

Air Force Institute of Technology

AFIT Scholar

Faculty Publications

2-2022

Cu²⁺ and Cu³⁺ Acceptors in β -Ga₂O₃ Crystals: A Magnetic Resonance and Optical Absorption Study

Timothy D. Gustafson

Air Force Institute of Technology

Nancy C. Giles

Air Force Institute of Technology

Brian C. Holloway [*]

Air Force Institute of Technology

Christopher A. Lenyk

Air Force Institute of Technology

J. Jesenovec

Washington State University

See next page for additional authors

Follow this and additional works at: <https://scholar.afit.edu/facpub>



Part of the [Atomic, Molecular and Optical Physics Commons](#)

Recommended Citation

Gustafson, T. D., Giles, N. C., Holloway, B. C., Lenyk, C. A., Jesenovec, J., McCloy, J. S., McCluskey, M. D., & Halliburton, L. E. (2022). Cu²⁺ and Cu³⁺ acceptors in β -Ga₂O₃ crystals: A magnetic resonance and optical absorption study. *Journal of Applied Physics*, 131(6), 065702. <https://doi.org/10.1063/5.0080502>








This Article is brought to you for free and open access by AFIT Scholar. It has been accepted for inclusion in Faculty Publications by an authorized administrator of AFIT Scholar. For more information, please contact AFIT.ENWL.Repository@us.af.mil.

Authors

Timothy D. Gustafson, Nancy C. Giles, Brian C. Holloway [*], Christopher A. Lenyk, J. Jesenovec, J. S. McCloy, M. D. McCluskey, and Larry E. Halliburton

RESEARCH ARTICLE | FEBRUARY 09 2022

Cu²⁺ and Cu³⁺ acceptors in β -Ga₂O₃ crystals: A magnetic resonance and optical absorption study

T. D. Gustafson ; N. C. Giles ; B. C. Holloway; C. A. Lenyk ; J. Jesenovec ; J. S. McCloy ; M. D. McCluskey ; L. E. Halliburton 



Journal of Applied Physics 131, 065702 (2022)

<https://doi.org/10.1063/5.0080502>



View
Online



Export
Citation

CrossMark

AIP Advances

Why Publish With Us?



25 DAYS
average time
to 1st decision



740+ DOWNLOADS
average per article



INCLUSIVE
scope

[Learn More](#)

Cu²⁺ and Cu³⁺ acceptors in β -Ga₂O₃ crystals: A magnetic resonance and optical absorption study

Cite as: J. Appl. Phys. **131**, 065702 (2022); doi: [10.1063/5.0080502](https://doi.org/10.1063/5.0080502)

Submitted: 1 December 2021 · Accepted: 16 January 2022 ·

Published Online: 9 February 2022



T. D. Gustafson,^{1,a)} N. C. Giles,¹ B. C. Holloway,¹ C. A. Lenyk,¹ J. Jesenovec,^{2,3} J. S. McCloy,^{2,3} M. D. McCluskey,^{2,4} and L. E. Halliburton^{5,a)}

AFFILIATIONS

¹Department of Engineering Physics, Air Force Institute of Technology, Wright-Patterson Air Force Base, Ohio 45433, USA

²Institute of Materials Research, Washington State University, Pullman, Washington 99164, USA

³Materials Science and Engineering Program, Washington State University, Pullman, Washington 99164, USA

⁴Department of Physics and Astronomy, Washington State University, Pullman, Washington 99164, USA

⁵Department of Physics and Astronomy, West Virginia University, Morgantown, West Virginia 26506, USA

^{a)}Authors to whom correspondence should be addressed: Timothy.Gustafson@protonmail.com and Larry.Halliburton@mail.wvu.edu

ABSTRACT

Electron paramagnetic resonance (EPR) and optical absorption are used to characterize Cu²⁺ (3d⁹) and Cu³⁺ (3d⁸) ions in Cu-doped β -Ga₂O₃. These Cu ions are singly ionized acceptors and neutral acceptors, respectively (in semiconductor notation, they are Cu⁻ and Cu⁰ acceptors). Two distinct Cu²⁺ EPR spectra are observed in the as-grown crystals. We refer to them as Cu²⁺(A) and Cu²⁺(B). Spin-Hamiltonian parameters (a g matrix and a ^{63,65}Cu hyperfine matrix) are obtained from the angular dependence of each spectrum. Additional electron-nuclear double resonance (ENDOR) experiments on Cu²⁺(A) ions give refined ⁶³Cu and ⁶⁵Cu hyperfine matrices and provide information about the nuclear electric quadrupole interactions. Our EPR results show that the Cu²⁺(A) ions occupy octahedral Ga sites with no nearby defect. The Cu²⁺(B) ions, also at octahedral Ga sites, have an adjacent defect, possibly an OH⁻ ion, an oxygen vacancy, or an H⁻ ion trapped within an oxygen vacancy. Exposing the crystals at room temperature to 275 nm light produces Cu³⁺ ions and reduces the number of Cu²⁺(A) and Cu²⁺(B) ions. The Cu³⁺ ions have an S = 1 EPR spectrum and are responsible for broad optical absorption bands peaking near 365, 422, 486, 599, and 696 nm. An analysis of loops observed in the Cu³⁺ EPR angular dependence gives 2.086 for the g value and 22.18, 3.31, and -25.49 GHz for the principal values of D (the fine-structure matrix). Thermal anneal studies above room temperature show that the Cu³⁺ ions decay and the Cu²⁺ ions recover between 75 and 375 °C.

Published under an exclusive license by AIP Publishing. <https://doi.org/10.1063/5.0080502>

I. INTRODUCTION

Copper serves as a deep acceptor in β -Ga₂O₃ and provides compensation for unintentional donors. Unlike the Zn acceptors in this wide bandgap semiconductor,^{1–3} singly ionized and neutral Cu acceptors differ only in the number of d electrons. The neutral Zn acceptors are small polarons where the hole is localized on one oxygen neighbor and the 3d shell of the Zn ion remains filled.¹ In contrast, the neutral Cu acceptors in β -Ga₂O₃ have the hole localized in the 3d shell. The singly ionized acceptors are Cu²⁺ ions (with the 3d⁹ configuration) and the neutral acceptors are Cu³⁺ ions (with the 3d⁸ configuration). As a result, the Cu acceptors are deep in β -Ga₂O₃ and are not expected to produce p-type conductivity.⁴

An interesting and unique property of the Cu acceptors in β -Ga₂O₃ (not seen with the more traditional Mg and Zn acceptors) is a significant photochromic response.⁵ Exposure to 275 nm light converts Cu²⁺ ions to Cu³⁺ ions and produces broad optical absorption bands in the visible and near ultraviolet regions. [Note: Throughout this report, ionic notation is used for the Cu acceptors, with an emphasis on the d shell occupancy. In semiconductor notation, the singly ionized and neutral acceptors are Cu⁻ and Cu⁰, respectively.]

In the present paper, we use electron paramagnetic resonance (EPR) and electron-nuclear double resonance (ENDOR) to characterize Cu²⁺ and Cu³⁺ ions in β -Ga₂O₃ crystals. These experimental techniques are well-suited to determine the electronic structure of

13 JULY 2023 18:55:18

the ground states of the Cu ions.^{6,7} Two distinct $S = 1/2$ EPR spectra from Cu^{2+} ions at octahedral Ga sites are observed in the as-grown Cu-doped crystals. The responsible ions are referred to as $\text{Cu}^{2+}(\text{A})$ and $\text{Cu}^{2+}(\text{B})$. A third EPR signal, with $S = 1$, is produced at room temperature with 275 nm light and is assigned to Cu^{3+} ions at an octahedral Ga site. Spin-Hamiltonian parameters are extracted from the angular dependence of each spectrum and atomic-scale models are developed. The $\text{Cu}^{2+}(\text{A})$ and Cu^{3+} spectra are the expected singly ionized and neutral Cu acceptors, respectively, in $\beta\text{-Ga}_2\text{O}_3$. They have no nearby defects. In contrast, the $\text{Cu}^{2+}(\text{B})$ ions have a defect at a nearest-neighbor oxygen site in the b - c plane. This perturbing defect is not identified in our study, but likely candidates are an OH^- ion, an oxygen vacancy, or an H^- ion trapped within an oxygen vacancy.

The present paper also describes the optical absorption features that are produced at room temperature with 275 nm light. Broad photoinduced absorption bands attributed to Cu^{3+} ions have peaks near 365, 422, 486, 599, and 696 nm. The 422, 599, and 696 nm bands are polarized (they are best seen with $E \parallel b$). After an exposure to 275 nm light, the three EPR spectra and the optical absorption bands are monitored during a series of thermal anneals at progressively higher temperatures (between 75 and 375 °C). These decay and recovery results help unravel the complexities of the roles played by the various defects in trapping electrons and holes during optical excitation of the Cu-doped $\beta\text{-Ga}_2\text{O}_3$ crystals.

There have been only a few studies of d^8 ions that are relevant to our present investigation. The observation of EPR spectra from Cu^{3+} and Ni^{2+} ions has been reported in $\alpha\text{-Al}_2\text{O}_3$ crystals, a material similar to $\beta\text{-Ga}_2\text{O}_3$.^{8,9} These papers provide insights into the expected properties of the Cu^{3+} ions in $\beta\text{-Ga}_2\text{O}_3$ crystals. Although optically detected magnetic resonance (ODMR) has revealed the presence of Cu^{2+} ions,¹⁰ there are no indications in the literature that stable Cu^{3+} ions can be formed in GaN. There are also no reports of EPR signals from Cu^{3+} ions in other III-V materials such as GaP and GaAs. The present paper provides a rare opportunity to establish the EPR and optical absorption properties of a d^8 ion in an important ultrawide-bandgap semiconductor.

II. EXPERIMENTAL DETAILS

The Cu-doped $\beta\text{-Ga}_2\text{O}_3$ crystals used in the present study were grown at Washington State University by the Czochralski (CZ) and vertical gradient freeze (VGF) methods.^{2,5,11,12} An iridium crucible was employed and the Cu doping level in the starting materials was 0.25 at. %. Growth proceeded in two steps. The initial seeding and pulling portion of the growth occurred over approximately 12 h. A pulling rate of about 2 mm/h was used. The CZ growth was then removed and the remaining melt was slowly cooled at an approximate rate of 1–2 °C/min to produce the VGF boule. Reference 13 provides additional growth details. The Cu content in the VGF material is an order of magnitude greater than in the CZ material.¹³ An increased hydrogen content is expected to accompany the increased Cu content. In general, the CZ and VGF crystals will not necessarily be similar because of variations in stoichiometry, nonuniform distributions of defects, and leaching of impurities from the crucible.

