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# Transition-metal ions in $\beta$ -Ga<sub>2</sub>O<sub>3</sub> crystals: Identification of Ni acceptors

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## ABSTRACT

Transition-metal ions (Ni, Cu, and Zn) in  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> crystals form deep acceptor levels in the lower half of the bandgap. In the present study, we characterize the Ni acceptors in a Czochralski-grown crystal and find that their (0/−) level is approximately 1.40 eV above the maximum of the valence band. Both Ni<sup>2+</sup> (3d<sup>8</sup>) and Ni<sup>3+</sup> (3d<sup>7</sup>) acceptors are present in the as-grown crystal. Also present are unintentional Ir<sup>3+</sup> (5d<sup>6</sup>) and Ir<sup>4+</sup> (5d<sup>5</sup>) donors. The neutral Ni<sup>3+</sup> acceptors have a low-spin S = 1/2 ground state and are easily monitored with electron paramagnetic resonance (EPR). Principal values of the g matrix for these acceptors are 2.131, 2.138, and 2.233. Although paramagnetic, the singly ionized Ni<sup>2+</sup> acceptors are not seen with EPR at X band (9.4 GHz). The Ir<sup>4+</sup> donors are monitored with EPR and with infrared absorption spectroscopy. Exposing the Ni-doped  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> crystal to 275 nm light at room temperature increases the concentration of Ni<sup>3+</sup> ions and reduces the concentration of Ir<sup>4+</sup> ions as electrons move from the acceptors to the donors. After illumination, heating the crystal above 375 °C restores the initial concentrations of the Ni<sup>3+</sup> and Ir<sup>4+</sup> ions. Broad optical absorption bands peaking near 303 and 442 nm are attributed to the Ni<sup>3+</sup> acceptors.

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## I. INTRODUCTION

Transition-metal ions, with their partially filled 3d shell, are easily incorporated in  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> crystals and can often be directly monitored with electron paramagnetic resonance (EPR). These ions prefer the sixfold Ga sites and can exhibit both donor and acceptor behavior. Of the transition-metal ions, Fe has been the most studied in  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>.<sup>1–12</sup> The Fe<sup>3+/2+</sup> acceptor level is 0.8 eV below the minimum of the conduction band,<sup>1,6</sup> and the Fe<sup>4+/3+</sup> donor level is 0.7 eV above the maximum of the valence band.<sup>10</sup> In conventional semiconductor notation, these are the (0/−) and the (+/0) levels, respectively. Chromium ions have also been extensively studied in  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> crystals, with their optical properties receiving much of the attention.<sup>13–21</sup> Sharp emission features appearing near 690 and 696 nm in  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> crystals are the

well-known R lines from the Cr<sup>3+</sup> ions. A value for the (0/−) acceptor level of Cr has not been experimentally established. Recently, Cu acceptors occupying sixfold Ga sites have been investigated in  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> crystals.<sup>22–24</sup> Neutral Cu<sup>3+</sup> acceptors have an S = 1 EPR spectrum and are responsible for intense optical absorption bands in the visible and near-ultraviolet regions. The (0/−) level of the Cu acceptors is 1.27 eV above the maximum of the valence band.<sup>23</sup> Additional EPR studies of transition-metal ions in  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> have focused on Ti, Mn, and Co.<sup>25–27</sup>

In the present paper, we use EPR to identify and characterize Ni acceptors in a doped  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> crystal. The EPR spectra show that the Ni<sup>3+</sup> (3d<sup>7</sup>) acceptors have a low-spin (S = 1/2) ground state, with six d electrons in the three t<sub>2g</sub> orbitals (↑↓ ↑↓ ↑↓) and one unpaired d electron in an e<sub>g</sub> orbital (↑). This deviation from Hund's rule for the d electrons is a result of a strong crystal field

