

**INTERSTITIAL AND SUBSTITUTIONAL Mn
IN GaAs AND GaP:
MAGNETIC RESONANCE STUDIES**

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ABSTRACT

We report the observation of a new EPR-center in GaAs and GaP. We identified these centers as an interstitial Mn-atom in its 2+ charge state probably surrounded by four nearest neighbor Ga-atoms. In addition we performed ENDOR-measurements on substitutional Mn²⁺ in GaAs, of which we give preliminary results. On the basis of these results we compare the localization of the 3d-electrons for substitutional and interstitial Mn²⁺ in GaAs.

1. Introduction

Transition metal impurities have been studied intensively by magnetic resonance techniques in various crystals [1, 2, 3, 4, 5]. In group IV semiconductors they favor interstitial positions, but have also been observed on substitutional sites [5]. In non-group IV compound semiconductors however, transition metal impurities so far have only been observed on substitutional sites. We report the first observation by electron paramagnetic resonance (EPR) of an isolated transition metal impurity on an interstitial position in a non-group IV semiconductor: Mn²⁺ in GaAs and GaP.

In this paper we will describe new EPR-spectra in GaAs and in GaP and their identification as interstitial Mn. A more extensive analysis of these new spectra will be reported elsewhere [6]. We also performed electron nuclear double-resonance (ENDOR) measurements on substitutional Mn²⁺ in GaAs of which we will give preliminary results. We will make a comparison of the delocalization of the electrons in the 3d-shell for substitutional and interstitial Mn.

2. Experiment

EPR and ENDOR measurements were carried out at K-band ($\nu \cong 23$ GHz) at 4.2K in dispersion mode. The GaAs sample was supplied to us by U. Kaufmann, was LEC grown and doped in the melt with Mn. The total Mn concentration was approximately 10^{17} cm⁻³. The GaP sample was neutron irradiated with thermal neutrons and was not intentionally doped with Mn.

3. Results

The new EPR-spectrum in GaP is shown in fig. 1. We label this spectrum GaP-NL1. The spectrum is isotropic. It clearly consists of six equidistant main lines split by hyperfine-interaction with a 100% abundant I=5/2 isotope. The spectrum is described by the following spin-Hamiltonian:

$$H = g\mu_B \mathbf{B} \cdot \mathbf{S} + AS \cdot \mathbf{I} - g_N\mu_N \mathbf{B} \cdot \mathbf{I}. \quad (1)$$

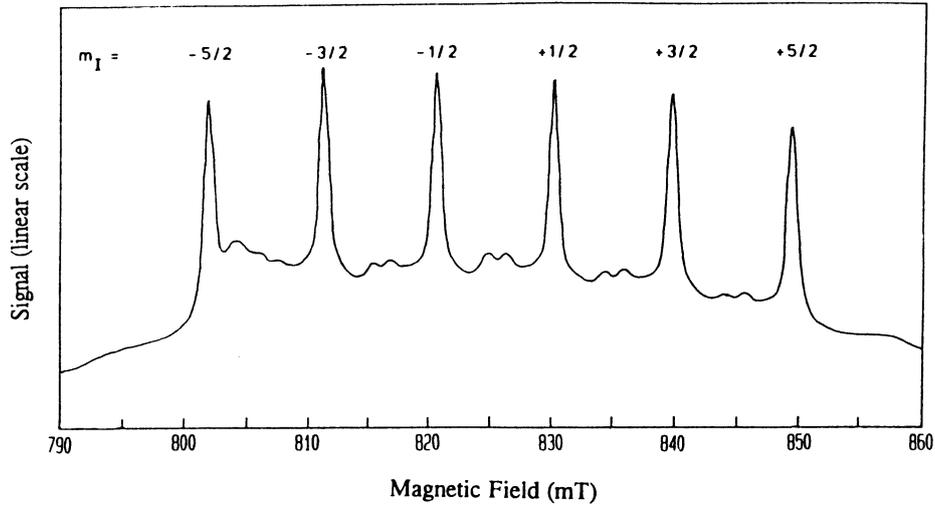


Figure 1: EPR spectrum of the GaP-NL1 center at K-band in dispersion mode at $T=4.2\text{K}$. The allowed $\Delta m_I = 0$ transitions are labelled with their m_I quantum number for the case $g > 0$, $g_N > 0$ and $A < 0$.

