Spintronics-based materials have attracted a lot of interest recently. By introducing spin as a degree of freedom existing technologies can be improved, e.g. smaller devices that consume less electricity, and are more powerful for certain types of computations as compared to present charge-based systems. A key point is that the magnetism be carrier-mediated, i.e. the magnetic state can be manipulated by electrical or optical means. Dilute magnetic semiconductors (DMS), i.e. semiconductors doped with low concentrations of magnetic impurities Mn, Cr, or Co, especially Mn doped GaAs, are generally thought to be good candidates to meet the requirements for spintronics applications. A central issue that has impeded the enhanced when the material is co-doped with acceptors, attempts to do this with holes has not been successful.

An alternative to a random alloy, (CVM) does a rather good job shown in Ref. 15 that the (CVM) does a rather good job of estimating \( T_c \) in random DMS alloys, and is expected to be comparably accurate here.
All the calculations are performed using supercells with periodic boundary conditions. The supercell we use includes 8ML in the [001] direction. We set the thickness of Mn layer to be 1 or 2 ML, which is comparable with the experiment setup. The inter-layer distance is chosen to be 6 ML which is an optimized value based on both speed and accuracy considerations. Checks show that further increase of the interlayer distance does not significantly affect the exchange interactions $T_c$. The lateral scale of the layers are chosen based on Mn concentration simulated. Both ordered and Special Quasi-Random Structures (SQS) are used to simulate Mn doping inside the δ layer.

Most of this effect can be traced to the strong crystallographic dependence of the magnetic exchange interactions. This can be seen by considering exchange interactions $J_{RR'}$ in Ga$_{1-x}$Mn$_x$As compounds of high Mn concentration (Fig. 4). While there is some variation between compounds, there is a tendency for the $J_{RR'}$ to be weak or even antiferromagnetic along the [001] axis, but to be more strongly ferromagnetic along the [110] axis. A similar result is found for the dilute random alloys.12 The origin of the strong crystallographic dependence can, at least in part, be explained in terms of the orbital character of the Mn d orbitals of $t_2$ and $e$ symmetry. Mn impurities in GaAs form a “dangling bond hybrid” level of $t_2$ symmetry which sits $\sim 0.1eV$ above the valence band maximum, and is an admixture of the Mn $d$ levels of $t_2$ symmetry $(xy, yz, \text{and } xz)$ and effective-mass like states derived from the top of the host valence band. Below the valence band top sit Mn $d$ orbitals of $e$ symmetry $(3z^2−r^2$ and $x^2−y^2$), which hybridize less strongly with the environment than the $t_2$ orbitals. As is well known, the $e$ states are filled, while the three $t_2$ states are partially filled with 2 electrons. (Mn, with 5 $d$ electrons and 2 $sp$ electrons, substitutes for Ga, with 3 $sp$ electrons. Thus Mn contributes 5 $d$ electrons and a hole.)

![FIG. 1: Dependence of $T_c$ on Mn concentration inside an superlattice consisting of a 1-2 ML thick δ-layer of Mn, sandwiched by a 6 ML thick GaAs layer. Mn are taken to form an ordered structure within the δ-layer. The x axis refers to the fraction of Ga atoms that are replaced by Mn in the layer considered. In the “m/n” label along x axis, m represents the number of ML in the Mn doped layer, and n is the total number of cation sites in the doped layer. Circles show mean-field results for comparison. The 2/2 system is predicted to be a frustrated spin glass; this is reflected in the figure by assigning $T_c=0$. Open diamond (circle) : $T_c$ for an SQS structure spread over 1ML at 50% concentration calculated within the CVM (MFA).](image1)

We first investigate a series of ordered δ-layers varying concentration within the layer for 1-2 ML superlattices. Fig. 1 shows the calculated $T_c$ for the Mn concentration in the δ-layer ranging between 1/4 and 1.

For bulk random alloys,15 the disorder in the Mn site positions rather strongly affects exchange interactions and reduces $T_c$. In the bulk Ga$_{1-x}$Mn$_x$As alloy, the predicted optimum $T_c$ was found to be $\sim 300K$ at $x=12\%$. Fig. 1 compares an ordered to a disordered configuration of Mn within the δ-layer in the 1/2 filling case (Mn position in the ML were simulated by an SQS structure). It is seen that the effect of disorder is to reduce $T_c$ slightly, just as in the bulk random alloy. (Note that mean-field theory incorrectly predicts $T_c$ increases with disorder, as was also found in the bulk alloy.)

Notably, the optimum $T_c$ for the δ-layer case occurs near 50% filling in a single ML and the optimum $T_c$ is near that predicted for the bulk case ($\sim 300K$ at $x=12\%$).

FIG. 1: Dependence of $T_c$ on Fermi level shift and excess hole concentration in a bulk SQS Ga$_{92}$Mn$_{8}$As$_{100}$ alloy. $E_F$ = 0 corresponds to the usual charge-neutral case.

![FIG. 2: Dependence of $T_c$ on the Fermi level shift and excess hole concentration in a bulk SQS Ga$_{92}$Mn$_{8}$As$_{100}$ alloy. $E_F$ = 0 corresponds to the usual charge-neutral case.](image2)
a function of Fermi level (thus altering the filling of the $t_2$ level), i.e., additional holes are modeled by simple Fermi level shifts. The $J_{RR'}$ and $T_c$ are maximal when the $t_2$ level contains approximately 3/2 electrons.

