RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 40, NUMBER 2 15 JULY 1989-I

Ga_i self-interstitial-related defect in GaP studied by optically detected magnetic resonance

W. M. Chen and B. Monemar
Department of Physics and Measurement Technology, Linköping University, S-581 83 Linköping, Sweden
(Received 17 April 1989)

We report the observation of a Ga_i self-interstitial-related defect in Cu- and Li-codoped GaP, by optical detection of magnetic resonance. This defect has a spin triplet as its lowest electronic excited state, giving rise to a deep midgap photoluminescence band peaking at about 1.05 eV. Strong and nearly isotropic four-line-structured hyperfine splittings resolved in the magnetic resonance spectra identify the Ga_i self-interstitial as part of a complex defect, which has an orthorhombic symmetry. The formation of a family of defect complexes associated with the Ga_i in GaP is also discussed.

Self-interstitials, vacancies, and antisites are the fundamental intrinsic lattice defects in semiconductors. In comparison to vacancies and antisites, which have been investigated intensively over the years in many semiconductors, very little is known about the self-interstitials. Noticeable progress has recently been made, however, with the aid of magnetic resonance techniques, in particular optical detection of magnetic resonance[1-4] (ODMR), and from theoretical calculations.[5] Kennedy and Spencer were able to detect Ga_i interstitials in $Al_{0.26}Ga_{0.74}As$ grown by molecular-beam epitaxy.[2] Rong and Watkins demonstrated the appearance of the isolated zinc interstitial in electron-irradiated ZnSe.[3] Recently, Lee reported the observation of the isolated Ga interstitial in oxygen-doped GaP.[4]

There has been a rapidly increasing interest in defect interactions in semiconductors over the last few years. Most of the intrinsic defects seem to appear in the form of complexes. One typical example is the technologically important defect *EL*2 in GaAs,[6] for which the most common model has been a weakly interacting arsenic-antisite–arsenic-interstitial pair (As_{Ga}-As_i).[7] We recently studied the interaction between the P_{Ga}-antisite and foreign impurities in GaP, and we have observed at least four different P_{Ga}-antisite related complexes, formed after copper and lithium diffusion,[8,9] or gold and lithium diffusion.[10]

In this paper we report on the interaction of the Ga_i self-interstitial with foreign impurities in GaP. A deep center is formed during copper and lithium diffusion, and this defect (denoted as Ga_i-*Y* below) is proved to be related to the Ga_i, giving rise to a strong hyperfine (HF) structured spin-triplet magnetic resonance spectrum, detected optically in the photoluminescence (PL) mode. The only previously identified defect of a similar type in a III-V compound was reported recently by Lee,[4] and by Godlewski and Monemar,[11] who argued that the four-line-HF-structured ODMR spectra in GaP:O were associated with a Ga_i-related defect (denoted as Ga_i-*X* below), challenging the previous interpretation of this spectrum as being related to oxygen.[12]

Different single-crystal GaP starting materials are used in this work, from Zn-doped *p* type, nominally undoped, to S- or Te-doped *n* type, all grown by the liquid encapsulated Czochralski method. They are diffused sequentially with Cu (~950 °C for 1 h) and Li (~400 °C for 4 h).

The ODMR setup employed in this work is a modified Bruker electron-spin-resonance (ESR) X-band spectrometer (Bruker 200-SRC) equipped with an Oxford ESR 10 continuous-flow helium cryostat and a cylindrical TE_{011} microwave cavity with optical access from all directions. The sample temperature can be varied from room temperature down to about 2 K with the aid of a second pump line. An Ar^+ laser (5145-Å line) or a Kr^+ laser (6471-Å line) was used to achieve above- or below-band-gap optical excitation, respectively. The photoluminescence signal was collected by a liquid-nitrogen-cooled Ge detector (North-Coast EO 817). The microwave-induced changes in the PL were detected by a lock-in technique, in phase with the chopped microwave radiation. For spectral studies the PL signals were dispersed by a 0.25-m Jobin-Yvon grating monochromator, before the detector.

