Electronic Structure of the Neutral Manganese Acceptor in Gallium Arsenide

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A new manganese-related isotropic electron-spin-resonance signal at $g=2.77$ has been observed in GaAs. It is shown to arise from the neutral Mn acceptor, Mn^0. The analysis gives an answer to the longstanding question of whether the structure of Mn^0 corresponds to $3d^4$ or to $3d^5$+hole. The data clearly favor the latter case, thus revealing that Mn is an exception within the $3d$ acceptor family in GaAs.

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Within the family of $3d$ transition-metal acceptors in gallium arsenide (GaAs), the manganese acceptor behaves unusually. This was evidenced already by the early observation that in its infrared absorption spectrum, just shortly before the onset of photoionization into the valence band, sharp spectral lines appear.[1] These result from optical transitions into shallow bound excited states, as $2P_{5/2}(\Gamma_8)$ and $2P_{5/2}(\Gamma_7)$, which are well accounted for by effective-mass theory.[2] From these data, the ionization energy of the neutral manganese acceptor can be determined with spectroscopic precision, at $E_v+113.0$ meV.[3] This value is the smallest one observed among $3d$ acceptors in GaAs; on the other hand, this value greatly exceeds the one predicted by effective-mass theory, E_v+26 meV.[2] The above-mentioned absorption spectrum,[1] as well as the donor-acceptor–type luminescence spectrum,[4] suggests that Mn behaves as a conventional acceptor in GaAs. On the other hand, magnetic susceptibility[5,6] and Faraday-rotation measurements[7] were interpreted as evidence that Mn is a typical $3d$ acceptor with the hole bound in the $3d$ shell. Thus the situation is controversial and the question arises how the electronic ground state of the neutral manganese acceptor in GaAs is properly described. According to the above mentioned results, the following two possibilities exist[8,9]:

(1) In a tight-binding case, the acceptor hole enters the $3d^5$ shell of the A^- core, resulting in a $3d^4$ configuration, then possibly undergoing a (static) Jahn-Teller distortion as observed for $Cr(3d^4)$ in GaAs[10] and other tetrahedrally coordinated semiconductors.

(2) Alternatively, the hole may be energetically favored by staying in a delocalized $^4S_{3/2}$ orbit around the $A^-(3d^5)$ acceptor core. In this case the manganese acceptor ground state will be drastically modified, by coupling between the spin of the delocalized hole, $j=\frac{3}{2}$, and that of the $A^-(3d^5)$ core, $S=\frac{5}{2}$.

In this Letter we present a new electron-spin resonance (ESR) signal in GaAs:Mn which is shown to arise from a cubic Mn-related spin-1 center. The ground-state g factors of the cubic $Mn^{3+}(3d^4)$ ion in tetrahedral symmetry are analyzed and are found to be incompatible with the experimental value of the new Mn signal. The g factor of a loosely bound hole, exchange coupled to the $A^-(3d^5)$ acceptor core, is calculated and is found to be in line with experiment. This analysis strongly supports model (2) and shows that Mn is an exception within the $3d$ acceptor family in GaAs.

Most samples used in this study were cut from a GaAs:Mn ingot doped in the melt. It was pulled from a pyrolytic BN crucible by the liquid-encapsulation Czochralski technique. Secondary-ion mass spectroscopy gave a total Mn concentration of 1.1×10^{17} cm^{-3}. Hall measurements showed that the material is p type with a room-temperature hole concentration of 4.5×10^{16} cm^{-3}. The ESR spectra were recorded at 9.4 GHz and at 35 GHz.

Figure 1 shows the 4.2-K ESR spectrum of GaAs:Mn. Three groups of lines centered around $g=2.00$, $g=2.77$, and $g=5.72$ are evident. The set of lines at $g=2.00$ is identified as the well-known[11,12] $\Delta M=1$ transition of the ionized Mn acceptor A^-, $Mn(3d^5)$. It is well visible also at temperatures above 20 K. In contrast, the lines near $g=5.72$ and $g=2.77$ disappear between 10 and 11 K. Note that the former line lies close to the half-field position of the latter one, thus suggesting that they correspond to $\Delta M=2$ and $\Delta M=1$ transitions of a spin-1 state, respectively. The two lines are isotropic in position indicative of a center with cubic symmetry and excluding a possible static Jahn-Teller distortion.

