Antiferromagnetic p-d exchange in ferromagnetic $Ga_{1-x}Mn_xAs$ epilayers

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The s,p-d exchange interaction of p-type $Ga_{1-x}Mn_xAs$ ($x<0.05$) epilayers is investigated by means of magnetoabsorption. The observed ferromagnetic-type splitting of fundamental absorption edge is explained by antiferromagnetic p-d exchange interaction, taking into account the Moss-Burstein effect, resulting from high hole concentration. [S0163-1829(99)05020-1]

The class of semiconducting compounds based on classical semiconductors, for which a controlled fraction of nonmagnetic cations is substituted by magnetic ions [called diluted magnetic semiconductors (DMS)] has been intensively studied during the last two decades.[1] The reason for this interest was the fact that DMS bridge the physics of semiconductors and the physics of magnetics. One of the most attractive features of DMS is the strong interaction between delocalized s- and p-type band electrons and localized d-type electrons of magnetic ions (called s,p-d exchange interaction). In particular this interaction yields band splittings of the order of 100 meV, which corresponds to the effective g factor of few hundreds.[1] The interaction for the conduction band (s-d exchange) is driven by a direct, potential exchange and should be always ferromagnetic (FM),[2] which is indeed the case for all DMS examples known so far.[1,3] On the other hand, a valence band p-d exchange is dominated by a kinetic exchange mechanism and can be both ferromagnetic and antiferromagnetic (AFM), depending on exchange channels, i.e., available paths for virtual electron jumps between the valence band and d orbitals of t symmetry.[3,4] For II-VI DMS based on Mn, Fe, and Co only AFM channels are possible, since all t spin-up orbitals are occupied, so the valence-band electrons can only jump to spin-down t orbitals. The situation is different for the ions with less than half-filled d shell (Cr, V, Ti, and Sc), for which some t spin-up orbitals are empty, making FM-type electron jumps possible.[4] Experiments showed FM p-d exchange for all Cr-based II-VI DMS studied so far,[5] which means that FM exchange prevails over AFM in these materials.

During recent years much interest was focused on DMS based on III-V compounds (GaAs and InAs) (Refs. 6–10) due to their possible use in optoelectronic devices and integrated circuits. Moreover, $In_xMn_{1-x}As$ and $Ga_{1-x}Mn_xAs$ reveal ferromagnetic behavior,[6–10] not observed in bulk II-VI DMS.[11] This ferromagnetism results most probably from Ruderman-Kittel-Kasuya-Yosida (RKKY) type interaction, triggered by high hole concentration (up to 10^{20} cm^{-3}).[10] The s,p-d exchange interaction for III-V Mn-DMS may be more complicated than II-VI DMS due to the complex nature of Mn impurity in these systems. Generally speaking, there are three different types of Mn centers possible to be found in III-V compounds. The most natural is substitutional Mn^{3+} (d^4 configuration), which was found in GaP,[12] but was not observed for GaAs. The second type of centers is a neutral acceptor A^0 built of d^4 core, with tightly bound electrons and weakly bound holes $(d^4+e)+h$.[13] The d^4 core with tightly bound electrons (d^4+e) can be viewed as a d^5 configuration. The A^0 center was observed in electron paramagnetic resonance (EPR) experiments for bulk GaAs doped with Mn ($x<0.001$),[13,14] but is missing in more Mn concentrated epilayers ($x\geqslant 0.005$).[14] The possible reason for its absence is high hole concentration, which yields screening of the Coulomb potential of (d^4+e), so the bound hole ionizes easily. The third type of Mn center is ionized acceptor A^- (d^4+e), arising from ionization of A^0. A^- is considered to be equivalent to d^5 configuration (i.e., Mn^{2+}). It thus should show in EPR characteristic six-line structures, resulting from hyperfine interaction with Mn nucleus spin. This expectation was confirmed in experiments done for both bulk crystals[15] and epilayers.[16]

