Ligand ENDOR on substitutional manganese in GaAs

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In this paper Ga ligand electron-nuclear double resonance measurements are reported on the substitutional Mn^{2+} center in GaAs. On the basis of these experiments it is concluded that the Mn^{2+} center is substitutional on a Ga site. From the electron paramagnetic resonance linewidth and the crystal-field parameter an estimate is made of the hyperfine interaction with the nearest-neighbor As atoms. The data are compared to those obtained for Fe^{3+} in III-V semiconductors. It is found that Mn^{2+} has a more localized character than the Fe^{3+} center. Finally, the quadrupole interaction of the Ga atoms is discussed.

I. INTRODUCTION

The 3*d* transition element atoms are very common impurities in a large number of host lattices.[1-4] Due to their high abundancies and high diffusivities they can easily enter a crystal and appear as intentional, as well as unintentional, dopants. In a group-IV elemental semiconductor they favor an interstitial position, although they have also been observed on substitutional sites in these materials.[4] In III-V compounds the situation is the opposite. Here the 3*d* transition-metal impurities favor the substitutional position, replacing a group-III atom.[3] The only interstitial transition element impurity in a III-V semiconductor reported so far is Mn^{2+} in GaAs and GaP.[5] Claims of the observation of interstitial Fe in GaP and GaAs have been made by Teuerle and coworkers on the basis of electron-nuclear double resonance (ENDOR) measurements,[6,7] but an analysis by Hage, Niklas, and Spaeth showed that the Fe atom should be assigned to a substitutional site.[8] Similarly, an isotropic signal at $g=5.85$ reported by Masterov *et al.*[9] and originally assigned to interstitial Mn with a $3d^7$ electron configuration was later shown by Schneider *et al.*[10] to be most probably due to the $\Delta m_S=\pm 2$ transitions of the neutral substitutional Mn center.

Although it has been observed on an interstitial position, Mn is most likely to occupy a substitutional position in GaAs, replacing a Ga atom. Once on a Ga site, it can form an isolated impurity or a complex with another dopant atom, such as Mn-Li,[11] Mn-O[12], Mn-Se,[13] and Mn-S.[14] The isolated substitutional Mn impurity in GaAs acts as an acceptor and has an energy level 113 meV above the valence band, which is the smallest value found for any 3*d* transition-metal impurity in this material. It has been observed by electron paramagnetic resonance (EPR) in two charge states: neutral, denoted by Mn^{3+},[10] and singly ionized, Mn^{2+}.[15,16] On the basis of an analysis of the *g* value of Mn^{3+}, Schneider *et al.* were able to determine the electron configuration of the charge state as $[Ar]3d^5$+loosely bound hole. The electron configuration of the ionized charge state is $[Ar]3d^5$ as follows from its effective spin $S=\frac{5}{2}$.

In this paper a ligand ENDOR study of the substitutional Mn^{2+} impurity in GaAs will be presented. The results will be compared to those of ENDOR experiments on Mn^{2+} in GaP,[17] and to ENDOR data as obtained for Fe^{3+}, which is isoelectronic to Mn^{2+}, in GaAs and GaP.[6,7]

II. EXPERIMENT

The material used in this study was kindly provided by Dr. U. Kaufmann of the Fraunhofer Institute for Applied Solid State Physics. The dimensions of the sample were $2\times2\times10$ mm^3, and it was cut from a GaAs:Mn ingot doped in the melt. The crystal was pulled from a pyrolytic BN crucible by the liquid-encapsulation Czochralski (LEC) technique. Secondary-ion-mass spectroscopy gave a total Mn concentration of 1.1×10^{17} cm^{-3}. Hall measurements showed that the material was *p* type with a room-temperature hole concentration of 4.5×10^{16} cm^{-3}. Since in the sample EPR spectra of both neutral and singly ionized charge states of substitutional Mn could be observed at 4.2 K, with comparable intensity, the Fermi level at this temperature must have been very close to the Mn acceptor level.