Small rectangular-shaped samples, approximately 2 mm on a side, were cut from the larger boules. EPR verified that unintentional Ir^{4+} and Fe^{3+} ions are present in the as-grown crystals. The observation of Fe is important, as the known angular dependence¹⁴ of the EPR spectrum from Fe^{3+} ions at octahedral Ga sites is used to precisely align the static external magnetic field along the crystal axes. In an earlier growth study, Galazka *et al.*¹⁵ identified the evaporation of Cu due to a high partial pressure as a problem when growing Cu-doped $\beta\text{-Ga}_2\text{O}_3$ crystals by the Czochralski method. A small overpressure (20 kPa) inside the furnace during growth helped to suppress Cu evaporation in the current study.¹³

At various places in the present paper, EPR is used to obtain the concentrations of defects. This is done by comparing the area under the EPR absorption signal (i.e., after integrating the first-derivative signal) to the area under the signal from a standard Bruker weak-pitch sample containing a known number of spins. With this method, relative concentrations of defects in a crystal are determined more precisely than absolute concentrations. We estimate that our absolute concentrations are accurate to within a factor of two (a primary source of error is the uncertainty in knowing the number of spins in the standard sample). An advantage of using EPR to determine defect concentrations is its ability to focus on specific charge states. Comparison to the Bruker weak-pitch EPR standard gave a concentration of $5.1 \times 10^{18} \text{ cm}^{-3}$ for the Ir^{4+} ions in an as-grown CZ crystal. A separate infrared absorption measurement¹⁶ of the intensity of the peak at 5153 cm^{-1} ($1.94 \mu\text{m}$) in the same sample gave $4.0 \times 10^{18} \text{ cm}^{-3}$ for the Ir^{4+} concentration, thus confirming the EPR result. The Fe^{3+} concentration, obtained from EPR, was approximately a factor of five lower than the Ir^{4+} concentration in this as-grown CZ sample. The Cu dopant and the unintentional impurities are not expected to be uniformly distributed in these boules.¹³

The $\beta\text{-Ga}_2\text{O}_3$ crystals have a monoclinic structure described by space group $C2/m$ (C_{2h}^3), with lattice constants $a = 12.214 \text{ \AA}$, $b = 3.0371 \text{ \AA}$, $c = 5.7981 \text{ \AA}$, and $\beta = 103.83^\circ$ at 273 K.^{17,18} Following the usual convention, the b direction is perpendicular to the mirror plane. The angle between the a and c axes is β and the c^* direction is defined to be perpendicular to the a - b plane. There are equal numbers of tetrahedral and octahedral Ga sites in the crystal, labeled Ga(1) and Ga(2), respectively. Oxygen ions occupy three crystallographically inequivalent sites in the crystal, labeled O(I), O(II), and O(III), and are distinguished by the number and types of Ga neighbors.

A Bruker EMX spectrometer, with a cylindrical TM_{110} resonator, was used to acquire the EPR spectra. ENDOR spectra were taken with a Bruker Elexsys E-300 spectrometer and a cylindrical TE_{011} resonator. These X-band spectrometers operated near 9.38 and 9.49 GHz, respectively. In the ENDOR experiments, the source of radio frequencies (restricted to the 1–120 MHz range) was frequency-modulated at 12.5 kHz. This gave first-derivative ENDOR signals. Oxford Instruments ESR-900 helium-gas flow systems were used to control the sample temperature and a Bruker nuclear magnetic resonance (NMR) gaussmeter provided corrections for the small difference in the magnetic field at the sample and the spectrometer's Hall sensor located on a magnet pole cap. A 275 nm LED from Thorlabs (Model M275L4), with an output power of 45 mW, was used to convert Cu^{2+} ions to Cu^{3+} ions. The

13 JULY 2023 18:55:18

effects of 325 and 442 nm wavelengths from a Kimmon IK Series He-Cd laser were also investigated. Optical absorption spectra were taken with a Cary 5000 spectrophotometer and an ultrabroadband (250 nm to 4 μm) fused-silica wire-grid polarizer (Thorlabs Model WP25M-UB). The optical absorption spectra were not corrected for surface reflection losses and scattering.

III. EPR FROM Cu^{2+} IONS

Two distinct Cu^{2+} ($S = 1/2$) EPR spectra, with resolved hyperfine structure, are observed in the as-grown Cu-doped $\beta\text{-Ga}_2\text{O}_3$ crystals. One spectrum, labeled $\text{Cu}^{2+}(\text{A})$, is best seen at temperatures below 80 K. Although the responsible defect is present at room temperature, short spin-lattice relaxation times cause its lines to broaden beyond recognition at higher temperatures. The second spectrum, labeled $\text{Cu}^{2+}(\text{B})$, can be easily seen at room temperature. The relative concentrations of the $\text{Cu}^{2+}(\text{A})$ and $\text{Cu}^{2+}(\text{B})$ ions depend on the growth conditions and vary from sample to sample. Results from two representative samples are included in our present study. Sample 1 was grown by the CZ method and has approximately equal initial concentrations of $\text{Cu}^{2+}(\text{A})$ and $\text{Cu}^{2+}(\text{B})$ ions. Sample 2 was grown by the VGF method and has an initial combined concentration of $\text{Cu}^{2+}(\text{A})$ and $\text{Cu}^{2+}(\text{B})$ ions that is slightly more than double that in sample 1. More important, the distribution of Cu among the two defects is very different in samples 1 and 2. When compared to sample 1, the initial concentration of $\text{Cu}^{2+}(\text{A})$ ions is three times less in sample 2 and the initial concentration of $\text{Cu}^{2+}(\text{B})$ ions is four times greater in sample 2. More simply stated, in sample 2, the concentration of $\text{Cu}^{2+}(\text{B})$ ions is about 12 times greater than the concentration of $\text{Cu}^{2+}(\text{A})$ ions. This is much different than the nearly equal concentrations found in sample 1. A second distinguishing feature for the two samples is the Fermi level: it is higher in sample 2 than in sample 1. The EPR, ENDOR, and optical absorption results in Secs. III–VI were obtained from sample 1, while the thermal decay results in Sec. VII were obtained from samples 1 and 2.

Most of the Cu^{2+} ions in our Cu-doped $\beta\text{-Ga}_2\text{O}_3$ crystals are located at octahedral Ga(2) sites. A few may also be at tetrahedral Ga(1) sites. Interstitial sites are unlikely for the Cu defects we observe. Thus far, computational studies of formation energies have found that Cu favors octahedral sites in $\beta\text{-Ga}_2\text{O}_3$.^{4,5,19–21} For both the fourfold Ga(1) and the sixfold Ga(2) sites, the Cu^{2+} ion is slightly larger than the Ga^{3+} ion. The effective ionic radii of Ga^{3+} and Cu^{2+} ions at fourfold sites are 47 and 57 pm, respectively, and their effective radii at sixfold sites are 62 and 73 pm.²² Closed shell Cu^+ ions have effective ionic radii of 60 and 77 pm at the fourfold and sixfold sites.

A. $\text{Cu}^{2+}(\text{A})$ ions

Figure 1 shows EPR spectra from the $\text{Cu}^{2+}(\text{A})$ ions. These data were taken at 40 K from sample 1 (a CZ-grown crystal). The microwave frequency was 9.379 GHz and the magnetic field was aligned along the a , b , and c^* directions in Figs. 1(a)–1(c), respectively. Comparison to a Bruker weak-pitch EPR standard sample gave an approximate concentration of $8.4 \times 10^{18} \text{ cm}^{-3}$ for these $\text{Cu}^{2+}(\text{A})$ ions. A stick diagram above the spectrum in Fig. 1(a) identifies the four Cu hyperfine lines resulting from the $I = 3/2$

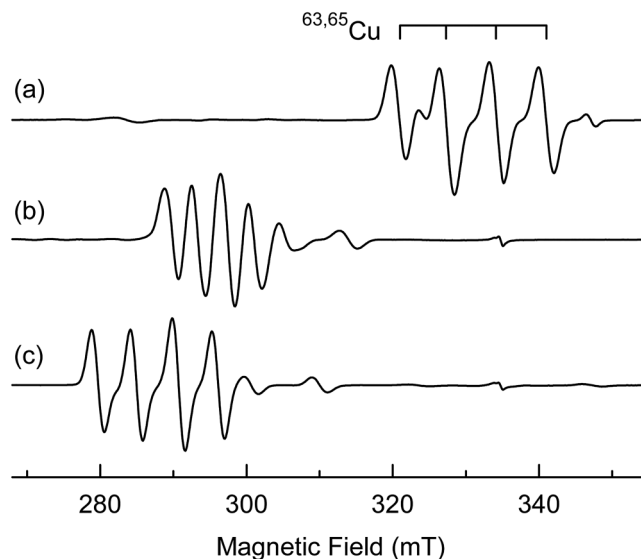


FIG. 1. EPR spectra from $\text{Cu}^{2+}(\text{A})$ ions in sample 1 (a Cu-doped $\beta\text{-Ga}_2\text{O}_3$ crystal grown by the Czochralski method). The spectra were taken at 40 K with a microwave frequency of 9.379 GHz. (a) Magnetic field along the a direction. The stick diagram above this spectrum identifies the ^{63}Cu and ^{65}Cu hyperfine lines. (b) Magnetic field along the b direction. (c) Magnetic field along the c^* direction.

nuclear spins of the ^{63}Cu and ^{65}Cu isotopes. Selection rules ($\Delta M_S = \pm 1$ and $\Delta m_I = 0$) for the allowed EPR transitions give $2I + 1$ lines. The natural abundances of the ^{63}Cu and ^{65}Cu isotopes are 69.15% and 30.85%, respectively, and their magnetic moments are $^{63}\mu = 2.2272\beta_n$ and $^{65}\mu = 2.3816\beta_n$, where β_n is the nuclear Bohr magneton.²³ Because the two isotopes have the same nuclear spin and similar magnetic moments, individual lines from the ^{63}Cu and ^{65}Cu nuclei are not resolved in Fig. 1 and only one set of four lines is observed for each direction of the magnetic field. In Figs. 1(b) and 1(c), two smaller and slightly broader lines from $\text{Cu}^{2+}(\text{B})$ ions are present just to the high-field side of the four lines from the $\text{Cu}^{2+}(\text{A})$ ions.

Figure 2 shows the angular dependence of the $\text{Cu}^{2+}(\text{A})$ EPR spectrum. Data were taken at 40 K while rotating the direction of the magnetic field in 10° steps from a to b , b to c^* , and c^* to a . The following spin-Hamiltonian, containing an electron Zeeman term, a hyperfine term, and a nuclear Zeeman term, describes these results,

$$H = \beta S \cdot g \cdot B + I \cdot A \cdot S - g_n I \cdot B. \quad (1)$$

The g and A matrices in Eq. (1) each have six independent parameters. These are the three principal values and the three Euler angles that define the directions of the principal axes. In Fig. 2, the EPR lines do not split into two branches in the middle portions of the a - b and b - c^* planes (although splittings in these planes are often seen for defects in monoclinic crystals).^{24,25} The lack of splitting indicates that the principal axes of the g and A

13 JULY 2023 18:55:18

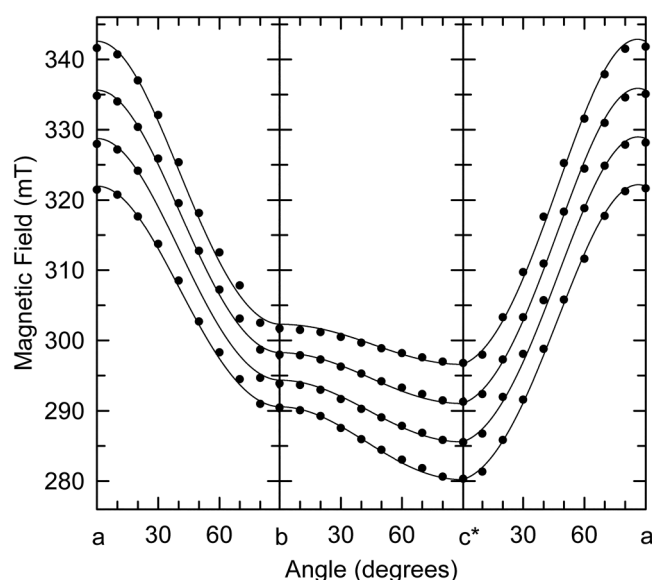


FIG. 2. Angular dependence of the EPR spectrum from $\text{Cu}^{2+}(\text{A})$ ions. The direction of the magnetic field is rotated from a to b , b to c^* , and c^* to a . Discrete points are from experiment. The solid lines were generated using the parameters in Table I.

matrices for the $\text{Cu}^{2+}(\text{A})$ ions are near the a , b , and c^* directions in the crystal. To extract values for the 12 parameters, the spin-Hamiltonian in Eq. (1) was rewritten as an 8×8 matrix ($S = 1/2$, $I = 3/2$) using the $|M_S, m_I\rangle$ basis set. This matrix was then repeatedly diagonalized (to obtain the energy eigenvalues) in a least-squares fitting routine. Input data for the fitting were the 177 pairs of magnetic field values and microwave frequencies representing the experimental points in Fig. 2. In the fitting process, the parameters in the g and A matrices were systematically varied until the predicted line positions agreed with the measured positions. “Best-fit” values for the spin-Hamiltonian parameters are listed in Table I. The Euler angles for each matrix have been converted in Table I to polar and azimuthal (θ, ϕ) pairs of angles, where θ is relative to the c^* axis and ϕ is relative to the a axis with positive rotation being from a toward b in the plane perpendicular to c^* . Principal values of the hyperfine matrix in Table I represent a “weighted average” of the two isotopes since individual lines from the ^{63}Cu and ^{65}Cu nuclei are not resolved in the EPR spectra. Recently, an EPR spectrum with similar spin-Hamiltonian parameters was assigned to Cu^{2+} ions unintentionally present in $\beta\text{-Ga}_2\text{O}_3$ powder.²⁶

The results in Table I allow us to develop a model for the $\text{Cu}^{2+}(\text{A})$ ions in $\beta\text{-Ga}_2\text{O}_3$. First, we review the notation and the coordinate system used to describe d orbitals. A “free” Cu^{2+} ($3d^9$) ion has a $^2D_{5/2}$ ground state ($S = 1/2$, $L = 2$). Within the crystal, in the presence of a crystalline electric field, the degeneracy of the five d orbitals is partially removed and only the lowest-lying states are thermally populated.²⁷ For a Cu^{2+} ion at the slightly distorted octahedral Ga(2) site in $\beta\text{-Ga}_2\text{O}_3$, the lowest state (occupied by the

TABLE I. Spin-Hamiltonian parameters for $\text{Cu}^{2+}(\text{A})$ ions in $\beta\text{-Ga}_2\text{O}_3$. Units for the principal hyperfine parameters are MHz. Uncertainties are estimated to be ± 0.001 for the g values, ± 2.0 MHz for the A principal values, and $\pm 1^\circ$ for the angles.

