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Electron paramagnetic resonance of Cu(d^9) in GaN

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Electron paramagnetic resonance of $\mathrm{Cu}^{2+}(d^9)$ has been detected optically in the visible and near-infrared luminescence of wurtzite GaN. Its effective $\mathcal{S}=1/2$ spin Hamiltonian parameters are $g_\parallel=\pm0.20(5)$, $g_\perp=+1.549(1)$, and $|^{63}A_\parallel|=550(50)$ MHz, and $|^{63}A_\perp|=570(5)$ MHz. A crystal field theory of the g values is presented, which identifies the ion as substitutional on the Ga sublattice. Possible mechanisms for its presence in the luminescence are discussed.

I. INTRODUCTION

The $3d$ transition element ions are common impurities in most semiconductors. The ability to study them by electron paramagnetic resonance (EPR) and optical spectroscopy via their partially filled inner d^n shells has provided a valuable probe not only of their important specific individual properties, but also of defect processes and interactions in general, in many of the traditional low to moderate band gap elemental and compound semiconductors. In the important wide band gap semiconductor GaN, such studies have also begun. In particular, EPR spectra of $\mathrm{Fe}^{3+}(d^5)$,[1] $\mathrm{Mn}^{2+}(d^5)$,[2] and $\mathrm{Ni}^{3+}(d^7)$,[2] have been reported, as has the photoluminescence (PL) associated with the internal d transitions of $\mathrm{V}^{3+}(d^2)$,[3,4] $\mathrm{Cr}^{4+}(d^2)$,[3] and $\mathrm{Fe}^{3+}(d^5)$.[1,5] In the present paper, we add the important impurity $\mathrm{Cu}^{2+}(d^9)$ to the list, presenting its EPR properties which we detect optically (ODEPR) in the visible and infrared luminescence of the material. (Above, we use the ''ionic'' notation, where, as has been universal in the above-referenced literature, the ion is viewed as replacing Ga^{3+} in the lattice. In the more relevant semiconductor notation, Fe^{3+}, being neutral with respect to the lattice, becomes $[\mathrm{Fe}]^0$, Cu^{2+} becomes $[\mathrm{Cu}]^-$, etc. In what follows, both notations will be used, the particular choice depending on the context in each case.)

II. EXPERIMENT

The sample studied was a high quality ≈ 500 μm thick free standing GaN single wurtzite crystal platelet grown at NEC by hydride vapor phase epitaxy (HVPE) using a facet-initiated epitaxial lateral overgrowth technique on a GaN-nucleated sapphire substrate which was subsequently removed. The details are described in Ref. 6. The sample was not intentionally doped, but n type, with $n<10^{17}$ cm^{-3}, and with very low dislocation content ($\sim 10^7$cm^{-2}). The c axis of the crystal was perpendicular to its platelet surfaces.

Most of the PL and ODEPR experiments to be described were performed under excitation with either the 351 or 364 nm line of an Ar^+ ion laser. The typical excitation power was ~ 20 mW. Detection of the luminescence was achieved in the visible by a silicon diode (EGG 250 UV) and in the near IR by a cooled Ge detector (North Coast EO817S), followed by lock-in detection synchronized to the frequency of a chopper in the excitation (for PL), or to the microwave on-off modulation frequency (for ODEPR). All PL and ODEPR studies were performed at pumped liquid He temperature (~ 1.7 K) in a 35 GHz ODEPR spectrometer which has been described elsewhere.[7]

III. RESULTS

The PL of the sample revealed several overlapping bands in the visible, the dominant one being the ''orange-red'' band centered at ~ 1.8 eV, often reported for HVPE material.[8,9] In the near IR, the 0.93 eV luminescence system identified[3,4] with V^{3+} was prominently observed, as was, more weakly, the 1.30 eV system[1,5] of Fe^{3+}.