The measurements of the ligand ENDOR spectrum were performed on a K-band ($\nu\approx23$ GHz) spectrometer at a temperature of 4.2 K. The spectrometer was tuned to dispersion and operated with microwave power of ≈10 μW incident in the cavity. The sample was mounted with the crystallographic $[01\bar{1}]$ direction along the cylindrical axis of the TE_{011} cavity and perpendicular to the rotation plane of the magnetic field.

III. RESULTS

In Fig. 1 the EPR signal of the GaAs:Mn sample is shown. It consists of two spectra belonging to interstitial (GaAs-*NL*1) (Ref. 5) and substitutional manganese atoms in the 2+ charge state.[15,16] The spectrum of the interstitial Mn atom consists of six sharp lines due to splitting by the hyperfine interaction with the 100% abundant $I=\frac{5}{2}$ Mn nucleus. The effective electron spin of this center is $S=\frac{5}{2}$, and the spectrum is described by the spin Hamiltonian

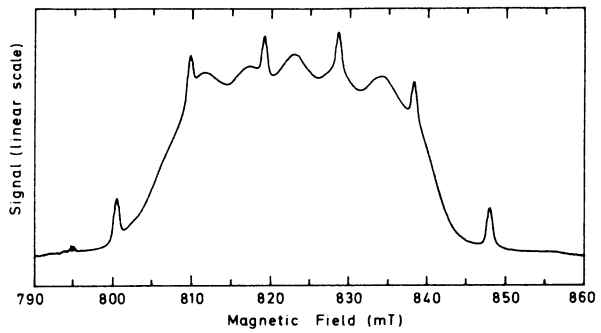

FIG. 1. EPR spectrum of the GaAs:Mn sample as measured in dispersion mode for the K microwave band ($\nu \approx 23$ GHz) at $T=4.2$ K.

$$H = g\mu_B \mathbf{B}\cdot\mathbf{S} + A\mathbf{S}\cdot\mathbf{I} , \tag{1}$$

with $g=2.0001$ and $A=-266.3$ MHz.

The other spectrum is assigned to substitutional Mn^{2+}. It also has an effective spin $S=\frac{5}{2}$, and the spin Hamiltonian describing it is given by Eq. (1) with a term H_{cf} incorporating the influence of the crystal field,

$$H_{cf} = a\tfrac{1}{6}[S_x^4+S_y^4+S_z^4-(\tfrac{1}{5})S(S+1)(3S^2+3S-1)] , \tag{2}$$

added to it. The parameters of the spin Hamiltonian can be determined as $g=2.0023$, $A=-162.6$ MHz, and $a=13\times10^{-4}$ cm^{-1}. For the substitutional Mn defect the resonance is also split into a sextet of lines by hyperfine interaction with the Mn nucleus. In addition, the individual $\Delta m_S=\pm1$ transitions are split by the crystal field. The linewidth of this spectrum, defined as the full width at half maximum, is found to be 5.6 mT. The ENDOR study reported here has been performed on this substitutional Mn^{2+} center.

In an ENDOR experiment the nuclear-magnetic-resonance spectrum is recorded and interactions involving the nuclear momenta of the center can be determined. Ga has two isotopes with a nonzero nuclear momentum: ^{71}Ga which has $I=\frac{3}{2}$, a 39.6% natural abundance, and a g_N value of 12.984 MHz/T, and ^{69}Ga, also with $I=\frac{3}{2}$, a natural abundance of 60.4%, and $g_N=10.219$ MHz/T.[18] The interactions involving the nuclear momentum of the Ga atoms on a certain site i can be described by the spin Hamiltonian

$$H_{\mathrm{Ga},i} = \mathbf{S}\cdot\mathbf{A}_i\cdot\mathbf{I}_i + \mathbf{I}_i\cdot\mathbf{Q}_i\cdot\mathbf{I}_i - g_{\mathrm{Ni}}\mu_N\mathbf{B}\cdot\mathbf{I}_i . \tag{3}$$

The first term describes the hyperfine interaction between the Ga nucleus and the paramagnetic spin system. The second term gives the nuclear quadrupole interaction, and the last term the nuclear Zeeman interaction.

