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Magnetic-resonance studies of interstitial Mn in GaP and GaAs

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We report the observation of an additional electron-paramagnetic-resonance (EPR) center in neutron-irradiated GaP. The center labeled as GaP-NL1 was further investigated with the electron-nuclear double-resonance technique. We also observed another, similar EPR center in GaAs doped with Mn, which we label as GaAs-NL1. On the basis of this study, we were able to identify these centers as an interstitial Mn atom probably surrounded by four nearest-neighbor Ga atoms. We note that this is an observation by the EPR technique of an interstitial transition-metal impurity in a III-V compound.

I. INTRODUCTION

Transition-metal impurities are studied most extensively by electron paramagnetic resonance (EPR).[1-5] Their spectra have been observed in the whole range of crystals from purely covalent (group-IV elemental semiconductors) to purely ionic (e.g., group I-VII salts). In the case of a compound crystal, single transition-metal impurities are usually found on substitutional sites replacing the cation. They can also form complexes with other atoms, while remaining on a substitutional site. In group-IV elemental semiconductors the situation is different. In these crystals, under normal diffusion conditions, transition-metal impurities favor interstitial positions,[5] although they are sometimes observed on substitutional sites. As part of a defect complex they can be on both substitutional and interstitial sites. To date, an isolated transition-metal impurity on an interstitial site has been reported only in group-IV semiconductors.

In this paper we report the observation of an EPR spectrum in neutron-irradiated GaP, which we label as GaP-NL1, and of an EPR spectrum in GaAs, which we label as GaAs-NL1. Both spectra are almost identical and we argue that they can be identified with an interstitial Mn ion. We note that this is an observation of an interstitial transition-metal impurity in a III-V compound semiconductor.

Due to its high abundance and usually high diffusivity, Mn is a very common impurity. In ionic crystal it exists preferentially in its 2+ charge state with a $3d^5$ electron configuration. In III-V semiconductors, isolated Mn has been observed to substitute for group-III atoms and to give rise to a deep level of acceptor character.[3] The possible charge states would then be either the neutral Mn^{3+} with electron configuration $3d^4$ (or $3d^5$+hole) or the singly ionized charge state Mn^{2+} with electron configuration $3d^5$.[6] In III-V semiconductors, substitutional Mn was also observed forming complexes with other impurities.[7-9] Until now interstitial manganese has only been observed in silicon.[4,10] Four different charge states of interstitial Mn in Si were detected: 2+, 1+, 0, and 1− with electron configurations $3d^5$, $3d^6$, $3d^7$, and $3d^8$, respectively. In addition to the interstitial, substitutional manganese in silicon has been observed by EPR;[4] two charge states were detected corresponding to the $3d^5$ and $3d^2$ electron configurations.

II. EXPERIMENT

The sample of $2\times2\times0.2$ mm^3 was cut from a GaP crystal which was not intentionally doped with Mn. The sample was irradiated with thermal neutrons perpendicular to the largest surface. The fluence of the neutrons was 1.4×10^{19} cm^{-2} and the ratio between thermal and fast neutrons was 1000:1. After this irradiation, the new EPR spectrum GaP-NL1 was observed. (The manganese-doped GaAs sample will be discussed in Sec. V.)

Measurements of electron paramagnetic resonance were performed at the X band (microwave frequency $\nu\cong9$ GHz) and the K band ($\nu\cong23$ GHz). The spectrometers were of the superheterodyne type with audio-frequency modulation of the magnetic field. The dispersion part of the magnetic susceptibility was observed at microwave powers of a few microwatts. The sample was mounted with the crystallographic $[0\bar{1}1]$ direction along the cylindrical axis of the microwave cavity and perpendicular to the rotation plane of the magnetic field.

Electron-nuclear double-resonance (ENDOR) experiments were carried out at the K band. For ENDOR measurements, the radio-frequency field was square wave modulated at 3.3 Hz to allow double phase-sensitive detection of the signal. The sample temperature during our experiments was 4.2 K or a few degrees above this value.

III. RESULTS

The GaP-NL1 spectrum, as recorded in the K band, is depicted in Fig. 1. It clearly consists of six nearly equidistant main lines of equal intensity and pairs of smaller lines in between the main lines. The spectrum is isotropic. It is quite similar to the spectrum reported by Wartewig[11] in Cr-doped GaAs and to the spectrum observed in Cr-doped InP by Schneider.[12] From its features it immediately follows that the observed splitting is due

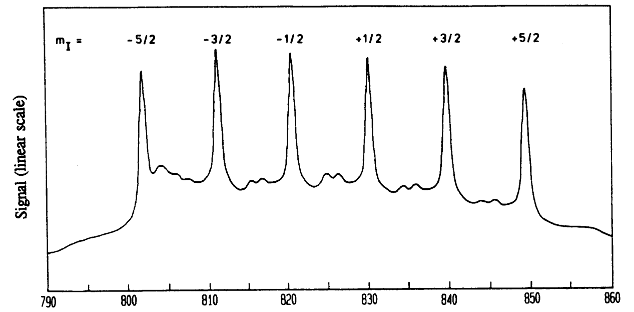

FIG. 1. EPR spectrum of the GaP-NL1 center at the K band in the dispersion mode at $T=4.2$ K. The allowed $\Delta m_I=0$ transitions are labeled with their m_I quantum number for the case $g>0, g_N>0$, and $A<0$.

to the hyperfine interaction with a 100% abundant magnetic nucleus with nuclear spin $I=\frac{5}{2}$.

