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OPTICAL DETECTION OF MAGNETIC RESONANCE FOR D-A RECOMBINATION LUMINESCENCE IN 6H-SiC*

G. D. Watkins,[(a)] Le Si Dang,[(a)†] K. M. Lee,[(a)] W. J. Choyke[(b)]

(a) Department of Physics, Lehigh University
Bethlehem, PA 18015, USA
(b) Westinghouse Research and Development Center
Pittsburgh, PA 15235, USA

ODMR is reported for donor-acceptor pair luminescence in 6H SiC containing nitrogen and aluminum. The donor resonance is isotropic, g=2.004±0.002. Resonances for the aluminum acceptor in three inequivalent silicon lattice sites are detected with $g_{\parallel}$=2.412±0.002, 2.400±0.002, and 2.325±0.002; and $g_{\perp}$=0. This indicates an effective-mass-like character for the acceptor, but with reduced orbital contribution due to the localization. Evidence for corresponding reduction in the spin-orbit splitting is cited.

I. Introduction

Silicon carbide (6H) containing aluminum displays a strong blue luminescence band at 2.65 eV which has been interpreted as arising from donor-acceptor pair (DA) recombination between nitrogen donors, always present, and the aluminum acceptors [1-3]. A typical spectral dependence of this luminescence at 1.7K is shown in Fig. (1a) for sample D142/GW-1, which is slightly n-type, the aluminum concentration being estimated at $\sim 10^{17}$ cm^{-3}. The two series Band C have been interpreted to arise from the difference ($\sim$50 meV) in ionization energy of the donor N substituted for carbon at inequivalent lattice sites in the 6H polytype, the well pronounced peaks within each series arising from coupling to LO lattice phonons $\sim$105 meV. Estimated differences in hole binding energy ($\sim$10 meV) at the inequivalent aluminum acceptor sites (silicon lattice) are too small to be resolved in the low temperature spectrum [2]. In this paper, we report optical detection of magnetic resonance (ODMR) [4] for this band, which confirms the donor-acceptor pair origin and sheds new light on the electronic structure of the aluminum acceptor.

II. Experimental Procedure

ODMR experiments were carried out at 35 GHz in a TE_{011} cavity made up of concentric rings [5], allowing large aperture for the optical beams. Magnetic fields up to 30 kG were produced by a superconducting magnet. The DA luminescence was excited with either the 350.7 and 356.4 nm lines of a Kr^+ laser or UV light from a 100 W Xe lamp. Audio frequency modulation of either the microwave power or the magnetic field was used and the corresponding synchronous changes in the luminescence intensity were observed in the direction of the magnetic field, using an RCA 4840 photomultiplier (S-20 response). Most measurements were made below the

*Research supported by NSF Grant No. DMR77-11309.
†Permanent address: Laboratoire de Spectrometrie Physique, Grenoble, France.

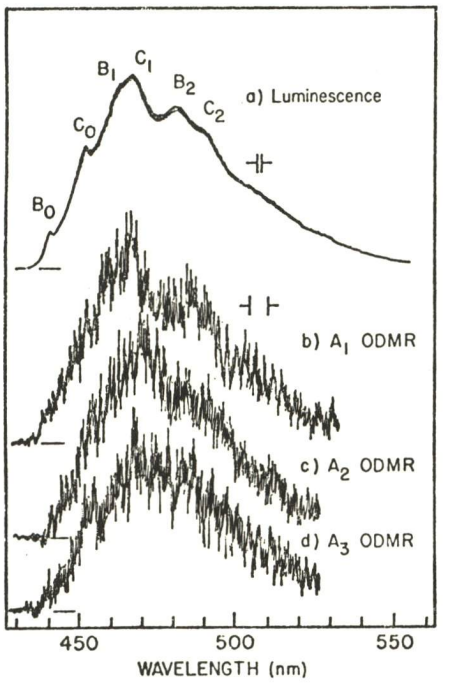

Fig. 1 Spectral dependence of luminescence and acceptor ODMR signals

λ-point of liquid helium, with the magnetic field rotating in a $(11\bar{2}0)$ plane.

