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Interstitial Mn as a new donor in GaP and GaAs: an EPR study

S.J.C.H.M. van Gisbergen, M. Godlewski [1], T. Gregorkiewicz and C.A.J. Ammerlaan
Natuurkundig Laboratorium der Universiteit van Amsterdam, Valckenierstraat 65, NL-1018 XE Amsterdam, Netherlands

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We report the observation of a new electron paramagnetic resonance centre in neutron-irradiated GaP and a similar new EPR centre in Mn-doped GaAs. Both centres have been identified as interstitial Mn and act as a donor. To our knowledge this is the first observation by EPR of an interstitial transition-metal impurity in a III–V compound. The implication of this new finding on the issue of Mn diffusion is discussed.

1. Introduction

Transition-metal impurities are very common in III–V semiconductors due to their usually high diffusivity and the high abundance of some of their isotopes [1–3]. They give rise to deep levels in the gap and therefore influence the electrical properties of the semiconductors considerably.

Transition-metal impurities in III–V semiconductors have sofar only been observed on substitutional sites replacing for the Group III atom [3]. In this paper we report the first observation by electron-spin resonance (EPR) of a transition-metal impurity on an interstitial site in a III–V semiconductor, namely Mn in GaAs and in neutron-irradiated GaP.

The GaAs sample was LEC-grown and doped in the melt with Mn. The total Mn concentration was approximately 10^{17} cm^{-3}. The GaP sample was unintentionally doped with Mn and neutron-irradiated with thermal neutrons. The ratio between thermal and fast neutrons was about 1000 : 1 and the fluence was 1.4×10^{19} cm^{-2}. The thickness of the sample was 0.3 mm.

Neutron irradiation is often used for neutron transmutation doping (NTD) of Si to obtain n-type material with a homogeneous donor distribution. For III–V materials only recently NTD has attracted some attention. In GaP, thermal neutrons convert Ga atoms into Ge and P into S. Since the cross-section of neutron capture by Ga is about 40 times larger than by P, the GaP is essentially doped with Ge. After neutron irradiation the Ge atoms are on interstitial positions and have to be moved to substitutional positions by annealing for which a typical temperature of 800 °C is used [4].

In this paper we will first show how the identification of the defect was achieved, then we will discuss the influence of the neutron irradiation on the creation of the interstitial Mn and finally we will discuss the implication that the existence of this new centre has on the diffusion of Mn in III–V semiconductors.

2. Identification of the defect

The newly discovered EPR spectrum, labelled GaP-NL1, as recorded in K-band ($\nu \approx 23$ GHz) is depicted in fig. 1. It clearly consists of six equidistant main lines of equal intensity, with pairs of smaller lines in between them. The spectrum is isotropic showing no angular dependence. From this it immediately follows that the observed splitting is due to the hyperfine interaction with a

[1] Permanent address: Institute of Physics, Polish Academy of Sciences, Al. Lotnikow 32/46, 02-668 Warsaw, Poland.

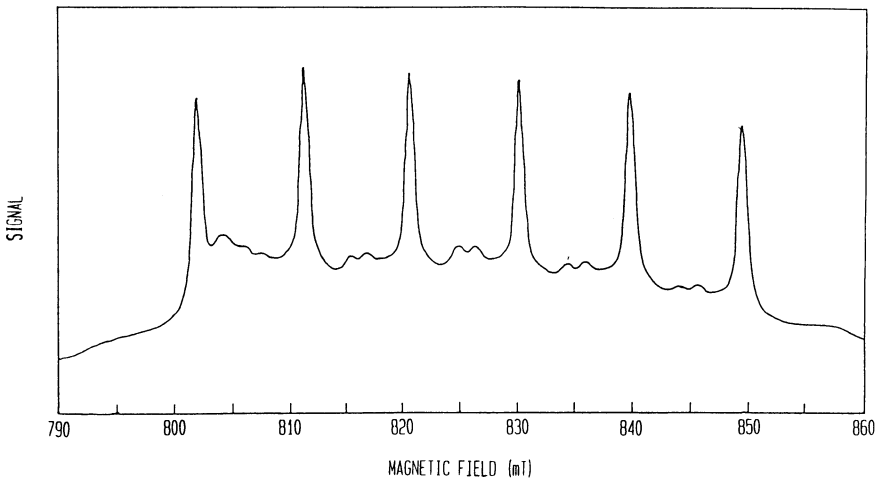

Fig. 1. EPR spectrum of the GaP-NL1 centre at K-band in dispersion mode at $T = 4.2$ K.