The spectrum can be described with the following spin-Hamiltonian:

$$H=g\mu_B\mathbf{B}\cdot\mathbf{S}+A\mathbf{S}\cdot\mathbf{I}-g_N\mu_N\mathbf{B}\cdot\mathbf{I}\ . \tag{1}$$

From the six main components of the GaP-NL1 spectrum, the following parameters were determined as $I=\frac{5}{2}$, $g=2.0006\pm0.0003$, and $A=\pm(266.4\pm0.5)$ MHz. The value of the effective spin S and the nuclear g_N value can be determined from further details of the spectrum, i.e., from the pairs of small lines between the six main resonances. These "forbidden" lines correspond to the transitions

$$|+\tfrac{1}{2},m_I\rangle\leftrightarrow|-\tfrac{1}{2},m_I-1\rangle$$

and

$$|+\tfrac{1}{2},m_I-1\rangle\leftrightarrow|-\tfrac{1}{2},m_I\rangle\ .$$

From the fact that they appear in the middle of the allowed $\Delta m_I=0$ transitions, it can be shown that the value of S should be odd (otherwise the forbidden transitions would be at positions close to the main lines). We calculated the splitting ΔB of the forbidden transitions up to third order in $A/g\mu_B B$ to be

$$\Delta B=2\frac{g_N\mu_N}{g\mu_B}B+b\frac{A^2}{g^2\mu_B^2B}-c\frac{A^3}{g^3\mu_B^3B^2}(2m_I-1)\ , \tag{2}$$

with $b=S(S+1)-\frac{1}{4}$ and $c=2S(S+1)-\frac{3}{4}$. For $S=\frac{1}{2}$, $\frac{3}{2}$, and $\frac{5}{2}$, this leads to $b=\frac{1}{2}, \frac{7}{2}, \frac{17}{2}$ and $c=\frac{3}{4}, \frac{27}{4}, \frac{67}{4}$, respectively. On the basis of Eq. (2), the effective electron spin and nuclear g value can be determined as $S=\frac{5}{2}$ and $g_N=10.5\pm0.5$ MHz/T, respectively. The successful fit requires g and g_N to be of the same sign which, for a significant physical interpretation, must be positive.

For the Hamiltonian in Eq. (1), the positions of the allowed $\Delta m_I=0$ transitions $|m_S,m_I\rangle\leftrightarrow|m_S-1,m_I\rangle$ are, up to second order in $A/h\nu$, given by[4]

$$g\mu B=h\nu+Am_I+[I(I+1)-m_I^2+m_I(2m_S-1)]A^2/2h\nu\ . \tag{3}$$

The second-order term splits lines with different values of m_S. The splitting is proportional to m_I. Thus, the lines with $m_I=\pm\frac{5}{2}$ are more split than the lines with $m_I=\pm\frac{1}{2}$. This splitting is often observed as line broadening, with the outermost lines $(m_I=\pm\frac{5}{2})$ more broadened than the innermost $(m_I=\pm\frac{1}{2})$ case. However, we do not observe such a pattern. We believe that this is due to internal stresses in the sample which are randomly distributed in both direction and magnitude.

The influence of stress can be described by an axial crystal field, which can be incorporated into the Hamiltonian, Eq. (1), by adding an extra term

$$H_{\rm st}=D[S_z^2-\tfrac{1}{3}S(S+1)]\ . \tag{4}$$

Since the stress is randomly distributed, it has to be averaged over all directions and magnitudes. The total effect of this is that all EPR lines, except the $m_S=+\frac{1}{2}$ to $-\frac{1}{2}$ transitions, are broadened and smeared out into a background signal for sufficiently large values of D. In the following we shall show that the average value is $D\approx250$ MHz from which we can deduce that the broadening of the $m_S=\pm\frac{3}{2}$ to $\pm\frac{1}{2}$ lines is approximately 25 mT and of the $m_S=\pm\frac{5}{2}$ to $\pm\frac{3}{2}$ lines approximately 50 mT. Thus, we only observe the $|+\frac{1}{2},m_I\rangle\leftrightarrow|-\frac{1}{2},m_I\rangle$ transitions, which show no broadening or shifting due to the term in Eq. (4).

For a $S=\frac{5}{2}$ and $I=\frac{5}{2}$ system, the observation of the forbidden $\Delta m_I=\pm1$ transitions can be either explained by an axial crystal field or by a cubic crystal field, as is done for Mn^{2+} in various crystals.[13–15] Both of these explanations lead to an angular dependence of the intensity of the forbidden lines, which is not observed. A randomly distributed axial crystal field due to internal stresses as described above, however, can account for the observation of those forbidden transitions and should not cause any angular dependence.