		Principal-axis directions		
Principal values		θ (deg)	ϕ (deg)	Directions in crystal
g matrix				
g_1	2.016	86.2	2.0	Near a
g_2	2.261	90.2	92.0	Near b
g_3	2.325	3.8	179.1	Near c^*
A hyperfine matrix (combined ^{63}Cu and ^{65}Cu)				
A_1	195	76.3	0.0	Near a
A_2	124	90.0	90.0	Near b
A_3	176	13.7	179.9	Near c^*

unpaired spin) will be either $(3z^2 - r^2)$ or $(x^2 - y^2)$. The (xy) , (yz) , and (xz) states are much higher in energy. If the Cu^{2+} ions were instead at a tetrahedral site, the ordering of the T_{2g} and E_g states would be reversed. The x , y , and z directions used to describe d orbitals at the octahedral Ga(2) site are defined within the GaO_6 octahedron and, thus, do not correspond to the a , b , and c crystal axes in the $\beta\text{-Ga}_2\text{O}_3$ crystal. We take the z direction to be near the a axis in the crystal, the x direction to be between the b and $-c$ directions, and the y direction to be between the b and c directions. This places the six neighboring oxygen ions in pairs around the Ga(2) site, roughly along the x , y , and z directions.

The g matrix for the $\text{Cu}^{2+}(\text{A})$ ions (see Table I) is approximately axial with $g_{\parallel} < g_{\perp}$. Its unique principal axis, associated with the smallest g value, is near the a direction in the crystal (or equivalently, the z direction). The two remaining perpendicular principal axes, corresponding to the larger, slightly inequivalent, g values, are close to the b and c directions in the crystal. An orthorhombic distortion is responsible for the minor inequivalence in these latter two g values and places their principal-axis directions nearly midway between the x and y and the x and $-y$ directions. The ordering of the principal g values (one smaller and two larger) is consistent with a model that has the Cu^{2+} ion at an octahedral Ga(2) site. An analysis of g matrices for $3d^9$ ions,^{28–30} when combined with our experimental g matrix in Table I, places the $\text{Cu}^{2+}(\text{A})$ unpaired spin (i.e., the hole) in a $(3z^2 - r^2)$ orbital aligned near the crystal’s a axis. A small contraction of the octahedron along the z direction or, equivalently, an expansion along x and y favors the $(3z^2 - r^2)$ orbital for the unpaired spin rather than the $(x^2 - y^2)$ orbital. There is no evidence from EPR that $\text{Cu}^{2+}(\text{A})$ ions have a nearby perturbing defect.

B. $\text{Cu}^{2+}(\text{B})$ ions

EPR spectra from the $\text{Cu}^{2+}(\text{B})$ ions in $\beta\text{-Ga}_2\text{O}_3$ are shown in Fig. 3. The data in Figs. 1 and 3 were obtained from sample 1 but with different measurement temperatures (40 K in Fig. 1 and room temperature in Fig. 3). At room temperature, the lines in the $\text{Cu}^{2+}(\text{A})$ spectrum are too broad to observe. The magnetic field was aligned along the a , b , and c^* directions in Figs. 3(a)–3(c),

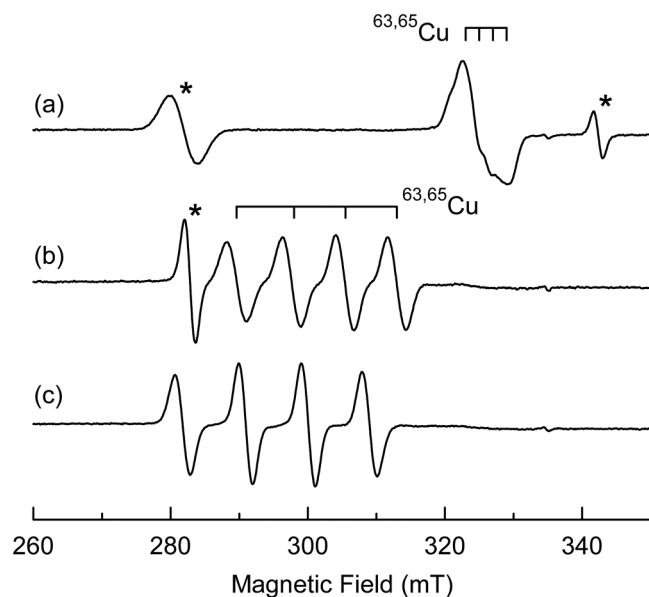


FIG. 3. EPR spectra from $\text{Cu}^{2+}(\text{B})$ ions in sample 1, taken at room temperature with a microwave frequency of 9.385 GHz. Stick diagrams above the spectra identify the ^{63}Cu and ^{65}Cu hyperfine lines. Lines marked with asterisks are from Fe^{3+} ions at octahedral Ga(2) sites. (a) Magnetic field along the a direction. (b) Magnetic field along the b direction. (c) Magnetic field along the c^* direction.

respectively. In Fig. 3, the approximate concentration of $\text{Cu}^{2+}(\text{B})$ ions is $9.7 \times 10^{18} \text{ cm}^{-3}$. The four Cu hyperfine lines are identified by a stick diagram above the spectrum in Fig. 3(b). When the magnetic field is along the a direction, the separation between the four lines is reduced to near zero and only a broad slightly distorted line is seen. Additional lines in Fig. 3, marked with asterisks, are from Fe^{3+} ions at octahedral Ga(2) sites.

The angular dependence of the $\text{Cu}^{2+}(\text{B})$ EPR spectrum, taken at room temperature, is shown in Fig. 4. These data were obtained while rotating the direction of the magnetic field from a to b , b to c^* , and c^* to a . The splitting of the EPR spectrum into two branches in the b - c^* plane in Fig. 4 indicates that there are two crystallographically equivalent, but magnetically inequivalent, orientations of the $\text{Cu}^{2+}(\text{B})$ ions.²⁵ The fitting method described in Sec. III A, combined with the spin-Hamiltonian in Eq. (1), was used to extract g and A matrices from the angular dependence of the $\text{Cu}^{2+}(\text{B})$ EPR spectrum. Input data were the 169 pairs of magnetic field values and microwave frequencies representing the experimental points in Fig. 4. The resulting “best-fit” values for the $\text{Cu}^{2+}(\text{B})$ parameters are listed in Table II. Directions of the principal axes in Table II are for one of the two crystallographically equivalent orientations of the $\text{Cu}^{2+}(\text{B})$ ions. The principal-axis directions for the other orientation are obtained by applying a reflection through the mirror plane of the crystal to the matrices in Table II. Principal values of the hyperfine matrix in Table II are again a “weighted average” for the ^{63}Cu and ^{65}Cu isotopes.

As can be seen when comparing the results in Tables I and II, the g matrices and the hyperfine matrices are significantly different

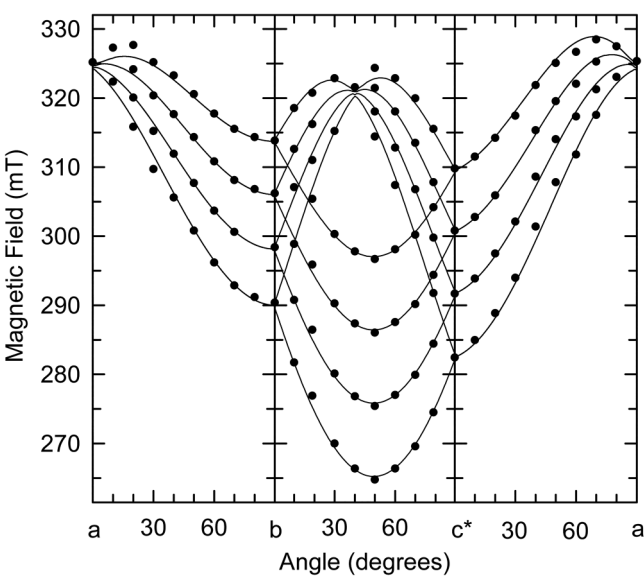


FIG. 4. Angular dependence of the EPR spectrum from $\text{Cu}^{2+}(\text{B})$ ions. The direction of the magnetic field is rotated from a to b , b to c^* , and c^* to a . Discrete points are from experiment. The solid lines were generated using the parameters in Table II.

for the $\text{Cu}^{2+}(\text{A})$ and $\text{Cu}^{2+}(\text{B})$ ions. Fitting the EPR angular dependence gave $g_{\parallel} < g_{\perp}$ for the $\text{Cu}^{2+}(\text{A})$ ions. A similar process gave $g_{\parallel} > g_{\perp}$ for the $\text{Cu}^{2+}(\text{B})$ ions. The g matrices for both defects are axial, but the direction of the unique principal axis is near the a direction for the $\text{Cu}^{2+}(\text{A})$ ions and between the b and c^* directions for one of the crystallographically equivalent orientation of the $\text{Cu}^{2+}(\text{B})$ ions (and between the $-b$ and c^* directions for the other orientation). In Table II, the hyperfine matrix for the $\text{Cu}^{2+}(\text{B})$ ions is also axial with its unique axis between the b and c^* directions (the same as the unique axis of the g matrix).

Although the $\text{Cu}^{2+}(\text{A})$ and $\text{Cu}^{2+}(\text{B})$ EPR spectra both represent Cu^{2+} ions at an octahedral site, their different g and hyperfine

TABLE II. Spin-Hamiltonian parameters for $\text{Cu}^{2+}(\text{B})$ ions in $\beta\text{-Ga}_2\text{O}_3$. Units for the principal hyperfine parameters are MHz. Uncertainties are estimated to be ± 0.001 for the g values, ± 2.0 MHz for the A principal values, and $\pm 1^\circ$ for the angles.

		Principal-axis directions		
Principal values		θ (deg)	ϕ (deg)	Direction in crystal
g matrix				
g_1	2.053	69.6	340.0	Between b and c^*
g_2	2.099	123.3	55.8	
g_3	2.387	40.6	95.7	
A hyperfine matrix (combined ^{63}Cu and ^{65}Cu)				
A_1	0	89.2	358.7	Between b and c^*
A_2	7	130.1	88.0	
A_3	354	40.1	89.7	

matrices indicate that they do not have the same environment. When combined with the results in Sec. VII, we conclude that a defect is located near the $\text{Cu}^{2+}(\text{B})$ ion. A different x, y, z coordinate system, then, is needed when describing the d orbitals. For the orientation of the $\text{Cu}^{2+}(\text{B})$ ion described in Table II, the z direction is placed midway between b and c (i.e., along the unique axes of the g and hyperfine matrices), the x direction is near a , and the y direction is midway between b and $-c$. With these x, y , and z directions, the g matrix in Table II is consistent with the unpaired spin (i.e., the hole) occupying an $(x^2 - y^2)$ orbital.^{28–30} A defect with an effective positive charge located at the oxygen site along the z direction makes the hole prefer the $(x^2 - y^2)$ orbital rather than the $(3z^2 - r^2)$ orbital.

