Electronic structure of Mn ions in (Ga,Mn)As diluted magnetic semiconductor

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The electronic structure of Mn in the diluted magnetic semiconductor (Ga,Mn)As was studied by means of electronic and spin-flip Raman scattering. The Mn ion was found to manifest itself in three different electronic configurations: (i) neutral Mn acceptor, i.e., Mn $3d^5$ inner-shell electrons with a weakly bound valence band hole, (ii) ionized Mn acceptor, i.e., $3d^5$ state, and (iii) neutral Mn in the $3d^4$ electronic configuration. The latter state undergoes a crystal-field splitting and a Jahn-Teller effect. The energy separation between the optical dipole active sublevels of the ${}^5T_2$ ground state is directly measured in the dynamic Jahn-Teller-effect regime. The Mn $3d^4$ state is assumed to play an important role for the ferromagnetism observed in diluted (Ga,Mn)As.

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I. INTRODUCTION

For many years, Mn-containing diluted magnetic semiconductors (DMS's) based on II-VI compounds have been the subject of intense fundamental studies because of the strong exchange interaction between the half filled $3d$ shell of the Mn^{2+} ions ($S_d=5/2$) and the charge carriers.[1] Recently, the interest for DMS's has been renewed because of their unique magnetic properties which make them interesting for semiconductor spin devices. This interest has stimulated the study of not only the traditional II-VI DMS's, but also of DMS's based on III-V compounds. The recent progress in growth techniques made cubic (Ga,Mn)As available, and the discovery ot its ferromagnetism made this material attractive for fundamental studies as well as for applications in devices based on spin-related phenomena.[2,3]

The origin of ferromagnetism in diluted (Ga,Mn)As is not yet well understood, as illustrated by the large number of recent publications devoted to theoretical investigations of this problem. The attempts to explain the ferromagnetic behavior in (Ga,Mn)As have used the following approaches: hole-mediated Ruderman-Kittel-Kasuya-Yoshida (RKKY) type interaction between local Mn moments,[2,4–6] Zener model,[6] virtual electron excitation from the magnetic impurity to the valence band,[7] Korringa-Kohn-Rostoker coherent-potential and local-density-approximation calculations,[4] as well as double-resonance mechanism, i.e., intra-atomic ferromagnetic exchange interaction between spins in resonant and localized states.[8] Most of these approaches are based on the assumption that, in the diluted regime, Mn enters GaAs in the same $3d^5+h$ or $3d^5$ electronic configuration as in the doping regime.[9–15] On the other hand, a ferromagnetic ion-ion ($3d^4$–$3d^5$) coupling has been predicted for mixed-valence DMS's.[16] A Müliken population analysis showed that the configuration of Mn in GaAs is compatible with either the $3d^5$ or the $3d^6$ configuration with noninteger occupation.[17] To fully understand the origin of ferromagnetism in (Ga,Mn)As it is necessary to clarify the electronic configuration in which Mn enters GaAs in the diluted regime.

In this paper, we study in detail the electronic and spin-flip Raman scattering (SFRS) of $Ga_{1-x}Mn_xAs$ with $x=0.006$–0.08. The transition from the doping to the diluted regime is found to be accompanied by dramatic changes in the Mn electronic structure. Our Raman-scattering investigations studies indicate that, in the diluted regime, Mn enters GaAs not only in the $3d^5+h$ and $3d^5$ configurations but also in the $3d^4$ state (i.e., a valence-band hole enters the d shell of the Mn ion). We assume that Mn ions in the $3d^4$ electronic configuration are relevant to the origin of ferromagnetism in diluted (Ga,Mn)As.

II. SAMPLES AND EXPERIMENTAL SETUP

The samples for the present study were grown by molecular-beam epitaxy on GaAs(001) substrates (semi-insulating, Si, or Zn doped). Prior to (Ga,Mn)As deposition, a GaAs buffer layer was grown at 600 °C. The substrate was then cooled to 250–300 °C for the growth of 500–1000 nm of (Ga,Mn)As. The growth rate was typically 4–10 nm/min and the As_4/Ga beam-equivalent-pressure (BEP) ratio was 25-50. Two groups of $Ga_{1-x}Mn_xAs$ samples have been studied, the Mn concentration being obtained from the lattice constant of the (Ga,Mn)As layer determined by high-resolution x-ray diffraction.[18] The samples of group A have a Mn content of $x\leqslant 0.012$. In the samples of group B the Mn content is in the range $0.02<x\leqslant 0.08$. Superconducting quantum interference device (SQUID) measurements were carried out in the temperature range 5–400 K to investigate the macroscopic magnetic properties of the samples and to confirm the absence of MnAs nanoclusters.