For $D\ll g\mu_B B$, the ratio R_{01} between the forbidden transitions $|m_S,m_I\rangle\leftrightarrow|m_S-1,m_I-1\rangle$ and $|m_S, m_I-1\rangle\leftrightarrow|m_S-1,m_I\rangle$ and the allowed $\Delta m_I=0$ transitions is given by[16]

$$R_{01}=\frac{1}{2}\left[\frac{3D}{4g\mu_BB}\right]^2\left[1+\frac{S(S+1)}{3m_S(m_S-1)}\right]^2\times[I(I+1)-m_I^2+m_I]\ . \tag{5}$$

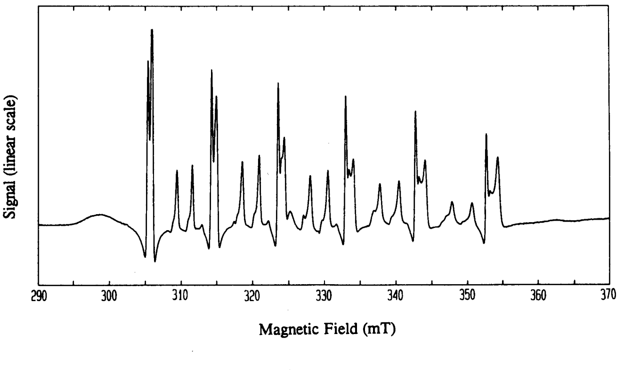

FIG. 2. EPR spectrum of GaP-NL1 at the X band in the dispersion mode at $T\approx6$ K.

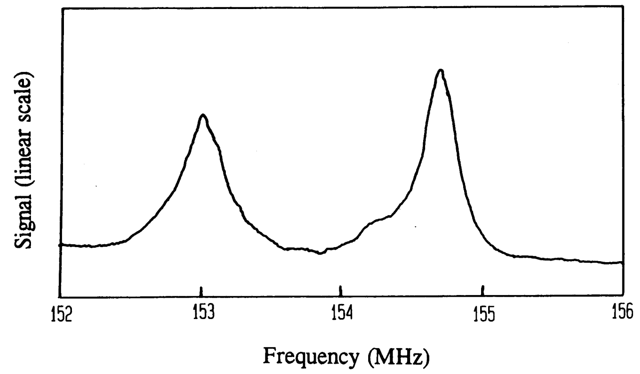

FIG. 3. Typical ENDOR spectrum as recorded on the K band ($\nu=23.149$ GHz) on the EPR line with $B=821.2$ mT and $m_I=-\frac{1}{2}$.

Here D can be taken as its averaged value. This relation is in good agreement with the experiment if we take $D\approx250$ MHz. This value for D for a randomly distributed stress is reasonable.[17]

The spectrum as recorded on the X band is shown in Fig. 2. It also consists of six groups of main lines with lines belonging to the forbidden $\Delta m_I=\pm1$ transitions between them. In this spectrum, the main lines are split into three components. Because of the randomly distributed axial crystal fields, all these lines belong to $m_S=+\frac{1}{2}$ to $-\frac{1}{2}$ transitions. The splitting is then probably due to an additional stress applied to part of the sample in the direction of the cylindrical axis of the microwave cavity. This stress may lead to a small displacement of the atoms from their normal site and thus to small changes in the values of g and A. The values for g and A which follow from the central lines are, however, identical to their K-band values. When compared with K-band results from Eq. (2), the splittings of the forbidden transitions are a further proof that $S=\frac{5}{2}$. Also, their intensities are consistent with those observed at the K band if we use Eq. (5).

ENDOR measurements were performed at the K band in the region of 100–160 MHz, where ENDOR lines on the $m_S=+\frac{1}{2}$ to $-\frac{1}{2}$ transitions were expected. The observed ENDOR lines are given in Table I. A typical ENDOR scan is given in Fig. 3, as observed on the EPR line at $B=821.2$ mT with $m_I=-\frac{1}{2}$ ($\nu=23.149$ GHz). From the ENDOR measurements the values of A and g_N could be determined to a greater accuracy with $A=\pm(266.83\pm0.1)$ MHz and $g_N=10.3\pm0.4$ MHz/T. Similar to the EPR measurements, the ENDOR measurements showed no angular dependence.