In the current ENDOR experiment the Ga neighboring shell of the substitutional Mn^{2+} center in GaAs which exhibits the largest hyperfine interaction has been analyzed. The sites in this shell have monoclinic-I symmetry, i.e., such are the symmetries of the corresponding **A** and **Q** tensors.

The ENDOR experiment is carried out at the $m_S=-\frac{1}{2}$ level of the $m_S=\frac{1}{2}$ to $-\frac{1}{2}$ EPR transition. This EPR transition can be observed at six values of the magnetic field split due to the hyperfine interaction with the Mn atom, with the splitting exceeding the EPR linewidth. The experiment is performed at two values of the magnetic field, corresponding to $m_{I,\mathrm{Mn}}=-\frac{3}{2}$ and $\frac{3}{2}$, respectively. At these two values of the magnetic field the intensity of the simultaneously present GaAs-*NL* 1 signal is minimal, which reduces the possibility that the ENDOR signals related to the GaAs-*NL* 1 center are also observed in the experiment. The two positions of the magnetic field differ by 17.41 mT; by comparing the ENDOR spectra recorded for these two values it is possible to determine directly the value of g_N from the observed shift of the line position. Since the ENDOR linewidth is typically 30 kHz, this can be done with an accuracy of ≈0.5 MHz/T. As GaAs consists of three isotopes with a nonzero nuclear momentum: ^{71}Ga with $g_N=12.984$ MHz/T, ^{69}Ga with $g_N=10.219$ MHz/T, and ^{75}As with $g_N=7.292$ MHz/T,[18] it is in this manner possible to assign directly an ENDOR signal to a specific isotope in GaAs.

In Fig. 2 the ENDOR spectrum is shown as recorded in the [111] direction for the two values of the magnetic field. From the observed shift of the lines it follows that they originate from hyperfine interactions with nuclei with $g_N=(12.5\pm0.5)$ MHz, which can be identified as ^{71}Ga atoms.

By performing scans in the [100], [111], and [011] directions, as well as in several other directions in the $(01\bar{1})$ plane, the **A** and **Q** tensors of the Ga shell could be determined. For ^{71}Ga they were found to be

$$\mathbf{A} = \begin{bmatrix} 15.28 & 1.00 & 0.71 \\ 1.00 & 15.28 & 0.71 \\ 0.71 & 0.71 & 15.20 \end{bmatrix} \mathrm{MHz} \tag{4}$$

and

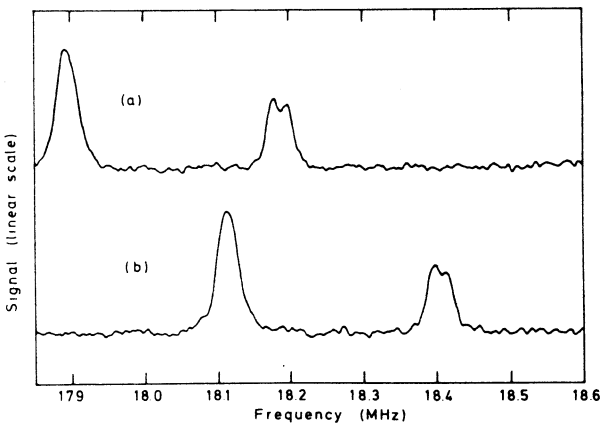

FIG. 2. Typical Ga ENDOR spectrum as recorded in the K microwave band ($\nu=23.117$ GHz) with the magnetic field in the [111] direction on the $m_S=\frac{1}{2}$ to $-\frac{1}{2}$ EPR line at (a) $B=816.06$ mT and (b) $B=833.47$ mT, corresponding to $m_{I,\mathrm{Mn}}=-\frac{3}{2}$ and $m_{I,\mathrm{Mn}}=\frac{3}{2}$, respectively.