In Fig. 1, we show the ODEPR signal, with $B\perp c$ axis, observed in the visible luminescence. In addition to signals at ~ 1.25 T ($g\sim 2$), which will be the subject of a subsequent publication, a four-line positive signal is observed at higher field. Its spectral dependence, estimated using various optical filters, reveals its source in the visible to be the dominant ''orange-red'' band at ~ 1.8 eV. It is also observed as a positive signal in the 0.93 eV V^{3+} band in the near IR. The

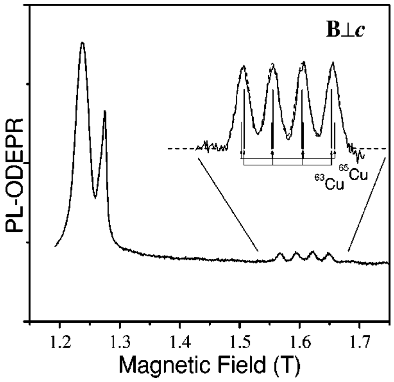

FIG. 1. ODEPR spectrum observed in the orange-red visible luminescence for **B**$\perp$ c axis. Shown also on an expanded scale is a simulation of the spectrum (dashed lines) resulting from hyperfine interaction with the two naturally occurring isotopes of Cu.

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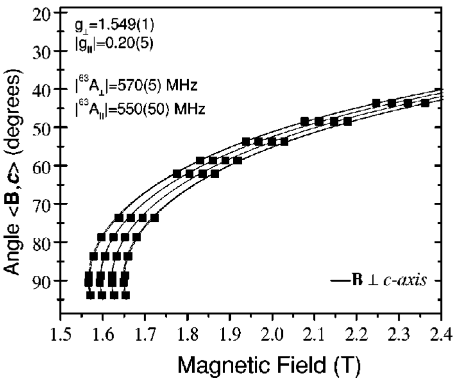

FIG. 2. Angular dependence of the Cu^{2+} spectrum.

signal is seen for both 351 and 364 nm excitation but is absent under 458–514 nm excitation, even though the relevant luminescence bands are still present. In a HVPE sample from a different source that contained the same luminescence bands, the signal was not observed.

Anticipating that it will be identified as arising from Cu, we show also in the figure the satisfactory match assuming hyperfine interaction with the two natural abundance $I=3/2$ isotopes of copper (69.2% ^{63}Cu, 30.8% ^{65}Cu, with $\mu^{65}/\mu^{63}=1.07$). The angular dependence of the spectrum is given in Fig. 2. The spectrum can be matched accurately, as shown in the figure, to the effective $\mathcal{S}=1/2$, $I=3/2$ Hamiltonian

$$\mathcal{H}=\mu_B\mathcal{S}\cdot\mathbf{g}\cdot\mathbf{B}+\mathcal{S}\cdot\mathbf{A}\cdot\mathbf{I}, \tag{1}$$

with $|g_\parallel|=0.20(5)$, $g_\perp=+1.549(1)$, and $|^{63}A_\parallel|=550(50)$ MHz, $|^{63}A_\perp|=570(5)$ MHz. (The signs of the parameters are not determined experimentally. However, the positive sign of $g_\perp$ will be established from the theoretical analysis in the next section.) The similarity of these distinctive parameters ($|g_\parallel|<|g_\perp|$, plus the $I=3/2$ hyperfine structure) to previously published values for $Cu^{2+}(d^9)$ in similar wurtzite materials[10] immediately identifies the defect as arising from $Cu^{2+}(d^9)$.

IV. THEORY

For a d^9 transition element ion in a wurtzite crystal such as GaN, the Hamiltonian for its free ion ^2D state can be written

$$\mathcal{H}=\mathcal{H}_{T_d}+\mathcal{H}_{s.o.}+\mathcal{H}_{C_{3v}}+\mathcal{H}_Z, \tag{2}$$

where the terms, in decreasing order, arise from the cubic crystal field, the spin-orbit interaction, the wurtzite trigonal field, and the Zeeman interaction. A typical result is shown in Fig. 3, where the specific order given for the resulting states reflects our conclusions to follow for the $Cu^{2+}(d^9)$ EPR spectrum being studied here. In particular, the indicated sign of the T_d crystal field, giving the $^2T_2$ state lowest, can be inferred directly from the theory of Mason *et al.*,[12] who treated the similar d^9 case of trigonally distorted interstitial Ni^+ in diamond. Their results showed that the sizable value we find for $|g_\perp|=1.549$ is only possible for one or the other of the two Γ_4 states arising from the $^2T_2$ state, the other three states having $g_\perp$ equal to or very close to zero. This therefore determines the sign of the T_d crystal field to be as shown in the figure, which is that expected for a substitutional site on the Ga sublattice.[13] The spin-orbit ordering shown in the next panel of the figure reflects the negative value of λ. The assignment for the sign of the trigonal crystal field in the last panel results from a detailed analysis of the g values, which we now develop.