IV. DISCUSSION

A. Identification of impurity

As already pointed out, the measurements clearly show that the defect consists of a 100% abundant $I=\frac{5}{2}$ isotope. Moreover, the simple hyperfine splitting indicates that only a single atomic species is involved in a well-defined site. The possible candidates with $I=\frac{5}{2}$ are Al, Mn, I, Pr, Eu, or Re. Of these, only Al and Mn have a 100% abundant isotope with the value of g_N in approximate agreement with the experiment [Mn, $g_N=10.553$ MHz/T and for Al, $g_N=11.004$ MHz/T (Ref. 18)]. Since aluminum has the electron configuration [Ne]$3s^23p$, it cannot form an $S=\frac{5}{2}$ state with $g\approx2$. Manganese has an electron configuration [Ar]$4s^23d^5$. The half-filled d shell forms an ^6S state with spin $S=\frac{5}{2}$. In a crystal there are two possible electron configurations which lead to $S=\frac{5}{2}$: [Ar]$4s^23d^5$ and [Ar]$3d^5$, belonging to neutral and doubly ionized manganese, respectively. For the neutral manganese, the $4s$ electrons would probably be moved to the $3d$ shell, as is the case in Si.[4] This would decrease the effective spin of the system to $S=\frac{3}{2}$, rendering this charge state inconsistent with the experiment. Even if the $4s$ electrons did not move to the $3d$ shell, the possibility of a neutral charge state would still not be consistent with experimental data, since the observed hyperfine constant is too large to be accounted for by neutral manganese as will be discussed later. We therefore conclude that the center contains a Mn atom in its doubly ionized 2+ charge state.

Since, for all centers involving an isolated Mn ion in its $3d^5$ configuration where the sign of the hyperfine constant has been determined, the sign is negative, we can also assume that the sign of the hyperfine parameter is negative for the GaP-NL1 center.

B. Hyperfine interaction

1. Origin of A

The hyperfine parameter A can be considered as having three parts: a contribution due to unpaired s electrons (Fermi contact interaction), a contribution due to

TABLE I. ENDOR frequencies as recorded on the K band ($\nu=23.296$ GHz) on the six $m_S=\frac{1}{2}$ to $-\frac{1}{2}$ transitions.

Magnetic field (mT)	808.09	817.34	826.75	836.26	845.89	855.62
ENDOR freq. (MHz)	109.30	110.45	110.54	111.75	113.03	114.46
	110.20	110.84	111.62	113.05	114.38	
	151.20	151.31	152.96	154.79	156.46	
		153.00	154.73	156.49	157.12	
				157.22		

spin-orbit coupling, and an orbital contribution.[19] The latter is zero in cubic symmetry, as is the case in our system. The spin-orbit part is related to the g-shift relative to the free electron's g_e. Here, $\Delta g = -0.0017 \pm 0.0003$. From this one can calculate that the contribution to the hyperfine interaction is very small (less than 1.2 MHz). We conclude that the hyperfine interaction is mainly caused by contact interaction.

The Fermi contact interaction means that the electron density is not zero on the Mn nucleus. It possibly originates from the residual spin density in the $4s$ orbital, polarization of the inner s orbitals by the spin density in the half-filled $3d$ shell, or spin-polarized valence-band orbitals. The last contribution is small and will be neglected here.[20]

A free Mn^{2+} ion with electron configuration $[Ar]3d^5$ has a hyperfine splitting due to the polarization of the $1s$, $2s$, and $3s$ electron shells by the half-filled $3d$ shell. This gives a hyperfine interaction, $A = -304$ MHz.[21] For a free neutral manganese atom with electron configuration $[Ar]4s^2 3d^5$, the hyperfine splitting is caused by polarization of the $1s$-$4s$ shells. Since the contribution of the $4s$ shell is $+256$ MHz, this leads to a total hyperfine constant $A = -48$ MHz for the neutral manganese atom. When the atom or ion is placed in a crystal, the absolute value of A can only be reduced (due to delocalization effects). This then rules out the possibility that the center consists of neutral manganese.

Consider a substitutional Mn with electron configuration $3d^5$ in a diamond or zinc-blende structure. The manganese ion will then form covalent bonds with its surrounding atoms. These bonds consist of a hybridized Mn orbital $(4s4p^3)$ and orbitals from the ligands. The degree of covalency indicates the partial filling of the $4s$ orbitals of Mn. In the case of a purely covalent bond, there will be a maximum of one electron in a $4s$ orbital. These binding orbitals will have no net spin, since each bond consists of two electrons and their spins pair off. However, the partially filled $4s$ orbitals can be spin polarized. Their contribution to the polarization is linear with occupation. For an occupation of one electron, it is $+128$ MHz (Ref. 21) with a sign opposite to the hyperfine interaction of the inner s shells. Therefore, the contribution from the partially occupied $4s$ orbitals can influence the magnitude of A considerably. With increasing covalency of the bonds between Mn and its ligands, the absolute value of the total core polarization decreases.

In covalent crystals there exists yet another mechanism that decreases the core-polarization contribution to the hyperfine interaction, namely, the delocalization of the $3d$ electrons. When these electrons are less localized in the region of the s orbitals, this leads to a smaller core polarization. This effect can be considerable since the effect of 40% delocalization or more has been determined by ENDOR experiments.[22]

Apart from the above-discussed core polarization, the $4s$ admixture with nonzero spin density can also contribute to the hyperfine interaction. For a fully occupied (purely spinlike) $4s$ orbital, the contribution is $+5036$ MHz.[23] Therefore, even a small $4s$ admixture can influence the hyperfine parameter A considerably. The sign of this contribution is positive and leads to a decrease of the absolute value of A.