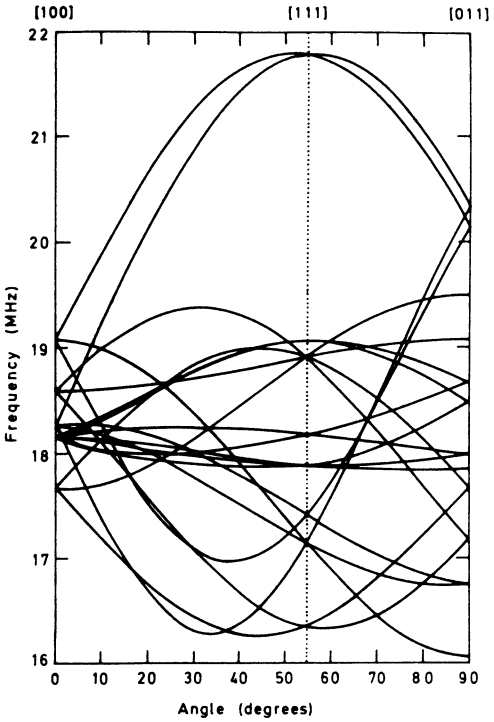

FIG. 3. Angular dependence of the ^{71}Ga ligand ENDOR spectrum for magnetic field $B=816.06$ mT.

$$\mathbf{Q}=\begin{bmatrix} -0.10 & 0.48 & 0.44 \\ 0.48 & -0.10 & 0.44 \\ 0.44 & 0.44 & 0.20 \end{bmatrix} \text{MHz} . \quad (5)$$

These results can alternatively be given by the principal values and directions:[2] $a=15.25$ MHz, $b=0.81$ MHz, $b'=0.16$ MHz, and $\theta_A=30.9°$ for the **A** tensor, and $q=\pm 0.46$ MHz, $q'=\pm 0.13$ MHz, and $\theta_Q=40.9°$ for the **Q** tensor. It should be noted here that in an ENDOR experiment only the relative signs of the components of the **A** and **Q** can be determined. For a physical interpretation in terms of the linear-combination-of-atomic-orbitals (LCAO) model the isotropic hyperfine constant a is assumed to be positive.

In Fig. 3 the simulated angular dependence is shown for the ^{71}Ga ENDOR transitions on the $m_S=-\frac{1}{2}$ level. The simulation is performed for $B=816.06$ mT, which corresponds to $m_{I,\mathrm{Mn}}=-\frac{3}{2}$.

IV. DISCUSSION

In this section the results of the ENDOR experiment will be analyzed and compared to ENDOR measurements performed on Mn^{2+} in GaP (Ref. 17) and Fe^{3+} in GaAs and GaP.[6,7] Similarly to the present case, in the ENDOR experiment for Mn^{2+} in GaP the **A** and **Q** tensors of the Ga shell showing the largest hyperfine interaction were detected. For the Fe^{3+} defect in GaAs and GaP, in addition, the interactions with other shells were recorded. The results of these experiments are summarized in Tables I and II, where the observed **A** and **Q** tensors are listed, respectively. For the Fe^{3+} center only the two shells with largest interactions have been given.

TABLE I. Parameters for the ligand hyperfine tensors for Mn^{2+} and Fe^{3+} centers in GaAs and GaP. Hyperfine parameters a, b, and b' are given in MHz, and θ_A in degrees.