In Fig. 1 we show ODMR spectra from the Ga_i-*Y* defect when the magnetic field **B** is along the ⟨100⟩ and the ⟨110⟩ crystalline directions. Such ODMR spectra have been consistently observed in both undoped and Te-doped GaP after Cu and Li diffusion. The strongest ODMR signals were obtained in *n*-type GaP with a Te concentration of about 7×10^{16} cm^{-3}. The ODMR signals were observed both by above-band-gap and by below-band-gap optical excitation. The optimized sample temperature was around 9 K, in order to suppress the background ODMR signals of another origin which dominated at lower temperatures.[13]

To investigate the defect center responsible for the observed ODMR transitions, we have studied the spectral dependence of the ODMR signal [Fig. 2(b)]. Clearly the broad PL band peaking at ~1.05 eV is responsible for the ODMR. The microwave-induced resonant transitions give rise to an increase in the PL intensity of the 1.05-eV band, i.e., a positive ODMR signal. In the same figure [Fig. 2(a)], we show a PL spectrum of the same sample in the midgap spectral region with above-band-gap excitation, with the same spectra resolution as that in Fig. 2(b). Besides the 1.05-eV PL band, there are two other broad PL bands appearing within the spectral region, one peaking at ~1.13 eV and the other at the lower-energy side of the 1.05-eV band. The former corresponds to a donor-

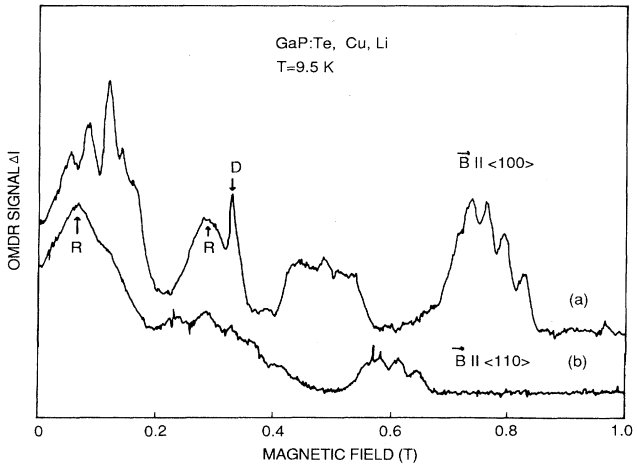

FIG. 1. ODMR spectrum for the Ga_i-Y defect in GaP taken at 9.5 K and 9.2 GHz with (a) $\mathbf{B}\|\langle 100\rangle$ and (b) $\mathbf{B}\|\langle 110\rangle$, by detecting the entire PL emission in Fig. 2(a) with a cooled Ge detector. The Ga_i (nuclear spin $I=\frac{3}{2}$ for both naturally abundant isotopes ^{69}Ga and ^{71}Ga) central hyperfine structure is clearly resolved. A donor resonance D ($g\approx 2$) and a background from other defects R can also be seen in the spectrum.

acceptor pair emission associated with the shallow Te donors, which gives rise to an isotropic donor resonance signal ($g\approx 2$) in the ODMR spectrum (as shown in Fig. 1), commonly observed for Te-doped GaP crystals. The latter PL band originates from the so-called P_{Ga}-B complex,[9] as evident from its characteristic ODMR spectrum

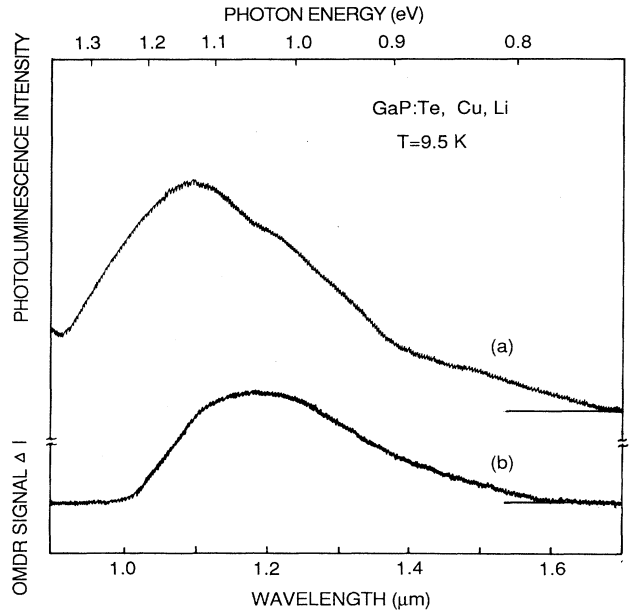

FIG. 2. (a) Midgap photoluminescence spectrum of Cu-Li-diffused bulk GaP:Te, taken at 9.5 K with Ar^+-laser optical excitation (5145-Å line). (b) Spectral dependence of the ODMR signal from the Ga_i-Y defect as shown in Fig. 1, taken at 9.5 K with the same spectral resolution as that in (a).

observed in the same crystal at a different temperature.