If this applies to both the $t_2$ and $e$ levels, the $t_2$ level should contribute a FM exchange, while the $e$ level should contribute a competing AFM exchange. To see to what extent this model describes the LDA exchange we resolve the mean-field estimate for $T_c$ into separate $l$ and $m$ contributions, that is

$$T_c^{\text{MFA}} = \sum_L T_{c,L}^{\text{MFA}}$$

and

$$T_{c,L}^{\text{MFA}} = \frac{2}{3} \sum_{RR'L'} J_{RR'L'}^{L'}$$

where $J_{RR'L'}$ is identical to Eq. (1) but with the sum over $LL'$ suppressed. Three compounds with high Mn concentration were studied: MnGa$_3$As$_4$ in the L1$_2$ structure, a four-atom SQS alloy Mn$_2$Ga$_2$As$_4$, and MnAs in the ZB phase. Data shown in Fig. 3 largely verifies this picture. The Table in Fig. 3 shows the $e$ levels consistently contribute antiferromagnetically. FM contributions from $t_2$ level decrease with increasing Mn concentration. In the high concentration limit (ZB MnAs) the picture of a $t_2$ derived impurity band is rather far removed from reality. Fig. 3 also shows site-resolved $J_{RR'}$. It shows that $J_{RR'}$ when $R$ points along [110] tend to be FM, while those pointing along [001] tend to be AFM. This tendency is compatible with symmetry of the $t_2$ orbitals, which point in the [110] directions and are FM coupled, while the $e$ orbitals point along the [001] are weak or even AFM coupled. Thus it seems that the LDA exchange interactions are rather strongly dependent on symmetry of the Mn orbitals rather than largely being a function of the Fermi surface, as RKKY-like models suppose.

The orientation dependence of $J$ has been studied previously by a number of authors, mostly in the dilute case where the Mn doping concentration is < 10%. One approach estimates $J$ from various FM-AFM configurations. However, such calculations are predicated on the assumption that large-angle rotations can map to a Heisenberg model (a perturbation theory valid for small rotations). More importantly, this approach is problematic especially for dilute case, because many $J$'s are required. The longer-ranged $J$s are important to describe $T_c$, where percolation is important. The more rigorously based linear-response technique explicitly calculates energy changes for small angle rotations. Many $J$s are calculated at once; and the range extends far beyond the unit cell. In any case, none of the preceding calculations yield AFM coupling in the [001] direction, because the competing antiferromagnetic interactions are much stronger at high concentrations, at least in the LDA. In the dilute case, we obtain both FM and AFM exchange coupling for [001] direction, which when averaged yields a small net coupling, similar to a CPA linear-response calculation. However, for high Mn doping in the $\delta$-doped case studied here, AFM becomes increasingly dominant along [001].

The crystallographic dependence of $J_{RR'}$ and the reduction of $J_{RR'}$ with Mn concentration, help to explain why $T_c$ is maximal for partial fillings of the $\delta$ layer (Fig. 1), and also suggest that $T_c$ will be optimal for a rather small $\delta$ layer thickness. To test this, we compute $T_c$ varying the number $\delta$ layers. We fix the total thickness of the supercell as 8ML and change the thickness of $\delta$-layer up to 8ML (corresponding to the bulk case). Each layer contains 50% Mn and 50% Ga (the 1-layer case corresponds to the “1/2” point in Fig. 1). Data is shown in Fig. 1. $T_c$ is optimal at 2ML, then decreases above that. (For thicknesses > 2 ML only $T_c^{\text{MFA}}$ is shown. CVM predicts a spin glass).

We now turn to the question: can $T_c$ be increased by co-doping to add holes? We can mimic addition of holes...
by Fermi level shifts (as before); alternatively we can dope the GaAs layer with an acceptor such as Be. In Ref. 10 δ-doped MnGaAs were grown in this way. Extra holes were supplied to the δ-layer by doping Be in the GaAs near (but not in) the δ-layer, to prevent compensating donors such as Mn interstitials from forming in the δ-layer.

In Fig. 5 the dependence of $T_c$ on the number of extra holes is presented. $T_c$ increases markedly by the addition of $\sim 1/2$ hole/Mn atom. Higher hole concentrations do not further increase $T_c$ (as in the random alloy). The difference between Fermi level shifts and using actual dopants can be explained in that the latter contains electrostatic shifts as a result of charge transfer from the Be dopants to the Mn layers, thus reducing hole confinement in the δ-layer. This confirms the experimental results for δ layer and also suggest a much higher $T_c$ for defect free samples compared with the best $T_c$ recorded to date.

In conclusion, we demonstrate a strong crystallographic dependence of magnetic exchange interactions in Ga$_{1-x}$Mn$_x$As, and show that it can be exploited in δ-doped Mn:GaAs structures to optimize $T_c$. We determine the size and concentration of δ-layers, and hole concentration that are predicted to result in an optimal $T_c$. Under optimal conditions (which entails superlattices to be grown sufficiently defect-free) $T_c$ is predicted to be well above room temperature.

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\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{fig4}
\caption{FIG. 4: Dependence of $T_c$ on the δ-layer thickness for an average Mn concentration of 50% per layer. Circles show mean-field results for comparison.}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{fig5}
\caption{FIG. 5: Dependence of $T_c$ on excess hole concentration for a 2ML δ-doped MnGaAs structure, with the δ-layer containing 50% Mn, as calculated by the CVM. Hole doping is modeled through artificial Fermi level shifts, or induced through the addition of Be in GaAs layers adjacent to the δ-layer.}
\end{figure}
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