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Tuning of the average *p-d* exchange in (Ga,Mn)As by modification of the Mn electronic structure

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An important parameter of the ferromagnetism of (Ga,Mn)As alloys is the average *p-d* exchange integral $N_0\beta$ since the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction parameter $J_{\mathrm{RKKY}} \propto (N_0\beta)^2$. We prove, by a detailed study of *p*-type $Ga_{1-x}Mn_xAs$ and *n*-type $Ga_{1-x}Mn_xAs:Te$ ($x < 0.005$) in the paramagnetic phase, that the magnitude and sign of $N_0\beta$ are strongly dependent on the local electronic configuration of the Mn ions. We find $N_0\beta > 0$ (ferromagnetic coupling) in *p*-type samples where the local Mn configuration is Mn^0_{Ga} ($3d^5$ +hole). In *n*-type samples, $N_0\beta < 0$ (antiferromagnetic coupling) with the local Mn configuration being Mn^-_{Ga} ($3d^5$). The average $N_0\beta$ in (Ga,Mn)As is not a material constant as widely believed. It can be tuned and can even change its sign, depending on the doping conditions of the Mn-containing layer.

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Currently, the favored magnetic semiconductors in the widespread area of spintronics are Mn-doped III-V semiconductors. The tremendous interest is caused by their compatibility with established III-V device technology. On the one hand, the Mn ions in these semiconductors act as acceptors providing free holes as carriers and, on the other hand, they carry the localized magnetic moments crucial for achieving magnetism. The Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction is commonly accepted as the underlying mechanism yielding ferromagnetism and high Curie temperatures.[1–4] As discussed by Dietl *et al.* on the basis of a mean-field Zener model, T_C values above 300 K should be achievable for $Ga_{1-x}Mn_xAs$ if a large value of x is accompanied by a corresponding increase of the hole concentration n_H. There exists, however, a discrepancy between experimental and theoretical values of T_C in Mn-containing GaAs. By specific annealing procedures, the T_C of as-grown samples may be increased,[5,6] but still the highest T_C reported so far for $Ga_{1-x}Mn_xAs$ is far below 300 K. The discrepancy is generally explained by compensation effects leading to $n_H \ll x$. It is known that Mn can easily occupy an interstitial site and act as a double donor.[7–11] Mahadevan and Zunger showed that such an interstitial Mn ion not only reduces n_H by codoping but also introduces an antiferromagnetic interaction if the interstitial ion is close to a Mn ion on a regular lattice site. A similar antiferromagnetic contribution is expected also for higher x for two neighboring Mn ions on regular lattice sites due to the Anderson superexchange interaction, well known from (II,Mn)VI diluted magnetic semiconductors.[12,13]

However, an aspect which has been entirely ignored so far is the influence of compensation on the average *p-d* exchange integral between the localized magnetic moments and the extended valence band states. The average *p-d* exchange is crucial for the ferromagnetism of (III,Mn)V semiconductors. The ferromagnetic coupling between the Mn spins in the RKKY picture is mediated by the free carriers. The exchange parameter and Curie temperature are given by

$$J_{\mathrm{RKKY}}(r) = -J_{pd}^2 \frac{\mu_0 m^* k_F^4}{\pi^3 \hbar^2} F(2k_F r), \tag{1}$$

$$T_C \propto J_{pd}^2 m^* x n_H^{1/3}, \tag{2}$$

where r is the distance between two interacting Mn ions and $F(x) = (\sin x - x \cos x)/x^4$ is the oscillating Friedel function of the product between the Fermi wave vector k_F and the distance between Mn ions r. m^* is the hole effective mass. The Fermi wave vector is proportional to $n_H^{1/3}$ where n_H is the hole density. The often used *p-d* exchange integral $N_0\beta$ is directly proportional to the coupling constant J_{pd} which describes the coupling between hole spins and Mn spins in the RKKY picture. N_0 denotes the number of unit cells per cm^3 and $\beta = \langle X|J|X\rangle$ is the exchange interaction parameter. If all Mn ions have the same electronic configuration, β (i.e., J) is equivalent to the microscopic interaction parameter for an individual Mn ion with the extended hole wave function. In the case of a random distribution of Mn ions with different electronic configurations the experimentally determined β is a weighted average of the microscopic parameters J of the Mn centers with different electronic configurations interacting with the extended hole state.