100% abundant magnetic nucleus with nuclear spin value $I = 5/2$. The smaller lines are due to spin forbidden $\Delta m_I = \pm 1$ transitions. The spectrum can be described with the following spin-Hamiltonian:

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

From this EPR spectrum and additional electron–nuclear double resonance (ENDOR) measurements the following parameters could be determined: $S = 5/2$, $I = 5/2$, $g = 2.0011 \pm 0.0003$, $A = \pm 266.4 \pm 0.1$ MHz and $g_N = 10.3 \pm 0.2$ MHz/T. From the values of S, I and g_N it immediately follows that the centre consists of a Mn atom in its $+2$ charge state with electron configuration $3d^5$. The simple pattern of the hyperfine splitting indicates that no further magnetic nuclei are involved. Because the spectrum is isotropic the centre consists of a single Mn atom on a site of T_d symmetry. Here three possibilities exist: a Ga site, a P site or an interstitial site. Since the EPR spectrum of Mn on a Ga site has already been observed and is distinctly different from our spectrum, this possibility can be ruled out [5].

Now we will discuss whether the Mn ion is substitutionally on a P site or on an interstitial site. In fig. 2 the relation between the absolute value of the hyperfine constant A and the cova-

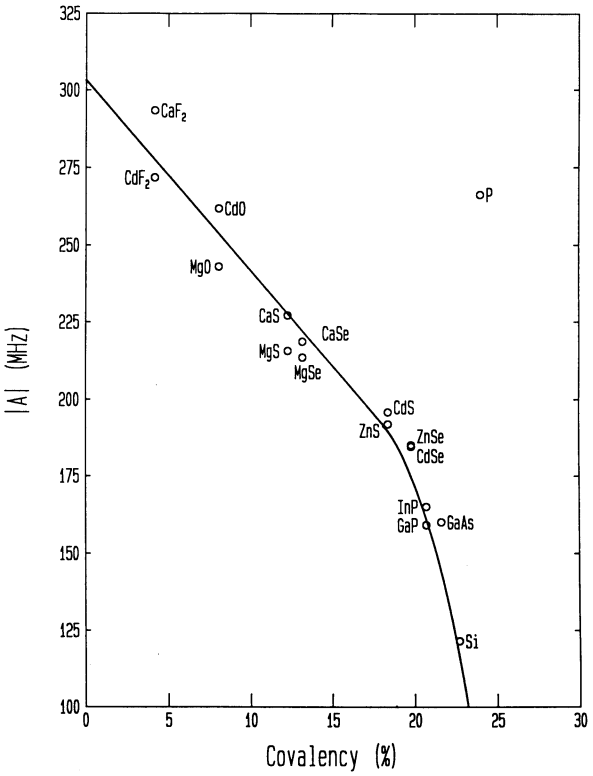

Fig. 2. Relation between the absolute value of hyperfine constant A and covalency of bonds between Mn and its nearest neighbours for substitutional Mn in various compounds. The point marked P is discussed in the text.

lency of the bond between Mn and its ligand is given for substitutional Mn in various compounds [6]. The covalency is defined as [7–9]

$$\left[1 - 0.16(x_A - x_{Mn}) - 0.035(x_A - x_{Mn})^2\right]/c, \quad (2)$$

where x_A and x_{Mn} are the electron negativity of the ligand and Mn ion respectively, and c is the number of ligands. As can be seen from fig. 2 the absolute value of A decreases monotonically with covalency. In this figure we have marked a point P, which was calculated for the model of the GaP-NL1 centre consisting of a substitutional Mn ion on a P site. Since this point lies far outside the curve we conclude this model to be highly unlikely.

For transition-metal impurities on interstitial sites however generally larger values for A are found when compared to substitutional sites [10]. The large value for A is then indicative of a Mn on an interstitial site. From the above-presented reasoning we therefore conclude that the centre consists of a Mn^{2+} ion on an interstitial site of T_d symmetry. In semiconductors interstitial Mn can very well be in its +2 charge state as is the case in Si [10].