The A^0 and A^- centers may give rise to different s,p-d exchange. The s-d exchange arises from interaction between d electrons of Mn ion, and s electrons of Mn, contributing to the conduction-band wave function. This is a one-center potential exchange and should be FM, irrespective of the nature of the Mn center [similarly as was for II-VI DMS (Ref. 2)]. The value of this exchange, characterized by exchange integral $N_0\alpha$, is probably not very different from $+0.2$ eV, the typical value for II-VI DMS. For p-d exchange the situation is different. The A^- (as being Mn^{2+}-like) offers only AFM exchange paths. On the other hand, A^0 can provide both AFM and FM channels.[17] The ferromagnetic exchange occurs due to bound hole, which is spin polarized and provides an empty spin-up electron state for spin-up electrons jumping from the valence band.[19] Experimentally, s,p-d exchange was studied by means of interband magnetospectroscopy. For bulk GaAs:Mn crystals, the observed exciton splitting is compatible with FM p-d exchange,[19,18] i.e., σ^- transitions occur at lower energy than σ^+ ones [which is opposite to AFM-type splitting typical for Mn-based II-VI DMS, where $E(\sigma^-)>E(\sigma^+)$ (Ref. 20)]. This was viewed as showing the dominant role of FM channels provided by A^0

TABLE I. Parameters of the used $Ga_{1-x}Mn_xAs$ samples.

Sample	Mn concentration x	Hole concentration (cm^{-3})	T_c (K)	$N_0\alpha - N_0\beta$ (eV)
563	0.032	10^{19}–10^{20}	36 ± 2	-2.1 ± 0.1
401	0.042	10^{19}–10^{20}	28 ± 2	-1.7 ± 0.1

centers, over the AFM paths offered by both A^0 and A^-.[19] On the other hand, magnetocircular dichroism (MCD) reflectance experiments performed on $Ga_{1-x}Mn_xAs$ epilayers[21] and superlattices[9] suggested AFM-type splitting at both E_0 (Γ point of the Brillouin zone) and E_1 (Λ point of the Brillouin zone) critical points, i.e., the same situation as for $Cd_xMn_{1-x}Te$. This result was interpreted as typical for A^- centers, as discussed above. Since no A^0 centers are present in the epilayers, at least above $x\simeq0.005$, there is no FM path for the p-d exchange. We should note, however, that reliability of reflectance MCD data may be questioned, in particular at E_0 critical point, due to the problem with light multiscattering in the epilayers.[21]

The information about p-d exchange in $Ga_{1-x}Mn_xAs$ was also derived from other experiments. Transport measurements data interpreted in terms of critical scattering models yielded the absolute value of $N_0\beta=3.3$ eV.[10] Analysis of magnetic data (Curie critical temperature) allowed us to estimate the absolute value of $N_0\beta$ between 1.0–1.25 eV.[22] Recent core-level photoemission study of $Ga_{0.926}Mn_{0.074}As$ gave $N_0\beta=-1.2$ eV, if A^- configuration was assumed.[23] Unfortunately the latter experiment, although in principle sensitive to the sign of $N_0\beta$, could not discriminate between A^0 and A^- configurations, which precluded definite conclusions about the character of p-d exchange.

In view of the above facts we performed magnetotransmission experiments on $Ga_{1-x}Mn_xAs$ epilayers, in the range of fundamental absorption edge (around E_0). The epilayers for testing were grown at Tohoku University, by the molecular-beam epitaxy technique, described in detail elsewhere.[6–10] We used two epilayers (samples 563 and 401), with Mn concentration $x=0.032$ and 0.042, as resulting from x-ray-determined lattice constants (Table I). The 2-μm-thick epilayers were grown on (100) GaAs substrate, with 200-nm $Al_{0.9}Ga_{0.1}As$ buffer layers. Both were p-type, with low-temperature hole concentration between 10^{19}–10^{20} cm^{-3}. The precise determination of hole concentration was not possible because of the dominance of the anomalous Hall effect over the ordinary Hall effect that yields carrier concentration.[24] The epilayers revealed ferromagnetic order at low temperatures, critical temperature T_c being about 30–40 K (Table I). For transmission measurements the substrate was removed by etching, after the sample was glued to the glass plate.