The complexity of the situation is illustrated by the wide range of values determined for $N_0\beta$ in (Ga,Mn)As. In paramagnetic GaAs:Mn for very small Mn concentrations ($\approx 10^{17}$ to 10^{19} cm^{-3}) a ferromagnetic *p-d* coupling ($N_0\beta > 0$) is commonly found.[14–16] These results were obtained by magneto-optical measurements, which offer direct access to $N_0\beta$ via the giant Zeeman splitting of the heavy-hole (HH) excitons in the Faraday geometry (corrected for diamagnetic shifts and for the normal Zeeman splitting):[12,13]

$$\Delta E_{\mathrm{HH}} = E_{\mathrm{HH}}(\sigma^+) - E_{\mathrm{HH}}(\sigma^-) \propto N_0(\beta - \alpha) \approx N_0\beta \tag{3}$$

because $|N_0\beta| \gg |N_0\alpha|$ where $N_0\alpha$ is the *s-d* exchange integral between the localized Mn $3d$ states and the extended

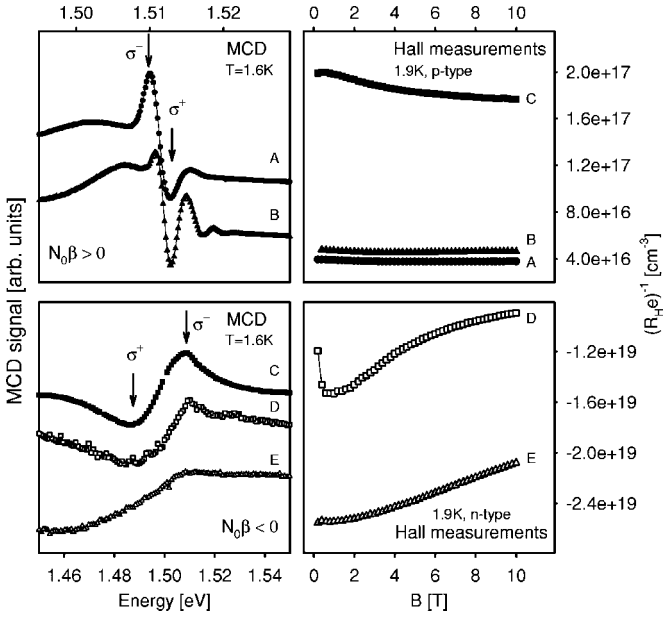

FIG. 1. Left: MCD spectra of GaAs:Mn (A,B) and GaAs:Mn,Te (C,D,E) samples taken at $H=1$ T for A to D, $H=3$ T for E. Right: corresponding Hall results.

conduction band states.[14] σ^+ and σ^- denote the circular light polarizations. In paramagnetic GaAs:Mn one finds $\Delta E_{\mathrm{HH}}>0$ whereas in (II,Mn)VI diluted magnetic semiconductors $\Delta E_{\mathrm{HH}}<0$ is always observed. This means that the coupling between the valence band states and the Mn moments is antiferromagnetic, $N_0\beta<0$.[12,13]

Ando *et al.*[17] observed $\Delta E_{\mathrm{HH}}<0$ and deduced $N_0\beta<0$ from magnetic circular dichroism (MCD) measurements in reflection on ferromagnetic $Ga_{1-x}Mn_xAs$ layers with x from 5% to 8% and n_H between 10^{19} and 10^{20} cm^{-3}. On the other hand, Szczytko *et al.*[30] observed $\Delta E_{\mathrm{HH}}>0$ on $Ga_{1-x}Mn_xAs$ alloys with $x\approx 0.04$, but also deduced $N_0\beta<0$, accounting for occupation effects. Matsukura *et al.*[18] determined the modulus $|N_0\beta|\approx 3.5$ eV from transport measurements assuming that the negative magnetoresistance curves above T_C arise solely from spin-disorder scattering between the hole spins and the Mn spins. Satoh *et al.*[19] determined values for $|N_0\beta|$ between 3.0 and 3.5 eV from the dependence of T_C on hole concentration. The latter two approaches are not direct measurements and are based on the strict validity of Eq. (1). Core-level photoemission experiments of $Ga_{0.926}Mn_{0.074}As$ gave a value of $N_0\beta=-1.2$ eV.[20] In general, it appears to be very difficult to extract reliable values for $N_0\beta$ from ferromagnetic samples. We show in what follows that the range of observed $N_0\beta$ values directly reflects the occurrence of Mn ions in two different charge states which differ in their electronic structure.