For excitation of spin-flip and electronic Raman scattering excitation we used the lines of Ar- and Kr-ion lasers, as well as a tunable Ti:saphier laser pumped by an Ar-ion laser. The laser power densities focused on the sample were in the range from 5 to 50 Wcm^{-2}. The Raman light was dispersed in a DILOR spectrograph and detected by a charge-coupled device (CCD) array. The experiments were carried out in the temperature range 4–200 K, in a continuous He-flow cryostat, and in magnetic fields up to 14 T, either in the backscattering Faraday or Voigt geometry. In Faraday geometry, the Raman spectra were recorded in $z(x,y)\bar{z}$ or $z(x,x)\bar{z}$ configuration, with $\bar{z}$ and z being perpendicular to the sample surface, and the linear polarization of the incident (x) and scattered (x or y) light parallel to the [001] or [011] crystal

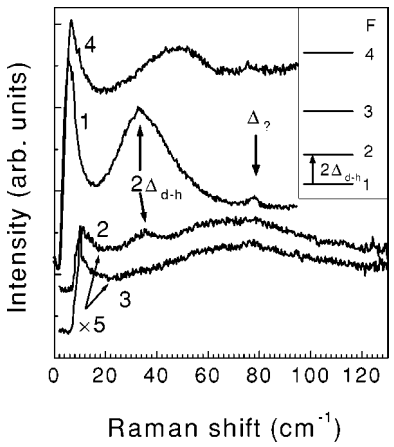

FIG. 1. Raman spectra of GaMnAs for samples of type A and B measured in resonance with the $E_0+\Delta_0$ gap. Raman spectra of the $2\Delta_{d\text{-}h}$ line for sample A1 taken at 4 K (spectrum 1) and 125 K (spectrum 4) together with the corresponding spectra for samples B1 (spectrum 2) and B2 (spectrum 3) taken at 4 K. The level diagram indicating $2\Delta_{d\text{-}h}$ transitions between the $F=1$ and $F=2$ acceptor states is shown in the inset.

axis. In Voigt geometry, we used the configuration $z(\sigma,\pi)\bar{z}$ or $z(\pi,\pi)\bar{z}$, with $\bar{z}$ and z perpendicular to the sample surface and to the magnetic field B, and σ or π denoting the linear polarizations of the incident (σ or π) and scattered (π) light with the electric-field vector of the light perpendicular (σ) or parallel (π) to B, which is parallel to the [001] or [011] crystal axis.

III. RESULTS AND DISCUSSION

The samples of group A, with low Mn content, show extremely weak near-band-gap photoluminescence (PL) due to the recombination of photoexcited free electrons with holes bound to neutral Mn acceptors ($e-A^0$); the PL band is centered at 1.411 eV.[19] In these samples, we did not detect any PL line related to the recombination of excitons bound to neutral Mn acceptors (A^0X).[13,15] In the samples of group B, with Mn content $0.02<x\leqslant 0.08$, we did not detect any near-band-gap PL.

A. Raman scattering involving complexes with Mn in $3d^5$ electronic configuration

The Raman spectra of the group-A samples show, under resonance excitation at the $E_0+\Delta_0$ gap,[20] a strongly polarized $2\Delta_{d\text{-}h}$ line, with a half width at half maximum (HWHM) of $\delta=24$ cm^{-1}, detected only in the $z(x,y)\bar{z}$ configuration. The $2\Delta_{d-h}$ line was also detected in Mn-doped GaAs samples with $N_{\mathrm{Mn}}\sim 0.7$–3.5×10^{18} cm^{-3}. Figure 1 shows Raman spectra of a diluted (Ga,Mn)As sample, recorded in $z(x,y)\bar{z}$ configuration, with $x\|[001]$, under zero magnetic field at two temperatures $T=4$ K and $T=125$ K (spectra 1 and 4, respectively). With increasing temperature, the broad asymmetric (long high-energy tail) $2\Delta_{d\text{-}h}$ line, centered at 35 cm^{-1} at $T=4$ K, shifts to higher energy. At $T=200$ K it is centered at 51 cm^{-1}. The intensity of the $2\Delta_{d\text{-}h}$ line decreases by approximately a factor of 5 with increasing temperature in the range 5–200 K (see solid circles in Fig. 3). A similar line, with a Raman shift of 34 cm^{-1} at $T=4$ K and HWHM of $\delta=15$ cm^{-1}, was also detected in a Mn-doped GaAs sample with $N_{\mathrm{Mn}}\sim 1.2\times 10^{18}$ cm^{-1}. However, its Raman shift was found to increase only up to 40 cm^{-1} in the same temperature range.