On the basis of a further analysis of the hyperfine constant A, the small linewidth and the absence of a crystal field splitting, we further come to the conclusion that the centre is very localized and that the Mn^{2+} ion probably has four Ga atoms as nearest neighbours [11]. We now assume that since the interstitial Mn is very localized, it forms deep levels in the gap. It then probably has only one or two levels in the gap, the Mn^{2+}/Mn^{+} and Mn^{+}/Mn^{0} level, making this defect a single or double donor.

The EPR spectrum as observed for the Mn-doped GaAs sample is shown in fig. 3. When compared to the GaP-NL1 spectrum in fig. 1 an additional spectrum can be distinguished. From the literature it can be identified as originating from substitutional Mn on a Ga site in GaAs [12]. The six sharp lines belong to a new spectrum in GaAs which we label GaAs-NL1. This spectrum is characterized by the same spin Hamiltonian as the GaP-NL1 spectrum with almost identical parameters. Therefore, on the basis of the preceding discussion we can identify it as a single Mn ion in its +2 charge state with electron configuration $3d^5$ on an interstitial site in GaAs probably surrounded by four Ga atoms.

3. Discussion

In the GaP only interstitial Mn was found, whereas in the GaAs sample both interstitial and substitutional Mn were present. Since only the GaP sample was neutron-irradiated, we believe

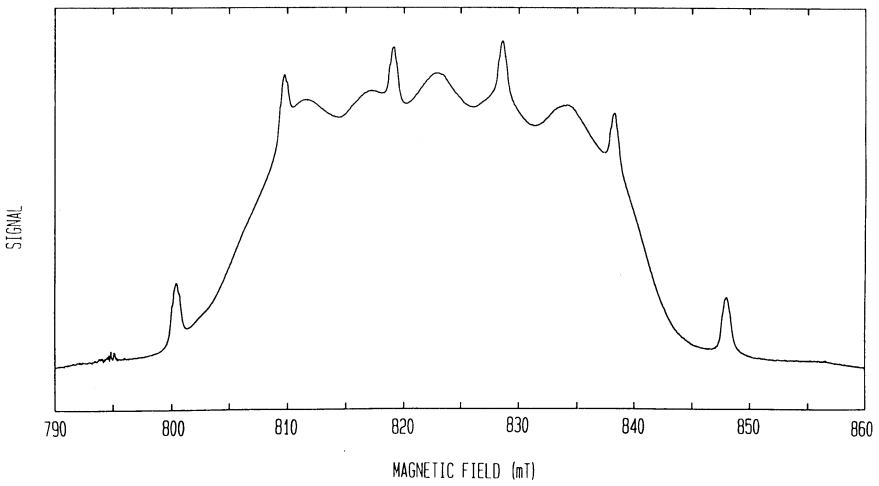

Fig. 3. EPR spectrum of GaAs doped with Mn at K-band for $\boldsymbol{B} \parallel [100]$.

that the neutron irradiation has caused substitutional Mn to move to interstitial positions. The most probable mechanism for this is that β and γ recoil processes, which occur during the transmutation of Ga atoms into Ge by thermal neutrons, are responsible for moving the Mn atoms to interstitial positions. This mechanism can explain the bulk concentration of interstitial Mn in the GaP sample, which was approximately 10^{15} cm^{-3}.

After annealing the sample for 1 h at 800 °C, which was necessary in order to move the Ge atoms from interstitial to substitutional positions, the interstitial Mn was no longer observed.

