Mn impurity in $Ga_{1-x}Mn_xAs$ epilayers

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Electron paramagnetic resonance was measured in $Ga_{1-x}Mn_xAs$/GaAs epilayers with $0.002 \leqslant x \leqslant 0.01$. Data were taken as a function of magnetic field orientation at low temperatures. The observed spectra were attributed to ionized Mn acceptor A^-. No neutral Mn acceptor centers were detected. The observed anisotropy of A^- is interpreted in terms of sizable demagnetizing fields resulting from ferromagnetic coupling between Mn ions. [S0163-1829(99)07235-5]

Manganese impurity in GaAs and other III-V compounds has been studied for a long time.[1–17] The present understanding of the situation can be summarized as follows: There are essentially three types of Mn centers in III-V compounds. The first one (we denote it center $C1$) is formed by substitutional manganese Mn^{3+}, which is in d^4 configuration, with the ground state spin $S=2$. This configuration is in fact equivalent to Cr^{2+} in II-VI compounds and should reveal all the features characteristic for that case, including static Jahn-Teller effect and magnetic anisotropy.[18,19] The second type of Mn center (center $C2$) occurs when the center $C1$ traps an electron and binds it tightly at the d shell. Such center can be regarded as a d^5 configuration, with $S=5/2$. The Mn center $C2$ is negatively charged and can therefore attract and (weakly) bind a hole, forming a (d^5+h) complex (center $C3$).[4] Due to an exchange interaction between the d-shell ($S=5/2$) and the bound hole ($j=3/2$), the groung state of $C3$ may have total angular momentum $J=4$ (for ferromagnetic interaction between the hole and the ion) or $J=1$ (for antiferromagnetic interaction). Centers $C1$ and $C3$ can be viewed as neutral acceptor centers A^0 (d^4) and A^0 (d^5+h), respectively, while center $C2$ as an ionized acceptor A^-. Experiments performed for GaP:Mn revealed the existence of both A^0 (d^4) and A^- centers.[17] In contrast A^0 ($d4$) centers were not observed in EPR for GaAs:Mn.[4] Moreover the available data (e.g., magnetization) do not match the behavior expected for a A^0 (d^4) center.[13,14,9,20] On the other hand in most GaAs:Mn crystals ionized acceptor centers A^- were observed in EPR. The EPR spectrum of A^- center reveals typical 6-line structure (resulting from electron hyperfine interaction with ^{55}Mn nucleus spin $I=5/2$), centered at $g^*=2.00$.[2,3] In some cases additional lines were observed for $g^*=2.77$ and $g^*=5.72$,[4] which were interpreted as triplet

transitions for $\Delta m=1$ and $\Delta m=2$, where Δm represents the change of angular momentum J_z.[4] These transitions were ascribed to A^0 (d^5+h) center with $J=1$ ground state. This model is corroborated by infrared (IR) spectroscopy data, which reveal acceptor level at about 0.113 eV above the top of the valence band.[1] Recently the spectrum of this acceptor was throughly studied under the presence of uniaxial stress and magnetic field.[13,14,21] The results give the strong support for the A^0 (d^5+h) impurity center. Also the magnetic data of GaAs:Mn could be successfully described taking into account A^0 (d^5+h) and A^- centers.[9,20] The lack of A^0 (d^4) centers was recently explained by configuration cluster-model calculations, which showed that for GaAs the ground state of neutral acceptor is dominated by (d^5+h) configuration.[22] It seems therefore rather well established that for bulk GaAs manganese impurity occurs either as a neutral (d^5+h) or ionized (d^5) acceptor center. Ionization of A^0 (d^5+h) give rise to p-type conductivity of this material.

For a long time the investigation of Mn impurity in III-V compounds was limited to bulk crystals and low Mn concentrations (below 0.1 molar MBE technology), which allowed the growth of $Ga_{1-x}Mn_xAs$ and $In_{1-x}Mn_xAs$ epilayers with significant Mn concentration (few molar quantum structures are very appealing from the point of view of fabrication of optoelectronic devices, which could be integrated in ICs). For this reason, as well as for attractive basic physics problems they offer, these materials have attracted considerable attention during recent years. Many interesting properties have been reported,[23–28] among them ferromagnetism of Mn ion system and strong magnetooptical effects.[29] The latter results from band splittings induced by s, p-d exchange interaction, between delocalized s and p band electrons and

localized d electrons of Mn ions. We note that such behavior is typical for so called diluted magnetic semiconductors (DMS, mostly based on II-VI compounds), intensively investigated during last two decades.[30]