Paramagnetic $Ga_{1-x}Mn_xAs$ and $Ga_{1-x}Mn_xAs:Te$ layers with $x<0.005$ were grown on GaAs substrates by metal-organic vapor-phase epitaxy (MOVPE). An (Al,Ga)As etch stop was grown prior to the growth of the paramagnetic layer. Thus, the substrate could be removed after growth to avoid any ambiguities in the magneto-optical experiments. A thorough characterization by photoluminescence, Hall effect, secondary-ion mass spectroscopy, high-resolution x-ray diffraction, and transmission electron microscopy measurements revealed that there is no interstitial Mn in the layers and all Mn is incorporated on group III lattice sites as acceptors. Codoping with Te on the group V lattice changes the majority carriers from holes to electrons. Superconducting quantum interference device measurements confirmed that the samples are paramagnetic.

Figure 1 summarizes MCD (left) and Hall (right) measurements at $T\approx 2$ K of a series of GaAs:Mn,Te samples with increasing Te content (from A to E). The Hall results show that samples A to C are p type, whereas D and E are n type. The small variations of the Hall constants with field are due to the magnetic-field-induced tuning of the disorder and the density of states typical for dilute magnetic semiconductors. The MCD measurements were performed in the transmission geometry on pieces of the specimens without substrate. A positive (negative) MCD signal corresponds to dominant σ^- (σ^+) absorption in the layer. Samples A and B exhibit $\Delta E_{\mathrm{HH}}>0$ whereas $\Delta E_{\mathrm{HH}}<0$ is observed for samples C to E. According to Eq. (3), this corresponds to $N_0\beta>0$ for the former samples and $N_0\beta<0$ for the latter. This proves unambiguously that the sign of the exchange integral $N_0\beta$ in GaAs:Mn is correlated with the type of conductivity. Sample C, which is only partly compensated, is an exception as will be discussed below. We obtain $N_0\beta\approx+2.5$ eV for the p-type samples[14] and estimate for n-type samples that $N_0\beta<0$ and $|N_0\beta|<5$ eV. It is worth noting that a negative $N_0\beta$ has been reported also for n-type $In_{1-x}Mn_xAs$ with x ranging from 0% to 12%.[21,22]

The sign reversal is a manifestation of the strong correlation between the local Mn configuration and the p-d exchange integral $N_0\beta$. For n-type conductivity (C and D) all of the Mn acceptors are compensated and A^- centers will be dominant. For p-type conductivity (A and B) basically two electronic configurations are possible: either a hole (h) is bound to the Mn acceptor at low temperatures or Mn itself changes from a high-spin state $S=5/2$ to an $S=4/2$ state.

To decide this question we have performed *ab initio* total energy calculations based on the density functional theory in the local spin-density approximation. The calculations are performed using the linear muffin-tin orbital Green's function method in the atomic sphere approximation[23] (for technical details see Ref. 24). The Green's function technique describes an *isolated* defect in an otherwise perfect crystal. Hence, energy levels of charged defects are obtained directly and need no background charge correction.

The fivefold orbital degeneracy of the Mn $3d$ level is lifted by the T_d site symmetry and the level splits into a doublet e and triplet t_2. The exchange interaction lifts the spin degeneracy. The $e\uparrow$ states are located within the valence bands; the $t_2\uparrow$ states are situated just above the upper valence band edge. The corresponding unoccupied $\downarrow$ states are above the conduction band edge. According to our calculation, the isolated negative Mn_{Ga} point defect in its $S=5/2$ high-spin state has the lowest total energy for any position of the Fermi energy E_F within the gap, independent of doping. For p-type samples the neutral Mn_{Ga}^0 defect in the $S=4/2$ high-spin state is by 0.36 eV higher in energy, the reason being the reduction of the exchange splitting by taking an electron out of the $t_2\uparrow$ state. Hence there is no other deep charge state for Mn_{Ga},