From the six main components of the GaP-NL1 spectrum, the following parameters were determined as $I=5/2$, $g = 2.0006 \pm 0.0003$ and $A = \pm 266.4 \pm 0.5$ MHz. In the Mn-doped GaAs sample we recorded a similar spectrum, which we label GaAs-NL1. It is characterized by $g = 2.0001 \pm 0.0003$ and $A = \pm 266.3 \pm 0.5$ MHz. A similar spectrum was also recorded by Wartewig [7] in Cr-doped GaAs and by Schneider [8] in Cr-doped InP. The pairs of small lines between the main lines belong to 'forbidden' $\Delta m_I = \pm 1$ transitions: $|+1/2, m_I\rangle \leftrightarrow |-1/2, m_I - 1\rangle$ and $|+1/2, m_I - 1\rangle \leftrightarrow |-1/2, m_I\rangle$. It will be explained later that these are $m_S = +1/2$ to $m_S = -1/2$ transitions. From the fact that they appear in the middle of the main lines it immediately follows that S is odd. The splitting of these lines ΔB is up to third order in $A/g\mu_B B$ given by:

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

with $b = S(S+1) - (1/4)$ and $c = 2S(S+1) - (3/4)$. For $S=1/2, 3/2$, and $5/2$, this leads to $b = 1/2, 7/2, 17/2$ and $c = 3/4, 27/4, 67/4$, respectively. On the basis of Eq. (2) the effective electron spin and nuclear g -value can be determined as $S=5/2$ and $g_N = 10.5 \pm 0.5$ MHz/T, respectively.

From further ENDOR experiments we could determine A and g_N more accurately to be $A = \pm 266.83 \pm 0.1$ MHz and $g_N = 10.3 \pm 0.4$ MHz/T.

The spin-Hamiltonian (Eq. 1) can not account for the intensities of the observed 'forbidden' transitions. In order to explain the observation of $\Delta m_I = \pm 1$ transitions, generally a cubic or axial crystal field is introduced [9, 10, 11]. Such a crystal field leads to an angular dependence of intensities of the 'forbidden' transitions which we do not observe. In order to explain the occurrence of $\Delta m_I = \pm 1$ transitions we introduce an internal stress, which is randomly distributed in both direction and magnitude. The influence of stress can be incorporated into the Hamiltonian, Eq. 1, by adding an extra term

$$H_{st} = D[S_z^2 - (1/3)S(S+1)]. \quad (3)$$

This randomly distributed stress leads to the observation of 'forbidden' $\Delta m_I = \pm 1$ transitions. 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 [12]

$$R_{01} = \frac{1}{2} \left(\frac{3 \langle D \rangle}{Ag\mu_B B} \right)^2 \left(1 + \frac{S(S+1)}{3m_S(m_S-1)} \right)^2 [I(I+1) - m_I^2 + m_I]. \quad (4)$$

Here $\langle D \rangle$ is the averaged value of D . For the GaP-NL1 spectrum we can determine that $\langle D \rangle \approx 250$ MHz. Such a value for the randomly distributed stress causes all EPR lines except the $m_S = +1/2$ to $m_S = -1/2$ to be broadened by more than 10 mT, so that they are smeared out into a background signal.

Without the random stress incorporated into the spin-Hamiltonian, each line would consist of five lines belonging to the five possible m_S to $m_S - 1$ transitions. Due to second-order effects these 5 transitions would be split by a factor which is proportional to m_I . This splitting would for the GaP-NL1 spectrum be observed as a broadening of the lines, with the outermost lines ($m_I = \pm 5/2$) more broadened than the innermost ones ($m_I = \pm 1/2$). However, since we only observe the $m_S = +1/2$ to $m_S = -1/2$ transitions, this broadening effect does not occur and each line is equally broadened.