Host lattice	Impurity	Ligand	a	b	b'	θ_A	Ref.
GaAs	Mn^{2+}	^{71}Ga	15.25	0.81	0.16	30.9	this
	Fe^{3+}	^{75}As	22.52	4.35	0	35.3	6,7
	Fe^{3+}	^{71}Ga	11.37	1.83	0	35.3	6,7
GaP	Mn^{2+}	^{71}Ga	14.90	0.88	0.17	32.0	17
	Fe^{3+}	^{31}P	24.78	5.95	0	35.3	6,7
	Fe^{3+}	^{71}Ga	11.22	1.85	0	35.3	6,7

A. Site identification

As mentioned above, in an analysis of the ENDOR data obtained for Fe^{3+} in GaAs and GaP, Teuerle and co-workers concluded that the Fe^{3+} atom was at an interstitial site.[6,7] This analysis was based on the fact that for neither of the two shells listed here has monoclinic-I symmetry, as expected from a substitutional defect, been observed. This may have been due to the ENDOR linewidth being so large that the authors could not observe a significant deviation of b' and q' from zero, and of θ_A and θ_Q from 35.3°. This made it impossible to determine the site of the Fe^{3+} atom on the basis of symmetry arguments. From an analysis of the localization of the paramagnetic electron system on the ligand atoms (GaP:Fe^{3+}) and of the quadrupole interaction (GaAs:Fe^{3+}) they concluded that the Fe^{3+} atom was on an interstitial site in both materials. A more complete analysis by Hage, Niklas, and Spaeth showed, however, that this site identification was not conclusive and that the Fe^{3+} was most probably on a substitutional site replacing a Ga atom.[8]

In the experiment performed here on the Mn^{2+} center, the situation is more clear because of the high resolution achieved in ENDOR. If one assumes that the largest Ga hyperfine interaction is with the nearest Ga atoms (a natural assumption always adopted for the development of ENDOR-based microscopic defect models), this leads to the conclusion that the Mn^{2+} is at a substitutional position replacing a Ga atom. Such a conclusion is based on the following reasoning. The fact that the g tensor has cubic symmetry implies that the Mn atom is at a site of T_d symmetry. There are four such positions in the GaAs lattice; substitutional on a Ga or As site, or interstitial

TABLE II. Parameters for the ligand quadrupole interaction tensors for Mn^{2+} and Fe^{3+} centers in GaAs and GaP. Quadrupole parameters q and q' are given in MHz, and θ_Q in degrees.

Host lattice	Impurity	Ligand	q	q'	θ_Q	Ref.
GaAs	Mn^{2+}	^{71}Ga	0.46	0.13	40.9	this
	Fe^{3+}	^{75}As	4.10	0	35.3	6,7
	Fe^{3+}	^{71}Ga	0.05	0	35.3	6,7
GaP	Mn^{2+}	^{71}Ga	0.50	0.10	43.0	17
	Fe^{3+}	^{71}Ga	0.08	0	35.3	6,7

with either Ga or As atoms as the nearest neighbors. For an interstitial position the symmetry of the Ga hyperfine interaction should be trigonal or tetragonal for Ga or As atoms as nearest neighbors, respectively. On a substitutional site the symmetry of the hyperfine interaction with the nearest Ga shell should be trigonal or monoclinic-I, depending on whether the Mn ion substitutes for As or Ga, respectively. The observed symmetry is monoclinic-I, which agrees only with the Mn^{2+} atom on a substitutional Ga position. It can therefore be concluded that the manganese atom in GaAs behaves similarly to iron, occupying the identical lattice site.