(i.e., the crystal field is greater than the exchange energy that tends to align the spins parallel).<sup>28,29</sup> An exposure to 275 nm light converts  $\text{Ni}^{2+}$  to  $\text{Ni}^{3+}$  and converts  $\text{Ir}^{4+}$  to  $\text{Ir}^{3+}$ . Monitoring the subsequent thermal decay of the photoinduced neutral  $\text{Ni}^{3+}$  acceptors when heated above room temperature allows us to determine a thermal activation energy and, thus, a value for the (0/−) level. In addition to a fundamental interest in Ni as a dopant, we note that this metal is widely used to form  $\beta\text{-Ga}_2\text{O}_3$  Schottky-barrier diodes. Recent reports have suggested Ni will diffuse into the semiconductor and produce a new interfacial compound that, upon annealing, improves the interface quality by reducing the trap-state density.<sup>30,31</sup>

Our study of Ni in  $\beta\text{-Ga}_2\text{O}_3$  has greatly benefited from the much earlier work on  $\text{Ni}^{2+}$  and  $\text{Ni}^{3+}$  ions in  $\alpha\text{-Al}_2\text{O}_3$  crystals, a material similar to  $\beta\text{-Ga}_2\text{O}_3$  except for a wider bandgap. Geschwind and Remeika<sup>28</sup> showed that  $\text{Ni}^{3+}$  ions replace  $\text{Al}^{3+}$  ions and have a low-spin  $S = 1/2$  ground state. Above 50 K, they observed a single isotropic EPR line with  $g = 2.146$ . In an extension of this work, Shen and Estle<sup>32</sup> showed that the angular dependence of the  $\text{Ni}^{3+}$  ions observed at 1.2 K is caused by a dynamic Jahn-Teller effect. According to Müller and Günthard<sup>33</sup> and Tippins,<sup>34</sup> the charge-transfer optical absorption bands from  $\text{Ni}^{3+}$  ions peak near 280 and 400 nm. Turning to the divalent charge state, Marshall *et al.*<sup>35</sup> described the strongly angular dependent  $S = 1$  EPR spectrum of the  $\text{Ni}^{2+}$  ions in  $\alpha\text{-Al}_2\text{O}_3$  and Müller and Günthard<sup>33</sup> reported an absorption band from  $\text{Ni}^{2+}$  ions that peaks near 400 nm in  $\alpha\text{-Al}_2\text{O}_3$ . An EPR signal from  $\text{Ni}^{2+}$  ions is not observed in the present study of  $\beta\text{-Ga}_2\text{O}_3$  because the crystal-field-splitting parameter  $D$  in the spin-Hamiltonian ( $H = \beta\mathbf{S}\cdot\mathbf{g}\cdot\mathbf{B} + \mathbf{S}\cdot\mathbf{D}\cdot\mathbf{S}$ ) is greater than the energy of the microwave photons.

## II. EXPERIMENTAL DETAILS

A Ni-doped  $\beta\text{-Ga}_2\text{O}_3$  crystal was grown at Washington State University by the Czochralski (CZ) method.<sup>24,36,37</sup> An iridium crucible, radio frequency heating, and a controlled  $\text{O}_2$  atmosphere were used. The Ni doping level in the starting materials was 0.25 at. %, and the pulling rate was approximately 2 mm/h. A small rectangular-shaped sample, with approximate dimensions of  $1 \times 2 \times 2 \text{ mm}^3$ , was cut from the larger boule for use in the present investigation. The edges of this sample were along the  $a$ ,  $b$ , and  $c$  directions, respectively. Because the distribution of dopants and impurities can be nonuniform in a boule, all the experimental results presented in this paper were taken from one sample. Additional information about the growth of  $\beta\text{-Ga}_2\text{O}_3$  crystals at Washington State University and the concentrations and distribution of dopants and impurities in these crystals can be found in Ref. 38.