Like in Refs. 13 and 15, we associate the $2\Delta_{d\text{-}h}$ line detected in diluted (Ga,Mn)As to transitions within the A^0 (neutral Mn acceptor) complex from the $F=1$ to the $F=2$ state (see the inset in Fig. 1). As shown in Refs. 9–11 and 13–15, the $F=1$ ground state is obtained via antiferromagnetic exchange interaction of Mn $3d^5$ electrons ($S_d=5/2$) and valence-band holes ($J_h=3/2$). The energy of the $2\Delta_{d\text{-}h}$ line is directly related to the antiferromagnetic exchange constant. In Mn-doped GaAs, the acceptor ground state consists of Mn $3d^5$ electrons weakly bound to a valence-band hole, so that the valence-band hole does not enter the Mn $3d$ shell. We assume that the strong nonuniform asymmetric broadening of the $2\Delta_{d\text{-}h}$ line, observed in diluted (Ga, Mn)As, is correlated with an increased p-d exchange energy in the diluted regime. This assumption is supported by the temperature dependence of the $2\Delta_{d\text{-}h}$ line position. The energy of the $2\Delta_{d\text{-}h}$ line maximum increases linearly with temperature in the range 4–150 K (with a rate of 0.1 cm^{-1}/K) and the line becomes asymmetric on the low-energy side at high temperatures (see spectrum 2 in Fig. 1). Further temperature increase leads only to an intensity decrease of the $2\Delta_{d\text{-}h}$ line. The dependence of the $2\Delta_{d\text{-}h}$ line energy on temperature can be explained as follows. A temperature increase leads first to a depopulation of the $F=1$ ground state of the neutral Mn acceptors with the smallest exchange (i.e., binding) energy. The maximum position at higher temperatures is determined by complexes with larger binding energy. In (Ga,Mn)As compensated by deep donors, such as As antisites known to be present in low-temperature-grown GaAs,[23] these complexes can be a hole bound to two (or a few) neighboring Mn ions.

The intensity of the $2\Delta_{d\text{-}h}$ line was found to depend strongly on the Mn content. Figure 1 shows low-temperature Raman spectra of the $2\Delta_{d\text{-}h}$ line recorded from sample A2 (spectrum 1) and two different samples B1 (spectrum 2) and B2 (spectrum 3) of group B (see Table I). The intensity of the $2\Delta_{d\text{-}h}$ line was found to decrease with increasing Mn content, and to totally disappear in the sample with a Mn content of about 6%. We correlate the disappearance of the $2\Delta_{d\text{-}h}$ line with increasing Mn content with the formation of an impurity band. In uncompensated (Ga,Mn)As this occurs for $x\geqslant 0.015$, when the average distance between neighboring neutral Mn acceptors becomes comparable to their Bohr radius of 8–10 Å.

The line labeled $\Delta_?$ in Fig. 1 was detected for crossed linear polarizations only in samples with $x\leqslant 0.015$. The origin of this line is not yet clear. We believe that it might be related to an impurity-induced one-phonon scattering.

In a magnetic field, we observed the strongly polarized Δ_d line with a magnetic-field-dependent Raman shift which can be be represented as $\Delta_d=g_d\mu_B B$ with $g_d=2.02$. This line

TABLE I. Parameters of the $Mn_xGa_{1-x}As$ DMS samples used in this work: Exchange constants $\Delta_{d\text{-}h}$, energy separation Δ_2 between Γ_1 and Γ_5 states, and inner Mn shell electrons g factors g_d measured by SFRS as well as paramagnetic (PM) or ferromagnetic (FM) type of magnetism and Curie temperature T_C measured by SQUID.