In particular for Ga$_{1-x}$Mn$_x$As epilayers with $x \leqslant 0.005$ reflectance magnetocircular dichroism (MCD) probing the band splittings, was found to be essentially the same as was for Cd$_{1-x}$Mn$_x te$.[29] This suggests that the character of the s, p-d exchange in the GaMnAs case is the same as for Mn-based II-VI DMS,[30–34] i.e., s-d exchange is ferromagnetic (exchange integral $N_0\alpha > 0$, where N_0 is number of unit cells in unit volume) and the p-d exchange is antiferromagnetic (exchange integral $N_0\beta < 0$). Such behavior may be expected for Mn center in the d^5 configuration (A^-), for which only antiferromagnetic exchange channels are available.[34] The s-d exchange, being a potential (direct) exchange is always ferromagnetic. This experimental observation in epilayers contradicts the magneto reflectance results for bulk GaAs:Mn ($x < 0.0001$), which showed exciton splitting compatible with ferromagnetic p-d exchange ($N_0\beta > 0$). That finding was interpreted in terms of new, ferromagnetic p-d exchange paths. Such paths can be provided by A^0 ($d^5 + h$) Mn centers, since the bound hole is spin polarized.[35] The observed difference in the band splitting for bulks and epilayers was then attributed to different abundance of A^- and A^0 ($d^5 + h$) centers: since only A^0 centers give rise to ferromagnetic p-d exchange, these centers must be present in bulk GaAs:Mn crystals. On the other hand in the GaMnAs epilayers A^- centers must dominate over the A^0 centers, so effectively the p-d exchange is antiferromagnetic.[29]

The concept of neutral and ionized Mn acceptors in GaMnAs was recently used to explain the ferromagnetism of Mn ion system.[36] The proposed double exchange mechanism relies critically on coexistence of A^0 and A^- centers, which can exchange one electron and this way provide (ferromagnetic) coupling between Mn ions.

To verify the above hypotheses it is therefore essential to establish the actual situation in the GaMnAs epilayers. In view of that we performed EPR measurements on the epilayers, as well as on the bulk GaAs:Mn crystals for reference. To provide direct relation to magnetooptical results, we used the same crystals, for which magnetooptical experiments were performed.

The examined bulk crystals were heavily doped with Mn on the level from 10^{17} cm^{-3} ($x = 5 \times 10^{-6}$) to 10^{19} cm^{-3} ($x = 5 \times 10^{-4}$). The manganese concentration was estimated from the magnetization of the sample, assuming that the magnetization is approximated by the Brillouin function with $S = 5/2$.[35] The usual methods, such as electron microprobe analysis or wet chemical analysis could not provide sufficient accuracy in this case. Actually, the exact Mn concentration for bulk crystals is not relevant. All the crystals were p type, having room temperature hole concentration on the level of 10^{18} cm^{-3}. Standard EPR experimental setup, operating at 9.5 GHz and temperature range 3–300 K was used. Similarly as in the previous experiments[4] we observed both A^- ($C2$) and A^0 ($C3$) centers. Figure 1 displays typical EPR spectra for two crystals (samples No. 1, $x = 5 \times 10^{-6}$ and No. 2, $x = 5 \times 10^{-4}$). Sample No. 1 reveals typical six-line spectrum, characteristic for A^- (Mn^{2+} center), centered at g factor 2.004, in good agreement with (Refs. 2,3). For
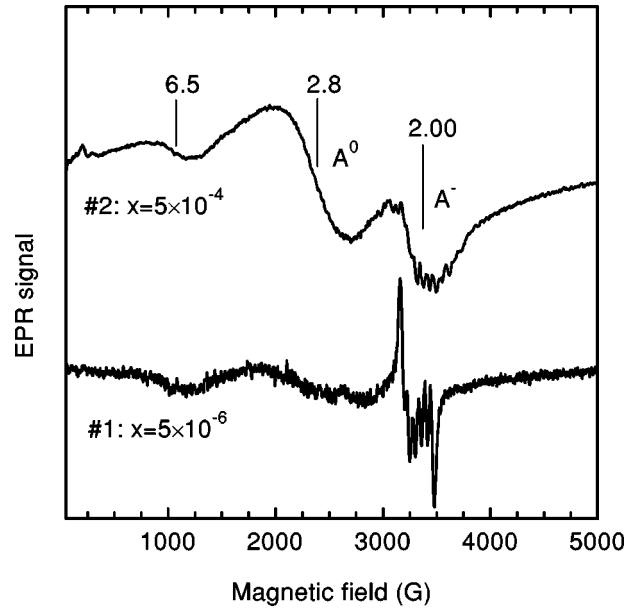