2. *Identification as interstitial Mn*

Let us now address in more detail the question on which site the Mn atom is located. Since the spectrum is isotropic, then the center has cubic symmetry. That limits its possible identification to a single Mn^{2+} atom at a site with T_d point-group symmetry. This could be a substitutional Ga or P position or either of two tetrahedral interstitial positions. One interstitial position has four nearest-neighbor Ga atoms and one has four nearest-neighbor P atoms. Substitutional Mn on a Ga site has already been observed by EPR.[24] The relevant spectrum is clearly different from the one observed here, so this possibility can be ruled out.

For a substitutional Mn in various compounds, the relation between the value of A and the covalency of the bond between Mn and its ligands is given in Fig. 4.[25] The covalency is defined as[26,27]

$$c = [1 - 0.16(x_A - x_B) - 0.035(x_A - x_B)^2]/z \;, \qquad (6)$$

where x_A and x_B are the electron negativity of the ligand and Mn ion, respectively, and z is the number of ligands. As can be seen from Fig. 4, the absolute value of A de-

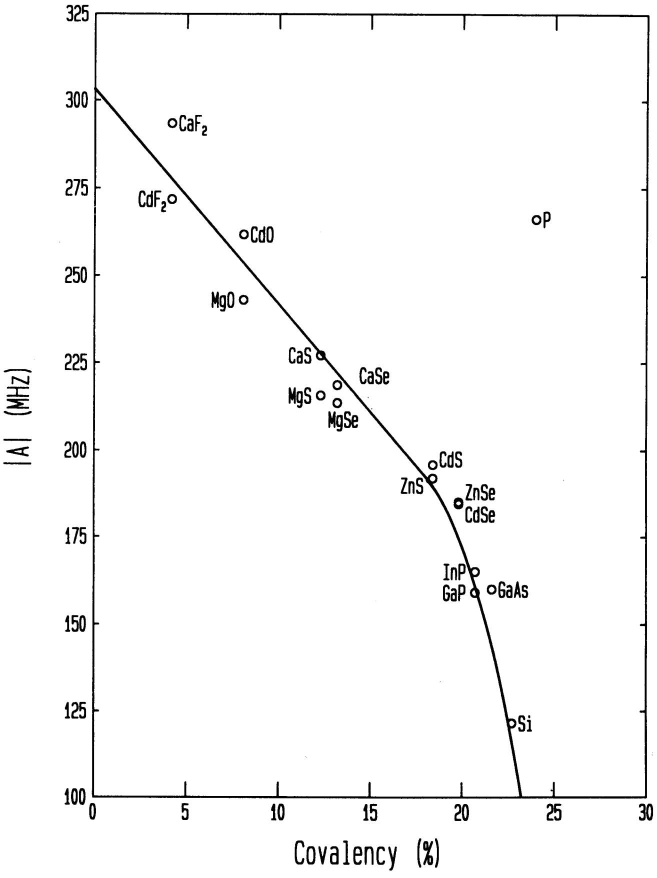

FIG. 4. Relation between the absolute value of hyperfine constant A and covalency of bonds between Mn and its nearest neighbors for substitutional Mn in various compounds. The point marked P is discussed in the text.

creases monotonically with the covalency. Between 0% and 18% covalency, the relation is linear; between 18% and 25%, A decreases even faster.

In Fig. 4, a GaP data point is shown for a substitutional Mn on a Ga site.[24] Since our A value is clearly different from previous substitutional site data, the new center GaP-NL1 might have its Mn at a P site. From Eq. (6) the covalency value for such a case can be calculated by taking x_B as the electron negativity of Mn, x_A as the electron negativity of Ga, and $z=4$ (on a P site the Mn is surrounded by four Ga atoms).[28] This procedure results in a covalency value of 24%. In Fig. 4 we have plotted this data as point P at the measured A value of 266.4 MHz. As can be seen, this point lies far outside the curve, rendering a substitutional P site as unlikely.

For transition-metal impurities on interstitial sites, larger values for A are generally found when compared to substitutional sites.[4] Our large A value is thus indicative of a Mn at an interstitial site. From this reasoning we therefore conclude that the center consists of a Mn atom on an interstitial site of T_d symmetry.

3. *Nearest-neighbor atoms*

In GaP, two interstitial sites of T_d symmetry are possible; they differ by a first-neighbor shell which can contain either four Ga or four P atoms. In what follows we present an argument leading to a defect model which has interstitial Mn surrounded by nearest-neighbor Ga atoms. The argument is based on a comparison between the interstitial and substitutional Mn centers in Si and those in GaP.