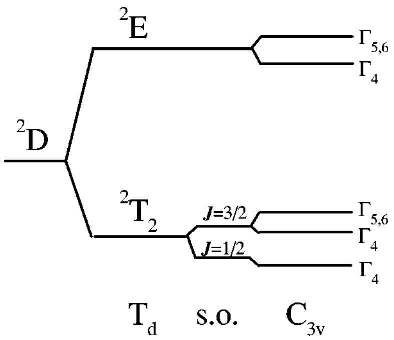

FIG. 3. Energy levels for Cu^{2+} substituting for Ga^{3+} in wurtzite GaN.

Consider first the spin-orbit and trigonal field interactions within the $^2T_2$ state, which we write, following the notation of Mason *et al.*,[12] as

$$\mathcal{H}_{s.o.}+\mathcal{H}_{C_{3v}}=\lambda\mathbf{L}\cdot\mathbf{S}-K[L_{z'}^2-L(L+1)/3], \tag{3}$$

where the z' axis is the $\langle 111\rangle$ wurtzite c-axis direction. (We here assume λ to be isotropic, and neglect the small effect on the $^2T_2$ states of off-diagonal matrix elements of the spin-orbit and trigonal crystal field terms between them and the distant ^2E states.) Taking advantage of the fact that within a T_2 state the matrix elements of $\mathbf{L}$ for the $L=2$ d functions are identical to those of a fictional $\mathcal{L}=1$ operator within p functions, but multiplied by a coefficient $\alpha=-1$, we label the unperturbed states by $M_{\mathcal{L}}=0,\pm1$ and $M_S=\pm1/2$, defined with respect to the z' axis. The resulting Hamiltonian matrix becomes

$$\begin{array}{c} |-1,-1/2\rangle \\ |+1,-1/2\rangle \\ |0,+1/2\rangle \end{array} \left\| \begin{array}{ccc} -\lambda/2-K & & \\ & \lambda/2-K & -\lambda/\sqrt{2} \\ & -\lambda/\sqrt{2} & +2K \end{array} \right\| \begin{array}{c} |+1,+1/2\rangle \\ |-1,+1/2\rangle \\ |0,-1/2\rangle \end{array} \tag{4}$$

which is identical in the basis either of the set of states shown on the left of the matrix, or of the Kramers conjugate set shown to the right. The resulting energies and wave functions[14] for the three Kramers doublets are

$$\Gamma_{4u}:\ E(\Gamma_{4u})=K/2+\lambda/4+\sqrt{(3K/2-\lambda/4)^2+\lambda^2/2},$$

$$|+1,-1/2\rangle\cos\delta+|0,+1/2\rangle\sin\delta, \tag{5}$$

$$|-1,+1/2\rangle\cos\delta+|0,-1/2\rangle\sin\delta,$$

$$\Gamma_{4l}:\ E(\Gamma_{4l})=K/2+\lambda/4-\sqrt{(3K/2-\lambda/4)^2+\lambda^2/2},$$

$$|+1,-1/2\rangle\sin\delta-|0,+1/2\rangle\cos\delta, \tag{6}$$

$$|-1,+1/2\rangle\sin\delta-|0,-1/2\rangle\cos\delta,$$

$$\Gamma_{5,6}:\ E(\Gamma_{5,6}) = -\lambda/2 - K,$$

$$|+1,+1/2\rangle, \tag{7}$$

$$|-1,-1/2\rangle,$$

where

$$\tan\delta = \frac{+\lambda/\sqrt{2}}{3K/2-\lambda/4-\sqrt{(3K/2-\lambda/4)^2+\lambda^2/2}}, \tag{8}$$

and Γ_{4u} denotes the higher energy Γ_4 state, Γ_{4l} the lower. With λ negative, the Γ_{4l} state is always the ground, lowest energy, state of interest to us.