B. Localization

From an analysis of the hyperfine constant A of the self-hyperfine interaction of Mn the localization of the paramagnetic electron system on the Mn nucleus itself can be determined. The dominating mechanism for this Fermi-contact interaction is spin polarization of the inner s orbitals by the spin density in the $3d$ shell.[19] A completely localized $3d^5$ shell gives rise to a Fermi-contact interaction of -304 MHz.[20] In addition to the s electrons of the inner shells, electrons localized in the bonds can also contribute to the Fermi-contact term. The electrons in the bonds have no net spin but lead to a partial filling of the Mn $4s$ shell, as is indicated by the degree of covalency of these bonds. The covalency c is defined as[21,22]

$$c=[1-0.16(x_{\mathrm{As}}-x_{\mathrm{Mn}})-0.035(x_{\mathrm{As}}-x_{\mathrm{Mn}})^2]\ , \quad (6)$$

where x_{As} and x_{Mn} are the electron negativities of the As and the Mn atoms, respectively.[23] From $x_{\mathrm{As}}-x_{\mathrm{Mn}}=0.74$ it follows that the bonds between Mn and As have a covalency of 86.4%. This means that Mn has 0.864 electrons localized in the $4s$ shell, whose contribution has to be taken into account. For a $3d^5$ shell completely localized on the Mn core the Fermi-contact contribution of a $4s$ shell with two electrons is $+256$ MHz.[20] The combined contribution of the $1s$, $2s$, $3s$, and partially filled $4s$ shells to the hyperfine constant can then be calculated as $-304+0.864\times0.5\times256$ MHz $=-193.4$ MHz for a fully localized $3d^5$ shell. As the observed hyperfine constant is -162.6 MHz, this implies that the paramagnetic electron system has a localization on the Mn shell of 84%.

To determine the core localization of the GaAs:Fe^{3+} center, it is assumed that for Fe the Fermi-contact interaction due to polarization of the s shells by a $3d^5$ shell is identical to that for Mn with a scaling factor $g_N(^{57}\mathrm{Fe})/g_N(^{55}\mathrm{Mn})$. From the observed hyperfine parameter $A=-15.24$ MHz for $^{57}Fe^{3+}$ in GaAs[24] and the difference in electron negativity between Fe and As of 0.2,[23] a core localization of 65% can be estimated for the Fe^{3+} center in GaAs.

To describe the localization on the ligand atoms, the wave function of the paramagnetic electron system Ψ is approximated by a linear combination of atomic orbitals (LCAO) at the central and ligand atoms. In this case $3d^5$ atomic wave functions for Mn^{2+} and Fe^{3+} sites, and $4s$ and $4p$, and $3s$ and $3p$ for Ga and As, and P, respectively, are used. The wave functions coefficients, η_i for localization, α_i for the s part, and β_i for the p part, are determined by comparing them to the values obtained by Hartree-Fock calculations of the free atom:

$$\eta_i^2\alpha_i^2=\frac{a_i}{a_f}\ , \quad (7)$$

$$\eta_i^2\beta_i^2=\frac{b_i-b_{\mathrm{dd},i}}{b_f}\ . \quad (8)$$

Here a_f and b_f are the free-atom hyperfine parameters.[25] The anisotropic hyperfine parameter b_i is reduced by $b_{\mathrm{dd},i}$, which describes the dipole-dipole interaction, originating from a contribution of the wave function on the central ion. For the whole shell j of ligand the atoms total localization is given by $\eta_j^2=N_j\eta_i^2$, where $N_j=4$ or 12 is the number of atoms in the shell of atom i. In Table III η_j^2, η_i^2, α_i^2, and β_i^2 are given for the first two shells of the Mn^{2+} and Fe^{3+} centers in GaAs and GaP. The data for the first As shell of the GaAs:Mn^{2+} defect are based on estimates as discussed in Secs. IV C and IV D.

From this result it follows that the combined localization of the Mn^{2+} defect in GaAs on the core and the first two shells is 91%, which makes it a very localized defect. For the Fe^{3+} defect in GaAs 78% is localized on the core and on the first two shells. This defect is therefore less localized than the Mn^{2+} center. From Table III it can also be concluded that hardly any differences can be observed for the localization of a Mn^{2+} center in GaAs and GaP.