So far, the only other material in which both substitutional and interstitial Mn have been observed is Si. In Si, interstitial Mn can be found in its 2+, 1+, 0, and 1− charge states. The 2+ charge state has electron configuration $3d^5$ and hyperfine constant $A=-160.41$ MHz. Substitutional Mn in Si is observed in its 2− and 1+ charge states. The 2− charge state has electron configuration $3d^5$ and $A=-121.5$ MHz. In GaP, substitutional Mn on a Ga site is observed in EPR in its 2+ charge state with electron configuration $3d^5$ and has $A=-159.16$ MHz. All EPR parameters on these centers are summarized in Table II.

First consider substitutional Mn. The Mn in Si and the Mn in GaP covalent bonds have covalency of 22.7% and 20.7%, respectively. This means that Mn in Si has $4\times0.227=0.908$ electrons in the 4*s* shell. This decreases the core-polarization contribution to the hyperfine interaction to −187.8 MHz. For substitutional Mn in GaP, there are $4\times0.207=0.828$ electrons in the 4*s* shell, which leads to a core-polarization contribution of −197.8 MHz. If we now assume that there is no admixture of spin density in the 4*s* shell, then the only other mechanism that can decrease the hyperfine constant is delocalization of the $3d^5$ shell. For Si this would then lead to a localization of 65% of the $3d^5$ electrons on the Mn core. Since we have neglected the admixture of 4*s* spin density, the calculated number represents the minimum localization value. For GaP, a minimal localization of the $3d^5$ shell on the Mn core of 80% can be calculated in a similar manner.

Let us now consider interstitial Mn. There are no covalent bonds between Mn and its ligands, so there will be no decrease in core polarization due to a partially occupied 4*s* shell. If we again do not consider admixture of spin density in the 4*s* shell, the only mechanism to decrease the hyperfine constant, compared to the free-ion case, is the delocalization of the 3*d* shell. For Si this would lead to a localization of 53% on the Mn core, which is much less than the relevant value for substitutional Mn. Such a result is unexpected since for substitutional Mn the covalent bonds between Mn and its ligands should lead to a smaller localization on the core. Since this is clearly not the case, the contribution of the 4*s* spin-density admixture must be larger for interstitial Mn than for substitutional Mn in Si. Such a situation is certainly plausible since, for substitutional Mn, 0.9 electrons are already in the 4*s* state forming covalent bonds, whereas these bonds are unoccupied in interstitial Mn. Admixture of the 4*s* spin density is then less likely for substitutional Mn.

For GaP, interstitial Mn would have a localization of 88% on the core if the 4*s* spin-density admixture were neglected. This value is larger than the minimal localization of substitutional Mn. Apparently the influence of the 4*s* spin-density admixture to interstitial Mn is less important than for Si. In order to explain this, the influence of the surrounding atoms on the 4*s* admixture should be taken into account. The surrounding of an interstitial Mn with nearest-neighbor Ga consists of the first shell formed by 4 Ga atoms at a distance of 2.72 Å, the second shell of 6 P atoms at 3.14 Å, and the third shell of 12 Ga atoms at 5.22 Å. For Mn with nearest-neighbor P, the surrounding is identical with P and Ga interchanged. Due to the localized character of the defect, let us first consider only the influence of the first two neighboring shells on the 4*s* admixture.

TABLE II. Values of g, A, and a for Mn with electron configuration $3d^5$ on substitutional and interstitial sites in Si, GaP, and GaAs. Values for Si are from Ref. 4, values for substitutional Mn in GaP and GaAs are from Refs. 24 and 9, respectively.

	Substitutional			Interstitial		
	g	A (MHz)	a (10^{-4} cm^{-1})	g	A (MHz)	a (10^{-4} cm^{-1})
Si	2.0058	−121.5	26.1	2.0066	−160.41	19.88
GaP	2.002	−159.16	10	2.0006	−266.83	<10
GaAs	2.0023	−162.6	13	2.0001	−266.3	<13

Let us first consider the charge difference between the Ga and P atoms. The binding of GaP is 87% covalent. If we assign the charges of the binding electrons according to this percentage to the Ga and P atoms, the net charge of the Ga atoms is negative and is $-0.47e$ and of the P atoms it is $+0.47e$. If we now assume that the influence of the second shell can be shielded by the first shell, but not vice versa, then this mechanism clearly favors the Ga atoms to be the nearest neighbors, since a negatively charged close surrounding will lead to less $4s$ admixture than a positively charged surrounding, due to electrostatic repulsion between $4s$ electrons and negatively charged ligands.

Let us further consider the difference in electron negativity between Mn and its surrounding atoms. We can expect that the smaller difference in electron negativity will result in less $4s$ admixture since the $4s$ orbitals are localized further away. The difference in electron negativity between Mn and Si, P, and Ga is 0.52, 0.89, and 0.18, respectively.[28] The difference in electron negativity is smaller for Ga when compared to Si, whereas it is larger for P. If we again assume some shielding of the second shell by the first shell, the small effect of $4s$ admixture for the interstitial Mn in GaP with respect to Si favors Ga to be the nearest neighbor.