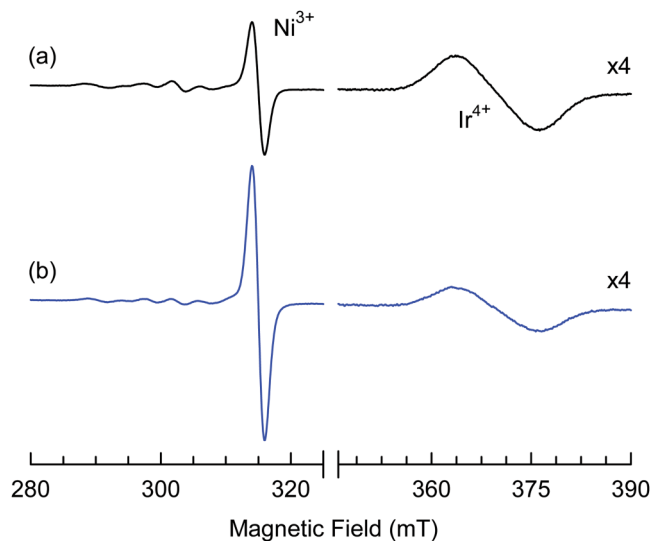
The EPR spectra were obtained with a Bruker EMX spectrometer and a cylindrical  $\text{TM}_{110}$  resonator (the microwave frequency was 9.39 GHz). An Oxford Instruments ESR-900 helium-gas flow system controlled the sample temperature and a Bruker NMR gaussmeter provided corrections for the small difference in the magnetic field at the sample and the spectrometer's Hall sensor. In addition to the  $\text{Ni}^{3+}$  ions, EPR verified that unintentional  $\text{Ir}^{4+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Fe}^{3+}$  ions were present in the as-grown crystal.

Approximate concentrations of these ions were obtained by comparing their spectra (intensities, linewidths, and number of lines) to a Bruker weak-pitch EPR standard sample. A 275 nm LED (Thorlabs Model M275L4), with an output power of 45 mW, was used to convert  $\text{Ni}^{2+}$  ions to  $\text{Ni}^{3+}$  ions. Infrared absorption spectra were obtained with a ThermoScientific Nicolet 8700 FTIR spectrometer. A white-light (QTH) source, a  $\text{CaF}_2$  beam splitter, a DTGS detector, and an ultrabroadband fused-silica wire-grid polarizer were used. Absorption spectra in the visible and near ultraviolet were taken with a Cary 5000 spectrophotometer.

The  $\beta\text{-Ga}_2\text{O}_3$  crystals have a monoclinic structure described by space group  $C2/m$  ( $C_{2h}^3$ ). Lattice constants at 273 K are  $a = 12.214 \text{ \AA}$ ,  $b = 3.0371 \text{ \AA}$ ,  $c = 5.7981 \text{ \AA}$ , and  $\beta = 103.83^\circ$ .<sup>39,40</sup> Following the usual convention, the  $b$  direction is perpendicular to the mirror plane. The angle between the  $a$  and  $c$  axes is  $\beta$  and the  $c^*$  direction is defined to be perpendicular to the  $a$ - $b$  plane. Tetrahedral and octahedral Ga sites in the crystal are 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 nearest Ga neighbors.<sup>41</sup> The low-spin  $\text{Ni}^{3+}$  ions are slightly smaller than the  $\text{Ga}^{3+}$  ions. Their effective ionic radii at sixfold coordinated sites are 56 and 62 pm, respectively.<sup>42</sup> The effective ionic radius of the larger  $\text{Ni}^{2+}$  ions at a sixfold site is 69 pm.

## III. EPR SPECTRUM FROM $\text{Ni}^{3+}$ ACCEPTORS

Figure 1(a) shows the EPR spectrum taken from an as-grown Ni-doped  $\beta\text{-Ga}_2\text{O}_3$  crystal. These data were obtained at 100 K,



**FIG. 1.** EPR spectra from  $\text{Ni}^{3+}$  acceptors and  $\text{Ir}^{4+}$  donors in a Ni-doped  $\beta\text{-Ga}_2\text{O}_3$  crystal. Both spectra were taken at 100 K with a microwave frequency of 9.3905 GHz. The slowly varying (static) magnetic field was along the  $b$  direction, and the microwave magnetic field was along the  $a$  direction. Intensities of the  $\text{Ir}^{4+}$  spectra have been increased by a factor of 4. (a) Before exposure to 275 nm light. (b) After an exposure to 275 nm light for 2 min while being held at room temperature.