Transmission was measured in the spectral range 1.4–2.0 eV, at temperature 2 K$<T<$60 K and magnetic field up to 5 T. Circularly polarized light was used. In order to double check the light polarity, $Ga_{1-x}Mn_xAs$ epilayers were measured simultaneously with $Cd_xMn_{1-x}Te$ thin samples, for which the sense of exciton splitting is well known. Typical absorption spectra are displayed in Fig. 1. No excitonic structure is visible in the available spectral range. Instead a broad edge is observed up to about 1.9 eV, above which transmission was too low to be reliable. Having in mind the broadness of the edge, the excitonic structure probably will not be observed even for thinner epilayers. Below about 1.5 eV, a rather weak structure is visible, which we ascribe to below-the-gap transitions. These transitions are irrelevant for the present discussion and will be discussed in detail elsewhere. Under external magnetic field, the edge splits for about 100 meV. Such strong edge splitting is characteristic for s,p-d exchange effects.[1,20] The most striking fact is that the σ^- edge is redshifted relatively σ^+ edge, i.e., in the opposite way than for $Cd_xMn_{1-x}Te$. The sense of the splitting is therefore the same as was for bulk GaAs:Mn,[19] i.e., it is of FM type. This result contradicts the reflectance MCD observation.[21,9]

Since in the energy range above 1.5 eV the absorption edge increases monotonously, it is likely that the above-the-band-gap transitions (in the sense of exciton energy) were not reached. Therefore, we were not able to determine the absolute value of σ^-,σ^+ energy gaps. Instead the band-gap splitting was evaluated as the relative edge shift (Fig. 1). We chose a possibly high absorption level for this evaluation to minimize the contribution of below-the-gap transitions. We note that choosing a different absorption level for our procedure, one obtains the values differing one from the other no more than 15% (which we thus assumed to be experimental uncertainty). The edge splitting evaluated this way is exemplified in Fig. 2 (as a function of magnetic field, at constant temperature) and Fig. 3 (as a function of temperature, at constant magnetic field). The splitting closely follows magnetization M of the epilayer, as measured using a superconducting quantum interference device (SQUID) magnetometer. Such behavior is a fingerprint of s,p-d induced band splittings, which typically are parametrized by the mean spin of magnetic ions $\langle S\rangle$.[1,25] A very fast saturation of the edge splitting with magnetic field (Fig. 2) reflects FM coupling between Mn ions. The increase of temperature suppresses

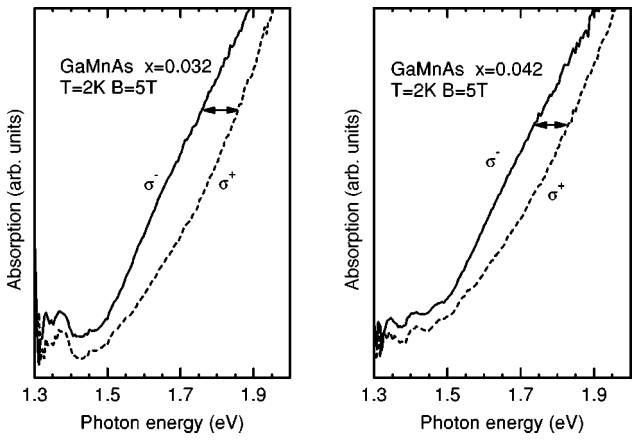

FIG. 1. Absorption edge of $Ga_{1-x}Mn_xAs$, $x=0.032$ (left plot) and 0.042 (right plot) at $T=2$ K and magnetic field $B=5$ T measured for σ^- and σ^+ polarized light. The double head arrow shows the splitting of the edge.