Summarizing, from the large hyperfine interaction parameter A, we conclude that the center GaP-NL1 consists of an interstitial Mn atom. By comparison with Mn centers in Si, we further identify the nearest-neighbor shell as most probably consisting of four Ga atoms.

C. Crystal-field parameter

For substitutional Mn in Si and GaP, and for interstitial Mn in Si, the EPR spectrum is not fully described by the spin Hamiltonian Eq. (1). An additional term has to be included that gives in account the crystal-field influence and is

$$H_{\mathrm{cf}}=(a/6)[S_x^4+S_y^4+S_z^4 -\tfrac{1}{5}S(S+1)(3S^2+3S-1)] \; . \qquad (7)$$

The crystal-field parameter a has been determined as 26.1×10^{-4} cm^{-1}, 19.88×10^{-4} cm^{-1}, and 10×10^{-4} cm^{-1} for substitutional Mn in Si, interstitial Mn in Si,[4] and substitutional Mn in GaP,[24] respectively. Since we only observe the $m_S=+\frac{1}{2}$ to $-\frac{1}{2}$ transitions and the value of a is determined from the angular dependence of the splitting of the other transitions, we cannot give a value for a for the GaP-NL1 spectrum.

The crystal field splits the $3d$-electron quintet into a t_2 orbital triplet and an e orbital doublet. The splitting between these two multiplets is usually denoted $10Dq$, where Dq is the crystal-field splitting parameter. The crystal field operates on the spatial part of the wave function and thus only affects systems with nonzero orbital momentum. A pure half-filled $3d$ shell, which in the presence of a crystal field consists of three electrons in t_2 orbitals and two electrons in e orbitals, forms a ${}^6S_{5/2}$ ground state which has no orbital momentum and will not experience the crystal-field influence. However, in a crystal, some admixture of ${}^4P_{5/2}$ occurs making $J=\frac{5}{2}$ the only good quantum number. This sixfold degenerate state is no longer an orbital singlet and can be split by a cubic crystal field into a quartet Γ_8 and a doublet Γ_7. The energy difference between those two levels is $3a$. In the presence of a magnetic field for $g\mu_B B \gg a$, the quantum numbers are m_J and the six relevant energy levels for the six m_J states are

$$\begin{aligned} W_{\pm1/2}&=\pm\tfrac{1}{2}g\mu_B B+pa \;, \\ W_{\pm3/2}&=\pm\tfrac{3}{2}g\mu_B B-\tfrac{3}{2}pa \;, \\ W_{\pm5/2}&=\pm\tfrac{5}{2}g\mu_B B+\tfrac{1}{2}pa \;. \end{aligned} \qquad (8)$$

Here $p=p(\theta)$ gives the angular dependence of the splitting. The crystal-field contribution in this formula also follows from Eq. (7). The actual value of the constant a depends on the spin-orbit interaction parameter λ which couples L and S momenta, and on the crystal-field-splitting parameter, Dq, which gives a major contribution to the energy difference between the ${}^6S_{5/2}$ and ${}^4P_{5/2}$ states and determines the amount of ${}^4P_{5/2}$ admixture. The value of a is proportional to $\lambda^4 Dq^n$, where n varies from 3 to 6.[29] Additionally, the Racah parameters B and C which arise from the Coulombic electron-electron interaction influence the value of a.[29]

We will now try to make an estimation for the value of a for a Mn^{2+} ion in a III-V compound. For Dq we will use the value as was determined from the crystal-field splitting for substitutional Mn^{2+} in GaP: $Dq=430$ cm^{-1}.[30] For a free Mn^{2+} ion, $\lambda=300$ cm^{-1}. For iron group ions the value of λ in solids is about 25% less than the free-ion value,[19,29] so we take $\lambda=240$ cm^{-1}. For the Racah parameters we take the free-ion values for the Mn^{2+} atom $C/B=3.5$ and $B=960$ cm^{-1}. Using these numbers, we calculate the crystal-field parameter (after Hall, Hayes, and Williams[29]) as $a=0.2\times10^{-4}$ cm^{-1}.

This value for a is about 2 orders of magnitude smaller than the a values for Mn in Si and substitutional Mn in GaP. This can be explained by the following mechanism. If the half-filled $3d$ shell becomes less localized on the Mn core, the localization on the ligand sites is increased. Within the linear combination of atomic orbitals model, the atomic orbitals at the ligand sites are then occupied and some of these have nonzero orbital momentum $l>0$. These orbitals give a spin-orbit interaction which is much stronger than the spin-orbit interaction at the Mn core thus increasing the a value.

In the preceding discussion on the hyperfine interaction, we found that the half-filled $3d$ shell is most delocalized for substitutional Mn in Si, which also has the largest value for a. Then, subsequently, interstitial Mn in Si and substitutional Mn in GaP show smaller delocalization and also their values for a are subsequently smaller (see Table II). For the interstitial Mn in GaP, the delocalization is even smaller. This leads us to the conclusion that the value for a will be smaller for this center than for the substitutional Mn in GaP. We have made an upper limit for the value of a for the GaP-NL1 center as $a<10\times10^{-4}$ cm^{-1}.