Candidates for this adjacent defect are an OH^- ion, an oxygen vacancy, or an H^- ion trapped within an oxygen vacancy. The observation of the two crystallographically equivalent, but magnetically inequivalent, orientations of the $\text{Cu}^{2+}(\text{B})$ ions (demonstrated by the splitting of the EPR spectrum into two branches in the b - c^* plane in Fig. 4) indicates that the perturbing defect is in the b - c^* plane at one of the four oxygen sites that are adjacent to the Ga(2) site where the $\text{Cu}^{2+}(\text{B})$ ion is located. More specifically, the perturbing defect is at one of the two O(I) sites or at one of the two O(III) sites. The defect could be on either site within a pair and thus would give two crystallographically equivalent orientations for the $\text{Cu}^{2+}(\text{B})$ ions. Our candidate defects (i.e., donors) have positive charge relative to the regular lattice and form a close-associate pair when next to a Cu^{2+} acceptor in the as-grown crystal. As an example of a nearby perturbation,³¹ we note that a Cu^{2+} ion substituting for a Ti^{4+} ion in TiO_2 , with an adjacent oxygen vacancy, has g and hyperfine matrices that are similar to those reported in Table II for the $\text{Cu}^{2+}(\text{B})$ ions.

IV. ENDOR FROM $\text{Cu}^{2+}(\text{A})$ IONS

Electron-nuclear double resonance (ENDOR) experiments are often used to identify nuclei that participate in an EPR spectrum. In our present case, it is already known that ^{63}Cu and ^{65}Cu are responsible for the four-line EPR spectra in Figs. 1 and 3. ENDOR, however, does give other useful information, namely, improved values of the Cu hyperfine parameters and, most important, the nuclear electric quadrupole matrices for the Cu nuclei. The strength of a quadrupole interaction is directly proportional to the electric field gradient at the nucleus. Because of the monoclinic crystal structure of $\beta\text{-Ga}_2\text{O}_3$, there is a large electric field gradient at each Cu^{2+} nucleus caused by the surrounding lattice (with enhancement by the Sternheimer antishielding factor).³² The unpaired spin residing primarily in a d orbital also makes a significant contribution to the electric field gradient at the Cu^{2+} nucleus. EPR experiments, by themselves, do not usually provide information about the nuclear electric quadrupole interactions (except when forbidden transitions are observed).³¹ With ENDOR, these interactions are directly measured.

Two representative ENDOR spectra obtained from the ^{63}Cu and ^{65}Cu nuclei in the $\text{Cu}^{2+}(\text{A})$ ions are shown in Fig. 5. The temperature is 13 K and the magnetic field is aligned along the a direction in the crystal. In an ENDOR experiment, the magnetic field is held constant at the center of an EPR line and the radio frequency (rf) is swept through a region of interest, giving signals when the rf

has the appropriate energy to “flip” a nuclear spin (selection rules for the ENDOR transitions are $\Delta M_S = 0$ and $\Delta m_I = \pm 1$).³³ The ENDOR spectrum in Fig. 5(a) was taken with the magnetic field fixed at the second (i.e., next-to lowest) EPR line in Fig. 1(a) and the spectrum in Fig. 5(b) was taken with the magnetic field set at the third EPR line. Additional ENDOR lines, expected in the 150–165 MHz region, are not present in the spectra in Fig. 5. This is because the upper limit of the rf amplifier in our ENDOR spectrometer was nominally 100 MHz and only a few of the lines appearing at higher frequencies were detected. The label above each line in Fig. 5 identifies the responsible nucleus as ^{63}Cu or ^{65}Cu .

Figure 6 shows the complete ENDOR angular dependence for the ^{63}Cu nuclei in the $\text{Cu}^{2+}(\text{A})$ ions. The discrete points are experimental results. These data were taken while rotating the direction of the magnetic field from a to b , b to c^* , and c^* to a . The following spin-Hamiltonian was used to determine the parameters that describe the angular data in Fig. 6,

$$H = \beta S \cdot g \cdot B + I \cdot A \cdot S + I \cdot P \cdot I - g_n \beta_n I \cdot B. \quad (2)$$

This is the same as the Hamiltonian in Eq. (1), except that a nuclear electric quadrupole term has been added. The nuclear electric quadrupole matrix P is traceless. Its principal values are proportional to e^2qQ , where eq is the electric field gradient and Q is the nuclear quadrupole moment. When using the fitting process to extract the A and P matrices from the angular dependence in Fig. 6, the g matrix was fixed at the values given in Table I. Input data were the 295 pairs of ENDOR frequencies and magnetic field values representing

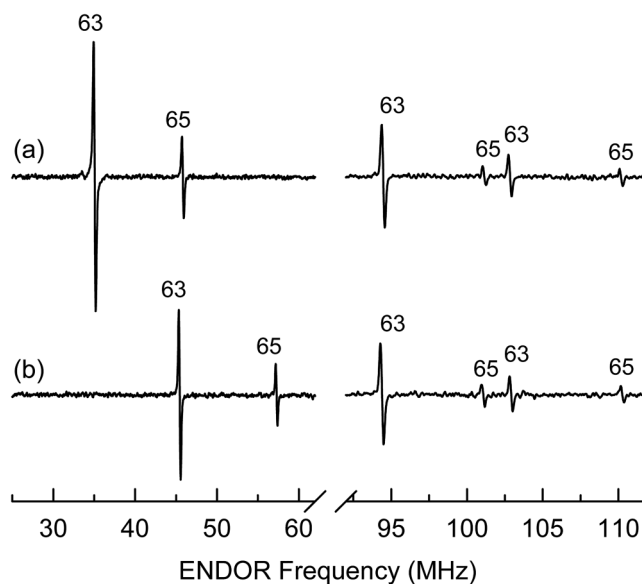


FIG. 5. ENDOR spectra from ^{63}Cu and ^{65}Cu nuclei in $\text{Cu}^{2+}(\text{A})$ ions. These spectra were taken at 13 K from sample 1. The microwave frequency was 9.490 GHz and the magnetic field was along the a direction. Labels above the lines identify the responsible Cu nucleus. (a) Magnetic field fixed at the second (next-to lowest) EPR line in Fig. 1(a). (b) Magnetic field fixed at the third (next to highest) EPR line in Fig. 1(a).

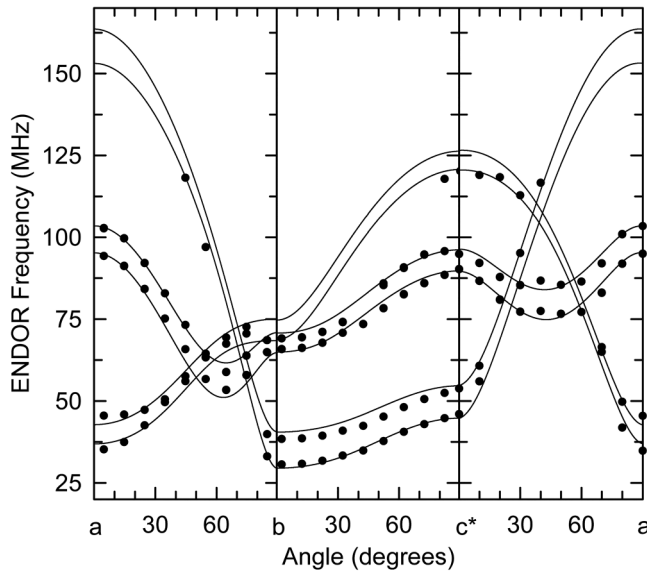


FIG. 6. Angular dependence of the ^{63}Cu ENDOR lines from the $\text{Cu}^{2+}(\text{A})$ ions. The direction of the magnetic field is rotated from a to b , b to c^* , and c^* to a . Discrete points are from experiment. The solid lines were generated using the parameters in Table III.

the experimental points in Fig. 6. The resulting “best-fit” values for the ^{63}Cu parameters are listed in Table III for the $\text{Cu}^{2+}(\text{A})$ ions. Corresponding values for the ^{65}Cu parameters are obtained by multiplying the hyperfine principal values in Table III by 1.069 and multiplying the quadrupole principal values by 0.924. These numerical factors are the ratios of nuclear magnetic moments and nuclear electric quadrupole moments, respectively, for the two Cu isotopes.²³ The principal-axis directions are the same for the two isotopes. For comparison, we note that Jeom and Lim³⁴ have used nuclear magnetic resonance (NMR) to determine the nuclear electric quadrupole parameters for ^{69}Ga and ^{71}Ga nuclei in $\beta\text{-Ga}_2\text{O}_3$ crystals.

TABLE III. Spin-Hamiltonian parameters from ENDOR for $\text{Cu}^{2+}(\text{A})$ ions in $\beta\text{-Ga}_2\text{O}_3$. Units for the principal hyperfine parameters are MHz. Uncertainties are estimated to be ± 0.5 MHz for the A principal values, ± 0.2 MHz for the P principal values, and $\pm 1^\circ$ for the angles.

		Principal-axis directions		
	Principal values	θ (deg)	ϕ (deg)	Directions in crystal
A hyperfine matrix for ^{63}Cu				
A_1	198.8	83.3	0.0	Near a
A_2	106.7	90.0	90.0	Near b
A_3	172.6	8.7	180.0	Near c^*
P nuclear electric quadrupole matrix for ^{63}Cu				
P_1	19.78	89.8	0.0	Near a
P_2	-6.99	90.0	90.0	Near b
P_3	-12.79	0.2	180.0	Near c^*

V. EPR FROM Cu^{3+} IONS

An $S = 1$ EPR spectrum appears when the Cu-doped $\beta\text{-Ga}_2\text{O}_3$ crystals are exposed at room temperature to ultraviolet light. At the same time, the EPR spectra from the $\text{Cu}^{2+}(\text{A})$ and $\text{Cu}^{2+}(\text{B})$ ions decrease in intensity. For both sample 1 and sample 2, the underlying electronic process leading to the formation of the $S = 1$ spectrum is efficiently driven by 275 nm (4.51 eV) light. We found that 325 nm (3.81 eV) light is considerably less efficient in both samples and 442 nm (2.81 eV) light has essentially no effect. This suggests that a threshold mechanism may be involved, with photon energies greater than midgap required.

The new $S = 1$ spectrum is assigned to Cu^{3+} ($3d^8$) ions. Although $S = 1$ spectra are usually studied with higher microwave frequencies,³⁵ we could easily identify lines due to the Cu^{3+} ions using our spectrometer operating near 9.4 GHz. Figure 7 shows the Cu^{3+} EPR spectrum taken at room temperature from sample 1 after an exposure to 275 nm light (the microwave frequency was 9.377 GHz and the magnetic field was along the a direction). The same Cu^{3+} spectrum, with nearly the same intensity, is produced with 275 nm light in sample 2. Long spin-lattice relaxation times allow the Cu^{3+} ions to be observed at room temperature. We estimate that the concentration of Cu^{3+} ions in Fig. 7 is approximately $1.4 \times 10^{19} \text{ cm}^{-3}$.