The partially resolved ^{55}Mn $(I=\frac{5}{2})$ hyperfine structure confirms that the center is due to manganese. For reasons to be discussed below it is assigned to the isolated, neutral Mn acceptor A^0. Although the position of the $g=2.77$ line is isotropic at 9.4 and 35 GHz, its peak-to-peak width ΔH changes significantly with magnetic field orientation. For $H\|\langle100\rangle$ the width has a minimum, $\Delta H\approx440$ G, while for $H\|\langle111\rangle$ it has a max-

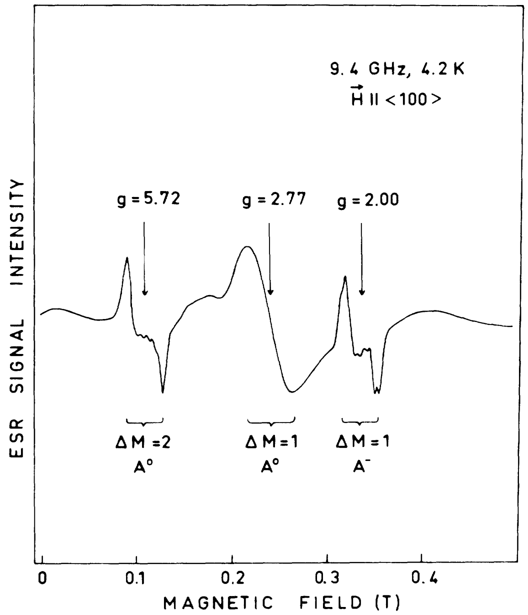

FIG. 1. ESR spectrum of *p*-type GaAs:Mn showing signals due to the neutral (A^0) and ionized (A^-) manganese acceptor.

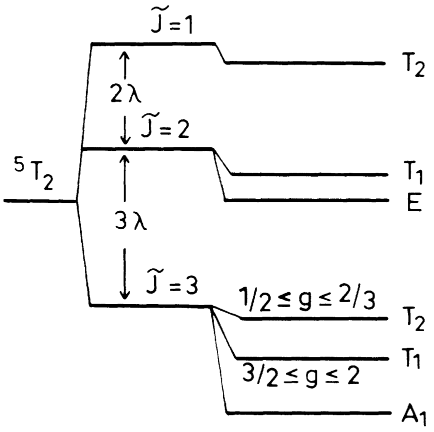

FIG. 2. Crystal-field ground state of Mn($3d^4$) in T_d symmetry and its splitting by first- and second-order spin-orbit interaction. Note that the model does not account for the Mn^0 ESR.

imum, $\Delta H \approx 670$ G. Such an orientation dependence of the linewidth has also been observed for the shallow boron acceptor in Si.[13]

Preliminary ESR measurements under externally applied uniaxial stress reveal that the A^0, $\Delta M=1$ line broadens rapidly under external stress in contrast to the other lines in Fig. 1. A clear-cut splitting has not yet been resolved, possibly because of stress inhomogeneities. The stress response of the A^0, $\Delta M=1$ line and the temperature dependence of its intensity, as well as its large g-shift, $\Delta g = g-2 = 0.77$, strongly indicate that a state with nonzero orbital angular momentum is involved.

We have already noted that the $g=5.72$ and $g=2.77$ signals in Fig. 1 result from $\Delta M=2$ and $\Delta M=1$ transitions of an effective $J=1$ state belonging to a cubic Mn center with orbital angular momentum in its ground state. Since the ESR of Mn($3d^5$) is well known,[11,12] it is natural to assign the new signals in *p*-GaAs:Mn to the neutral Mn acceptor state $\mathrm{Mn}^0_{\mathrm{Ga}}$. It is now shown that these signals cannot be understood within model (1) but can be accounted for within model (2).

For model (1), i.e., Mn($3d^4$), the splitting of the $^5T_2$ (D) crystal-field ground state by first- and second-order spin-orbit interaction is shown in Fig. 2.[14] It is seen that a T_1 and a T_2 triplet lie above the singlet A_1 ground state. *A priori* it cannot be excluded that the Mn^0 resonances result from one of these triplet states. The energetic positions of T_1 and T_2 above A_1 have been calculated following the procedure exemplified for Cr($3d^4$) in II_B-VI compounds.[14,15] With use of reasonable estimates for the crystal-field parameter the spin-orbit and spin-spin coupling constants of Mn($3d^4$) in GaAs, we find that T_1 and T_2 lie 13 and 23 cm^{-1} above A_1, respectively. This result remains unaffected if a dynamic Jahn-Teller effect were operative since such an effect would quench the first-order but not the second-order spin-orbit interaction.[16] Thus T_1 and T_2 are depopulated at 4.2 K and ESR due to these states should not occur. In addition the g factors of T_1 and T_2 are incompatible with the measured g value of 2.77. They are given by $|g(T_1)| = \frac{2}{3} g_{\tilde{J}=3}$ and $g(T_2) = \frac{1}{2} g_{\tilde{J}=3}$, where $g_{\tilde{J}=3} = \frac{1}{3}(4-k)$ is the Landé g factor of the $\tilde{J}=3$ spin-orbit level[17] in Fig. 2. The orbital reduction factor k could contain contributions from covalency effects and from a possible dynamic Jahn-Teller effect. It could therefore range between ≈ 1 and ≈ 0. Correspondingly, $\frac{3}{2} \le g(T_1) \le 2$ and $\frac{1}{2} \le g(T_2) \le \frac{2}{3}$, and this is seen to be incompatible with the experimental g value.