D. Linewidth

The linewidth of a substitutional transition-metal impurity is considerably larger in III-V compounds than in Si. This is due to the higher abundance of nuclear magnetic moments. (In GaP or GaAs, every ion in the lattice has a nuclear magnetic moment while in Si only approximately 5% do.) For substitutional transition-metal impurities in GaP, the main contribution to the linewidth comes from the hyperfine interaction with the surrounding P atoms. These are four equivalent nuclei with $I=\frac{1}{2}$ and lead to hyperfine splittings which are not resolved in EPR. The experimental linewidth is therefore proportional to the hyperfine coupling with the surrounding P atoms.

In this study we have already concluded that Mn is at an interstitial site of tetrahedral symmetry with four Ga atoms in the nearest-neighbor shell. Ga also has a nonzero nuclear moment, so hyperfine interaction with the first shell will contribute to the linewidth.

The linewidth of the GaP-NL1 spectrum is 0.6 mT. For a III-V compound, this number is very small and comparable to the linewidth of Mn impurity in silicon, where almost no hyperfine interactions with the surrounding shells are present. The small linewidth indicates then that the hyperfine interaction with the surrounding Ga atoms is very small and, since those have a nonzero nuclear magnetic moment, the localization on the ligands is very small. Such a conclusion is in good agreement with the large value of A, which is also indicative of a very localized character of the spin density.

V. INTERSTITIAL Mn IN GaAs

EPR experiments were performed on GaAs doped with Mn, which was grown by the liquid-encapsulated Czochralski technique. The EPR spectrum as recorded on the K band is shown in Fig. 5. It consists of two spectra: one that has been attributed to substitutional Mn on a Ga site and a new spectrum similar to the one observed by Wartewig.[11] The spectrum of substitutional Mn in GaAs is characterized by $g=2.0023$, $A=\pm162.6$ MHz, and $a=13\times10^{-4}$ cm^{-1}.[9] The new spectrum, which we label GaAs-NL1, is isotropic and can be described by the same spin Hamiltonian as the GaP-NL1 spectrum [Eq. (1)] with parameters $I=\frac{5}{2}$, $g=2.0001\pm0.0003$ and $A=\pm(266.3\pm0.5)$ MHz. These values are almost identical to the ones observed for GaP-NL1. Since no forbidden $\Delta m_I=\pm1$ transitions could be distinguished, we could not determine the values of S and g_N. However, since the values of g, A, and I are almost identical to the values of the GaP-NL1 spectrum and since the GaAs contains Mn, we identify this center on the basis of our discussion of the GaP-NL1 spectrum as interstitial Mn in GaAs on a site of T_d symmetry most probably surrounded by four nearest-neighbor Ga atoms. As we have done for the GaP-NL1 center, we can give as an upper limit for the crystal-field parameter the value for substitutional Mn, so $a<13\times10^{-4}$ cm^{-1}.

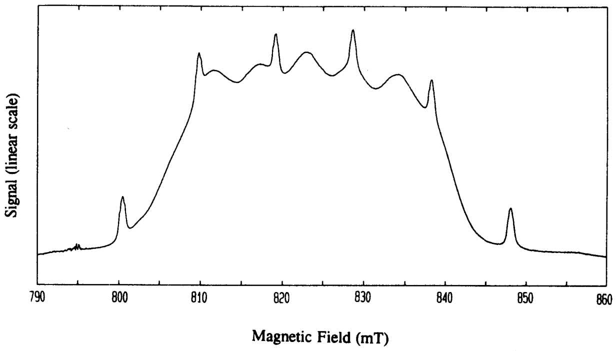

FIG. 5. EPR spectrum of GaAs doped with Mn at the K band.

The value of A is almost identical for both the GaP-NL1 and GaAs-NL1 centers. If we first compare the values of the hyperfine constant for substitutional Mn in GaP and GaAs, we arrive at -159.16 and -162.6 MHz, respectively. These values only differ by 3.5 MHz while these centers have different nearest neighbors (P and As, respectively) and are much more delocalized than the interstitial Mn centers. It is therefore not surprising that, for interstitial Mn in both GaP and GaAs, the hyperfine constants are almost identical, since those centers are very localized and the nearest neighbors are the same in both materials, namely, Ga.

VI. CONCLUSION

We have observed a new EPR spectrum in neutron-irradiated GaP. The spectrum is characterized by $S=\frac{5}{2}$, $I=\frac{5}{2}$, $g=2.0006$, $A=-266.8$ MHz, and $g_N=10.3$ MHz/T and is labeled GaP-NL1. We also observed the same spectrum in GaAs doped with Mn. This spectrum we label GaAs-NL1. This study identified the center as a single Mn atom at an interstitial site of T_d symmetry with, most probably, four nearest-neighbor gallium atoms.

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