The following spin-Hamiltonian (with $S = 1$ and $I = 3/2$) describes the Cu^{3+} EPR spectrum:

$$H = \beta S \cdot g \cdot B + S \cdot D \cdot S + I \cdot A \cdot S - g_n \beta_n I \cdot B. \quad (3)$$

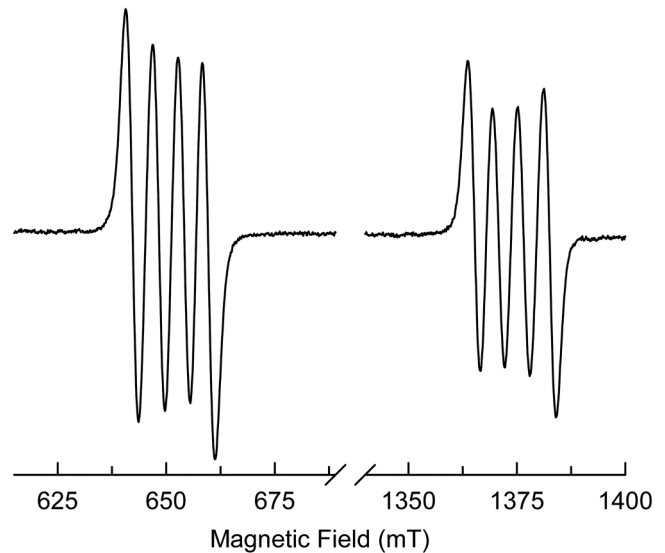


FIG. 7. EPR spectrum from Cu^{3+} ions in sample 1 (a CZ-grown $\beta\text{-Ga}_2\text{O}_3$ crystal). The Cu^{3+} ions were produced at room temperature with 275 nm light. This spectrum was taken at room temperature with the magnetic field along the a direction and a microwave frequency of 9.377 GHz. The four lines in each set represent ^{63}Cu and ^{65}Cu hyperfine interactions.

13 July 2023 18:55:18

Electron Zeeman, fine structure (i.e., zero-field splitting), hyperfine, and nuclear Zeeman terms are included.³⁶ Here, the D matrix represents the spin-orbit and spin-spin couplings between the 3d electrons averaged over their spatial distributions.³⁷ There are two groups of four lines, centered near 0.653 and 1.375 T, in the spectrum in Fig. 7. The separation of lines within each group is approximately 6.2 mT and is the result of hyperfine interactions with ⁶³Cu and ⁶⁵Cu nuclei. As expected, the strengths of these Cu³⁺ hyperfine interactions in β -Ga₂O₃ are similar to those reported for Cu³⁺ in α -Al₂O₃.⁸ More importantly, the two sets of lines in Fig. 7 are separated by 0.722 T. This large separation is caused by the zero-field splitting and, thus, directly demonstrates the S = 1 nature of the Cu³⁺ spectrum.

The angular dependence of the Cu³⁺ EPR spectrum (for our X-band microwave frequency) is shown in Fig. 8. Data were taken for rotations in the *a*-*b* and the *b*-*c** planes. Here, we ignore the relatively small Cu hyperfine splittings and plot only the centers of the two four-line groups. This angular dependence is unusual, as lines are only detected when the direction of the magnetic field is near *a* or *c**. There were no EPR lines for most directions of the magnetic field because the zero-field splittings are larger than our microwave frequency. The spin-Hamiltonian in Eq. (3), after removing terms involving the nuclear spin, is used to extract parameters from the experimental data in Fig. 8. We assume an isotropic g matrix, as our limited angular data do not allow a full determination of the g matrix. This is, however, a good approximation, since the anisotropy of g matrices is usually minimal for d⁸ spin systems.^{8,9} Because the loops in Fig. 8 are centered on the *a* and the *c** directions, the principal axes of the D matrix must be along the *a*, *b*, and *c** directions in the crystal. Also, the D matrix is traceless. Together, this leaves only three parameters to be determined (a g value and two principal values of the D matrix). Input data for the fitting program were the microwave frequency (9.377 GHz), two magnetic fields from the *a* spectrum (0.653 and 1.375 T), and one magnetic field from the *c** spectrum (0.934 T). The “best-fit” values for the Cu³⁺ spin-Hamiltonian parameters are given in Table IV.

Figure 9 illustrates the origin of the “loops” in the Cu³⁺ angular dependence (see Fig. 8).^{38,39} In this figure, energy levels are plotted vs the strength of the magnetic field (hyperfine effects are not included). The magnetic field is oriented along the *a* direction in Fig. 9(a) and is rotated 12° from *a* toward *b* in Fig. 9(b). EPR transitions are indicated by vertical red lines having lengths corresponding to the microwave frequency. With the field along *a*, the two EPR lines are separated by 722 mT, as seen in Fig. 9(a). When the direction of the magnetic field is rotated away from *a*, the two energy levels begin to separate and the two EPR lines move closer. At 12° in Fig. 9(b), they have moved to a separation of 518 mT. The two energy levels continue to diverge as the angle from *a* is increased and the EPR lines continue to converge. Beyond 18°, the separation between the two energy levels is greater than the microwave frequency, and EPR transitions no longer occur.

VI. PHOTOINDUCED OPTICAL ABSORPTION

Figure 10 shows optical absorption from sample 1 before and after an exposure to 275 nm light. These spectra were taken at room temperature with unpolarized light propagating along the *a* direction in the crystal. Two absorption peaks, near 2.90 eV

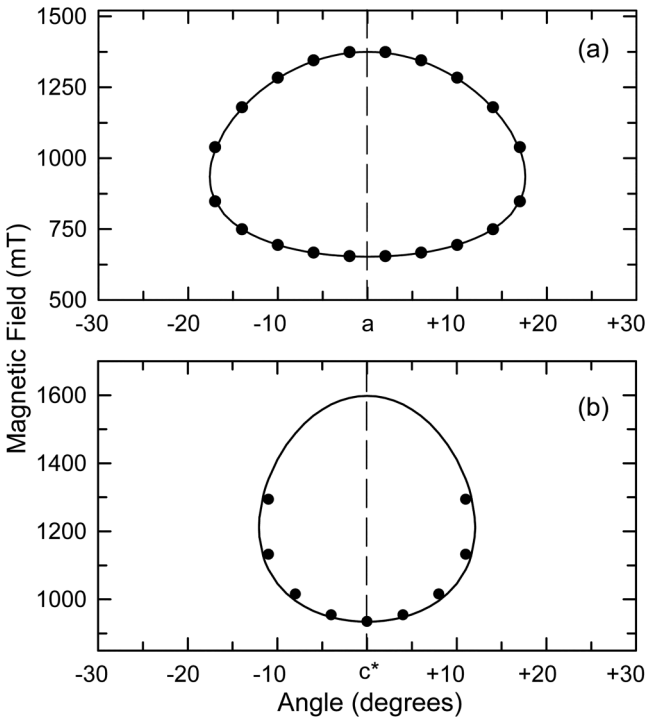


FIG. 8. Angular dependence of the Cu³⁺ EPR spectrum. (a) The direction of the magnetic field is rotated in the *a*-*b* plane. (b) The direction of the magnetic field is rotated in the *b*-*c** plane. Experimental results are represented by discrete points. The solid lines were generated using the parameters in Table IV. There are no experimental points above 1.40 T in the lower plot because of the high-field limit of the magnet.

13 JULY 2023 18:55:18

(428 nm) and 3.48 eV (356 nm), are present in the “before light” spectrum. These absorption features have been attributed to the presence of deep singly ionized Ir⁴⁺ donors.^{2,40} The primary effect of the 275 nm light is the production of a broad double-peaked absorption in the region from 2.4 to 3.7 eV (517–335 nm). These photoinduced absorption features have been assigned by Jesenovec *et al.*⁵ to Cu³⁺ ions. Additional photoinduced absorption is seen between 1.6 and 2.3 eV (775–540 nm).

TABLE IV. Spin-Hamiltonian parameters for Cu³⁺ ions in β -Ga₂O₃. Units for the zero-field parameters are GHz. The values for g, D₁, and D₂ were determined by fitting experimental results. D₃ is obtained from D₁ and D₂ using the traceless nature of D. Uncertainty in the D values is estimated to be ± 0.2 GHz.

	Principal values	Direction of principal axis
	g matrix (isotropic)	
g	2.086	
	D matrix (zero-field parameters)	
D ₁	22.18	Near <i>a</i>
D ₂	3.31	Near <i>b</i>
D ₃	-25.49	Near <i>c</i> *

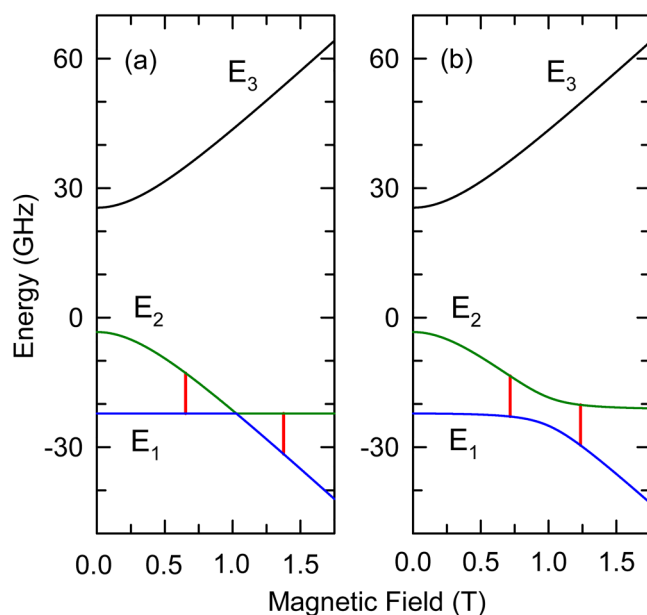


FIG. 9. Energy levels as a function of magnetic field for Cu^{3+} ions ($S = 1$) in a Cu-doped $\beta\text{-Ga}_2\text{O}_3$ crystal. Observed transitions (i.e., EPR lines) are indicated by red vertical lines. (a) Magnetic field along the a direction. (b) Magnetic field 12° from a toward b .

A more detailed look at the photoinduced absorption from sample 1 is provided in Fig. 11. The spectra in this figure were taken at room temperature with light propagating along the a direction and polarized either $E \parallel b$ or $E \parallel c^*$. Before the exposure to 275 nm light, only the absorption at the band edge shows a polarization effect, shifting from 4.70 eV for $E \parallel b$ to 4.45 eV for $E \parallel c^*$. Intrinsic transitions from multiple valence bands to the conduction band minimum are responsible for this shift (selection rules govern their polarizations).^{41–43} After the exposure to 275 nm light, significant polarization effects are seen in the photoinduced bands associated with the Cu^{3+} ions. Two bands peaking near 3.40 and 2.55 eV dominate the spectrum with $E \parallel c^*$. Additional absorption is seen with $E \parallel b$. In the inset to Fig. 11, the spectrum taken with $E \parallel c^*$ has been subtracted from the spectrum taken with $E \parallel b$. The resulting “difference” spectrum shows an intense peak near 2.94 eV and smaller peaks near 2.07 and 1.78 eV. Our results in Fig. 11 suggest that there are five bands associated with the Cu^{3+} ions, two at 365 and 486 nm best seen with $E \parallel c^*$, and three at 422, 599, and 696 nm best seen with $E \parallel b$. These same five absorption bands are also present, with similar intensities, in sample 2 after exposure to 275 nm light.

Blumberg *et al.*⁸ showed that the three absorption bands observed in the visible and near-ultraviolet for Cu^{3+} ions in $\alpha\text{-Al}_2\text{O}_3$ are explained by a Tanabe–Sugano energy level diagram^{44–46} constructed for $3d^8$ ions in a cubic field. A similar approach is appropriate for our present case. The Cu^{3+} ions in $\beta\text{-Ga}_2\text{O}_3$ are in a distorted octahedron, and this should cause a further splitting of levels and possibly introduce polarization effects, thus supporting

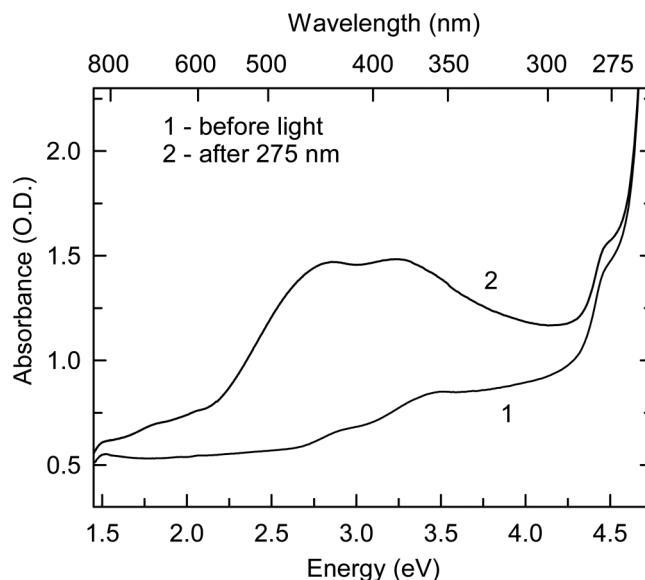


FIG. 10. Optical absorption spectra from sample 1, taken at room temperature with unpolarized light propagating along the a direction in the crystal. Spectrum 1 was taken before exposure to light. Spectrum 2 was taken after exposure to 275 nm light.

