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P_{Ga}-antisite-related neutral complex defect in GaP studied with optically detected magnetic resonance

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A triplet ($S=1$) spectrum for a deep P_{Ga}-antisite-related complex defect in (Cu,Li)-codoped GaP has been studied with optical detection of magnetic resonance. The defect has a ⟨110⟩ orientation, and a hyperfine interaction in agreement with P_{Ga} is clearly resolved, although the magnitude of the $\vec{A}$ tensor is considerably reduced compared to the isolated P_{Ga} defect. The electronic structure of the defect is consistent with a strongly localized electron-hole pair, recombining radiatively at a neutral defect, suggested to be a P_{Ga}-Cu_{Ga} pair. The anisotropic behavior of the $\vec{g}$ tensor (and in part the $\vec{D}$ tensor) is explained as mainly due to a residual spin-orbit interaction of the bound hole.

Anion antisite defects in III-V semiconductors are of considerable fundamental and technological interest. Isolated, such defects were predicted to be stable in III-V materials,[1] and have since been identified experimentally in several compounds, such as GaP,[2] GaAs,[3] and InP.[4] The isolated anion antisite defects are generally concluded to be nonradiative recombination centers, from studies of optically detected magnetic resonance (ODMR) in GaP (Refs. 5 and 6) and GaAs.[7] In these materials, the singly ionized deep donor state in a cubic symmetry was shown to be involved.[5-7]

In addition to isolated antisite defects, complexes of the P_{Ga} defect and unidentified impurities have been observed in GaP, by electron paramagnetic resonance (EPR) ($S=\frac{1}{2}$),[8] and ODMR ($S=1$).[5] Both these defects give resonance spectra with a resolved ligand hyperfine (hf) structure due to interaction of P_{Ga} with three nearest-neighbor P atoms. The electronic structure of these defects is not understood in detail.[5,8] A neutral complex defect tentatively identified as the Cu_{Ga}-As_{Ga} pair has recently been studied in GaAs.[9]

In this Rapid Communication, we report ODMR data for another deep neutral isolated complex in GaP, shown to be antisite related with a resolved central hyperfine interaction from the P_{Ga} nuclear spin. The defect has been observed only in bulk GaP, diffusion doped with both Cu and Li. The center gives preferentially radiative recombination, unlike isolated antisite centers in GaP, from an excited $S=1$ triplet "bound-exciton" state to a spin-free $S=0$ ground state of the defect. The defect is ⟨110⟩ oriented, characteristic of a substitutional pair on one sublattice. It is argued that the defect identity is Cu_{Ga}-P_{Ga} at nearest-neighbor sites, allowing both electron and hole to be strongly localized at the defect. The ODMR data presented below allow the deduction of a consistent model of the electronic structure of the defect.

The samples used in this investigation were prepared from nominally undoped liquid-encapsulated-Czochralski-(LEC) grown GaP, diffusion doped sequentially with Cu and Li, as previously described.[10] ODMR measurements were performed at temperatures around 4 K in a 9-GHz cylindrical cavity, with a modified Bruker 200-SRC ESR spectrometer. The photoluminescence (PL) signal was detected with a cooled North Coast EO-817 Ge detector, via a Jobin-Yvon 0.25-m grating monochromator.

In the near-band-gap energy region these samples show PL spectra related to neutral complexes involving both Cu and Li. Optical spectra and ODMR data for these defects are reported separately.[10,11] In the midgap energy region, strong broad PL bands appear in these samples, as shown in Fig. 1. The PL spectrum of particular interest in this work has a no-phonon region at about 1.3 eV, and the associated broad phonon wing peaks at about 1.05 eV (Fig. 1).

