles in Fig. 1. Using the bulk values of the effective spin and temperature[2] in the calculations, corresponding to the $x$ values in the well and barrier layers, we obtain the dashed line in this figure. As can be seen, there is a marked discrepancy between theory and experiment for intermediate values of the magnetic field. It might be thought that one possible reason for this was that the actual temperature of the sample had been raised above 1.6 K as a result of laser heating. However, this would have affected also the Zeeman splitting in the barrier region. The observed Zeeman splitting of the barrier transition of sample 1 is shown in the inset to Fig. 1 against a plot of the calculated splitting of a $Cd_{0.906}Mn_{0.094}Te$ layer (assuming a random distribution of the Mn ions and bulk values for $S_{\rm eff}$ and $T_{\rm eff}$) at $T=1.6$ K. This figure demonstrates clearly that laser heating of the sample is negligible and that the DMS material in the barriers is responding essentially as bulk. The difference between the calculated and the observed exchange shifts in the well region can also not be explained by a change in the exciton binding energy, because the calculated binding energy for this transition decreases monotonically from 13.9 meV at 0 T to 13.4 meV at 8 T. This difference also cannot be accounted for by interface effects resulting in an increase in $T_0$ in the monolayers of the well next to the barrier region. Hence, since the observed saturation value of the exchange shift for both samples 1 and 2 (see Fig. 2 below) is consistent with the same effective value of $x$, we are led to conclude that, if clustering is responsible for the observed effects, then such a clustering of the Mn ions does not change $\bar{x}$ but leads to an increased effective antiferromagnetic coupling between them, which in turn enhances $T_0$ in these regions.

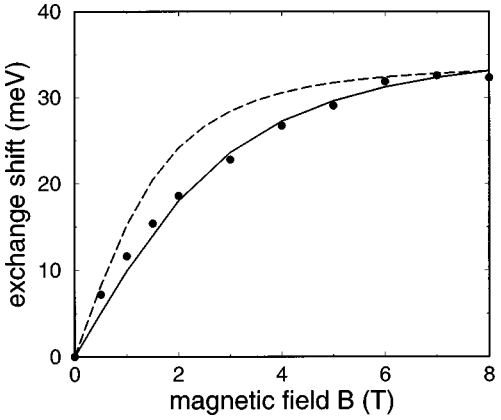


FIG. 2. Exchange shift of sample 2. (The meaning of the symbols is the same as in Fig. 1.)

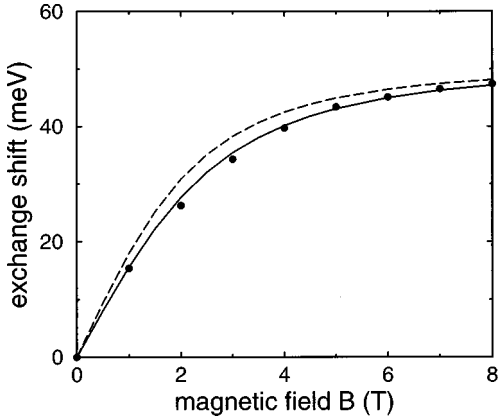


FIG. 3. Exchange shift of sample 3. (The meaning of the symbols is the same as in Fig. 1.)

In the past, agreement between theoretical and experimental curves has been achieved by adjusting the semiphenomenological parameter $T_0$ in a mean-field type approach. However, it is obvious that, even in a random alloy, $T_0$ will vary on a microscopic scale due to fluctuations in the alloy composition. In a similar manner, $T_0$ is affected by alloy clustering. Given that clustering may well stem from interface effects, we will assume, in what follows, that the corresponding variation in $T_0$ will be a function of the position in the well region determined by, e.g., the conditions of growth in a given molecular-beam-epitaxy system. The Mn ions could, for instance, be distributed randomly over the first few monolayers in the well region but with a gradual increase in the amount of clustering over the following monolayers. (*A priori*, this distribution is, of course, unknown. However, from the fabrication point of view, it is not unreasonable to assume a nonlinear dependence for a nonequilibrium growth process. We will come back to this point later.) To be specific, we chose a quadratic dependence of $T_0(z)$ in the well layer of the form

$$T_0(z) = T_0^m + (T_0^b - T_0^m)\left(\frac{z}{z_0}\right)^2,$$

where $T_0^m$ is the maximum value of $T_0$ occurring at the interface to the barrier material, $T_0^b$ is the bulk value of $T_0$ for this particular Mn concentration, and $z_0$ describes the spatial extent of the alloy clustering. The parameters used in the calculations were $N_0\alpha = 220$ meV, $N_0\beta = -880$ meV (Ref. 2), $m_{hh}^* = 0.6$, $m_e^* = 0.096$ (Ref. 24) and $\epsilon_r = 10.6$.