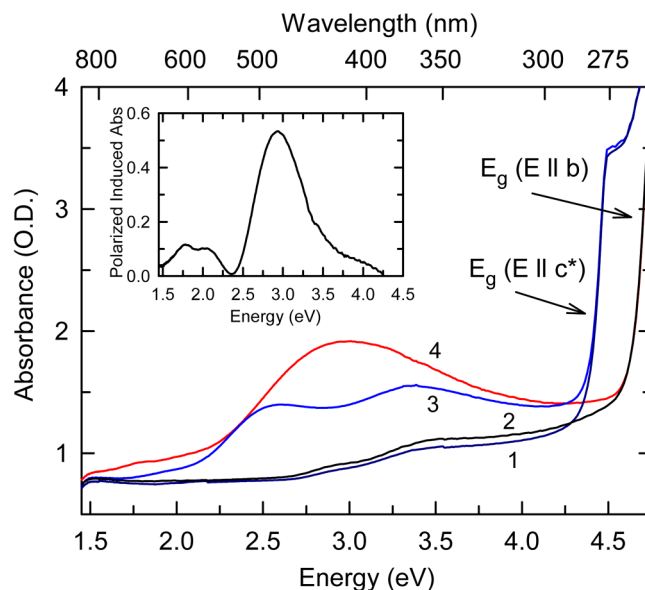


FIG. 11. Polarization effects in the optical absorption from Cu^{3+} ions in sample 1. Spectrum 1 (with $E \parallel c^*$) and spectrum 2 (with $E \parallel b$) were taken before exposure to 275 nm. Spectrum 3 (with $E \parallel c^*$) and spectrum 4 (with $E \parallel b$) were taken after exposure to 275 nm. The inset shows the difference spectrum produced when spectrum 3 ($E \parallel c^*$) is subtracted from spectrum 4 ($E \parallel b$).

our assignment of the five photoinduced bands in Fig. 11 to Cu^{3+} ions. A theoretical/computational study of the expected optical absorption from Cu^{3+} ions in $\beta\text{-Ga}_2\text{O}_3$ will help in the interpretation of the experimental spectra.

Samples 1 and 2 differ in one respect. The two absorption bands attributed to Ir^{4+} ions, at 2.90 and 3.48 eV in the “before light” spectrum in sample 1 (see Fig. 10), are not observed in the “before light” spectrum from sample 2. This result indicates that the Fermi level is higher in sample 2, with most of the iridium present as Ir^{3+} ions (i.e., neutral donors).

VII. THERMAL RECOVERY RESULTS

The decay of the Cu^{3+} EPR spectrum and Cu^{3+} optical absorption bands and the recovery of the Cu^{2+} EPR spectra have been monitored as a crystal is heated stepwise above room temperature. These results for samples 1 and 2 are shown in Figs. 12–15. Before beginning each series of thermal annealing steps, the crystal was reset by heating to 500 °C. This removed the effects of previous illuminations and restored the crystal to its as-grown state. Then, the crystal was exposed at room temperature to 275 nm light for 2 min. Next, the crystal was heated in 25 °C steps, from 75 to 375 °C. For each step, after pre-heating a small tube furnace to a set temperature, the crystal was quickly positioned at the center of the furnace and removed after 2 min. Following the 2 min anneal, the crystal was either placed in the microwave cavity and an EPR spectrum was taken at 40 K or placed in the spectrophotometer and an optical absorption spectrum was taken at room temperature. After recording the spectrum, the process was repeated at the next higher temperature. For each sample, EPR data were collected during one

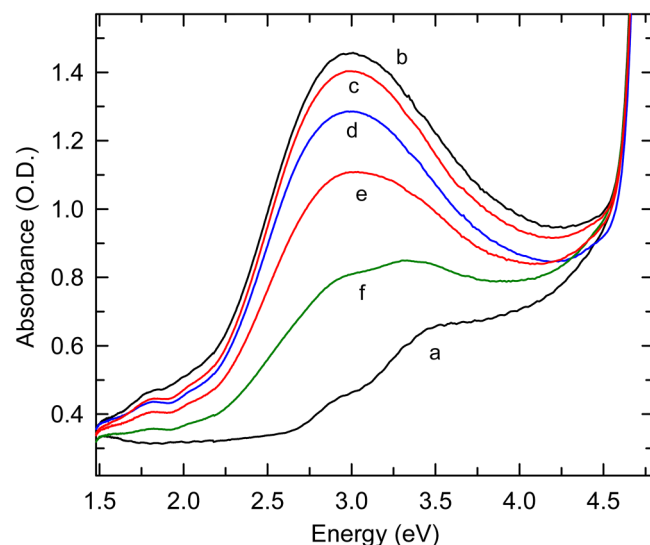


FIG. 12. Thermal decay of Cu^{3+} optical absorption in sample 1. Spectra were taken at room temperature with light polarized $E \parallel b$ and propagating along the a direction in the crystal. Spectrum a was taken before exposure to 275 nm light. Spectrum b was taken after exposure to 275 nm light. Spectra c, d, e, and f were taken after heating to 225, 250, 300, and 325 °C, respectively.

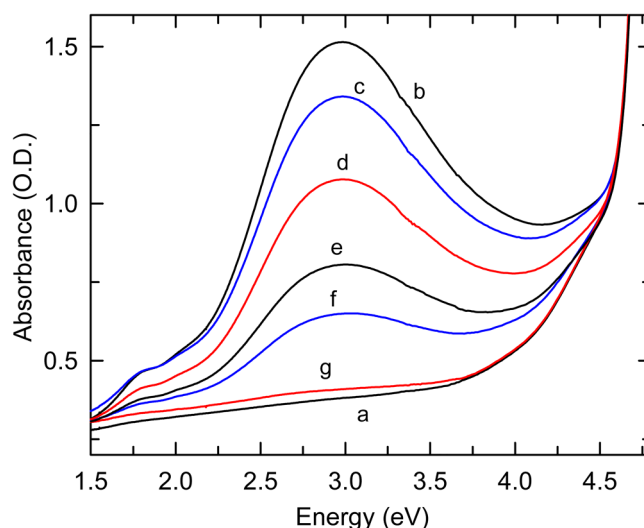


FIG. 13. Thermal decay of Cu^{3+} optical absorption in sample 2. Spectra were taken at room temperature with light polarized $E \parallel b$ and propagating along the a direction in the crystal. Spectrum a was taken before exposure to 275 nm light. Spectrum b was taken after exposure to 275 nm light. Spectra c, d, e, f, and g were taken after heating to 100, 125, 150, 175, and 325 °C, respectively.

series of heating steps, and optical absorption data were collected during an identical, but separate, series of heating steps.

Data describing the thermal decay of the Cu^{3+} optical absorption bands in sample 1 (CZ-grown) are shown in Fig. 12. These spectra were taken with light propagating along the a direction in the crystal and polarized with $E \parallel b$. With this polarization of the spectrometer light, the bands peaking at 365, 422, and 486 nm are all present and strongly overlap. Although spectra were taken every 25 °C, only a subset of these spectra is plotted in Fig. 12. A similar set of absorption data for sample 2 (VGF-grown) is shown in Fig. 13. The absorption bands in Figs. 12 and 13 are very similar, in both shape and intensity, which agrees with our observations in Sec. V that the concentrations represented by the Cu^{3+} EPR signal are nearly the same in sample 1 and sample 2. This leads us to conclude that the photoinduced optical absorption bands in Figs. 11 and 12 and the EPR spectrum in Fig. 7 are from the same defect, namely, the isolated Cu^{3+} neutral acceptor at an octahedral Ga site.

The thermal decay results for the EPR spectra observed in sample 1 are shown in Fig. 14. Intensities of the $\text{Cu}^{2+}(\text{A})$, $\text{Cu}^{2+}(\text{B})$, Cu^{3+} , and Ir^{4+} EPR spectra are plotted as a function of heating temperature. Starting on the left side of the plot, the first two sets of data points represent intensities of the EPR spectra before and immediately after exposure to the 275 nm light. The intensities of the $\text{Cu}^{2+}(\text{A})$, $\text{Cu}^{2+}(\text{B})$, and Ir^{4+} spectra are normalized to their initial values before 275 nm light and the intensity of the Cu^{3+} spectrum is normalized to its value immediately after illuminating with the 275 nm light. Heating steps begin with the data points at 75 °C. Normalized production and decay results for optical absorption (measured at 422 nm in Fig. 12) are also included in Fig. 14. The Ir^{4+} and $\text{Cu}^{2+}(\text{A})$ EPR spectra both decrease by more than half

13 JULY 2023 18:55:18

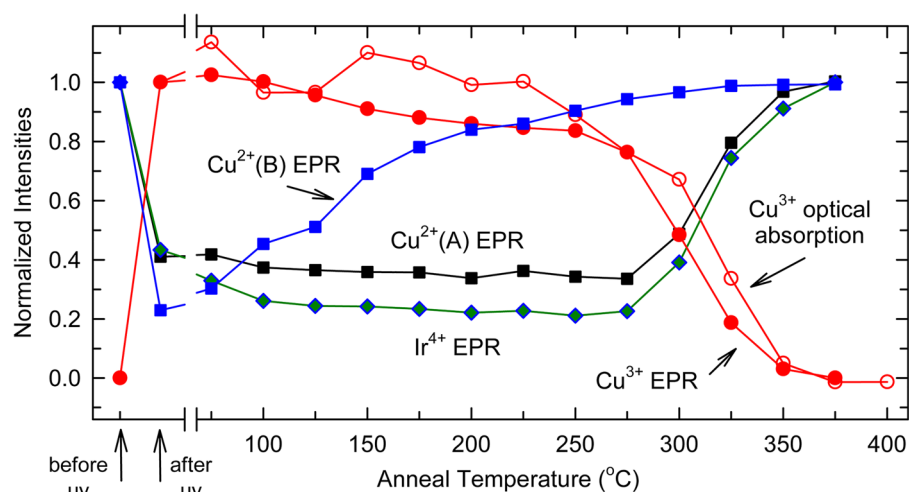


FIG. 14. Thermal decay and recovery of EPR and optical absorption spectra in sample 1 (CZ grown). Intensities of $\text{Cu}^{2+}(\text{A})$ EPR (black squares), $\text{Cu}^{2+}(\text{B})$ EPR (blue squares), Cu^{3+} EPR (red closed circles), Cu^{3+} optical absorption (red open circles), and Ir^{4+} EPR (green diamonds) are shown.

and the Cu^{3+} EPR and optical absorption spectra appear when the 275 nm light is turned on, whereas heating in the 275–375 °C region restores the initial Ir^{4+} and $\text{Cu}^{2+}(\text{A})$ spectra and destroys the Cu^{3+} spectra. Although 275 nm light initially reduces both of their intensities, the $\text{Cu}^{2+}(\text{A})$ and $\text{Cu}^{2+}(\text{B})$ ions have significantly different recovery behaviors during the subsequent heating. There is a small decrease in the Cu^{3+} EPR spectrum in the 75–200 °C region that appears to correlate with the recovery of the $\text{Cu}^{2+}(\text{B})$ ions.