The Zeeman interaction for each state is given by

$$\mathcal{H}_Z = \mu_B(2\mathbf{S}+k\mathbf{L})\cdot\mathbf{B}, \tag{9}$$

where a factor $k \leqslant +1$ (assumed isotropic) has been included to account for possible reduction of the orbital contribution. With the wave functions given above, we calculate the x', y', and z' Zeeman matrix elements of Eq. (9) between the states of each Kramers doublet, and equate them to those of Eq. (1), where the matrix elements of the effective spin operator $\mathcal{S}$ are given by the Pauli spin matrices. From this, we obtain, with $g_{z'} = g_{\parallel}$ and $g_{x'} = g_{y'} = g_{\perp}$,

$$\Gamma_{4u}:\ g_{\parallel} = -(2+k)\cos 2\delta - k,$$

$$g_{\perp} = 1 - \cos 2\delta - \sqrt{2}k \sin 2\delta, \tag{10}$$

$$\Gamma_{4l}:\ g_{\parallel} = (2+k)\cos 2\delta - k,$$

$$g_{\perp} = 1 + \cos 2\delta + \sqrt{2}k \sin 2\delta, \tag{11}$$

$$\Gamma_{5,6}:\ g_{\parallel} = 2(1-k),$$

$$g_{\perp} = 0. \tag{12}$$

The signs of the Γ_4 g values above result from labeling the Zeeman upper "+1/2" and lower "−1/2" effective $\mathcal{S} = 1/2$ states in the same order as given in Eqs. (5)–(7). Reversing the assignment would have reversed the signs of $g_{z'}$, but, at the same time, would have reversed the signs of $g_{y'}$ so that then $g_{y'} = -g_{x'}$. The product $g_{x'}g_{y'}g_{z'}$ would remain the same in either case, as required, being the only sign property that is experimentally measurable.[15] However, because of the further requirement of C_{3v} symmetry, we demand $g_{x'} = g_{y'}$, and the assignments above and the resulting g values given in Eqs. (10)–(12) are therefore uniquely determined for the particular choice (relative sign) of the wave functions within each Kramers pair given by Eqs. (5) and (6). (It is important to compare the matrix elements with those of the Pauli matrices as we have done, rather than simply calculate the energy splittings, which would not have caught this important point. The Pauli matrix behavior of the effective spin Hamiltonian is essential to describe the dynamic response of the system and is therefore a requirement.[16])

As pointed out by Abragam and Bleaney[17] in the similar case of d^1, the expressions for the g values given above for the two Γ_4 states describe an ellipse on a plot of $g_{\parallel}$ vs $g_{\perp}$. In Fig. 4, we show the result, with several values for k, and, on it, we indicate the range covered for each Γ_4 doublet vs the trigonal parameter K/λ. We include also the two possible positions on the graph for the g values determined here, which, as shown, are matched in the ground Γ_{4l} state by $k = 0.25$, $K/\lambda = +0.26$, or $k = 0.34$, $K/\lambda = +0.20$. We have therefore now finally established that K is indeed negative, as we indicated in Fig. 3. This, in turn, provides further confirmation of the model (if one were necessary), in that a negative sign for K is predicted for the crystal field experienced by the positive d^9 hole for four negatively charged nitrogen nearest neighbors in T_d symmetry, but under compression along the c axis, as expected for wurtzite GaN, with its lattice value of $c/a < 1.6333$. We see further from the figure that $g_{\perp}$ must be positive. However, not having experimentally measured $g_{x'}g_{y'}g_{z'} = g_{\parallel}g_{\perp}^2$, we cannot choose between the two possibilities $g_{\parallel} = \pm 0.2$. Accepting this, we have determined that $k \sim 0.3$ and $K \sim +0.23\lambda$.

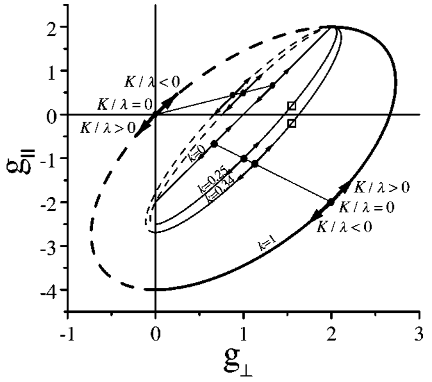

FIG. 4. Locus of the Γ_4 g values for d^9 vs selected values of k. The solid lines cover the range for the ground Γ_{4l} state and the dashed lines for Γ_{4u} vs K/λ. The two possible positions for the Cu^{2+} g values are also shown (squares), which lead to the values $k = 0.25$, $K/\lambda = +0.26$ or $k = 0.34$, $K/\lambda = +0.20$.