Sample	Mn content x	Δd-h (meV)	Δ2 (meV)	g_d	T_C(K)
A1	0.006	-2.1 ± 0.1	2.85 ± 0.02	$+2.02\pm0.01$	PM
A2	0.01	-2.1 ± 0.1	2.85 ± 0.02	$+2.02\pm0.01$	PM
B1	0.039	-2.2 ± 0.1	2.85 ± 0.02	$+2.02\pm0.01$	PM
B2	0.063		2.85 ± 0.02	$+2.02\pm0.01$	30 FM

was detected only in Raman spectra measured in the $z(\sigma,\pi)\bar{z}$ Voigt configuration, as displayed in Fig. 2(a), and only at temperatures above 50 K (see solid squares in Fig. 3). The intensity of the Δ_d line increases gradually up to $T\sim150$ K and slowly drops above $T\sim170$ K. The Δ_d line was also detected in Mn-doped GaAs with $N_{\mathrm{Mn}}\sim0.7$–3.5×10^{18} cm^{-3}.

The Δ_d Raman line is related to spin-flip transitions within the Zeeman-split $3d^5$ multiplet of Mn^{2+} ions (ionized acceptor A^-), i.e., transitions with d-electron spin change $\Delta S_d=+1$ [see the inset in Fig. 2(a)]. Observation of the

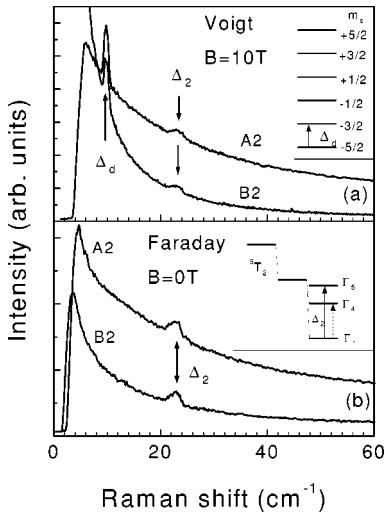

FIG. 2. Raman spectra of GaMnAs for samples of type A and B measured in resonance with E_0 gap. (a) Raman spectra of samples A2 and B2 for $B=10$ T measured at $T=140$ K in the $z(\sigma,\pi)\bar{z}$ Voigt configuration. The inset shows the energy levels of the Mn^{2+} ion in a magnetic field and indicates the origin of the Δ_d Raman line. (b) Raman spectra of samples A2 and B2 for $B=0$ T measured at $T=140$ K in the $z(x,y)\bar{z}$ Faraday configuration. The labels Δ_d and Δ_2 are explained in the text. The inset shows the energy levels of the Mn^{3+} ($3d^4$) crystal-field ground state ($^5T_2$) in T_d symmetry as well as its splitting by first- and second-order spin-orbit interaction. The origin of the Δ_2 Raman line is indicated. The solid arrow indicates the electric dipole allowed optical transition Δ_2, while the dashed arrow indicates a transition allowed in magnetic dipole approximation.

type-Δ_d line and its replicas (up to $n=5$) in Mn-doped GaAs has recently been reported;[13,15] the lines were correlated to spin-flip transitions within the d shell of $n\times$ Mn ions induced by photoexcited excitons in the A^0X complexes (n is the number of Mn ions in the exciton volume). In diluted (Ga,Mn)As, spin-flip transitions within the Mn d shell are induced by the electron or light-hole part of photoexcited e-h pairs. The difference between the doping and the diluted regime manifests itself in the selection rules. The SFRS process in Mn-doped GaAs is mediated by neutral Mn acceptors bound to excitons; therefore spin flip is observed either in Faraday or in Voigt geometry (for details, see Ref. 15). In diluted (Ga,Mn)As, like in bulk II-VI DMS's,[22] this process occurs only in Voigt geometry. Contrary to Mn-doped GaAs (and also contrary to II-VI DMS's), the SFRS process in diluted (Ga,Mn)As occurs only at temperatures $T\geqslant50$ K. At low temperatures most of the Mn ions are occupied by valence-band holes thus forming neutral Mn acceptors (A^0), where holes and $3d^5$ electrons couple antiferromagnetically forming a complex with a modified g factor.[9–15] The temperature increase leads to thermal activation of the holes from the bound to the excited state, presumably to the impurity band, and the ionized Mn acceptors (A^-) give rise to the SFRS process with transitions within the Mn d inner shell. We have estimated the activation energy of the holes to be $\varepsilon_0\sim4$ meV.