A relatively simple explanation of the primary photoinduced process emerges from the data in Fig. 14. In sample 1, with a lower Fermi level, electrons and holes produced by the 275 nm light are trapped at Ir^{4+} ions and $\text{Cu}^{2+}(\text{A})$ ions, respectively, and form Ir^{3+} ions (neutral donors) and Cu^{3+} ions (neutral acceptors). In other words, the light transfers electrons from the singly ionized $\text{Cu}^{2+}(\text{A})$ acceptors to the singly ionized Ir^{4+} donors (e.g., an electron from the valence band is excited to an Ir^{4+} ion and the hole left in the valence band is trapped by a Cu^{2+} ion). Upon heating, the Ir^{3+} and Cu^{3+} ions become thermally unstable between 275 and 375 °C. One

(or both) of these neutral defects releases charge that then moves to the other defect, thus restoring the Ir^{4+} ions and $\text{Cu}^{2+}(\text{A})$ ions to their pre-illumination concentrations. We use the approximation $E \approx 25kT_m$ to estimate a thermal activation energy for this recovery process.^{47–50} Here, T_m corresponds to the temperature where half of the neutral Cu^{3+} acceptors have decayed and half the Ir^{4+} ions have recovered. From Fig. 14, T_m is near 315 °C (or 588 K). This gives a thermal activation energy near $E = 1.27$ eV.

Since the $\text{Ir}^{3+/4+}$ donor level has been experimentally determined to be 2.25 eV below the conduction band minimum,⁵¹ we attribute the decay of the Cu^{3+} ions and recovery of the Ir^{4+} ions in Fig. 14 to the thermal excitation of electrons from the valence band to the neutral Cu acceptors (or equivalently, the release of holes to the valence band). With this interpretation, our analysis of the Cu^{3+} thermal decay places the $(0/-)$ level of the isolated Cu acceptor approximately 1.27 eV above the valence-band maximum. Recently, Cai *et al.*⁴ predicted that the $(0/-)$ level of Cu in $\beta\text{-Ga}_2\text{O}_3$ is 2.02 eV above the valence band maximum. These experimental and calculated

13 July 2023 18:55:18

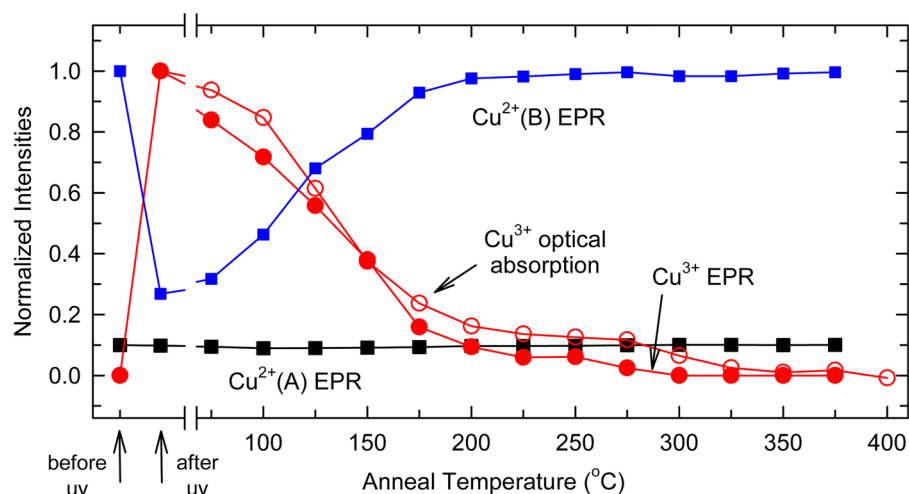


FIG. 15. Thermal decay and recovery of EPR and optical absorption spectra in sample 2 (VGF grown). Intensities of $\text{Cu}^{2+}(\text{A})$ EPR (black squares), $\text{Cu}^{2+}(\text{B})$ EPR (blue squares), Cu^{3+} EPR (red closed circles), and Cu^{3+} optical absorption (red open circles) are shown.

values for the Cu (0/−) acceptor level are in reasonable agreement and follow the trend seen for the Mg and Zn (0/−) levels in β -Ga₂O₃ of experimental values being lower than computational values.^{1,52}

We now turn to sample 2, grown by the VGF method, and show the thermal decay and recovery of photoinduced defects in Fig. 15. As was noted earlier, there are significant differences between samples 1 and 2. In sample 2, the initial concentration of Cu²⁺(B) ions is 12 times greater than the concentration of Cu²⁺(A) ions, whereas the initial concentrations of these two defects are nearly equal in sample 1. Also, sample 2 has a higher Fermi level that causes nearly all the iridium donors to initially be in the non-EPR-active neutral Ir³⁺ charge state. In contrast, most of the iridium ions in sample 1 are initially present as singly ionized Ir⁴⁺ ions. Infrared absorption gave a value of $1.0 \times 10^{17} \text{ cm}^{-3}$ for the “before light” concentration of Ir⁴⁺ ions in sample 2 compared to a “before light” value of $4.0 \times 10^{18} \text{ cm}^{-3}$ for Ir⁴⁺ ions in sample 1.

In Fig. 15, the intensities of the Cu²⁺(B) and Cu³⁺ EPR spectra are plotted as a function of heating temperature after an exposure to 275 nm light. Production and decay results for the Cu³⁺ optical absorption (measured at 422 nm in Fig. 13) are also included. The Cu²⁺(A) EPR data have been added in Fig. 15 but are not normalized because the intensities are much reduced compared to Cu²⁺(B) and do not change significantly with temperature. Figures 14 and 15 can be directly compared since the same steps were followed when taking data. As can be seen, sample 2 is very different from sample 1. The Cu²⁺(B) ions play a central role in sample 2. Their decrease with light and their thermal recovery directly correlates with the production and decay of the Cu³⁺ ions. This is different from sample 1 where there was little connection between the Cu³⁺ and Cu²⁺(B) ions during heating.

The results in Fig. 15 suggest that 275 nm light converts Cu²⁺(B) ions to Cu³⁺ ions in sample 2. Since the concentration of Ir⁴⁺ ions is small in sample 2, another defect must be serving as the electron trap during illumination. Both observations can be explained if Cu²⁺(B) ions play a dual role [i.e., if the probability for a Cu²⁺(B) ion to trap a hole and become a Cu³⁺ ion is nearly equal to the probability for a Cu²⁺(B) to trap an electron and become a Cu⁺ ion]. Unfortunately, the mechanisms that lead to this dual behavior have not been clearly identified. One possible scenario that would be consistent with much of the data is based on an OH[−] ion being the adjacent defect for the Cu²⁺(B) ions. The 275 nm light could cause the OH[−] ion to disassociate into an O^{2−} ion and an H⁺, with the H⁺ moving away from the Cu²⁺ ion and bonding to a more distant oxygen ion.^{53,54} After the dissociation of the OH[−] ion, the Cu²⁺ ion, now with no adjacent defect, could trap a hole and become a Cu³⁺ ion. The remaining Cu²⁺(B) ions, with the adjacent OH[−] ion, could trap electrons and become Cu⁺ (3d¹⁰) ions. These Cu⁺ ions would have no unpaired spins and, thus, no EPR signal (this would account for the lack of an observable electron trap in Fig. 15). Electrons thermally released from these Cu⁺ ions in the 75–175 °C range would recombine with holes at the Cu³⁺ ions. Another possible scenario begins with an H[−] ion trapped within an oxygen vacancy as the adjacent defect for the Cu²⁺(B) ions. This latter model has been explored by Jesenovec *et al.*⁵ A final determination of the mechanisms leading to the production and thermal decay of the Cu³⁺ ions in VGF-grown crystals, such as sample 2, must await further experimental and computational results.

VIII. SUMMARY

Two $S = 1/2$ EPR spectra, labeled Cu²⁺(A) and Cu²⁺(B), are observed in as-grown Cu-doped β -Ga₂O₃ crystals grown by the CZ and VGF methods. The Cu²⁺(A) ions occupy Ga(2) sites with no nearby defect and have the unpaired spin in a $(3z^2 - r^2)$ orbital. The Cu²⁺(B) ions, also at Ga(2) sites, have the unpaired spin in an $(x^2 - y^2)$ orbital because of a defect located at a neighboring oxygen site in the b - c plane. ENDOR provides further characterization of the Cu²⁺(A) ions. Exposure at room temperature to 275 nm light produces Cu³⁺ ions and decreases the intensities of the Cu²⁺(A) and Cu²⁺(B) spectra. The Cu³⁺ ions have an $S = 1$ EPR spectrum and are responsible for broad optical absorption bands peaking near 365, 422, 486, 599, and 696 nm. Spin-Hamiltonian parameters are determined for the three EPR spectra.

A series of stepwise thermal anneals after an illumination show that the decay of the Cu³⁺ ions and the recovery of the Cu²⁺(A) and Cu²⁺(B) ions happen in the 75–375 °C range, with the CZ-grown and the VGF-grown crystals having quite different responses. The CZ-grown crystal has a simple behavior, as expected for the high-quality material containing few unintentional defects. When the 275 nm light is on the CZ crystal at room temperature, singly ionized Ir⁴⁺ donors convert to neutral Ir³⁺ donors by trapping electrons and singly ionized Cu²⁺(A) acceptors convert to neutral Cu³⁺ acceptors by trapping holes. Subsequent heating, without light, allows the Cu³⁺ acceptors to release holes to the valence band near 315 °C. An activation energy for this process is estimated to be 1.27 eV. This, in turn, places the (0/−) level for Cu acceptors in β -Ga₂O₃ approximately 1.27 eV above the valence band maximum.

The behavior of the VGF crystal during illumination and subsequent heating is more complex and reflects the presence of large concentrations of unintentional defects (possibly hydrogen and/or oxygen vacancies). In contrast to the CZ crystal, where the Cu³⁺ ions decay near 315 °C when they release holes, the Cu³⁺ ions in the VGF crystal decay near 125 °C when electrons are released from an unidentified electron trap (most likely Cu⁺ ions). The details of the mechanisms involved in the formation and decay of Cu³⁺ ions in the VGF material are not well understood at this time.

ACKNOWLEDGMENTS

T.D.G. was supported at the Air Force Institute of Technology by an NRC Research Associateship Award. Work at WSU was supported by the Air Force Office of Scientific Research under Award No. FA9550-21-1-0507 monitored by Dr. Ali Sayir. Any opinions, findings, and conclusions or recommendations expressed in this paper are those of the authors and do not necessarily reflect the views of the United States Air Force.

AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

DATA AVAILABILITY

The data that support the findings of this study are available within the article.