The angular dependence of the Ga_i-Y ODMR spectrum was measured, when $\mathbf{B}$ is rotated in the $(1\bar{1}0)$ crystalline plane. The experimental data can be fitted by a spin Hamiltonian for a spin triplet:

$$H_s=\mu_B\mathbf{B}\cdot\mathbf{g}\cdot\mathbf{S}+\mathbf{S}\cdot\mathbf{D}\cdot\mathbf{S}+\mathbf{I}\cdot\mathbf{A}\cdot\mathbf{S}. \quad (1)$$

The first and second terms are the linear electronic Zeeman and fine-structure terms, respectively. The third term describes the central hyperfine (CHF) interaction between an electronic spin $\mathbf{S}$ and a nuclear spin $\mathbf{I}$. $S=1$ for the spin triplet and $I=\frac{3}{2}$ is immediately deduced from the overall four-line CHF splitting in the ODMR spectra. A basis set of wave functions, $|S=1,M_S,I=\frac{3}{2},m_I\rangle$ (where $M_S=-1,0,+1$ and $m_I=-\frac{3}{2},-\frac{1}{2},+\frac{1}{2},+\frac{3}{2}$), was used in the diagonalization of Eq. (1) with the aid of a computer program. The evaluated spin-Hamiltonian parameters are given in Table I.

The electronic g value obtained for the Ga_i-Y center is nearly isotropic and close to $+2$, as commonly observed for spin triplets in GaP.[14] The fine-structure D tensor is very anisotropic and of a large magnitude, however, reflecting a strong low-symmetry crystal field (whose origin will be discussed in more detail below). The CHF tensor is found to be nearly isotropic with $A_1=4.0\times10^{-6}$ eV. Overlapping with it, another isotope of $I=\frac{3}{2}$ is present, whose A-tensor amplitude is evaluated to be about $A_2=5.0\times10^{-6}$ eV. They are argued below to arise from the two naturally abundant Ga isotopes, ^{69}Ga (60.4%) and ^{71}Ga (39.6%), both with a nuclear spin of $\frac{3}{2}$. The symmetry for the Ga_i-Y center is deduced, from the angular dependence of the ODMR spectra, to belong to the symmetry group C_{2v}. The crystal field is strongest, however, along the $\langle 100\rangle$ crystalline direction.

Based on the present experimental data the electronic structure of the Ga_i-Y defect can be discussed either in terms of a two-electron model or in terms of a deep bound-exciton (BE) model. In the first model the observed 1.05-eV PL emission is interpreted as a radiative transition between an excited state of the Ga_i^+ (denoted as Ga_i^{+*}) to the ground state of Ga_i^+, i.e.,

$$Ga_i^{+*}\rightarrow Ga_i^{+}+h\nu. \quad (2)$$

The first bound electron in this case should lie at an a_1

TABLE I. The spin Hamiltonian parameters for the Ga_i-Y defect in GaP, where $x=[110]$, $y=[\bar{1}10]$, and $z=[001]$.

Parameters	Values
g tensor	
$g_x=g_y=g_z$	2.0
D tensor (10^{-5} eV)	
D_x	−1.14
D_y	−2.33
D_z	3.47
A tensor (10^{-6} eV)	
A_1 (^{69}Ga)	4.0
A_2 (^{71}Ga)	5.0

state to account for the nearly isotropic and strong CHF interaction, whose magnitude is close to one-half of that for the same electron bound to the isolated T_d-site Ga_i in its Ga_i^{2+} charge state ($^2A_1$).[4] This is due to the relation $\mathbf{A}=(\mathbf{A}_{e1}+\mathbf{A}_{e2})/2$, i.e., the magnitude of the resultant A tensor for the spin triplet should be one-half of the sum of the A tensors for the two electrons, provided that the second electron is loosely bound and the influence from the coupling term related to $\Delta\mathbf{A}=(\mathbf{A}_{e1}-\mathbf{A}_{e2})/2$ is negligible. The observed strongly anisotropic D tensor and the low symmetry for this defect would have to be explained in terms of a large lattice distortion (due to, e.g., the Jahn-Teller effect) driving the Ga_i away from its T_d site.