C. Linewidth

The broadening of the EPR lines of the Mn^{2+} and Fe^{3+} centers in GaAs is caused mainly by unresolved ligand hyperfine interaction. In general, for all ligand atoms the isotropic part of the hyperfine interaction is much larger than the anisotropic one: $a_i \gg b_i$. Under these conditions it is possible to relate the standard deviation ΔB of a Gaussian profile to the isotropic hyperfine parameters. Assuming no crystal-field broadening and equal linewidth of all the components, one obtains

$$(\Delta B)^2=\frac{1}{3g^2\mu_B^2}\sum_i I_i(I_i+1)a_i^2\ , \quad (9)$$

TABLE III. Localization η_j^2 (shell j), η_i^2 (atom site i), and the amount of s and p character (α_i^2 and β_i^2) on the first two shells for Mn^{2+} and Fe^{3+} centers in GaAs and GaP, in percents. For the As shell of GaAs:Mn^{2+}, values estimated from the linewidth and crystal field are used.

Host lattice	Impurity	Ligand	η_j^2	η_i^2	α_i^2	β_i^2
GaAs	Mn^{2+}	^{75}As	3.88	0.97	13.4	86.6
		^{71}Ga	3.46	0.29	34.1	65.9
	Fe^{3+}	^{75}As	5.10	1.27	12.1	87.9
		^{71}Ga	8.19	0.68	10.7	89.3
GaP	Mn^{2+}	^{71}Ga	3.58	0.30	32.2	67.8
	Fe^{3+}	^{31}P	6.35	1.59	11.7	88.3
		^{71}Ga	8.14	0.68	10.7	89.3

where the summation runs over all ligand atoms.

The experimentally observed linewidth at half maximum $(\Delta B)_{FWHM}=5.6\times10^{-3}$ T corresponds to standard deviation $\Delta B=2.38\times10^{-3}$ T and $(\Delta B)^2=5.65\times10^{-6}$ T^2. Using the hyperfine constant a as determined in the ENDOR experiment, the contribution to $(\Delta B)^2$ from the Ga shell can be calculated as $(\Delta B)^2_{Ga}=3.42\times10^{-6}$ T^2. This implies that for the contribution of the As shell $(\Delta B)^2_{As}\leq 2.23\times10^{-6}$ T^2. From this it follows that the maximum value for the isotropic hyperfine interaction with the nearest-neighbor As atoms is 19 MHz. Under the assumption that the paramagnetic electron system of Mn^{2+} is mostly localized within the first two ligand shells, the actual value of the isotropic hyperfine constant of this As shell should be close to this number.

D. Crystal field

The splitting of the ground state, $3a$, depends on the spin-orbit interaction parameter λ, crystal-field splitting parameter $10Dq$, and Coulombic electron-electron interaction characterized by Racah parameters B and C.[26]

The values of a for the Mn^{2+} and Fe^{3+} defects in GaAs can be estimated in the following manner. The values of Dq can be derived as 390 cm^{-1} for Mn^{2+}, and 300 cm^{-1} for Fe^{3+}.[27–29] For such values $n=3$. The value for λ, which is generally 25% less in solids than for the free ion, is estimated as 300 and 330 cm^{-1} for Mn^{2+} and Fe^{3+}, respectively.[26,30,31] For the Racah parameters the values $B=960$ cm^{-1} and $C/B=3.5$ are taken. Using these numbers the crystal-field parameters can be calculated as $a=0.4\times10^{-4}$ cm^{-1} for Mn^{2+}, and $a=0.2\times10^{-4}$ cm^{-1} for Fe^{3+}.[26] These values are much smaller than the ones actually observed in GaAs, which are $a=13\times10^{-4}$ cm^{-1} for Mn^{2+} and $a=340\times10^{-4}$ cm^{-1} for Fe^{3+}. The discrepancy can be explained by taking into account the spin-orbit interaction at the ligand sites[32] which can be much larger than on the central ion due to the contribution from the p orbitals, whose total admixture may be much larger than that of the $^4P_{5/2}$ state. The crystal-field parameter that originates from ligand spin-orbit interaction is then proportional to