The full line in Fig. 1 was generated with values of $T_0^m = 5.9$ K and $z_0 = 140$ Å. Figure 2 shows the same curves as Fig. 1 but for sample 2. Here the full line was generated with values of $T_0^m = 6.5$ K and $z_0 = 70$ Å. In comparison, the bulk value of $T_0$ for $x = 0.036$ is 1.26 K (Ref. 2). This demonstrates clearly that a clustering of the Mn ions with a concomitant increase in the effective temperature can account for the experimental results. Furthermore these results indicate that there is an appreciable portion of the well region that is responding essentially as bulk.

Finally, we repeated the experiments for a quantum well with larger values of $x$ and $y$ (sample 3 in Fig. 3). These measurements showed similar results to those obtained for samples 1 and 2 only on a reduced scale. In terms of the present interpretation, this would indicate that clustering effects are more pronounced in samples with low Mn ion concentrations. The structural details of all samples together with the parameters used in the calculations are summarized in Table I.

### B. The $Zn_{1-x}Mn_xSe$ system

Heimbrodt *et al.*[25] performed magneto-optical studies on $Zn_{1-x}Mn_xSe$ layers of varying width sandwiched between nonmagnetic ZnSe barrier layers. The Mn concentration was chosen to be $x = 0.04$ in order to form a spin superlattice at zero magnetic field. Under the application of an external magnetic field the $Zn_{1-x}Mn_xSe$ layer constitutes the well region of the resulting quantum-well structure in $\sigma^+$ optical polarization. Based on a comparison of theory and experiment (see Fig. 4 below) Heimbrodt *et al.*[25] were led to the conclusion that there appeared to be a strong *increase* in the effective Mn ion concentration of the $Zn_{1-x}Mn_xSe$ layers with decreasing layer thickness. (Alternatively, for future reference, we note that this could be described as a strong *decrease* in the effective Mn ion concentration with increasing layer thickness.) Calculations by these same authors also indicated that neither the enhanced paramagnetism at the interfaces nor interface roughness was sufficient to explain the

TABLE I. Structural details of the samples and parameters used in the calculations. $L_w$ denotes the well width in Å and $E_0$ the zero-field exciton energy in meV. $T_0$ is in units of K.

| Sample | $L_w$ | $y$ ($x$) | $E_0$ | $T_0^m$ ($z_0$/Å) | $T_0^b$ |
|---|---|---|---|---|---|
| 1 | 150 | 0.036 (0.094) | 1661.9 | 5.9 (140) | 1.26 |
| 2 | 75 | 0.036 (0.095) | 1674.8 | 6.5 (70) | 1.26 |
| 3 | 84 | 0.072 (0.266) | 1742.6 | 4.5 (60) | 2.20 |

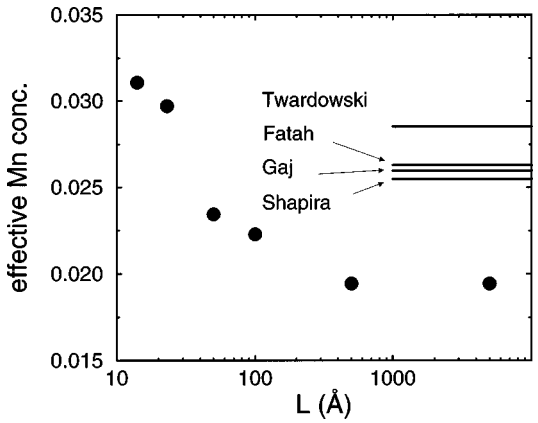


FIG. 4. Effective Mn ion concentration in $Zn_{0.96}Mn_{0.04}Se$ layers of varying width $L$. The data points (full circles) were obtained by Heimbrodt *et al.* (Ref. 25). The bulk values (horizontal lines) were taken from Twardowski *et al.* (Ref. 27), Fatah *et al.* (Ref. 3), Gaj *et al.* (Ref. 2) and Shapira (Ref. 8).

strong increase of the paramagnetic behavior, and suggested an increase of the exchange integrals $N_0\alpha$ and $N_0\beta$ as an explanation of the increasing Zeeman splitting with decreasing layer thickness.[26] In what follows, we will show that the experimental observations of Heimbrodt *et al.*[25] can also be explained by Mn ion clustering.