On the other hand, for model (2) exchange coupling, $\epsilon \mathbf{S}\cdot\mathbf{j}$, of the delocalized hole, $j=\frac{3}{2}$, with the ionized acceptor core, $S=\frac{5}{2}$, results in the sublevels $J=S+j=1$, 2, 3, 4, being energetically located at 0, 2ϵ, 5ϵ, and 9ϵ, respectively. Thus a $J=1$ ground state is obtained if *antiferromagnetic* coupling ($\epsilon>0$) of the hole with the $3d^5$ acceptor core is assumed. Corresponding eigenvectors of the $J=1$ state spanned in a $|m_S,m_j\rangle$ basis, are calculated[18] as

$$\begin{aligned}
|1,+1\rangle &= \tfrac{1}{2}\sqrt{2}\,|\tfrac{5}{2},-\tfrac{3}{2}\rangle - \tfrac{1}{10}\sqrt{30}\,|\tfrac{3}{2},-\tfrac{1}{2}\rangle + \tfrac{1}{10}\sqrt{15}\,|\tfrac{1}{2},\tfrac{1}{2}\rangle - \tfrac{1}{10}\sqrt{5}\,|-\tfrac{1}{2},\tfrac{3}{2}\rangle,\\
|1,0\rangle &= \tfrac{1}{5}\sqrt{5}\,|\tfrac{3}{2},-\tfrac{3}{2}\rangle - \tfrac{1}{10}\sqrt{30}\,|\tfrac{1}{2},-\tfrac{1}{2}\rangle + \tfrac{1}{10}\sqrt{30}\,|-\tfrac{1}{2},\tfrac{1}{2}\rangle - \tfrac{1}{5}\sqrt{5}\,|-\tfrac{3}{2},\tfrac{3}{2}\rangle, \qquad (1)\\
|1,-1\rangle &= -\tfrac{1}{2}\sqrt{2}\,|-\tfrac{5}{2},\tfrac{3}{2}\rangle + \tfrac{1}{10}\sqrt{30}\,|-\tfrac{3}{2},\tfrac{1}{2}\rangle - \tfrac{1}{10}\sqrt{15}\,|-\tfrac{1}{2},-\tfrac{1}{2}\rangle + \tfrac{1}{10}\sqrt{5}\,|\tfrac{1}{2},-\tfrac{3}{2}\rangle.
\end{aligned}$$

From these wave functions eigenvalues of the Zeeman operator appropriate,

$$\mathcal{H} = g_S \mu_{\mathrm{B}} \mathbf{H} \cdot \mathbf{S} + g_1' \mu_{\mathrm{B}} \mathbf{H} \cdot \mathbf{j} + g_2' \mu_{\mathrm{B}} (H_x j_x^3 + H_y j_y^3 + H_z j_z^3), \tag{2}$$

are obtained, the isotropic g factor being

$$g_{J=1} = \tfrac{7}{4} g_S - \tfrac{3}{4} g_1' + \tfrac{41}{20} g_2'. \tag{3}$$

The g factor of the $3d^5$ manganese acceptor core is known from electron-spin resonance: $g_S = 2.003$.[11,12] Representative values for g_1' and g_2' of holes bound at acceptors, as carbon and tin, have been inferred from Zeeman studies of acceptor-bound excitons.[19] For the deep acceptor tin in GaAs, $E_A = E_v + 167$ meV, bound-hole g' values of $g_1' = +0.78$ and $g_2' = -0.07$ have been quoted.[19] If we adopt these values for GaAs:Mn a g factor of $g_{J=1} = 3.0$ is then predicted from Eq. (3) for the neutral manganese acceptor in GaAs. This value is not too far from the one determined by ESR, $g = 2.77$, thus clearly favoring model (2).