FIG. 1. The EPR spectrum of GaAs doped with Mn obtained at $T = 3.8$ K for samples No. 1 ($x = 5 \times 10^{-6}$) and No. 2 ($x = 5 \times 10^{-4}$). Microwave frequency: 9.51 GHz. The g-factor values 2.00, 2.8, and 6.5 are marked. The EPR markers were removed from the spectra for clarity.

sample No. 2 in addition to the A^- structure around $g = 2.00$,[42] two other lines are visible: the first one for $g_1 = 2.8$ and the second one for $g_2 = 6.5$ (Fig. 1). Both g_1 and g_2 are fairly isotropic with a rotation of the sample relative to the magnetic field. Following Ref. 4 we ascribe these two lines to the transitions within A^0 triplet. We note that the second transition occurs at slightly lower magnetic filed than expected for ideal triplet, for which $g_2 = 2g_1$. This discrepancy was present in all samples, although g_2 changed slightly from sample to sample (from 5.7[4] to 6.2-6.8 for our samples), while g_1 remains rather constant. Such behavior can hardly be explained by local uniaxial strains, described by DS_z^2 term in Hamiltonian. Such sample dependent strain would vary the energy of the first transition, leaving the second one unchanged. Leaving this problem apart, we conclude that structures typical for A^0 centers are pronounced in some bulk crystals, while in the others (such as sample No. 1) they are practically missing. Although some traces of weak structures around $g = 2.8$ and 6.6 could be observed, it is apparent that A^0 centers, if present in sample No. 1, are much less numerous than the A^- centers. We note that MCD measured on sample No. 1 was found compatible with AFM p-d exchange, while magnetoreflectance of sample No. 2 showed FM-type exciton splitting.[35] These observations are in full agreement with the model for the p-d exchange mentioned above.[29]

The Ga$_{1-x}$Mn$_x$As epilayers, which were studied had much more higher Mn concentration than bulk crystals (x between 0.002 and 0.01) and thickness between 0.5 and 2 μm. In particular we used the sample with x=0.005, which was previously investigated by MCD.[29] For the details of the growth process and the basic transport properties we refer to Refs. 23–27. EPR was measured as a function of temperature from about 3 K to room temperature and as a function of magnetic field orientation relatively the epilayer. For all the
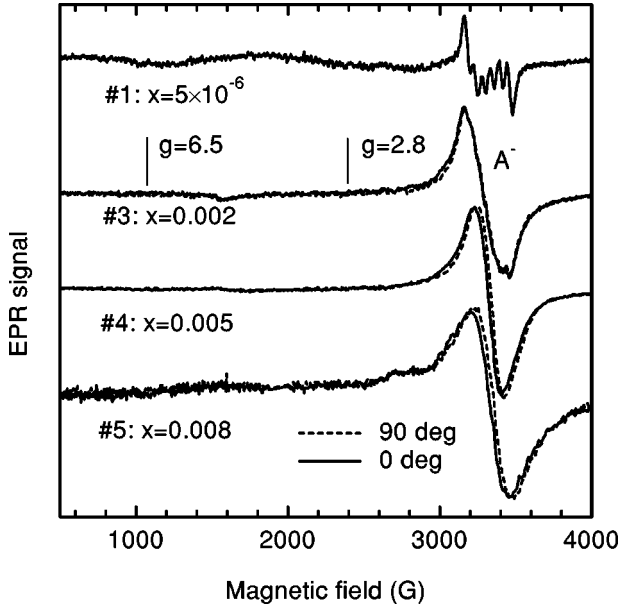
FIG. 2. The EPR spectra of GaMnAs epilayers (No. 3, $x = 0.002$ at T=3.9 K and No. 4, $x = 0.005$ at 3.4 K) for magnetic field parallel ($0°$) and perpendicular ($90°$) to the epilayer. For comparison the spectrum of bulk sample No. 1 is also shown. The EPR markers were removed from the spectra for clarity.