Keeping the latter in mind, we turn our attention first to the experimentally determined values of the effective Mn ion concentration $\overline{x}$. Figure 4 shows values of $\overline{x}$ for $Zn_{0.96}Mn_{0.04}Se$. The full circles represent the data points obtained by Heimbrodt *et al.*[25] in $Zn_{1-x}Mn_xSe$ layers of varying thickness $L$. In comparison, the four horizontal lines mark values of $\overline{x}$ determined in bulk material for this concentration. With regard to the latter, the largest value was obtained by an interpolation of the data points by Twardowski *et al.*[27] The next smaller value, which represents the result of a numerical calculation utilizing the spin-pairing model (with a *random* distribution of the magnetic ions) of Fatah *et al.*,[3] virtually coincides with the two smallest values displayed in Fig. 4 and representing the data points of $\overline{x}$ in $Cd_{0.96}Mn_{0.04}Te$ obtained by Gaj *et al.*[2] and in $Zn_{0.96}Mn_{0.04}Se$ by Shapira.[8] However, the crucial point to note from Fig. 4 is that, within the experimental uncertainties, the data points of $\overline{x}$ corresponding to Heimbrodt's epilayers (with $L=500$ Å and 5000 Å) lie significantly below the accepted values of $\overline{x}$ for bulk $Zn_{0.96}Mn_{0.04}Se$ with a *random* distribution of the Mn ions. We suggest that this *reduction* in the paramagnetic response of Heimbrodt's epilayers, with respect to the bulk, arises from a clustering of the paramagnetic Mn ions. Similarly, from the work described in the preceding section, we could anticipate that we might be able to account for Heimbrodt's results on narrower wells without the need for clustering. This is indeed the case as shown below.

We now turn to the measurements of Heimbrodt *et al.*[25] in more detail. Table II shows the measured and calculated exchange shifts for Heimbrodt's $Zn_{0.96}Mn_{0.04}Se$ layers of width $L$ at $B=7.5$ T (the calculations have also been checked at intermediate field values with similar results). The 500 and 5000 Å ZnMnSe layers are the epilayers. The parameters used in the calculations were $N_0\alpha=260$ meV, $N_0\beta=-1310$ meV (Ref. 27), $\gamma_1=3.77$, $\gamma_2=1.24$, $m_e^*=0.17$ (Ref. 29), $T=1.8$ K and $\epsilon_r=10.6$. (We note in this regard that the set of exchange parameters employed in the present calculations have smaller values than other sets reported in the literature.[1] Employing the latter sets would give rise to even larger discrepancies between theory and experiment.) For the following considerations we will assume that the same amount of interface disorder is present in all $Zn_{1-x}Mn_xSe$ layers arising from the uniformity of conditions during a given molecular-beam-epitaxy growth run.

Applying a magnetic field of 7.5 T to a $Zn_{0.96}Mn_{0.04}Se$ layer should give rise to an energy shift of the band edge of $\approx 50$ meV.[3,8] Therefore the results displayed in Table II lead to two important conclusions. First, since the calculated exchange shifts for the 100 Å $Zn_{1-x}Mn_xSe$ layer (and also for the two epilayers) without clustering are always larger than the experimental value (and are relatively insensitive to the quality of the interface), this suggests that the effective Mn concentration $\overline{x}$ in this region is reduced due to clustering effects of the Mn ions. *A priori*, we do not know the extent of Mn ion clustering. However, since, e.g., the 14 Å layer can be fitted without clustering (i.e. assuming only the presence of interface disorder and utilizing the ''random'' bulk value of $\overline{x}$ everywhere else) suggests that clustering effects