The randomly distributed stress also explains why we do not observe a cubic crystal field, which one would expect for a system with $S=5/2$. Such a crystal field demonstrates itself in a $p(\theta)$ angular dependence of the line position of all $\Delta m_I = 0$ transitions except for the $m_S = +1/2$ to $m_S = -1/2$ transitions. For these transitions a cubic crystal field doesn't lead to any angular dependence. Since these are the only transitions we observe, no effect of any crystal field is measured.

4. Identification of interstitial Mn

From the simple hyperfine splitting it follows that the impurity consists of a single atom in a well defined site. The atom involved has a 100% abundant $I=5/2$ isotope with $g_N = 10.3 \pm 0.4$ MHz/T, from which it can be identified as Mn. Mn can have an effective spin $S=5/2$ in its neutral charge state (Mn^0 , electron configuration $[Ar]4s^23d^5$) and in its 2+ charge state (Mn^{2+} , electron configuration $[Ar]3d^5$).

The spectrum is isotropic, so the Mn atom is on a site of T_d symmetry. This can either be a substitutional position, replacing for a Ga or a P atom, or an interstitial position. In the following we will demonstrate on the basis of an analysis of the hyperfine constant A that the GaP-NL1 center is an interstitial Mn atom in its 2+ charge state.

For all Mn centers where the sign of A has been determined, it is negative. We will therefore assume that the sign of A for the GaP-NL1 and the GaAs-NL1 centers is also negative.

The mechanism dominating the hyperfine interaction for a cubic defect with $g \approx 2$ is the Fermi-contact interaction. For Mn the $S=5/2$ state is formed by a half-filled 3d-shell which has no spin-density on the Mn nucleus. The Fermi-contact interaction is then caused by core polarization of the occupied s-orbitals by the electrons in the 3d-shell. For an isolated Mn^0 the 1s-4s shells can be polarized, which leads to a hyperfine constant $A = -48$ MHz, whereas for an isolated Mn^{2+} ion the 1s-3s shells are polarized and $A = -304$ MHz[13]. When an 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 is a neutral Mn atom and we can conclude that it consists of a Mn^{2+} ion.

When a Mn^{2+} ion is placed in a crystal the following mechanisms will decrease the absolute value of A . There may be admixture of a 4s-orbital with non-zero spin density to the wavefunction of the electrons in the 3d-shell. This then leads to direct Fermi-contact interaction. The sign of this interaction is positive, so this leads to a decrease of A . An additional mechanism will decrease $|A|$, when the Mn^{2+} ion is placed on a substitutional site. The Mn will then

form (partly) covalent bonds with its surrounding atoms. These bonds will consist of $4s4p^3$ hybridized orbitals and orbitals from the ligands. These bonds will be filled with electrons which are spin-paired off. The $4s$ -orbital of the Mn is then partially filled, and the electrons in these orbitals can be spin-polarized by the $3d$ -electrons. This contribution has a positive sign and is $+128$ MHz for a fully covalent bond.

A third mechanism which leads to a decrease of $|A|$ for Mn^{2+} in a crystal is the delocalization of $3d$ -electrons. On substitutional sites this delocalization is generally larger when the Mn makes more covalent bonds with its surrounding atoms and it is generally larger for a Mn^{2+} on a substitutional site than on an interstitial site.

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. 2 [14]. The covalency is defined as [15, 16]

$$c = [1 - 0.16(x_A - x_B) - 0.035(x_A - x_B)^2]/z, \quad (5)$$

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

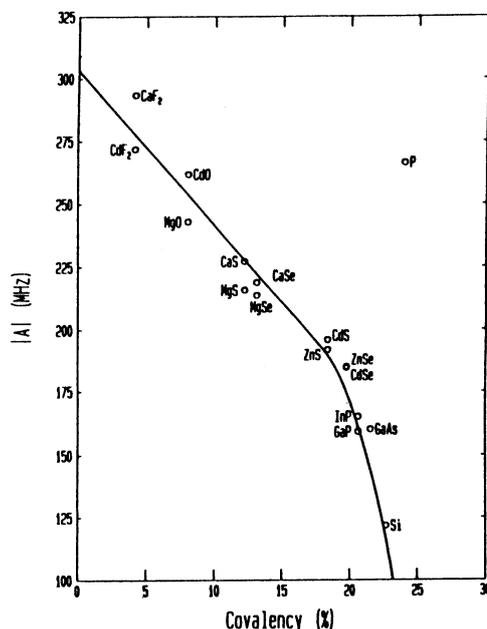


Figure 2: Relation between the absolute value of hyperfine constant A and covalency of bonds between Mn and its nearest neighbors for substitutional Mn in various compounds. The point marked P is discussed in the text.