B. Raman scattering involving Mn in $3d^4$ electronic configuration

For resonance excitation at the E_0 gap,[20] in zero magnetic field and at temperatures $T\geqslant90$ K, we detected a crossed-polarized Δ_2 Raman line at 23 cm^{-1}. Corresponding Raman spectra are shown in Fig. 2(a) for the $z(\sigma,\pi)\bar{z}$ Voigt configuration and Fig. 2(b) for the $z(x,y)\bar{z}$ Faraday configuration. This line was found to be absent at low temperatures and to appear abruptly at $T\sim90$ K (see solid triangles in Fig. 3). The intensity of this line was found to increase with temperature up to $T\sim160$–180 K. A further increase of temperature leads to a slow decrease of its intensity. The line was found not to be sensitive to the magnetic field, i.e., no

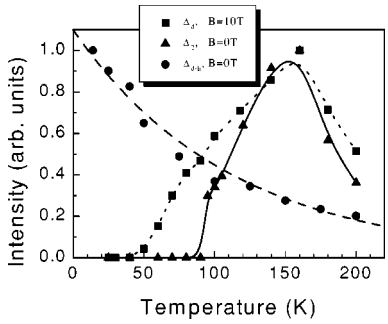

FIG. 3. Raman intensities as a function of temperature for sample A1. The temperature dependences for the $2\Delta_{d\text{-}h}$ (solid circles) and Δ_2 (solid triangles) lines are shown for $B=0$ T, while the dependence for the Δ_d (solid squares) line is displayed for $B=10$ T and Voigt geometry. The solid, dashed, and dotted lines are drawn to guide the eye.

shift or splitting of this line in a magnetic field was observed, neither in Faraday nor in Voigt geometry. In contrast to the Raman lines discussed above, the Δ_2 line was observed *only* in the diluted regime for all samples of groups A and B, but *not* in Mn-doped GaAs.

A similar line observed in II-VI DMS, (Ref. 21) with a magnetic-field-independent Raman shift, was correlated to transitions between the ground $|F=0,m_F=0\rangle$ and first-excited $|F=1,m_F=0\rangle$ states of antiferromagnetically coupled Mn ions. If the line $\Delta_2=23\ \mathrm{cm}^{-1}$, detected in diluted (Ga,Mn)As, were attributed to this transitions, then at high temperatures [in the case of diluted (Ga,Mn)As for $T \geqslant 90$ K] one would expect to find a Raman line corresponding to transitions between the next excited states, i.e., between $|F=1,m_F=0\rangle$ and $|F=2,m_F=0\rangle$, with energy separation 46 cm^{-1}. No line was observed at this energy in any of the diluted (Ga,Mn)As samples studied. The polarization properties of the Δ_2 line [observed in the $z(x,y)\bar{z}$ configuration] are also in contradiction with this model predicting an unpolarized character of the $|F=0,m_F=0\rangle$ to $|F=1,m_F=0\rangle$ transition. Hence we exclude this model for the explanation of the Δ_2 line.

The origin of the Δ_2 line can be explained by assuming that, in diluted (Ga,Mn)As, Mn reveals itself not only in the $3d^5$ but also in the $3d^4$ electronic configuration. In the latter state, a valence-band hole enters the Mn $3d^5$ core shell, resulting in the $3d^4$ configuration. The free-ion $3d^4$ ground state is ^5D similar to Cr in II-VI compounds or in GaAs as well as to Mn in GaP.[24–26] The crystal field of tetrahedral symmetry splits this state into a ^5E orbital doublet and a $^5T_2$ orbital triplet, the latter being the ground state. The first- and second-order spin-orbit coupling will further split the degeneracies of the spin orbitals. The corresponding energy-level scheme is depicted in the inset of Fig. 2(b). According to a calculation in Ref. 10, the Γ_4 and Γ_5 triplet states are estimated to lie 13 and 23 cm^{-1} above the Γ_1 singlet state. Transitions from the ground Γ_1 to the Γ_4 and Γ_5 states [arrows up in the inset of Fig. 2(b)] are allowed in the optic magnetic dipole and electric dipole approximations, respectively.[27] Furthermore, Raman transitions between Γ_1 and Γ_5 states are allowed by symmetry selection rules only for the $z(x,y)\bar{z}$ configuration.[28] Consequently, we attribute the Δ_2 Raman line detected at 23 cm^{-1} in crossed polarizations to transitions between the Γ_1 ground state and the Γ_5 excited state. The magnetic-field dependence of the Δ_2 line agrees with this assignment. In a magnetic field, we expect a splitting of this line into three components, due to Zeeman splitting of the Γ_5 state. However, only transitions between states with $\Delta m=0$ are allowed. This electronic configuration of the Mn ion is also valid if we take into account a dynamic Jahn-Teller effect, since such an effect quenches the first-order but not the second-order spin-orbit interaction.[29]