III. Experimental Results

Figure (2a) shows the ODMR spectrum for sample D142/GW-1 at 1.7K. The spectrum consists of four lines, whose g-values, determined from the (effective spin ½) Zeeman expression

$$h\nu = g(\theta)\mu_B H \ , \qquad (1)$$

are plotted in Fig. (2b) vs. θ, the angle between the applied magnetic field $\vec{H}$ and the crystal c-axis. The spectral dependence of the transitions, determined by inserting a monochromator before the photomultiplier reveals that each is present throughout the whole band. This is illustrated in Figs. (1b-d) for the three anisotropic lines.

We identify the isotropic line D as due to the nitrogen donor, the g-value,

$$g_D = 2.004 \pm 0.002, \qquad (2)$$

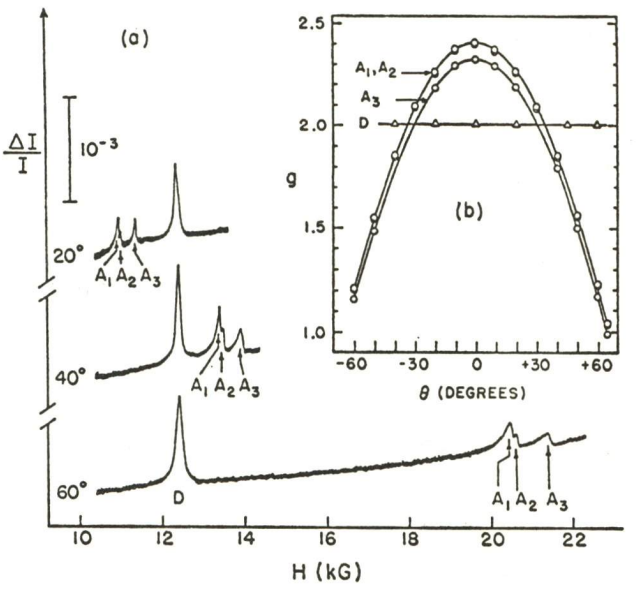

Fig. 2 a) ODMR spectra at 1.7K
b) Angular dependence of the lines

in good agreement with the EPR results for nitrogen in 6H SiC of Woodbury and Ludwig [6]. We identify the anisotropic lines, A_i, as due to the aluminum acceptor at non-equivalent lattice sites, with

$$g_i(\theta) = (g_{\parallel})_i \cos\theta, \qquad (3)$$

$$\begin{aligned}(g_{\parallel})_1 &= 2.412 \pm 0.002,\\ (g_{\parallel})_2 &= 2.400 \pm 0.002,\\ (g_{\parallel})_3 &= 2.325 \pm 0.002.\end{aligned} \qquad (4)$$

IV. Discussion

The presence of both donor and acceptor spectra confirms the distant DA recombination origin of the band. For the 6H polytype, there are three equally abundant but inequivalent silicon lattice sites, which can be classified as cubic (k_1, k_2) or hexagonal (h) local symmetry, when considering the three nearest

neighbor shells [1]. We therefore assign the three anisotropic spectra to aluminum acceptors at these sites. The assignment to specific ones must await further studies.

Now consider the g-factors of the acceptor. The maximum of the valence band is at the Γ point (k=0) in all polytypes of SiC. Recent studies of the fundamental absorption edge have been interpreted to indicate that the 6H hexagonal crystal field is larger than the spin-orbit splitting λ, which is about 7 MeV for free excitons [7]. Therefore J=L+S is no longer a good quantum number and the valence band structure should be as shown in Fig. 3. The uppermost valence band state is the doublet $(P_+\alpha, P_-\beta)$, where $P_\pm = (P_x \pm iP_y)/\sqrt{2}$ are the L=1 orbital states split from P_z by the hexagonal crystal field, and α,β are the spin up and down states, respectively.