There are some difficulties in explaining the experimental results on basis of the above model, however. First of all, transitions between two-electron states are, in general, believed to be nonradiative (Auger type), in contrast with the quite strong PL emission observed for the Ga_i-Y defect. Also, if the spin triplet of the excited Ga_i^{+*} state originates from the excited state of the primary bound electron, the CHF interaction would be expected to differ from half the value of that in its Ga_i^+ ground state, which is not the case. Furthermore, the excited state of the second electron could not explain the large energy separation of 1.25 eV from its ground state, since this electron is believed to be loosely bound at the Ga_i^+, as evident from its negligible contribution to the CHF splitting. In view of these facts the model of a defect complex (to be discussed below) seems to be more likely in this case.

In the second model, a BE recombination (annihilation of an interacting electron-hole pair) at the Ga_i-Y defect complex is considered to be responsible for the 1.05-eV PL band. Here Y represents an acceptor part of the complex. A hole tightly bound to such a defect may readily have a quenched orbital angular momentum, in the presence of a dominating low-symmetry crystal field.[15] The deep BE at the Ga_i-Y complex, composed of a hole with a quenched orbital angular momentum and a primarily bound electron centered at the Ga_i (in the Ga_i^{2+} state), may produce a spin singlet-triplet pair at its lowest-excited state, with the triplet lying at lower energy.[14] The g tensor for such a spin triplet is related to the corresponding quantities for the individual particles by $\mathbf{g}_{ex}=(\mathbf{g}_e+\mathbf{g}_h)/2$, where $\mathbf{g}_{ex}$, $\mathbf{g}_e$, and $\mathbf{g}_h$ denote the g tensor for the BE, the electron, and the hole, respectively. The observed nearly isotropic $\mathbf{g}_{ex}$ of about $+2$ agrees well with the model of the deep BE, where the quenching of the hole orbital angular momentum is nearly complete, giving rise to $g_h \approx 2$. The electron g value is commonly observed to be around $+2$ in GaP,[16] both for shallow and deep donors. The strong fine-structure interaction (strongest for all spin-triplets in GaP observed so far) is induced mainly by the magnetic dipole-dipole interaction between the electron and the hole and by a possible spin-orbit coupling for the hole.[17] However, we believe the former cause is dominant in this case.

The key results from the ODMR study is the resolved four-line-structured CHF splitting, indicating the involvement of a defect atom with a nuclear spin of $\frac{3}{2}$. In the samples under study, there are three types of atoms present which all have a nuclear spin of $\frac{3}{2}$, i.e., Ga [^{69}Ga (60.4%) and ^{71}Ga (39.6%)], Cu [^{63}Cu (69.2%) and ^{65}Cu (30.8%)], and Li [^{7}Li (92.5%)]. The Cu atoms can be excluded because the ratio of the nuclear gyromagnetic moments between the two isotopes, about 1.071, disagrees with the observed value of about 1.25. (The other isotope of the Li atom, ^{6}Li, has a nuclear spin of 1 and natural abundance of 7.5%, which disagrees from the experimental observations.) The ratio of the nuclear gyromagnetic moments of 1.271 for Ga is indeed, within experimental error, consistent with the experimental value of 1.25. Theoretical expectations predicted that a Ga_P antisite should have a T_2 state in which the spin density has a node at the center,[5] which cannot explain the strong and nearly isotropic CHF interaction observed in the experiments. The only plausible candidate is a Ga_i. Theory did predict an A_1 state for the T_d-site Ga self-interstitials,[5] which is in full agreement with the experimental data. The observation of an A value nearly half of the A value for the isolated Ga_i (Ref. 5) further supports the model.