The static tetragonal $T\otimes\epsilon$ Jahn-Teller distortion reduces the symmetry to D_{2d}, and thus lifts the degeneracy of the $^5T_2$ ground state, leaving an orbital singlet $^5B_2$ lowest state with spin $S=2$. The first- and second-order spin-orbit coupling splits $^5B_2$ in three sublevels ($\hat{\Gamma}_1\hat{\Gamma}_2$, $\hat{\Gamma}_4$, and $\hat{\Gamma}_5$). Only the optic magnetic dipole transitions $\hat{\Gamma}_5\rightarrow\hat{\Gamma}_4$ and $\hat{\Gamma}_1\hat{\Gamma}_2\rightarrow\hat{\Gamma}_5$ are allowed which could explain the observed disappearance of the Δ_2 line at low temperature. The static Jahn-Teller effect manifests itself typically in anisotropic electronic paramagnetic resonances (EPR's) in the low-temperature range, $T\simeq 10-30$ K, both in Cr-doped GaAs and in II-VI compounds.[24,25] At slightly higher temperatures, the EPR spectrum exhibits isotropic behavior, due to the dynamic Jahn-Teller effect which averages the anisotropic low-temperature spectra.[29] As mentioned above, our assignment of the Δ_2 line would still be valid if we assume such a dynamic Jahn-Teller effect in diluted (Ga,Mn)As.[29] Thus the temperature behavior of the Δ_2 Raman line observed in diluted (Ga,Mn)As can be explained by a model assuming a transition from the static (low temperature) to the dynamic ($T\geqslant 90$ K) Jahn-Teller effect. In diluted (Ga,Mn)As, this transition is accompanied by changes of the selection rules, resulting in the activation of the Δ_2 Raman line. The disappearance of the Δ_2 Raman line at low temperatures can also be explained within this model. At low temperatures, the ground state of Mn ions in $3d^4$ configuration is modified by the exchange interaction with neighboring ions, either in $3d^4$ or $3d^5$ electronic state (see below).

The observation of the Δ_2 Raman line in (Ga,Mn)As DMS's indicates that, in the diluted regime, Mn enters GaAs in $3d^4$ electronic configuration. This finding can explain the origin of ferromagnetism in diluted (Ga,Mn)As. In view of this Mn-ion configuration, the ferromagnetism can occur either via the kinetic *p-d* exchange or the double-resonance mechanism. The former was proposed to explain the ferromagnetism in Cr-based II-VI DMS's.[30–32] Since Mn^{3+} ions (i.e., $3d^4$ electronic configuration) in Mn-based III-V DMS's are similar to Cr^{2+} ions in Cr-based II-VI DMS's (i.e., triplet ground state), the model of kinetic exchange interaction can be applied to our case. This model predicts a hybridization-induced valence-band hole/ion interaction via orbital coupling, in addition to the usual spin-spin coupling.[33] The former term makes the kinetic exchange interaction (for Mn^{3+} and Cr^{2+} ions) sensitive to the Jahn-Teller effect.

The double-resonance mechanism, proposed to explain the ferromagnetism in mixed-valence manganites of perovskite structure,[34,35] assumes exchange interaction between pairs of Mn ions in different electronic configurations (e.g., $3d^5$-$3d^4$ pairs). According to this model, one extra *d* electron jumps virtually from one ion to the other via the *p* orbital of neighboring anions. A similar model has recently been developed to explain the magnetic properties of mixed Mn^{2+}-Mn^{3+} III-V DMS's.[16] This model can thus also be applied to our case because of the coexistence of Mn ions in both electronic configurations.

Our Raman scattering study shows that in diluted (Ga,Mn)As, Mn enters GaAs in three different electronic configurations. First, there are neutral Mn acceptors, with strong *antiferromagnetic* interaction between the Mn $3d^5$ inner-shell electrons and weakly bound valence-band holes.[9–15] The number of isolated neutral Mn acceptors decreases with increasing Mn content, due to the formation of an impurity band. Second, there are ionized Mn acceptors in the $3d^5$ electronic state. With increasing number of ionized

Mn acceptors, the importance of the ion-ion ($3d^5$-$3d^5$) exchange interaction—which is *antiferromagnetic* in nature in all known II-VI DMS's (Ref. 36)—is enhanced. Third, there are Mn ions in the $3d^4$ configuration, which can give rise to *ferromagnetism* via kinetic or double-resonance exchange interaction, as discussed above.