It is interesting to note that in a magnetic field the hole spin $\mathbf{j}$ orients *opposite* to that of the ionized-acceptor core, $\mathbf{S}$, since, e.g., $\langle +1 | S_z | +1 \rangle = +\frac{7}{4}$ and $\langle +1 | j_z | +1 \rangle = -\frac{3}{4}$. This fact apparently accounts for the sign reversal of circular polarization of luminescent donor-acceptor recombination in GaAs:Mn, as compared to GaAs:Zn, which was observed by Karlik *et al.*[20]

In the ESR spectra ^{55}Mn nuclear $(I = \frac{5}{2})$ hyperfine sextet splittings are apparent; see Fig. 1. That of the A^- state, 52×10^{-4} cm^{-1}, agrees with the value reported previously.[11,12] ^{55}Mn hyperfine splitting, 84×10^{-4} cm^{-1}, of the A^0 state is only resolved for the $\Delta M = 2$ transition (see Fig. 1) which is less broadened by random crystalline strains than the $\Delta M = 1$ transitions. This value is close to the ^{55}Mn hyperfine splitting expected from Eqs. (1) for the contribution of the $3d^5$ core: $\frac{7}{4} \times 52 \times 10^{-4}\ \mathrm{cm}^{-1} = 91 \times 10^{-4}\ \mathrm{cm}^{-1}$.

The fact that ESR of a neutral acceptor is observed *without* application of external uniaxial stress is remarkable in itself. However, for GaAs:Mn the acceptor's ground-state wave functions, Eqs. (1), are a mixture of stress-insensitive spin-only m_S states and highly stress-sensitive orbital m_j states. The contribution of the latter to the ESR linewidth is strongly reduced for GaAs:Mn: For instance, for stress along the z axis, the splitting of the $J = 1$ state is proportional to $\langle \pm 1 | j_z^2 | \pm 1 \rangle - \langle 0 | j_z^2 | 0 \rangle = \frac{3}{10}$, being only 15% that of a pure m_j state, $\langle \pm \frac{3}{2} | j_z^2 | \pm \frac{3}{2} \rangle - \langle \pm \frac{1}{2} | j_z^2 | \pm \frac{1}{2} \rangle = 2$.

An important question which remains to be answered concerns the magnitude of the exchange coupling $\epsilon \mathbf{S} \cdot \mathbf{j}$. An estimate can be inferred from a pronounced inelastic phonon scattering observed in p-GaAs:Mn at low temperatures, by thermal conductivity[21,22] and ultrasonic absorption[23] measurements. The data reveal existence of an excited level, at 2–3 meV, which may well be identified with the first excited state, at $W_{J=2} = 2\epsilon$, of the neutral manganese acceptor. Although rather small, these energies, 2–3 meV, corresponding to 480–720 GHz, still greatly exceed those of the microwave quanta in our ESR experiments. This accounts for practically identical g factors observed at 9 and 35 GHz. The excited level may also cause an Orbach-type relaxation which could explain the disappearance of the A^0 ESR lines above 11 K.

Attention should also be drawn to measurements of the static paramagnetic susceptibility as reported by Andrianov and co-workers[5,6] for p-GaAs:Mn. From their data we obtain for the effective number of Bohr magnetons $p_{\mathrm{eff}} = 3.9 \pm 0.1$ for the neutral manganese acceptor. This value is in good agreement with the one predicted by ESR, $p_{\mathrm{eff}} = g_J [J(J+1)]^{1/2} = 3.92$, for a $J = 1$ ground state with $g_J = 2.77$. Van Vleck–type paramagnetism, arising from admixture of $J = 2$ wave functions into the $J = 1$ ground state, is also evident; this can be exploited for obtaining an independent estimate for the position of the $J = 2$ level, as will be reported elsewhere. It must finally be mentioned that Masterov *et al.*[24] have observed an ESR spectrum for p-GaAs:Mn in which, apart from $A^-(3d^5)$-state ESR signals, the $\Delta M = 2$ transition of the A^0 state is clearly apparent whereas the $\Delta M = 1$ transition is not visible. This indicates severe strains to be present in their sample which can broaden the $\Delta M = 1$ transition beyond detection. Obviously, an assignment[24] of the ESR signal to a neutral manganese interstitial must be discarded.

In conclusion, we have presented strong evidence that the electronic ground state of the neutral manganese acceptor in GaAs is formed by a delocalized hole weakly coupled to the $A^-(3d^5)$ acceptor core—and not to a tight-binding $3d^4$ configuration. Thus manganese in GaAs, possibly also in InP and GaP, appears to be a rather anomalous member of the $3d$-transition metal family in compound and elemental semiconductors.

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