It is interesting to note the close similarity of the Ga_i-Y defect studied in this work with the Ga_i-X defect reported previously.[12] Firstly, they both give rise to PL bands in the midgap region with an energy difference less than 0.3 eV, indicating their similar binding energies. This might be explained by the argument that the defect potential is predominantly induced by the Ga_i^{2+}. A similar situation was observed for P_{Ga}-related complexes, all of which exhibited similar binding energies due to the dominating potential of the P_{Ga}^{4+}.[8-10] Secondly, the PL bands associated with the two Ga_i-related defects are both featureless with a half width (full width at half maximum) of about 250 meV. This implies that they have similar strength in coupling to the lattice.

In conclusion, we have studied a Ga_i self-interstitial-related defect named Ga_i-Y in GaP, which has a spin triplet in its electronic excited state, by optically detected magnetic resonance. The radiative transition of this center gives rise to a PL band peaking at 1.05 eV, with zero-phonon electronic transition energy at around 1.25 eV. The assignment of the Ga_i as a constitute of the defect has been identified unambiguously by the central-hyperfine structure resolved in the experiments. This work belongs to one of very few cases in semiconductors where the self-interstitial is clearly identified. The results demonstrate the tendency of pairing of Ga_i with other defects to form complexes. Further work on the kinetics of the defect formation and on the ligand hyperfine structure by optically detected electron and nuclear double resonance (ODENDOR) is highly desired, as well as theoretical calculations.

We are grateful to H. P. Gislason and M. Linnarsson for providing some of the GaP samples used in this investigation.

[1]K. M. Lee, K. P. O'Donnell, J. Weber, B. C. Cavenett, and G. D. Watkins, Phys. Rev. Lett. **48**, 37 (1982).

[2]T. A. Kennedy and M. G. Spencer, Phys. Rev. Lett. **57**, 2690 (1986).

[3]F. Rong and G. D. Watkins, Phys. Rev. Lett. **58**, 1486 (1987).

[4]K. M. Lee, in *Defects in Electronic Materials,* edited by M. Stavola, S. J. Pearton, and G. Davies, Materials Research Society Symposia Proceedings, Vol. 104 (Materials Research Society, Pittsburgh, 1988), p. 449.

[5]G. A. Baraff and M. Schlüter, Phys. Rev. Lett. **55**, 1327 (1985).

[6]G. M. Martin and S. Makram-Ebeid, in *Deep Centers in Semiconductors,* edited by S. Pantelides (Gordon and Breach, New York, 1986), p. 389.

[7]H. J. von Bardeleben, D. Stievenard, J. C. Bourgoin, and A. Huber, Appl. Phys. Lett. **47**, 970 (1985).

[8]W. M. Chen, H. P. Gislason, and B. Monemar, Phys. Rev. B **36**, 5058 (1987).

[9]W. M. Chen, B. Monemar, and M. Godlewski, Phys. Rev. B **37**, 2564 (1988).

[10]W. M. Chen, B. Monemar, and M. E. Pistol, Mater. Sci. Forum **38–41**, 899 (1989).

[11]M. Godlewski and B. Monemar, Phys. Rev. B **37**, 2752 (1988).

[12]M. Gal, B. C. Cavenett, and P. Smith, Phys. Rev. Lett. **43**, 1611 (1979).

[13]The existence of such an optimum temperature is due to the fact that the time constants (e.g., lifetimes, spin-lattice relaxation times, spin-flip times, etc.) of different radiative centers are in general quite different. This is similar to the case of P_{Ga}-related complexes in GaP (see Ref. 9).

[14]W. M. Chen, M. Godlewski, B. Monemar, and H. P. Gislason, in Ref. 4, p. 443.

[15]B. Monemar, U. Lindefelt, and M. E. Pistol, J. Lumin. **36**, 149 (1986).

[16]See, e.g., *Landolt Börnstein: Numerical Data and Fundamental Relationships in Science Technology,* edited by O. Madelung, M. Schnitz, and H. Weiss (Springer-Verlag, Berlin, 1980), Vol. 17.

[17]B. Monemar, W. M. Chen, and M. Godlewski, Mater. Sci. Forum **38–41**, 769 (1989).