Competition between the *ferromagnetic* and *antiferromagnetic* exchange interactions determines the magnetic properties of diluted (Ga,Mn)As. The data summarized in Table I illustrate such competition. The paramagnetic A1 and A2 samples, with low Mn content, show coexisting intense $\Delta_{d\text{-}h}$, Δ_2, and Δ_d Raman lines [see Figs. 1 and 2(a) and 2(b)]. Sample B1, which according to its Mn content could be ferromagnetic,[37] exhibits in fact paramagnetic behavior.[38] The Raman spectrum of this sample (see spectrum 2 in Fig. 1) shows the presence of the $2\Delta_{d\text{-}h}$ line, which is typical for Mn-doped GaAs and diluted (Ga,Mn)As with $x \sim 0.01$. We believe that the paramagnetic behavior of sample B1 is due to dominant neutral Mn acceptors, or complexes in which a hole is bound to two neighboring Mn ions. Formation of this latter complex is more probable in samples with high Mn content and strong compensation by deep donors, such as As_{Ga} antisites. In sample B2, which shows ferromagnetic behavior ($T_C \sim 30$ K), neutral Mn acceptors or complexes where a hole is bound to two Mn ions were not detected (see spectrum 3 in Fig. 1).

We believe that Mn ions in $3d^4$ electronic configuration are relevant to the origin of ferromagnetism in diluted (Ga,Mn)As. In contrast, neutral Mn acceptors (or complexes in which a hole is bound to a few Mn ions) as well as pairs of Mn ions contribute to produce a paramagnetic behavior. Evidence for the type of ferromagnetic exchange interaction (either kinetic or double-resonance exchange interaction) related to the Mn $3d^4$ state could be gained from infrared spectroscopy and EPR analysis.

IV. CONCLUSIONS

We have studied the electronic structure of Mn ions in diluted $Ga_{1-x}Mn_xAs$ by electronic and spin-flip Raman scattering. Depending on temperature and Mn content x, three different electronic configurations have been identified.

Mn $3d^5$ ions with a weakly bound valence-band hole (A^0 complex) and ionized Mn acceptors in $3d^5$ configuration were observed for Mn contents of $x \leqslant 0.04$ and $0.006 \leqslant x \leqslant 0.08$, respectively. Specifically for diluted material, Mn in the $3d^4$ configuration has been identified at temperatures $T \geqslant 90$ K and for Mn contents $0.006 \leqslant x \leqslant 0.08$. The $3d^4$ state undergoes a static (low-temperature) or dynamic ($T \geqslant 90$ K) Jahn-Teller effect. The energy separation between the lowest singlet and triplet sublevels of the $^5T_2$ ground state has been measured to be $\Delta_2 = 23$ cm^{-1}. We believe that Mn ions in the $3d^4$ electronic configuration are relevant for the origin of ferromagnetism in diluted (Ga,Mn)As semiconductors.

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[1] J.K. Furdyana, J. Appl. Phys. **64**, R29 (1988).

[2] H. Ohno, H. Munekata, T. Penney, S. von Molnár, and L.L. Chang, Phys. Rev. Lett. **68**, 2664 (1992).

[3] H. Ohno, A. Shen, F. Matsukura, A. Oiwa, A. Endo, S. Katsumoto, and Y. Iey, Appl. Phys. Lett. **69**, 363 (1996).

[4] H. Akai, Phys. Rev. Lett. **81**, 3002 (1998).

[5] J. König, H.-H. Lin, and A.H. MacDonald, Phys. Rev. Lett. **84**, 5628 (2000).

[6] T. Dietl, H. Ohno, and F. Matsukura, Phys. Rev. B **63**, 195205 (2001).

[7] V.I. Litvinov and V.K. Dugaev, Phys. Rev. Lett. **86**, 5593 (2001).

[8] J. Inoue, S. Nonoyama, and H. Itoh, Phys. Rev. Lett. **85**, 4610 (2000).

[9] I.Ya. Karlik, I.A. Merkulov, D.N. Mirlin, L.P. Nikitin, V.I. Perel', and V.F. Sapega, Fiz. Tverd. Tela **24**, 3550 (1982) [Sov. Phys. Solid State **24**, 2022 (1982)].