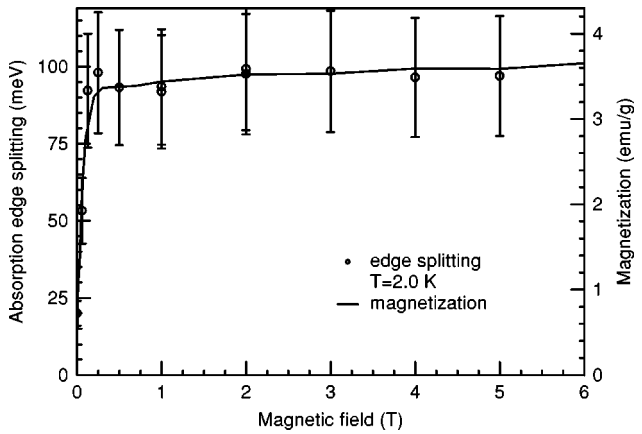

FIG. 2. Absorption edge splitting as a function of magnetic field at $T=2$ K of $Ga_{1-x}Mn_xAs$, $x=0.032$ (sample 563). The solid line shows magnetization of the same epilayer, corrected for diamagnetic contribution of the substrate.

magnetization and this way the band splitting is reduced (Fig. 3). In summary, the splitting is proportional to the magnetization (Fig. 4). Assuming the usual formula for the band splitting:[26] $\Delta E=(N_0\alpha-N_0\beta)x\langle S\rangle$, where $N_0\alpha$, $N_0\beta$ are s-d and p-d exchange constants, respectively, one gets the exchange parameters $N_0\alpha-N_0\beta=-2.1$ eV (sample 563) and -1.7 eV (sample 401). We used the relation $\langle S\rangle = -m_{\rm mol}/(g\mu_B x N_{\rm av})M$, where $m_{\rm mol}$ is molar mass, g is the electron g factor, μ_B is the Bohr magneton, and $N_{\rm av}$ is the Avogadro constant. A comment must be made about different values of the obtained parameters. First of all, we should note that the obtained values are very sensitive to the absolute value of magnetization, which scales with the epilayer thickness. It is probably reasonable to assume about 20% uncertainty of the latter, which yields a magnetization scaling factor between 0.8 and 1.2. This way uncertainty of the epilayer thickness could accommodate the difference in the exchange parameters. On the other hand, the difference in band splittings may be expected for the crystals with different hole concentration, as discussed below. We note that the obtained values are close to the result obtained for bulk

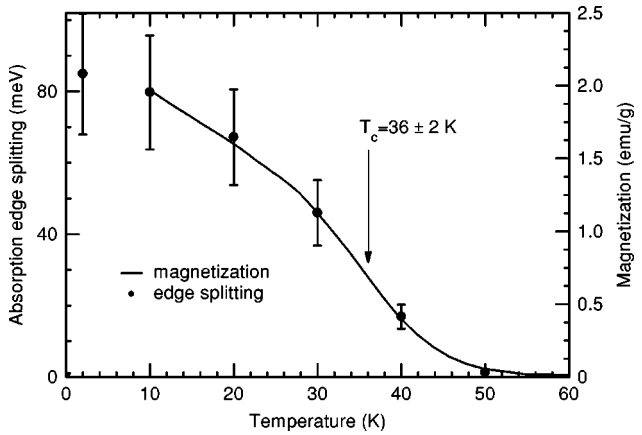

FIG. 3. Absorption edge splitting as a function of temperature at $B=0.02$ T of $Ga_{1-x}Mn_xAs$, $x=0.032$ (sample 563). The solid line shows magnetization of the same epilayer, measured at magnetic field $B=0.01$ T, corrected for diamagnetic contribution of the substrate. The arrow shows ferromagnetic transition temperature.

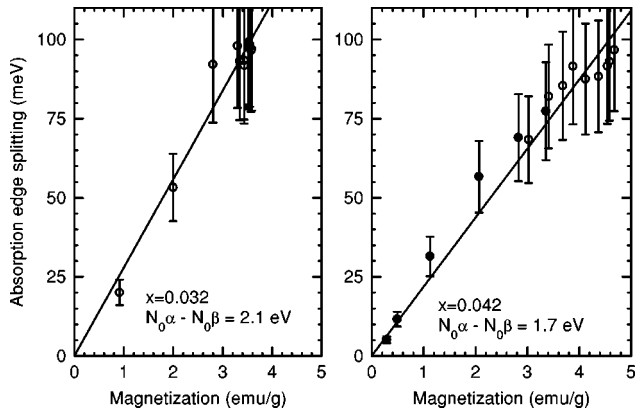

FIG. 4. Absorption edge splitting as a function of magnetization of $Ga_{1-x}Mn_xAs$, $x=0.032$ (left plot) and 0.042 (right plot). The straight lines correspond to $N_0\alpha-N_0\beta=-2.2$ eV and -1.7 eV, respectively. Open circles were obtained at $T=2$ K while solid circles at $T>5$ K.