We will now discuss the influence of interstitial Mn on the diffusion of Mn in III–V semiconductors. The mechanism of diffusion of Mn in intrinsic GaAs is in the literature assumed to be the following [13]: Two arsenic vacancies combine to form a divacancy. This divacancy is the vehicle by which manganese moves from one gallium site to another. The reactions involved are:

$$\mathrm{Mn}_{\mathrm{Ga}}^{-} + 2\,\mathrm{V}_{\mathrm{As}}^{+} \rightleftharpoons (\mathrm{V}_{\mathrm{As}}\mathrm{Mn}_{\mathrm{Ga}}\mathrm{V}_{\mathrm{As}})^{+}, \tag{3}$$

$$(\mathrm{V}_{\mathrm{As}}\mathrm{Mn}_{\mathrm{Ga}_1}\mathrm{V}_{\mathrm{As}})^{+} + \mathrm{Ga}_{\mathrm{Ga}_2} \rightleftharpoons (\mathrm{V}_{\mathrm{As}}\mathrm{Mn}_{\mathrm{Ga}_2}\mathrm{V}_{\mathrm{As}})^{+} + \mathrm{Ga}_{\mathrm{Ga}_1}. \tag{4}$$

The general temperature dependence of the diffusion coefficient can be described by the Arrhenius relationship:

$$D = D_0 \exp(-\epsilon/kT). \tag{5}$$

The activation energy ϵ for the diffusion of Mn in intrinsic GaAs is 2.49 eV [13]. For the diffusion of Mn in heavily doped p-type GaAs however the activation energy is much smaller: $\epsilon = 1.24$ eV [14], and the diffusion goes much faster. The faster diffusion in p-type GaAs is ascribed to a mechanism in which a substitutional manganese captures three holes and forms an interstitial manganese and a gallium vacancy (we assume the charge states to be different than in ref. [14]):

$$\mathrm{Mn}_{\mathrm{s}}^{0} + 3\,\mathrm{p} \rightleftharpoons \mathrm{Mn}_{\mathrm{i}}^{2+} + \mathrm{V}_{\mathrm{Ga}}^{+}. \tag{6}$$

Since the diffusion goes much faster in heavily p-type doped GaAs, we assume that this diffusion mechanism plays a relevant role in p-type material and not in intrinsic material, due to the dependence of the mechanism on the concentration of holes.

For a sample in which the second diffusion mechanism plays a relevant role and which is quenched rapidly from higher temperatures, it is reasonable to assume that it contains some interstitial Mn, as for our sample.

4. Conclusion

We have observed new EPR spectra in GaAs and in neutron-irradiated GaP. The spectra have been identified as interstitial Mn in its +2 charge state on a site of T_d symmetry probably surrounded by four Ga atoms. In the GaP sample the manganese atoms have probably been moved to interstitial positions by β and γ recoil processes associated with the neutron irradiation. The interstitial Mn probably plays an important role in the diffusion process of Mn in III–V semiconductors and can account for the fact that the Mn diffusion is much faster in p-type material than in intrinsic material.

References

[1] Landolt–Börnstein Vol. 2.9, Eds. J. Bartels, H. Borchers, H. Hausen, K.-H. Hellwege, Kl. Schäfer and E. Schmidt (Springer, Berlin, 1962).
[2] Landolt–Börnstein Vol. 22b, Eds. O. Madelung and M. Schulz (Springer, Berlin, 1989).
[3] B. Clerjaud, J. Phys. C 18 (1985) 3615.
[4] A. Huber, F. Kuchar and J. Casta, J. Appl. Phys. 55 (1984) 353.
[5] P. van Engelen and S.G. Sie, Solid State Commun. 30 (1979) 515.
[6] J.C.M. Henning, Phys. Lett. A 24 (1967) 40.
[7] L. Pauling, The Nature of the Chemical Bond, 3rd ed. (Cornell University Press, Ithaca, NY, 1960).
[8] N.B. Hannay and C.P. Smyth, J. Am. Chem. Soc. 68 (1946) 171.
[9] W. Gordy and W.J.O. Thomas, J. Chem. Phys. 24 (1956) 439.
[10] G.W. Ludwig and H.H. Woodbury, in: Solid State Physics, Vol. 13, Eds. F. Seitz and D. Turnbull (Academic Press, New York, 1962) p. 223.
[11] S.J.C.H.M. van Gisbergen, M. Godlewski, T. Gregorkiewicz and C.A.J. Ammerlaan, Phys. Rev. B, submitted.
[12] N. Almeleh and B. Goldstein, Phys. Rev. 128 (1962) 1568.
[13] M.S. Seltzer, J. Phys. Chem. Solids 26 (1965) 243.
[14] E.A. Skoryatina, Sov. Phys. Semicond. 20 (1986) 1177.