Strong ODMR signals were observed with PL detection in the broad band of Fig. 1; the resonances were due to an enhancement of the PL signal. Typical examples of such ODMR spectra are shown in Fig. 2 for the magnetic field

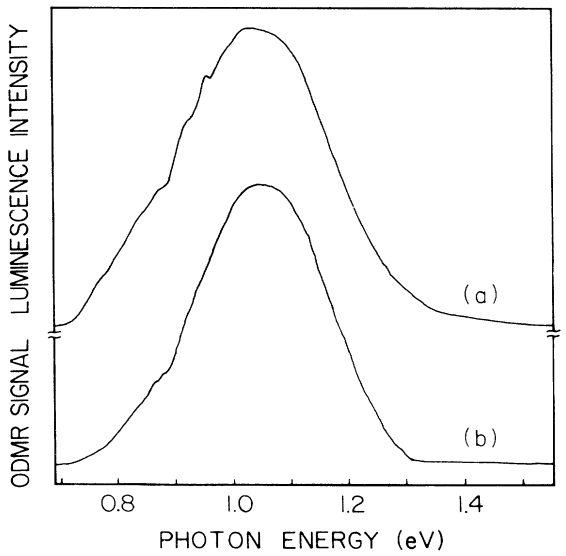

FIG. 1. (a) Infrared photoluminescence spectrum at 4 K of Cu-Li diffusion-doped bulk GaP. (b) Spectral dependence of the ODMR signal (see Fig. 2) at 4 K, showing that the entire PL spectrum in (a) is contributing to the ODMR.

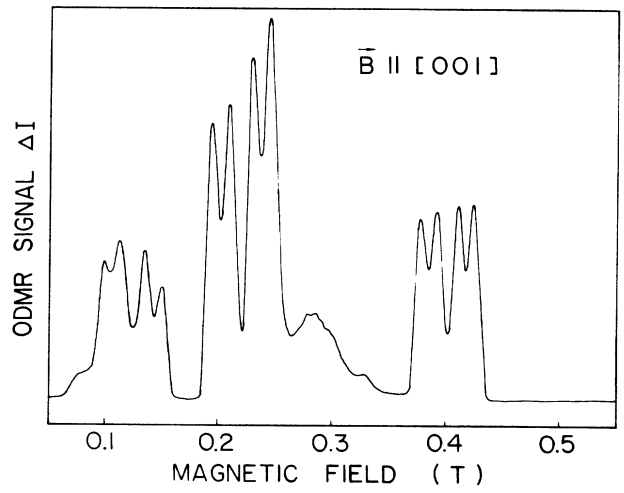

FIG. 2. ODMR spectrum taken at 4 K and 9.23 GHz with **B** ∥ [001], by detecting the entire PL band in Fig. 1 with a Ge detector. The P_{Ga} (nuclear spin $I=\frac{1}{2}$) central hyperfine structure is resolved. The weak background in the spectrum is due to overlap with similar spectra from other complex defects.

B along the [001] crystalline axis of the sample. The weaker background in the spectrum is due to overlap with other Cu- and Li-related spectra which give dominating ODMR signals at elevated temperatures.[12,13] The spectral dependences of these Cu- and Li-related ODMR signals coincide with the broad PL spectrum in Fig. 1. The angular dependence of the ODMR spectrum was measured in detail, as shown in Fig. 3. A computer fit of the experimental data was performed, using a general spin Hamiltonian for a spin triplet ($S=1$):

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

The first and second terms are the linear Zeeman and fine-structure terms, respectively; the third one describes the hyperfine interaction between a "spin" **S** of electronic origin and a nuclear-spin **I**. A basis set of spinlike wave functions for both electrons and holes was used in the diagonalization of Eq. (1). The evaluated parameters of the Hamiltonian in Eq. (1) are given in Table I, for best fit to the data.

An inspection of Fig. 3 suggests that a hyperfine interaction with a nucleus with spin $I=\frac{1}{2}$ is present, from the doublet splitting of all resonances. This spectrum also shows that the nucleus should have a 100% abundance, i.e., P atoms are the only natural candidates. The maximum splitting along [110] in Fig. 3, together with the nearly axial behavior of both $\vec{\vec{g}}$ and $\vec{\vec{D}}$ tensors, immediately suggests that the defect should be a ⟨110⟩-oriented substitutional pair. In this case P_{Ga} should be one of the constituents, since a complex involving interstitial P is unlikely in this case, considering the determined defect symmetry. P_{Ga}-antisite defects are expected to be present in the LEC bulk GaP material used in this work. The other constituent of the pair is believed to be Cu_{Ga}, introduced by the Cu diffusion.