The Zeeman effect on these states can be described by

$$\mathcal{H} = \mu_B \vec{H} \cdot (g_L \vec{L} + g_S \vec{S}) \ , \tag{5}$$

with L=1, S=1/2. Here g_L and g_S are the g-factors associated with the orbital angular momentum and the spin, respectively. For $g\mu_B H << \lambda$, this leads for the Γ_9 uppermost state to

$$g(\theta) = g_{\parallel}(\Gamma_9)\cos\theta; \quad g_{\parallel}(\Gamma_9) = 2\, g_L + g_S. \tag{6}$$

For the "atomic-like" case of the free hole (g_L=1), eq. (6) predicts $g_{\parallel}(\Gamma_9)$=4.0. It is interesting to note, however, that in 6H SiC, $g_{\parallel}$ has been observed to be systematically smaller as the hole becomes more bound: 3.2 from magneto-optic studies of the exciton bound to the neutral donor nitrogen [8], 2.85 from similar studies for the exciton bound to the charged state of the radiation produced CH center [9], and, in this paper, 2.3-2.4 for the aluminum acceptor. The cosθ angular dependence is observed in each of these cases. We interpret this to indicate that the bound hole remains effective-mass-like, reflecting the Γ_9 character of the top valence band state, but that the orbital contribution, g_L, is progressively reduced as the hole becomes more localized. From the $(g_{\parallel})_i$ values for the three acceptors, eq. (6) gives g_{L1}=.205, g_{L2}=.199, and g_{L3}=.161.

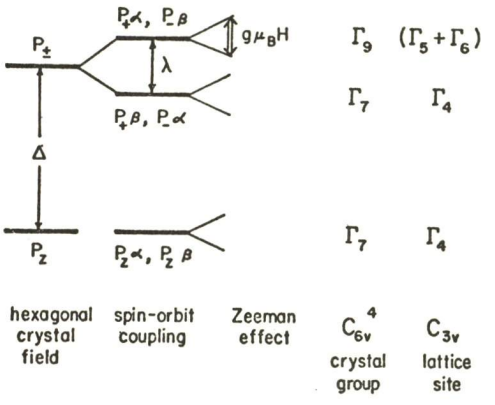

Fig. 3 The states at the top of the valence band (k=0)

Let us now consider possible mechanisms for the orbital reduction: (i) Localization alone can produce reduction because the relative magnitude and sign of the contributions to the orbital matrix elements from atoms on each of the sublattice shells surrounding the aluminum center will be modified [10,11]. (ii) As pointed out by Morgan [12], reduction due to the dynamic Jahn-Teller effect may also be important for bound hole states in semiconductors. Its importance should also increase with localization because the competing elastic energy stored in the lattice decreases linearly with the volume of the hole orbit.

Both mechanisms may also produce reduction in the spin-orbit splittings between the $(\Gamma_5+\Gamma_6)$ and Γ_4 states of the acceptor [12-13]. Assuming a similar reduction, we can make a rough estimate of the reduced spin-orbit values as $\lambda_i \cong g_{Li}\lambda_o$, where $\lambda_o=7$ meV, the free exciton value [7]. This predicts $\lambda_1, \lambda_2 \sim 1.4$ meV and $\lambda_3 \sim 1.1$ meV.

Recent Raman scattering studies [14] in aluminum-doped 6H SiC have detected strong zero field transitions at 1.32 and 1.12 meV, in close agreement with our predicted values. The geometry of the experiment was with the applied magnetic field perpendicular to the c-axis. Under these conditions, eq. (5) produces no Zeeman splittings of the $(\Gamma_5+\Gamma_6)$ or Γ_4 states but their separation is given by

$$E(\Gamma_5+\Gamma_6) - E(\Gamma_4) \cong (\lambda_i^2 + \mu_B^2 g_S^2 H_\perp^2)^{\frac{1}{2}} . \qquad (7)$$

This is precisely the observation of Scott et al. [14]. They interpreted the zero field splittings as arising from bound exciton exchange, perhaps at an impurity titanium. Our results suggest that the correct interpretation is the reduced spin-orbit interaction λ_i at the aluminum acceptors. We believe this provides a more reasonable explanation of their results because significant exciton concentrations should not have been generated with the long wavelength laser excitation used in their studies. The observed Raman selection rules and cross-sections can also be shown to agree with this new interpretation, but the nature of the transition must be considered as orbital-flip ($\Delta M_L=2$) rather than spin flip ($\Delta M_S=1$) [15].

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