epilayers with low Mn content ($x < 0.01$) only a single EPR line was observed with the g factor around 2.00 ($H = 3.3$ kG). We exemplify this situation in Fig. 2, where spectra of samples with $x = 0.002$ (No. 3) and 0.005 (No. 4) are shown. We ascribe the observed lines to the A^- center. The identification is based on the following arguments: (i) Since A^- was easily visible for bulk GaAs:Mn, we expect this should also be the case for GaMnAs epilayers, (ii) Mn is the dominant impurity, so it should dominate the EPR absorption (the possible other impurities should contribute much less to EPR absorption), (iii) the effective g factor of the observed line agrees well with the center of the 6-line A^- structure observed for bulk crystals. Moreover the width of the considered line is practically the same as A^- center. We believe that the line we observe results from broadening of the 6-line structure with increasing Mn concentration. Such broadening is well known for II-VI Mn-based DMS (Ref. 37) and is probably visible for bulk sample No. 2 (Fig. 1).[42] We stress that we were well aware of the possible low-temperature (LT) GaAs buffer layer contribution to EPR absorption. However, the characteristic lines originated from antisite AsGa were not visible. In particular the line with g factor around 1.6,[38] which should not be masked by any other lines and than could be used as a fingerprint of AsGa, was absent. This is probably due to small thickness of the buffer layer and higher growth temperature, than typical for LT GaAs.[38] The other possible reason is that microwave must pass through GaMnAs epilayer before penetrating the substrate, which weakens AsGa absorption.

The A^- line in the epilayers shows weak anisotropy as the magnetic field is rotated from the in-plane direction (we denote it as $0°$ configuration) to a direction perpendicular to the epilayer ($90°$ configuration), as shown in Fig. 2. The anisotropy is practically absent in $x = 0.002$ sample, but increases with increasing Mn content (the line shift between $0°$

and $90°$ configurations is 12–15 G for $x = 0.005$ and 28–32 G for $x = 0.008$, depending on the epilayer piece) (Fig. 3). Interpreting this anisotropy one should keep in mind that at low temperatures Mn ions in GaMnAs are ferromagnetically coupled,[23–27] so the epilayer magnetization is sizable and the demagnetizing field effects can be important. Assuming standard ferromagnetic resonance (FMR) formulas, with crystalline anisotropy neglected:[39]

$$\omega_0 = \gamma(H_{90°} - 4\pi M), \quad \gamma = g\mu_B/\hbar, \quad (1)$$

$$\omega_0 = \gamma[H_{0°}(H_{0°} + 4\pi M)]^{1/2} \quad (2)$$

for $90°$ and $0°$ configurations, respectively one can estimate both the g factor and the average (local) magnetization M. In the case of $x = 0.005$ sample one gets $g = 2.020$ and $M(H = 3.3\text{kG}, T = 3.4\text{K}) = 0.64$ emu/cm^3. Magnetization of the magnetic epilayer measured using a SQUID magnetometer at the same temperature and magnetic filed (3.3 kG) is 1.8 emu/cm^3, which is about 3 times larger value than that estimated from EPR. We note here that the value of the measured magnetization (per unit volume) rely critically on the epilayer thickness. The difference between technological thickness we used to evaluate M and the real thickness may be the source of large uncertainty of the measured magnetization. Having in mind the simplicity of the model [Eqs. (1) and (2)], in particular neglected crystalline anisotropy, we consider both g factor and magnetization in reasonable agreement with expectations for A^- center. Additional argument for the above interpretation is temperature dependence of the EPR anisotropy, which decreases with increasing temperature [cf. Eqs. (1) and (2)]. For the sample with $x = 0.005$ the difference between resonance position at $0°$ and $90°$ configurations drops by a factor of 3 between 5 and 10 K and becomes unmeasurable above 20 K. This behavior is in agreement with magnetization temperature dependence, which decreases by a factor of 3 from 3 to 10 K and furthermore by a factor of 2 from 10 to 20 K. The similar temperature dependence was observed for the sample with $x = 0.008$.