TABLE II. Exchange shift at $B=7.5$ T for $Zn_{0.96}Mn_{0.04}Se$ layers of varying width $L$. The calculations are for (a) $Zn_{1-x}Mn_xSe$ layers responding like ''random'' bulk material with perfectly abrupt interfaces, (b) including enhanced paramagnetism at the interfaces (otherwise perfect interfaces), (c) interface disorder of amount $\chi=0.2$ on a single monolayer scale (Ref. 28) (this means that 20% of the Mn ions are removed from one monolayer of the $Zn_{1-x}Mn_xSe$ layer and transferred into one monolayer of the ZnSe layer) including the altered paramagnetic response of each individual monolayer at the interface,[12] and (d) the presence of interface disorder, enhanced paramagnetism, and increasing amounts of alloy clustering (the values in parentheses were fitted without alloy clustering). Experimental values were taken from Ref. 25. All energies are in meV.

| $L$/Å | (a) | (b) | (c) | (d) | experiment |
|---|---|---|---|---|---|
| 14 | 12.7 | 13.9 | 16.2 | (16.2) | 16.5 |
| 23 (26) | 22.2 | 23.1 | 24.8 | (27.0) | 28.4 |
| 50 | 37.0 | 37.4 | 37.9 | 36.7 | 36.7 |
| 100 | 45.4 | 45.5 | 45.6 | 39.6 | 39.9 |
| 500 | 50.1 | | | 39.0 | 39.0 |
| 5000 | 50.1 | | | 38.6 | 38.6 |

lose importance for small layer thicknesses. This conclusion is consistent with the findings in the $Cd_{1-x}Mn_xTe$ system described in the preceding section.

Second, the results in Table II also show that the calculated exchange shift for the 23 Å layer is always too small compared with the experimental value. However, assuming the same amount of interface disorder to be present in all $Zn_{1-x}Mn_xSe$ layers and choosing the well to be one monolayer wider than the value determined via the reflection high-energy electron diffraction (RHEED) pattern[25] gives good agreement with experiment. This is indicated by the value in parentheses in Table II representing the calculation for a 26 Å layer without clustering. These results confirm that the observed exchange shifts in the narrower wells can be accounted for without the need to invoke clustering. For the wider wells a functional dependence of $\overline{x}$ on the well width, of the type described in the preceding section, could have been employed. However there is no unique solution to the problem. Hence a simpler approach was adopted. A constant value of $\overline{x}$ was chosen for the whole of the well region except for the first 26 Å where the bulk value of $\overline{x}=0.026$ was employed. The resultant fit to the data is shown in Table II and the values of $\overline{x}$ were 0.0247, 0.0221, 0.019, and 0.019 for the 50, 100, 500, and 5000 Å well widths, respectively. This shows a steady decrease in $\overline{x}$ with increasing well width which is consistent with an increasing amount of clustering for the wider wells until a ''saturation'' point is reached for the degree of clustering.

Finally, we note that a similar behavior has recently been reported by Heimbrodt *et al.*[26] in $Zn_{1-x}Mn_xSe$ layers of varying widths with $x=0.12$. Here the situation is complicated by the occurrence of indirect excitons. Nevertheless, a comparison shows that Heimbrodt's epilayers for this case have also a reduced value of $\overline{x}\approx 0.032$ compared with the calculated value of 0.041 in $Zn_{0.88}Mn_{0.12}Se$ bulk material with a random distribution of the Mn ions.[3,26]

## IV. DISCUSSION

In the $Cd_{1-x}Mn_xTe$ system described here we found that clustering can extend over an appreciable region of the well layer with a significant increase in the value of $T_0$ near one of the interfaces with the barrier material. However, the value of $T_0$ in the region of the opposite interface is close to that of bulk material. This suggests that the first few monolayers of the $Cd_{1-x}Mn_xTe$ well material are grown randomly with a successive increase in the amount of Mn ion clustering for the following monolayers (produced, e.g., as a response to the increasing strain energy in the system). The effect of clustering appears to be more pronounced in samples with low Mn concentrations.