[10] J. Schneider, U. Kaufmann, W. Wilkening, M. Baeumler, and F. Köhl, Phys. Rev. Lett. **59**, 240 (1987).

[11] N.S. Averkiev, A.A. Gutkin, E.B. Osipov, and M.A. Reshchikov, Fiz. Tverd. Tela **30**, 765 (1988) [Sov. Phys. Solid State **30**, 438 (1988)].

[12] M. Linnarsson, E. Janzén, B. Monemar, M. Klevermann, and A. Thilderkvist, Phys. Rev. B **55**, 6938 (1997).

[13] V.F. Sapega, T. Ruf, and M. Cardona, Solid State Commun. **114**, 573 (2000).

[14] A.K. Bhattacharjee and C. Benoitá la Guillaume, Solid State Commun. **113**, 17 (2000).

[15] V.F. Sapega, T. Ruf, and M. Cardona, Phys. Status Solidi B **226**, 339 (2001).

[16] J. Blinowski, P. Kacman, and J. A. Majewski, in *Proceedings of the 12th International Conference on High Magnetic Fields in the Physics of Semiconductors II* Würzburg, Germany, Edited by G. Landwehr and W. Ossau (World Scientific, Singapore, 1996), p. 861.

[17] S. Sanvito, P. Ordejón, and N.A. Hill, Phys. Rev. B **63**, 165206 (2001).

[18] The relaxed lattice constant of the (Ga,Mn) As layer was first calculated assuming that the (Ga,Mn) As layer is fully strained on the GaAs(001) substrate and that (Ga,Mn) As has the same elastic constant as GaAs. To derive the Mn concentration, Vegard's law was applied, assuming the value of 0.598 nm for the lattice constant of ''zinc-blende-like'' MnAs, and neglecting the lattice-constant change due to the possible presence of As_{Ga} point defects.

[19] W. Schairer and M. Schmidt, Phys. Rev. B **10**, 2501 (1974).

[20] R. Trommer and M. Cardona, Phys. Rev. B **17**, 1865 (1978).

[21] D.U. Bartholomew, E.-K. Suh, S. Rodriguez, A.K. Ramdas, and R.L. Aggarwal, Solid State Commun. **62**, 235 (1987).

[22] A. Petrou, D.L. Peterson, S. Venugopalan, R.R. Galazka, A.K.

Ramdas, and S. Rodriguez, Phys. Rev. B **27**, 3471 (1983).
[23] D.C. Look, J. Appl. Phys. **70**, 3148 (1991).
[24] J.T. Vallin and G.D. Watkins, Phys. Rev. B **9**, 2051 (1974).
[25] J.J. Krebs and G.H. Stauss, Phys. Rev. B **16**, 971 (1977).
[26] J. Kreissl, W. Ulrici, M. El-Metoui, A.-M. Vasson, A. Vasson, and A. Gavaix, Phys. Rev. B **54**, 10508 (1996).
[27] J.T. Vallin, G.A. Slack, S. Roberts, and A.E. Hughes, Phys. Rev. B **2**, 4313 (1970).
[28] J. Wagner and M. Ramsteiner, Phys. Rev. B **36**, 6688 (1987).
[29] F.S. Ham, Phys. Rev. **138**, A1727 (1965).
[30] A.K. Bhattacharjee, Phys. Rev. B **46**, 5266 (1992).
[31] J. Blinowski and P. Kacman, Phys. Rev. B **46**, 12298 (1992).
[32] A.K. Bhattacharjee, Phys. Rev. B **49**, 13987 (1994).
[33] W. Mac, N. T Khoi, A. Twardowski, J.A. Gaj, and M. Demianiuk, Phys. Rev. Lett. **71**, 2327 (1993).
[34] C. Zenner, Phys. Rev. **82**, 403 (1951).
[35] P.W. Anderson and H. Hasegava, Phys. Rev. **100**, 675 (1955).
[36] B.E. Larson, K.C. Hass, H. Ehrenreich, and A.E. Carlsson, Phys. Rev. B **37**, 4137 (1988).
[37] F. Matsukura, H. Ohno, A. Shen, and Y. Sugawara, Phys. Rev. B **57**, 2037 (1998).
[38] According to SQUID measurements most of our samples with 3–7% Mn content reveal ferromagnetism with different T_C. Sample B1 with 3.9% paramagnetic was selected intentionally to demonstrate the competition between three Mn states in the DMS regime.