13 July 2023 18:55:18

REFERENCES

- ¹T. D. Gustafson, J. Jesenovec, C. A. Lenyk, N. C. Giles, J. S. McCloy, M. D. McCluskey, and L. E. Halliburton, "Zn acceptors in β -Ga₂O₃ crystals," *J. Appl. Phys.* **129**, 155701 (2021).
- ²J. Jesenovec, J. Varley, S. E. Karcher, and J. S. McCloy, "Electronic and optical properties of Zn-doped β -Ga₂O₃ Czochralski single crystals," *J. Appl. Phys.* **129**, 225702 (2021).
- ³D. Skachkov and W. R. L. Lambrecht, "Computational study of electron paramagnetic resonance parameters for Mg and Zn impurities in β -Ga₂O₃," *Appl. Phys. Lett.* **114**, 202102 (2019).
- ⁴X. Cai, F. P. Sabino, A. Janotti, and S.-H. Wei, "Approach to achieving a *p*-type transparent conducting oxide: Doping of bismuth-alloyed Ga₂O₃ with a strongly correlated band edge state," *Phys. Rev. B* **103**, 115205 (2021).
- ⁵J. Jesenovec, C. Pansegrau, M. D. McCluskey, J. S. McCloy, T. D. Gustafson, L. E. Halliburton, and J. B. Varley, "Persistent room-temperature photodarkening in Cu-doped β -Ga₂O₃," *Phys. Rev. Lett.* (in press).
- ⁶J.-M. Spaeth and H. Overhof, *Point Defects in Semiconductors and Insulators Determination of Atomic and Electronic Structure from Paramagnetic Hyperfine Interactions* (Springer-Verlag, Berlin, 2003).
- ⁷J. A. Weil and J. R. Bolton, *Electron Paramagnetic Resonance: Elementary Theory and Practical Applications*, 2nd ed. (John Wiley and Sons, Hoboken, NJ, 2007).
- ⁸W. E. Blumberg, J. Eisinger, and S. Geschwind, "Cu³⁺ ion in corundum," *Phys. Rev.* **130**, 900 (1963).
- ⁹S. A. Marshall, T. T. Kikuchi, and A. R. Reinberg, "Paramagnetic resonance absorption of divalent nickel in α -Al₂O₃ single crystal," *Phys. Rev.* **125**, 453 (1962).
- ¹⁰C. Bozdog, K. H. Chow, G. D. Watkins, H. Sunakawa, N. Kuroda, and A. Usui, "Electron paramagnetic resonance of Cu(d⁹) in GaN," *Phys. Rev. B* **62**, 12923 (2000).
- ¹¹M. Saleh, A. Bhattacharyya, J. B. Varley, S. Swain, J. Jesenovec, S. Krishnamoorthy, and K. Lynn, "Electrical and optical properties of Zr doped β -Ga₂O₃ single crystals," *Appl. Phys. Express* **12**, 085502 (2019).
- ¹²M. Saleh, J. B. Varley, J. Jesenovec, A. Bhattacharyya, S. Krishnamoorthy, S. Swain, and K. Lynn, "Degenerate doping in β -Ga₂O₃ single crystals through Hf-doping," *Semicond. Sci. Technol.* **35**, 04LT01 (2020).
- ¹³J. Jesenovec, C. Rempke, J. Huso, B. Dutton, P. Toews, M. D. McCluskey, and J. S. McCloy, "Photodarkening and dopant segregation in Cu-doped β -Ga₂O₃ Czochralski single crystals," *J. Cryst. Growth* **578**, 126419 (2022).
- ¹⁴M. L. Meil'man, "EPR of Fe³⁺ ions in β -Ga₂O₃ crystals," *Sov. Phys. Solid State* **11**, 1403 (1969).
- ¹⁵Z. Galazka, K. Irmscher, R. Schewski, I. M. Hanke, M. Pietsch, S. Ganschow, D. Klimm, A. Dittmar, A. Fiedler, T. Schroeder, and M. Bickermann, "Czochralski-grown bulk β -Ga₂O₃ single crystals doped with mono-, di-, tri-, and tetravalent ions," *J. Cryst. Growth* **529**, 125297 (2020).
- ¹⁶C. A. Lenyk, N. C. Giles, E. M. Scherrer, B. E. Kananen, L. E. Halliburton, K. T. Stevens, G. K. Foundos, J. D. Blevins, D. L. Dorsey, and S. Mou, "Ir⁴⁺ ions in β -Ga₂O₃ crystals: An unintentional deep donor," *J. Appl. Phys.* **125**, 045703 (2019).
- ¹⁷S. Geller, "Crystal structure of (β -Ga₂O₃)," *J. Chem. Phys.* **33**, 676 (1960).
- ¹⁸J. Åhman, G. Svensson, and J. Albertsson, "A reinvestigation of β -gallium oxide," *Acta Cryst. C* **52**, 1336 (1996).
- ¹⁹H. Yan, Y. Guo, Q. Song, and Y. Chen, "First-principles study on electronic structure and optical properties of Cu-doped β -Ga₂O₃," *Physica B* **434**, 181 (2014).
- ²⁰C. Tang, J. Sun, N. Lin, Z. Jia, W. Mu, X. Tao, and X. Zhao, "Electronic structure and optical property of metal-doped Ga₂O₃: A first principles study," *RSC Adv.* **6**, 78322 (2016).
- ²¹C. Zhang, F. Liao, X. Liang, H. Gong, Q. Liu, L. Li, X. Qin, X. Huang, and C. Huang, "Electronic transport properties in metal doped β -Ga₂O₃: A first principles study," *Physica B* **562**, 124 (2019).
- ²²R. D. Shannon, "Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides," *Acta Cryst. A* **32**, 751 (1976).
- ²³N. J. Stone, "Table of nuclear magnetic dipole and electric quadrupole moments," *At. Data Nucl. Data Tables* **90**, 75 (2005).
- ²⁴T. D. Gustafson, E. M. Golden, E. M. Scherrer, N. C. Giles, A. A. Grabar, S. A. Basun, D. R. Evans, J. E. Slagle, and L. E. Halliburton, "Photoinduced trapping of charge at sulfur vacancies and copper ions in photorefractive Sn₂P₂S₆ crystals," *J. Appl. Phys.* **129**, 085702 (2021).
- ²⁵E. M. Scherrer, N. C. Giles, T. E. R. Dodson, A. A. Grabar, D. R. Evans, S. A. Basun, J. E. Slagle, and L. E. Halliburton, "Charge trapping by iodine ions in photorefractive Sn₂P₂S₆ crystals," *J. Chem. Phys.* **153**, 144503 (2020).
- ²⁶J. E. Stehr, D. M. Hofmann, J. Schörmann, M. Becker, W. M. Chen, and I. A. Buyanova, "Electron paramagnetic resonance signatures of Co²⁺ and Cu²⁺ in β -Ga₂O₃," *Appl. Phys. Lett.* **115**, 242101 (2019).
- ²⁷J. E. Wertz and J. R. Bolton, *Electron Spin Resonance: Elementary Theory and Practical Applications* (McGraw-Hill Book Company, New York, NY, 1972), Chap. 11.
- ²⁸A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions* (Oxford University Press, 1970), Chap. 7, pp. 455–466.
- ²⁹Z. Šroubek and K. Ždánkský, "Electron spin resonance of Cu²⁺ ion in CdWO₄, ZnWO₄, and MgWO₄ single crystals," *J. Chem. Phys.* **44**, 3078 (1966).
- ³⁰B. N. Misra and R. Kripal, "Studies of the ground state wave function and the *g*-anisotropy of the Cu²⁺ ion in different lattices," *Chem. Phys.* **19**, 17 (1977).
- ³¹A. T. Brant, S. Yang, N. C. Giles, M. Z. Iqbal, A. Manivannan, and L. E. Halliburton, "Oxygen vacancies adjacent to Cu²⁺ ions in TiO₂ (rutile) crystals," *J. Appl. Phys.* **109**, 073711 (2011).
- ³²F. J. Adrian, "Structural implications of nuclear electric quadrupole splittings in high-*T_c* superconductors," *Phys. Rev. B* **38**, 2426 (1988).
- ³³J. R. Harmer, "Hyperfine spectroscopy (ENDOR)," in *EPR Spectroscopy: Fundamentals and Methods*, edited by D. Goldfarb and S. Stoll (John Wiley & Sons, Chichester, 2018), Chap. 16, pp. 331–357.
- ³⁴T. H. Yeom and A. R. Lim, "Study of nuclear quadrupole interactions and quadrupole Raman processes of ⁶⁹Ga and ⁷¹Ga in a β -Ga₂O₃: Cr³⁺ single crystal," *J. Magn. Reson.* **200**, 261 (2009).
- ³⁵A. Schnegg, "Very-high-frequency EPR," in *EPR Spectroscopy Fundamentals and Methods*, edited by D. Goldfarb and S. Stoll (John Wiley & Sons, Chichester, 2018), Chap. 27, pp. 581–602.
- ³⁶J. Telsner, "EPR interactions (zero-field splittings)," in *EPR Spectroscopy: Fundamentals and Methods*, edited by D. Goldfarb and S. Stoll (John Wiley & Sons, Chichester, 2018), Chap. 3, pp. 29–62.
- ³⁷G. D. Watkins, "EPR and ENDOR studies of defects in semiconductors," in *Identification of Defects in Semiconductors, Semiconductors and Semimetals*, edited by M. Stavola (Academic Press, 1998), Chap. 1, Vol. 51A, p. 14.
- ³⁸J. R. Pilbrow, G. R. Sinclair, D. R. Hutton, and G. J. Troup, "Asymmetric lines in field-swept EPR: Cr³⁺ looping transitions in ruby," *J. Magn. Reson.* (1969) **52**, 386 (1983).
- ³⁹B. J. Gaffney and H. J. Silverstone, "Simulation methods for looping transitions," *J. Magn. Reson.* **134**, 57 (1998).
- ⁴⁰J. R. Ritter, J. Huso, P. T. Dickens, J. B. Varley, K. G. Lynn, and M. D. McCluskey, "Compensation and hydrogen passivation of magnesium acceptors in β -Ga₂O₃," *Appl. Phys. Lett.* **113**, 052101 (2018).
- ⁴¹N. Ueda, H. Hosono, R. Waseda, and H. Kawazoe, "Anisotropy of electrical and optical properties in β -Ga₂O₃ single crystals," *Appl. Phys. Lett.* **71**, 933 (1997).
- ⁴²T. Onuma, S. Saito, K. Sasaki, T. Masui, T. Yamaguchi, T. Honda, and M. Higashiwaki, "Valence band ordering in β -Ga₂O₃ studied by polarized transmittance and reflectance spectroscopy," *Jpn. J. Appl. Phys.* **54**, 112601 (2015).
- ⁴³K. A. Mengle, G. Shi, D. Bayerl, and E. Kioupakis, "First-principles calculations of the near-edge optical properties of β -Ga₂O₃," *Appl. Phys. Lett.* **109**, 212104 (2016).
- ⁴⁴Y. Tanabe and S. Sugano, "On the absorption spectra of complex ions 1," *J. Phys. Soc. Jpn.* **9**, 753 (1954).
- ⁴⁵Y. Tanabe and S. Sugano, "On the absorption spectra of complex ions 2," *J. Phys. Soc. Jpn.* **9**, 766 (1954).
- ⁴⁶S. Sugano, Y. Tanabe, and H. Kamimura, *Multiplets of Transition-Metal Ions in Crystals* (Academic Press, New York, 1970).

- ⁴⁷J. T. Randall and M. H. F. Wilkins, "Phosphorescence and electron traps I: The study of trap distributions," *Proc. R. Soc. London A* **184**, 366 (1945).
- ⁴⁸A. G. Milnes, *Deep Impurities in Semiconductors* (John Wiley and Sons, New York, 1973), Chap. 9, pp. 227–228.
- ⁴⁹R. W. Klaffky, B. H. Rose, A. N. Goland, and G. J. Dienes, "Radiation-induced conductivity of Al_2O_3 : Experiment and theory," *Phys. Rev. B* **21**, 3610 (1980).
- ⁵⁰Y. Jiang, N. C. Giles, and L. E. Halliburton, "Persistent photoinduced changes in charge states of transition-metal donors in hydrothermally grown ZnO crystals," *J. Appl. Phys.* **101**, 093706 (2007).
- ⁵¹J. R. Ritter, K. G. Lynn, and M. D. McCluskey, "Iridium-related complexes in Czochralski-grown $\beta\text{-Ga}_2\text{O}_3$," *J. Appl. Phys.* **126**, 225705 (2019).
- ⁵²C. A. Lenyk, T. D. Gustafson, S. A. Basun, L. E. Halliburton, and N. C. Giles, "Experimental determination of the $(0/-)$ level for Mg acceptors in $\beta\text{-Ga}_2\text{O}_3$ crystals," *Appl. Phys. Lett.* **116**, 142101 (2020).
- ⁵³L. Gomes and S. P. Morato, "Resonant OH (photodissociation in alkali halide crystals)," *Phys. Rev. B* **55**, 8743 (1997).
- ⁵⁴J. A. Joens, "The dissociation energy of $\text{OH}(X^2\Pi_{3/2})$ and the enthalpy of formation of $\text{OH}(X^2\Pi_{3/2})$, ClOH , and BrOH from thermochemical cycles," *J. Phys. Chem. A* **105**, 11041 (2001).