The results of Heimbrodt *et al.*[25] on $Zn_{1-x}Mn_xSe$ layers are interesting. However, for narrow wells they can be accounted for in terms of ''conventional'' interface effects[19] (i.e. interface roughness and enhanced paramagnetism) whereas for wider wells we need to invoke varying amounts of Mn ion clustering across the layer. To be specific, in order to interpret the experimental results[25] in the ZnSe/$Zn_{1-x}Mn_xSe$ system we need to invoke the following assumptions. First, small scale interface disorder (of the same amount) is present in all $Zn_{1-x}Mn_xSe$ layers. This is consistent with recent calculations[19] that show that the latter is the case in almost all the quantum-well structures reported in the literature to date. Second, there is a certain degree of Mn ion clustering present in the $Zn_{1-x}Mn_xSe$ layers which changes gradually across the layer width and results in a reduction in the effective Mn concentration.

The calculations above suggest that different material systems can contain different degrees of alloy clustering and that the latter could have a spatial distribution. A common trend appears to be that, when the Mn ion concentration changes abruptly at an interface, the amount of clustering that results varies with the number of monolayers grown. The first few monolayers show a random distribution of Mn ions after which the clustering steadily increases as the growth proceeds. It appears also that samples with low Mn ion concentrations display a greater degree of clustering than samples with high $x$ values.[25,26] It is natural to speculate on the reason for the difference in the clustering observed in the present author's samples and those of Heimbrodt *et al.*[25] In this connection we note that molecular-beam-epitaxy growth, although apparently simple in principle, has subtle complications in practice. Thus, e.g., it is well known that the growth of semiconductor $A$ on semiconductor $B$ can be different from the growth of semiconductor $B$ on semiconductor $A$.[20,21] The degree of clustering of a given alloy will be dependent on many features associated with the growth process–e.g. the growth temperature, the growth rate, the degree of purity of the source materials and the quality of the substrate, etc. It could also be dependent on whether an external energy source (e.g. a laser beam or a high-energy electron beam producing a RHEED pattern) is incident on the growing surface, since such energy sources could influence surface mobilities and the ability of surface adatoms to overcome local energy barriers. In view of this it is clear that different growth techniques, e.g. molecular-beam epitaxy, vapor phase deposition etc., and even different growth chambers using the same growth technique but different growth rates are likely to produce various amounts and distributions of alloy nonrandomness. Alloy clustering can give rise, in principle, to the three different effects described in (i) to (iii) in the introduction. Hence we attribute the difference in the degree of alloy clustering which is needed to account for the present author's results and that of Heimbrodt *et al.*[25,26] to the difference in the growth conditions prevailing in the growth chamber.

It is also natural to consider possible alternative explanations of the results described in the present paper. However, in view of the fact that the values for well width and barrier composition were checked independently, such explanations cannot be readily found. For example, one *a priori* possibility is that the growth parameters are not fully under control and that the Mn ion concentration is varying across the well region. If, however, this was the case, then it is difficult to understand why the saturated splitting observed in the CdTe/$Cd_{1-x}Mn_xTe$ structures is consistent with the same nominal $x$ value for two quantum wells of different width. Yet again one would expect, from the growth viewpoint, that, if anything, any spatial variation in the Mn ion concentration would occur in the immediate vicinity of an interface of a magnetic and a nonmagnetic material. However, the exchange shift of the narrow quantum-well structures re-

ported by Heimbrodt *et al.*[25] can be accounted for by assuming the same constant value of $x$ across the well region of the structure. On this same line of reasoning one would not expect the $x$ value of the wider wells to be less than the constant $x$ value of the narrow wells, which is what is required in order to account for the exchange shifts reported by Heimbrodt *et al.*[25]

## V. CONCLUSION

We have argued that, as a result of the strongly localized carrier wave functions in diluted magnetic semiconductor quantum wells, magneto-optical measurements are a suitable tool for investigating alloy clustering. In this context, exchange shift experiments have been shown to be consistent with the occurrence of a clustering of the magnetic Mn ions in both $Cd_{1-x}Mn_xTe$ and $Zn_{1-x}Mn_xSe$ quantum-well systems. However, the exact distribution of the alloy clustering is difficult to assess, since the exciton Bohr radii in these quantum-well structures still extends over several tens to hundreds of angströms.

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*Present address: Dept. of Medical Physics, Cookridge Hospital, Leeds LS16 6QB, U.K.

†Electronic address: t.stirner@physics.hull.ac.uk

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