The most important observation is that no A^0 was observed in any of the investigated epilayers (Fig. 2 and Table I). No lines around the field corresponding to $g = 2.7$ and $g = 5 - 6$ were visible. Certainly the demagnetizing field could shift the A^0 lines, but for low concentrations ($x < 0.01$) this shift would not exceed 100 G. Therefore the A^0 line should still occur around 2.4 kG, i.e. far away from 3.3 kG, where the A^- line is located. Since in bulk crystals we were able to observe A^0 center, the result for epilayers can be viewed as evidence that the A^0 centers are practically absent in the epilayers. The likely reason for such a situation is the high free hole concentration in the epilayers,[23–27] which screen the Coulomb potential of d^5 (A^-) center and reduce the hole binding energy. This way holes easily ionize and only A^- centers are left. This idea was already proposed in Refs. 29 and 22. Some other mechanisms preventing holes from being bind can also be imagined.

Finally we comment on $Ga_{1-x}Mn_xAs$ epilayers with higher Mn concentration ($x > 0.02$), basing on the preliminary data obtained so far.[43] Although the detailed discussion will be presented elsewhere, we only note here that in gen-
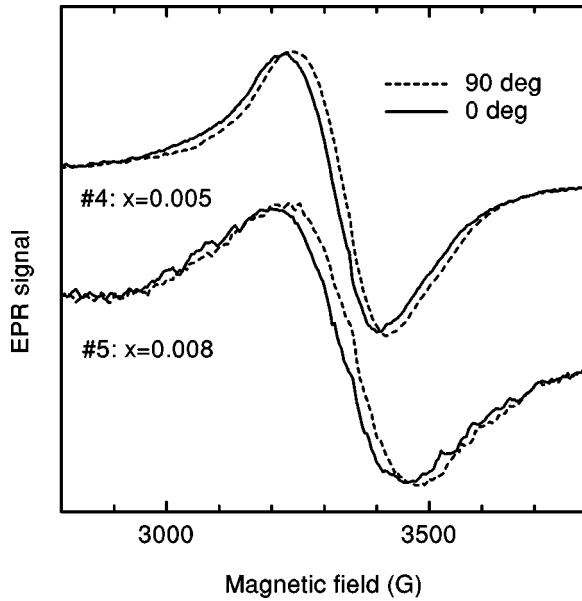
FIG. 3. The anisotropy of EPR spectra of Ga$_{0.995}$Mn$_{0.005}$As (No. 4) and Ga$_{0.992}$Mn$_{0.008}$As (No. 5). The observed difference for magnetic field parallel ($0°$) and perpendicular ($90°$) to the epilayer yields the following parameter values: No. 4 - $g=2.020$ and $M(H=3.3$ kG, $T=3.4$ K$)=0.64$ emu/cm^3, No. 5 - $g=2.018$ and $M(H=3.3$ kG, $T=6$ K$)=1.75$ emu/cm^3. The EPR markers were removed from the spectra for clarity.

eral the EPR spectra reveal multiline structures, which vary from sample to sample. Such situation may suggest different crystal phases, but also may point out the presence of impurities other than A^0 and A^-, which were generated during the growth process. Nevertheless it was not possible to as-

TABLE I. Studied Ga$_{1-x}$Mn$_x$As samples. The character of previously observed p-d exchange interaction (Refs. 29,35) is denoted in MCD column. The presence of the centers A^- and A^0 for a particular sample is marked in the last two columns.

Sample	x	MCD	A^-	A^0
No. 1 (bulk)	5×10^{-6}	AF	yes	no
No. 2 (bulk)	5×10^{-4}	F	yes	yes
No. 3 (epilayer)	0.002		yes	no
No. 4 (epilayer)	0.005	AF	yes	no
No. 5 (epilayer)	0.008		yes	no

sign any of the observed lines to the A^0 center. We note that if the argument of reduced binding hole energy of A^0 center is correct for small x, it should be even more relevant for the epilayers with higher x, since the hole concentration increases with x.[23–27] Therefore it is likely that A^0 centers are negligible in the epilayers studied so far. The dominant Mn center seems to be ionized acceptor A^-. This conclusion is decisive for interpretation of optical and magnetic properties of GaMnAs epilayers. First it supports hypothesis of antiferromagnetic p-d exchange for this material, as we discussed above. Second the absence (or negligible abundance) of A^0 centers makes double exchange d-d mechanism[36] ineffective. In view of that RKKY-type coupling between Mn ions[40,41] seems to be dominant mechanism triggering ferromagnetism of GaMnAs.

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