V. DISCUSSION AND SUMMARY

Cu^{2+}(d^9) has been observed by ODEPR in GaN. The sign of the cubic and weak C_{3v} crystal fields that it experiences identifies it as substitutional on the Ga sublattice. As such, its charge state in the lattice is $[\mathrm{Cu}]^-$, identifying the defect as a deep acceptor in its un-ionized (negative) charge state. The very small value for $g_{\parallel} = \pm 0.2$ reveals strong admixtures of spin and orbital states in its ground Kramers state, which we have demonstrated to result from comparable magnitudes determined for the competing spin-orbit (λ) and wurtzite trigonal crystal field (K) interactions. The small value for the orbital reduction factor $k \sim 0.3$ suggests the role of $4p$ admixtures into the t_2 d states (producing contributions of the opposite sign) and/or covalency effects which spread the d states partially into its neighbors.

Its detection as a positive signal in the ODEPR indicates that it is involved in a spin-dependent process of some kind that contributes to both the broad 1.8 eV and sharp 0.93 eV zero-phonon-line luminescence system. It cannot arise from the emitting excited state itself because it is absent under 458–514 nm excitation which still produces the luminescence. This suggests therefore a spin-dependent hole transfer to $[\mathrm{Cu}]^-$,

$$[\mathrm{Cu}]^- + h^+ \rightarrow [\mathrm{Cu}]^0, \qquad (13)$$

which, in turn, provides a direct or indirect feeding mechanism for the luminescence, but not the only one. We can tentatively rule out the possibility that the emissions arise directly from the excited captured hole state of $[\mathrm{Cu}]^0$, where the broad 1.8 eV transition might be a direct transition to the ground neutral state of the ion, with the 0.93 eV transition an alternative path via an internal d-to-d transition. Although this would be the conventional explanation for seeing the Cu^{2+} (i.e., $[\mathrm{Cu}]^-$) resonance in these two specific bands, it conflicts directly with the previous identification[3,4] of the 0.93 eV luminescence system as an internal d-to-d transition within the d^2 configuration of V^{3+}, i.e., $[\mathrm{V}]^0$.[18] It appears to conflict also with our failure to observe the Cu^{2+} resonance in a HVPE sample from a different source that displayed the same luminescence bands.

The evidence strongly suggests therefore that the copper involvement is instead simply to supply an excitation path to other centers that luminesce. A possible mechanism is as follows. Spin-dependent hole transfer to $[\mathrm{Cu}]^-$ could produce an excited effective mass (EM) hole state of $[\mathrm{Cu}]^0$. In a shallow large orbit, the hole could, in turn, be transferred to different emitting centers, aided by a sufficiently long lifetime local recombination to the ground state of $[\mathrm{Cu}]^0$. In this scenario, the normally deep Cu acceptor simply acts as a conduit for the hole via its excited EM states.

ACKNOWLEDGMENTS

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[10] Compare, for example, to the results in Ref. 11 for Cu^{2+} in ZnO, where $g_\parallel = 0.74$, $g_\perp = 1.531$, and $A_\parallel = 585$ MHz, $A_\perp = 693$ MHz.

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[13] Viewed either in the ionic model, with the substitutional ion surrounded by four negative nitrogen ions, or in the covalent model, with the negative covalent bond charge between copper and its four bonded nitrogen neighbors, the sign of the predicted crystal field for the inner d electrons is the same, causing the ${}^2T_2$ state to be lowest.

[14] For clarity, we adopt the same (arbitrary) definitions of the wave functions (in terms of sin δ and cos δ) as that in Ref. 12. Note, however, that our $|+1\rangle$, $|0\rangle$, and $|-1\rangle$ states correspond to their $-|T_2^+\rangle$, $+|A_1\rangle$, and $+|T_2^-\rangle$ states, respectively, the sign change being required so that the matrix elements of **L** between them remain $\alpha = -1$ times those of p functions.

[15] A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions* (Clarendon Press, Oxford, 1970), pp. 138–139. The sign of the product $g_{x'}g_{y'}g_{z'}$ can be determined experimentally by establishing which circular component of the microwave magnetic field causes the EPR transition.

[16] We are grateful to Frank Ham for pointing this out to us.

[17] A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions* (Ref. 15), pp. 417–426.

[18] Note, however, that the internal transitions for two holes in $\mathrm{Cu}^{2+}(d^8)$ and two electrons in $\mathrm{V}^{3+}(d^2)$ are formally equivalent except for the order of the levels. Is it possible therefore that the 0.93 eV system might actually be coming from copper? No ODEPR identification of V has been reported for the 0.93 eV luminescence.