The parameters in Table I allow interesting conclusions to be drawn on the electronic structure of the corresponding defect. The spin triplet can be considered to originate from a bound electron-hole pair, involving a spinlike hole

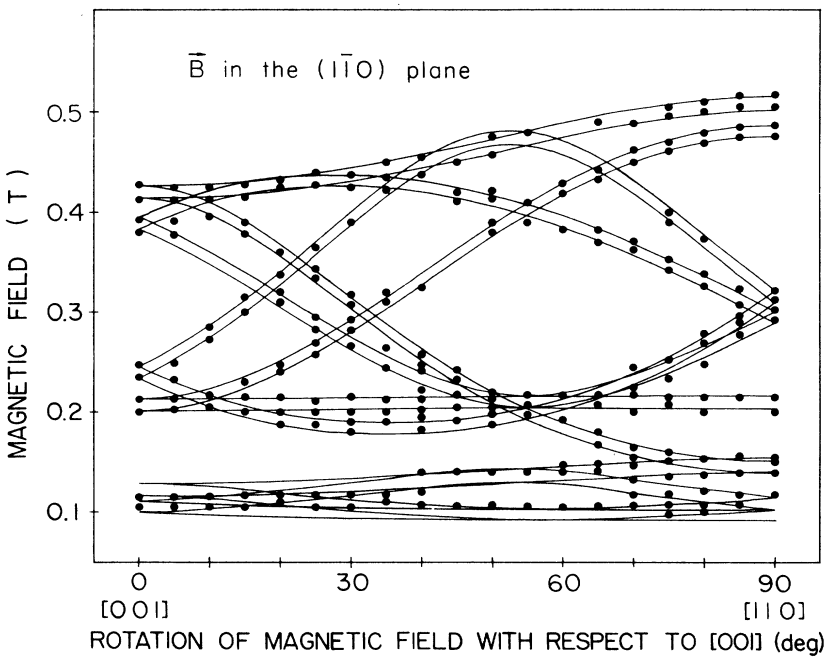

FIG. 3. Angular dependence of the ODMR spectrum, such as the one shown in Fig. 2, for rotation of the sample with **B** in the (1$\bar{1}$0) plane. The dots show experimental data after exclusion of the contributions from weak overlapping spectra from other complex defects. The full lines are calculated from a Hamiltonian, with parameters given in Table I.

TABLE I. Spin Hamiltonian parameters for the P_{Ga}-antisite complex in GaP discussed in this work.

Major defect axes	$\vec{g}$ tensor	$\vec{\vec{D}}$ tensor	$\vec{\vec{A}}$ tensor
$\hat{x} \parallel [001]$	$g_x = 1.96$	$D_x = 0.93 \times 10^{-5}$ eV	$A_x = 1.6 \times 10^{-6}$ eV
$\hat{y} \parallel [1\bar{1}0]$	$g_y = 1.72$	$D_y = 0.75 \times 10^{-5}$ eV	$A_y = 1.1 \times 10^{-6}$ eV
$\hat{z} \parallel [110]$	$g_z = 2.27$	$D_z = -1.68 \times 10^{-5}$ eV	$A_z = 1.4 \times 10^{-6}$ eV