GaAs:Mn crystals [$N_0\alpha-N_0\beta=-2.3$ eV (Ref. 19)]. However, in the point of view of a different exchange mechanism we describe below, the coincidence seems to be accidental.

The previous interpretation of the magneto-optic data assumed direct transitions in the center of the Brillouin zone (E_0 critical point). This is correct for bulk GaAs:Mn crystals, for which hole concentration is relatively low. However, for the epilayers with hole concentration ranging between 10^{18}–10^{20} cm^{-3}, the fact that the top of the valence band is empty (filled with holes) must be taken into account, since the Fermi energy E_F can be up to about 300 meV below the top of the valence band. Consequently, the Moss-Burstein shift of the absorption edge becomes sizable and is different for transitions originating from different valence subbands split by s,p-d exchange interaction (Fig. 5). It appears that in such case, for FM s-d exchange ($N_0\alpha>0$) and AFM p-d exchange ($N_0\beta<0$), σ^+ transitions occur at higher energy than σ^- ones (Fig. 5), i.e., the edge splitting is FM type. Had one assumed $N_0\beta>0$ (FM p-d exchange), the AFM-type

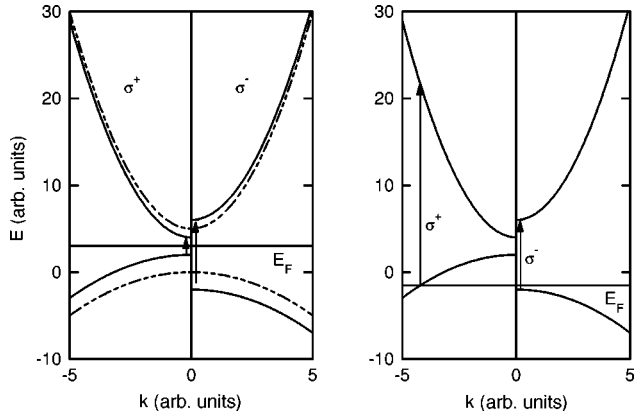

FIG. 5. The scheme of $Ga_{1-x}Mn_xAs$ band structure (only conduction and hh valence bands are shown) split by FM s-d exchange ($N_0\alpha>0$) and AFM p-d exchange ($N_0\beta<0$). The bands in the absence of exchange are denoted by dotted lines. Optical transitions for σ^+ and σ^- are shown in the case of low hole concentration (Fermi level in the gap, left plot) and for high hole concentration (Fermi level below top of the valence band, right plot).