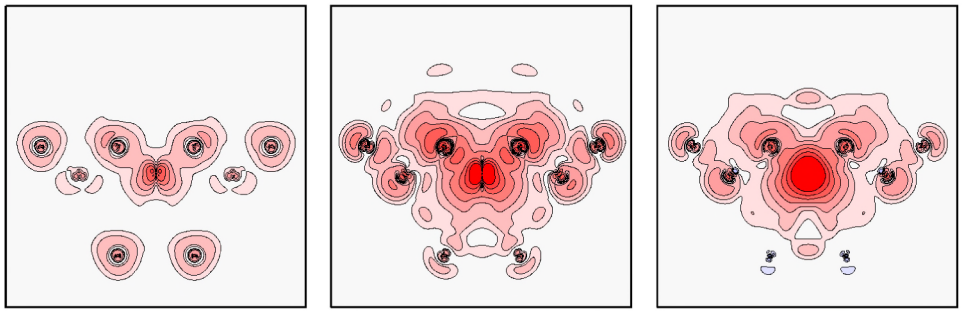

FIG. 2. Logarithmic contour plots of magnetization densities of the isolated Mn_{Ga}^{-} point defect with an additional valence band hole in a (110) GaAs plane. Left: the density of the valence band hole; center: density of the $t_2\uparrow$ gap state; right: total magnetization density of $t_2\uparrow+e\uparrow$. (Two contour lines correspond to one decade in density.)

except for a neutral charge state where a shallow valence band hole is bound to the negative deep acceptor (A^0). This result agrees with the electron paramagnetic resonance (EPR) result of Schneider *et al.*[25] that the neutral charge state of Mn_{Ga} is in a $3d^5+h$ state rather than in a $3d^4$ state.

In Fig. 2 we compare the magnetization density of the valence band hole with the respective densities of the $t_2\uparrow$ gap state and the total magnetization density of the high-spin state of Mn_{Ga}^{-} ($t_2\uparrow+e\uparrow$). Clearly, as is typical for a shallow state, the hole state is much more delocalized than the t_2 gap state. This state in turn extends much further than the remarkably compact total magnetization density.

These predictions are further corroborated by studies of the local electronic structure of the Mn ion. Figure 3 shows spin-flip Raman spectra of *p*-type GaAs:Mn (sample B of Fig. 1) taken with the laser excitation close to the band gap. The observed signals are paramagnetic resonance signals arising from multiple spin flips within the Zeeman-split ground state of the Mn $3d$ configuration.[26] The signals have g factors of 2.77 and 5.54. Schneider *et al.* demonstrated that A^- with a $3d^5$ configuration and A^0 with a $3d^5+h$ configuration can be distinguished in EPR experiments due to their different g values. They reported $g=2.0$ and 2.77 for the A^- and A^0 centers, respectively, interpreting the difference by a $3d^5$ ground state for A^-, while for A^0 a $3d^5+h$ ground state was inferred. Thus, the spin-flip signals in the *p*-type samples A and B originate solely from A^0 centers as there is no evidence for signals with $g=2.0$. This is different for the Te-doped samples (C and E) as can be seen from the EPR spectra in Fig. 3, taken at 9.5 GHz. The EPR spectrum observed in sample C consists of the A^- signal with six hyperfine lines centered at $g=2.0$ and an additional broad resonance line at a resonance field near 0.18 T with a linewidth of about 0.08 T. The broad resonance line can only be due to the A^0 center, because it appears just at the average field of the two signals at $g=2.77$ and 5.72 ascribed to the fine-structure transitions ($\Delta M=1$, $\Delta M=2$) of the A^0 center. In our case the fine structure is not resolved but is exchange narrowed into a single line in the center of gravity of the original fine structure. This narrowing process is driven by the exchange interaction of the localized acceptor with the charge carriers, as is typically observed in the electron spin resonance (ESR) of localized moments in metals.[27] Therefore, the partly compensated sample C has A^0 and A^- centers. The EPR spectrum of sample E consists of the A^- signal only.