In Fig. 2 a datapoint is shown for substitutional Mn in GaP and GaAs. These points are taken from the well-known EPR-spectra of substitutional Mn in GaP and GaAs, where the Mn replaces the Ga atom [17, 18]. Since our A value is clearly different from previous substitutional site data, if the new center GaP-NL1 is substitutional Mn, it has to be a Mn^{2+} atom replacing for a P atom. For this model we calculated the covalency [19] and plotted this as datapoint 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 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.

In the GaP lattice there are two possible interstitial sites of T_d symmetry, one with four Ga atoms as nearest neighbors and one with four P atoms as nearest neighbors. In order to determine on which site the Mn^{2+} is located we compare the interstitial Mn^{2+} center in GaP to the one in Si. It can be shown [6] that for Mn^{2+} in Si the 4s admixture with non-zero spin density, as discussed above, is larger than for the GaP-NL1 center.

In order to explain this, the influence of the surrounding atoms on the 4s admixture should be taken into account. We assume that the influence of the outer shells is shielded by the first shell of surrounding atoms, so that the main influence originates from the nearest neighbor shell of atoms.

Let us now consider the difference in electron negativity between Mn and its surrounding atoms. We can expect that a smaller electron negativity of the surrounding atoms compared to the electron negativity of Mn will result in less 4s admixture since the 4s orbitals are localized further from the nucleus than the 3d orbitals. The difference in electron negativity between Si and Mn ($x_{Si} - x_{Mn}$) is 0.52 and between Ga and P and Mn it is 0.18 and 0.82, respectively [19]. The difference in electron negativity is smaller for Ga when compared to Si whereas for P it is larger. Since we have less 4s admixture for interstitial Mn^{2+} in GaP than in Si, this favors Ga atoms to be nearest neighbors.

Summarizing, we have observed in GaP a new spectrum, GaP-NL1, which we identified as interstitial Mn^{2+} probably surrounded by Ga atoms. On the basis of a similar analysis we can also identify the GaAs-NL1 center as interstitial Mn^{2+} surrounded by Ga atoms.

5. Substitutional and interstitial Mn in GaAs

In addition to the experiments on interstitial Mn in GaP and GaAs we performed ENDOR measurements on substitutional Mn^{2+} in GaAs. This center has electron configuration $[Ar]3d^5$. Its EPR spectrum is characterized by $S=5/2$, $g = 2.0023$, $A = -162.6$ MHz and $a = 13 \times 10^{-4} \text{ cm}^{-1}$ (a is the crystal field splitting parameter) [18]. From an analysis of the hyperfine constant A we determined the localization of the $3d^5$ -electrons on the Mn ion to be approximately 80%. From preliminary data of our ENDOR experiment we could in an LCAO approximation estimate the amount of localization on the surrounding atoms. We found that on the first surrounding shell, which consists of four As atoms, on each atom approximately 2% was localized. On the next shell, which consists of twelve Ga atoms the localization was approximately 1% per atom. In the rest of the lattice only a few percent is located total, making this center a very localized defect.

For interstitial Mn in GaAs and GaP the localization is even higher. We found that at least 88% of the $3d^5$ -electrons was localized on the Mn ion [6].

6. Conclusion

We have for the first time observed by EPR a transition metal impurity in a non-group IV semiconductor on an interstitial site, namely Mn^{2+} in GaAs and GaP. The Mn^{2+} was probably surrounded by four Ga atoms as nearest neighbors.

In addition we performed ENDOR measurements on substitutional Mn^{2+} in GaAs. We found that the substitutional Mn was approximately 20% delocalized, whereas the interstitial Mn was maximally 12% delocalized.

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