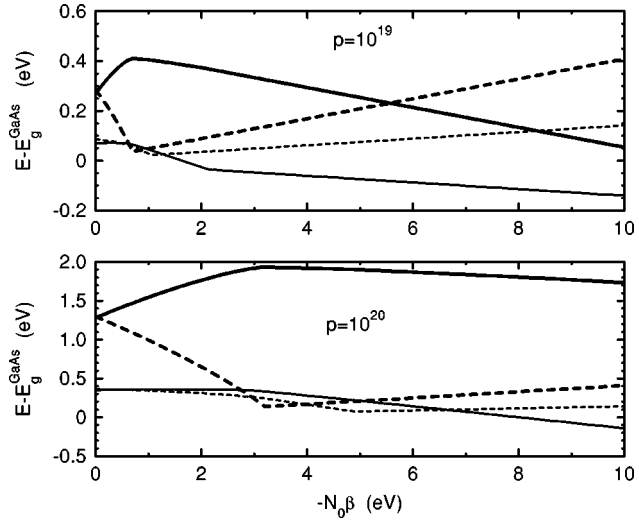

FIG. 6. The interband transition energies calculated for *p*-type $Ga_{1-x}Mn_xAs$ with hole concentration $p=10^{19}$ cm^{-3} (upper plot) and $p=10^{20}$ cm^{-3} (lower plot) as a function of *p-d* exchange integral. The thick lines denote transitions from the hh band, while the thin lines are from the lh band; σ^+ transitions are depicted by solid lines and σ^- by dashed ones. Energy is measured relatively to the band gap of pure GaAs. Parabolic bands have been assumed with $m_e=0.0665m_0$, $m_{hh}=0.47m_0$, and $m_{lh}=0.082m_0$ as well as saturated spin $\langle S\rangle=5/2$, $x=0.032$, and $N_0\alpha=+0.2$ eV. The nonzero splitting at $N_0\beta=0$ is the consequence of the constant, nonzero $N_0\alpha$ value.

splitting $[E(\sigma^-)>E(\sigma^+)]$ would be observed. In other words, due to the Moss-Burstein shift, the sense of the edge splitting is opposite to the sign of $N_0\beta$ (assuming typical values of $N_0\beta$ and $N_0\alpha$). We stress that the Moss-Burstein shift is the primary reason of this splitting inversion. The role of *p-d* interaction is rather to polarize the hole subbands, which differentiate the Moss-Burstein transition energies. Only if the valence-band exchange energy overcomes Fermi energy E_F, the regular (AFM for $N_0\beta<0$) splitting pattern is restored. The discussed model is presented in Fig. 6, where transition energies (measured relatively pure GaAs gap) are plotted for heavy (hh) and light (lh) holes versus $-N_0\beta$. Parabolic GaAs bands were assumed ($m_e=0.0665m_0$, $m_{hh}=0.47m_0$, and $m_{lh}=0.082m_0$), as well as saturated spin $\langle S\rangle=5/2$, $N_0\alpha=+0.2$ eV, and $x=0.032$. The hole concentrations 10^{19} and 10^{20} cm^{-3} were used. It is apparent that both hh and lh split in a FM way for AFM *p-d* exchange, as long as its magnitude is not too large. For very (unrealistically) large $N_0\beta$, AFM-type splitting is restored. We note that the band splitting (for saturated spin) depends on the hole concentration. This way the exchange parameter determined as the ratio of band splitting and saturated magnetization would be also hole concentration dependent.

The obtained result is in qualitative agreement with our experimental observation. Precise comparison and this determination of $N_0\beta$ can hardly be done due to rather large uncertainty of hole concentration of our epilayers. The model predicts sizable blueshift of the hh and lh energy gap, even in the absence of exchange interaction (i.e., for $B=0$). For $p=10^{20}$ cm^{-3}, hh transitions would be shifted beyond our actual spectral range, so in such case the observed absorption edges would be due to lh transitions. The calculated splitting would match the observed one if $N_0\beta=-2$ eV was assumed. On the other hand, for $p=10^{19}$ cm^{-3}, both hh and lh transitions would be in our spectral range. In this case we would most probably observe hh transitions, which are about three times more intense than lh ones. However, the resulting $N_0\beta=-0.2$ eV seems to be too small. Thus information about actual hole concentration is crucial for use and verification of the described model. We believe that in spite of its simplicity—i.e., neglect of the band tailing, highly possible in our heavily doped epilayers—the presented interpretation describes the essence of the actual situation for *p*-type $Ga_{1-x}Mn_xAs$, which is AFM *p-d* exchange interaction, resulting from A^- Mn centers.

We note that the transitions from the valence bands filled with electrons (like those in E_1 critical point) should reveal AFM-type splitting, since there is no Moss-Burstein effect for such bands. This seems to be supported by reflectance MCD data for E_1 transitions. The data at this critical point, highly above fundamental absorption edges, are free of epilayer multiscattering problems and this way are much more reliable than the data at E_0. The latter one, as we mentioned, should be considered with great care. This is also suggested by the very recent transmission MCD, which shows FM-type splitting at E_0 and confirms AFM-type splitting at E_1.[11]

Finally, we note that as a consequence of our model, semi-insulating $Ga_{1-x}Mn_xAs$ (with a valence band filled with electrons) should show AFM-type splitting of the fundamental absorption edge, directly reflecting AFM character of *p-d* exchange. The experimental data of such crystals are not available at the moment.

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