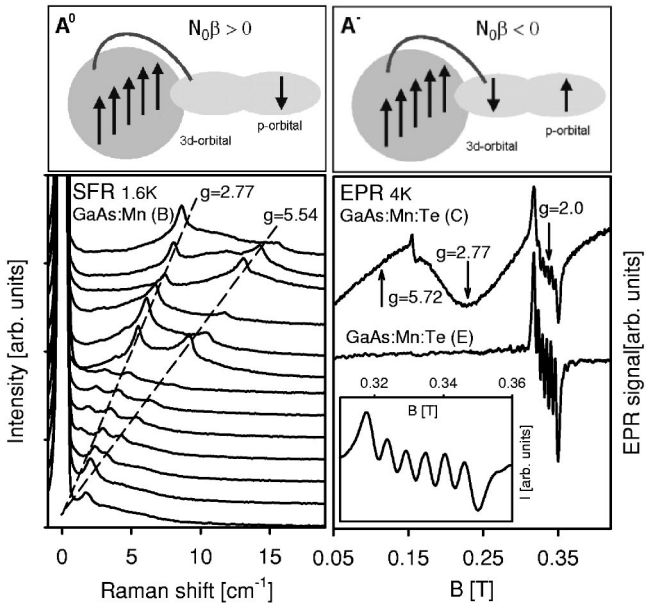

FIG. 3. Left: Spin-flip Raman spectra of *p*-type GaAs:Mn (sample B); the magnetic field ranges from 0 to 6 T in 0.5 T steps. Right: EPR spectra at $T=4$ K of GaAs:Mn,Te (samples C and E). Inset: hyperfine structure of A^- line (sample E). Top: Schematic representation of the mechanism leading to $N_0\beta>0$ and $N_0\beta<0$.

As Mn in ferromagnetic $Ga_{1-x}Mn_xAs$ samples is not solely incorporated on Ga sites but is also incorporated as an interstitial acting as a double donor,[7–11] this means that, in ferromagnetic samples, Mn ions on Ga sites are to a certain extent compensated. Consequently, A^- and A^0 centers are often observed simultaneously in EPR experiments on molecular-beam-epitaxy-grown ferromagnetic $Ga_{1-x}Mn_xAs$.[28,29]

The correlation of the sign of $N_0\beta$ with the local electronic configuration of the Mn ion can be understood qualitatively by considering virtual jumps of the p electrons to the d states and back (see top graphs of Fig. 3). In the case of half-filled d shells as in Mn^{2+} in a II-VI semiconductor, or even in the case of $Fe^{2+}(3d^6)$ or $Co^{2+}(3d^7)$ with more than half-filled d shells in II-VI semiconductors, the spin has to be aligned antiferromagnetically, as jumps are possible only into the unoccupied spin $3d$ states. Therefore, also in *n*-type GaAs:Mn,Te the coupling of the p orbital to the half-filled $3d^5$ with all spins aligned is antiferromagnetic. For ions with less than half-filled d shells, like $Cr^{2+}(3d^4)$ in II-VI semiconductors, a ferromagnetic coupling[31] is observed, as the spin of the hopping electron according to Hund's rule should be aligned parallel to those already located in the d shell. A Mn $3d^5+h$ center in GaAs behaves somewhat similarly to the

$3d^4$ state of Cr in II-VI semiconductors. The hole with a polarized spin can accommodate preferentially valence band electrons with a spin parallel to the spins of the 3*d* electrons, i.e., the *p-d* coupling is ferromagnetic.

In various theoretical and experimental papers a constant value of $N_0\beta$ is used.[1–4] A T_C variation is then solely determined by the Mn and free-carrier concentrations. The strong correlation of $N_0\beta$ and the type of Mn center, established in this work, implies that the average $N_0\beta$ is usually not a constant. The $N_0\beta$ value must be ill defined in $Ga_{1-x}Mn_xAs$ with x of several percent and a high degree of compensation. It will be an average determined by the ratio of A^- to A^0. Therefore, it is essential to incorporate the dependence of $N_0\beta$ on the local Mn configuration in current theories.

In conclusion, the magnitude as well as the sign of the *p-d* exchange integral $N_0\beta$ depend strongly on the local electronic configuration of the Mn ion. Controlling the local electronic structure of the Mn ion will offer additional ways of tuning *p-d* coupling in ferromagnetic (III,Mn)V compounds. This may be an important tool in the future for raising the Curie temperatures of these ferromagnetic semiconductors above room temperature.

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