and a spinlike electron. Spinlike holes occur when the bound hole states become orbitally nondegenerate through the action of a local strain field of low symmetry, which dominates over the spin-orbit interaction on the hole.[14] The rather strong residual anisotropy of the $\vec{g}$-tensor $\vec{g}_{ex}$ observed in this case (about $\pm 14\%$) is interpreted as mainly due to the bound hole. The observed effective $\vec{g}$ tensor can, to a good approximation, be written as $\vec{g}_{ex} = \frac{1}{2}(\vec{g}_e + \vec{g}_h)$, where $\vec{g}_e$ and $\vec{g}_h$ are the individual $\vec{g}$ tensors for electron and hole, respectively, provided that the electron-hole exchange interaction is large, so that the singlet state $S=0$ does not interfere with the triplet.[15,16] The bound electron could in principle also have some spin-orbit-induced anisotropy, but such effects have not previously been observed to be important in GaP.[2-4,15] The magnitude of the observed g shift points to a bound hole state with intermediately strong localization, also experiencing a local strain field of moderate strength,[14] while the electron is regarded as the most strongly bound particle, as may be expected for a P_{Ga} complex.[5,6] The $\vec{\vec{A}}$ tensor is anisotropic, which may be understood by considering the total bound-exciton (BE) wave function rather than the wave function for a single bound electron. The numerical values found for the $\vec{\vec{A}}$ components are about a factor of 3 smaller than what has previously been observed for P_{Ga} complexes.[5] We tentatively interpret this observation as an effect of the close nearest-neighbor configuration of the P_{Ga}-Cu_{Ga} pair, whereby the strength of the P_{Ga} donor impurity potential is partly canceled by the rather strong hole-attractive Cu_{Ga} potential nearby.

The $\vec{\vec{D}}$ tensor is diagonalized with the same principal axes as the $\vec{g}$ tensor; its magnitude is about a factor of 3 larger than for the P-$P_3(Y)$ defect previously studied.[5] This is expected if the $\vec{\vec{D}}$ tensor has a strong contribution from spin-orbit interaction effects for one or both bound carriers, in agreement with the large g shift found in this work [but not for the P-$P_3(Y)$ defect].[5] The contribution to $\vec{\vec{D}}$ from electron-hole magnetic dipole-dipole interaction should also be important in this case, since both carriers are rather strongly localized. The sign of the components of the $\vec{\vec{D}}$ tensor were determined by monitoring the circular polarization of the PL at resonance in the Faraday configuration, using a photoelastic modulator.

The relatively strong effects of spin-orbit interaction on the $\vec{g}$ and $\vec{\vec{D}}$ tensors in this work are consistent with the model of a substitutional pair as the defect identity. In this case only a moderately strong local strain field is expected, compared to the case of neutral complex defects involving interstitials,[12,15] where the local strain field is generally expected to be very strong. A weaker local strain field combined with a reasonably strong localization of the bound hole gives rise to a rather strong spin-orbit-induced coupling between the spin triplet and the excited states of the bound exciton, which are split off by the local strain field.[14]

The conclusions drawn in the above discussion are consistent with a geometrical model for the defect as a P_{Ga}-Cu_{Ga} pair. P_{Ga} is a double donor and Cu_{Ga} a double acceptor in GaP; both give rise to deep levels as isolated defects. A complex of Cu_{Ga}-P_{Ga} is therefore a neutral defect. The ground state of such a defect is most naturally suggested to be the case of full charge transfer between the P_{Ga} and Cu_{Ga} atoms, to complete the bonds locally. The P_{Ga} electron-attractive potential would be weakened by Cu_{Ga}, but obviously would still dominate the complex. The electron would be bound in a slightly more shallow state than for the case of isolated P_{Ga}, as evident from the binding energy of the BE and from the reduced value of the hf interaction compared to PP_4.[5,6] Likewise, the binding energy for the bound hole would be decreased from the case of isolated Cu_{Ga}.[17] The sum of the binding energies for isolated P_{Ga} and Cu_{Ga} is $(1.1+0.5) \approx 1.6$ eV, while the same sum for the P_{Ga}-Cu_{Ga} pair bound exciton studied in this work is about 1.0 eV.

In summary, we present in this communication the first results of a study of an antisite-related neutral complex defect in GaP, argued to be the P_{Ga}-Cu_{Ga} substitutional pair. The ODMR data presented here are related to an excited state of the defect, comprising a strongly bound electron-hole pair. The internal structure of this $S=1$ state is determined in detail by the data, and is also explained in terms of a realistic physical model for such a strongly localized electron-hole pair. A more detailed account of the ODMR data of this defect will be published later.

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