$$a \propto \left[\sum_i \lambda_i \eta_i^2 \beta_i^2\right]^4 , \tag{10}$$

where the summation runs over each shell, and λ_i is the spin-orbit interaction of the atoms in shell i. The values of λ for Ga and As are assumed to be equal. If only the first two shells are taken into account, then it is possible from a comparison of the observed p localization in the Ga shell of GaAs:Mn^{2+} and in the Ga and As shells of GaAs:Fe^{3+}, and from the value for a in both materials to make an estimate of the p localization in the As shell of GaAs:Mn^{2+}. From this a localization of 0.84% in the p orbitals per atom is calculated, which corresponds to an anisotropic hyperfine constant $b_i=3.58$ MHz if the dipole-dipole contribution $b_{dd,i}=0.77$ MHz is taken into account.

E. Quadrupole interaction

The quadrupole interaction at the Ga ligand atoms arises from the point charge of the central ion q_c, from the unpaired spin density and corresponding charges in the p orbitals of the Ga atom q_b, and from lattice relaxation q_r.[8] The contribution q_c originates from the electric-field gradient at the Ga atoms due to the charge of the central ion. If the screening of this field gradient by the nearest-neighbor As atoms is neglected,[33] q_c is given by[34]

$$q_c=\frac{ee_cQ(1-\nu_\infty)}{4\pi\varepsilon_0 2I(2I-1)r^3} . \tag{11}$$

Here e_c is the effective charge of the central ion which is taken to be the charge of the core plus the charge of its paramagnetic electron system for as far as it is localized within the nearest-neighbor shell. For ^{71}Ga the nuclear quadrupole moment Q is 0.11×10^{-24} cm^2, and the Sternheimer antishielding factor is $\nu_\infty=-9.8$.[35]

The quadrupole interaction arising from the paramagnetic electron localized in the p orbitals of a ligand atom is related to the measured anisotropic hyperfine constant by[17,32]

$$q_b=\frac{Se^2Q(1-R)}{2I(2I-1)\varepsilon_0\mu_0 g\mu_B g_N\mu_N}(b_i-b_{dd,i}) , \tag{12}$$

with R the atomic antishielding factor, which is -0.13 for Ga,[35] and S the spin of the system.

The contribution from the lattice relaxation q_r originates from movements of the (charged) ligand atoms toward the smaller central impurity ion. In addition to this effect, the relaxation of atoms in the lattice will alter the wave functions of the binding electrons, also leading to an electric-field gradient at the ligand nuclei. This contribution can be considerable, as the quadrupole interaction of a single $4p$ orbital can, with Eq. (12), be calculated as 37 MHz.

The quadrupole interaction at the nearest Ga shell of the Mn^{2+} defect in GaAs is found to be $q=\pm0.46$ MHz. For this center $q_c=-0.02$ MHz and $q_b=0.07$ MHz. In order to account for the observed result q_r has to be equal to 0.42 or -0.51 MHz. Such values can be achieved by assuming a relaxation of the nearest-neighbor As atoms toward the Mn^{2+} ion.

V. CONCLUSIONS

Ligand ENDOR measurements are performed on the nearest Ga shell of Mn^{2+} in GaAs. It is concluded that the Mn^{2+} atom is at a substitutional site replacing a Ga atom. The hyperfine interaction with the nearest-neighbor As atoms is estimated from the EPR linewidth and the crystal-field parameter. The Ga quadrupole interaction can be accounted for by relaxation of the As

atoms toward the central ion. From a comparison with ENDOR measurements performed on the Fe^{3+} center in GaAs and GaP, and Mn^{2+} in GaP all these centers are found to be very similar, with the Fe^{3+} defect having a more delocalized character than Mn^{2+}.

ACKNOWLEDGMENTS

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