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with the magnetic field along the  $b$  direction and a microwave frequency of 9.3905 GHz. The prominent line at 315.0 mT is assigned to  $\text{Ni}^{3+}$  ions at octahedral Ga(2) sites and the much broader, and less intense, line at 370.5 mT is due to  $\text{Ir}^{4+}$  ions, also at Ga(2) sites. Lenyk *et al.*<sup>43</sup> have previously used EPR and infrared absorption to characterize  $\text{Ir}^{4+}$  ions in  $\beta\text{-Ga}_2\text{O}_3$ . The  $\text{Ni}^{3+}$  and  $\text{Ir}^{4+}$  (acceptor and donor) concentrations in Fig. 1(a) are  $0.54 \times 10^{19}$  and  $2.32 \times 10^{19} \text{ cm}^{-3}$ , respectively. Much of the difference in these concentrations is explained by the presence of unseen  $\text{Ni}^{2+}$  ions. [Note: Because of the large anisotropy in the  $g$  matrix of the  $\text{Ir}^{4+}$  ions, the intensity of the  $\text{Ir}^{4+}$  EPR signal when the static magnetic field is along the  $b$  direction depends strongly on whether the microwave magnetic field in the resonator is along the  $a$  or  $c^*$  direction.] Weaker signals from  $\text{Cu}^{2+}$ (A) and  $\text{Cu}^{2+}$ (B) ions<sup>23</sup> and  $\text{Fe}^{3+}$  ions<sup>44</sup> are present in Fig. 1(a) in the magnetic field region slightly below the  $\text{Ni}^{3+}$  signal. The concentration of  $\text{Cu}^{2+}$ (B) ions is nearly a factor of 10 greater than the concentration of  $\text{Cu}^{2+}$ (A) ions. In the as-grown crystal, the combined concentrations of the  $\text{Cu}^{2+}$ (A) and  $\text{Cu}^{2+}$ (B) ions and the concentration of the  $\text{Fe}^{3+}$  ions are approximately a factor of 10 and a factor of 15 lower, respectively, than the  $\text{Ir}^{4+}$  concentration.

After taking the spectrum in Fig. 1(a), the crystal was warmed to room temperature and exposed to 275 nm light for 2 min while being held at this higher temperature. The crystal was then returned to 100 K, and the spectrum in Fig. 1(b) was taken. These spectra in Figs. 1(a) and 1(b) were obtained with identical spectrometer settings and, thus, can be directly compared. In each spectrum, the  $\text{Ir}^{4+}$  signals have been increased by a factor of 4. The exposure at room temperature to 275 nm light increased the intensity of the  $\text{Ni}^{3+}$  signal and decreased the intensity of the  $\text{Ir}^{4+}$  signal. Their concentrations in Fig. 1(b), after the exposure to 275 nm light at room temperature, are  $1.32 \times 10^{19}$  and  $1.60 \times 10^{19} \text{ cm}^{-3}$ , respectively. The  $\text{Cu}^{2+}$  and  $\text{Fe}^{3+}$  signals, with smaller initial intensities, both decreased during exposure to the 275 nm light. The concentration of  $\text{Cu}^{2+}$ (B) ions changed from  $2.2 \times 10^{18}$  to  $1.5 \times 10^{18} \text{ cm}^{-3}$ , and the concentration of  $\text{Fe}^{3+}$  ions changed from  $1.5 \times 10^{18}$  to  $0.9 \times 10^{18} \text{ cm}^{-3}$ .

The angular dependence of the  $\text{Ni}^{3+}$  EPR spectrum is shown in Fig. 2. Data were obtained in  $10^\circ$  steps as the direction of the static magnetic field was rotated in the  $a$ - $b$ ,  $b$ - $c^*$ , and  $c^*$ - $a$  planes. The absence of fine-structure in the angular dependence verifies that the  $\text{Ni}^{3+}$  ( $d^7$ ) ions in  $\beta\text{-Ga}_2\text{O}_3$  have a low-spin  $S = 1/2$  ground state. Also, the observation of a single line in each plane provides information about the principal-axis directions of the  $g$  matrix. As described in the recent EPR study of  $\text{Ir}^{4+}$  ions in  $\beta\text{-Ga}_2\text{O}_3$ ,<sup>43</sup> the monoclinic  $C2/m$  space group permits a defect located at sixfold Ga(2) sites to have two different, but crystallographically equivalent, orientations of the principal axes of its  $g$  matrix. For the  $\text{Ni}^{3+}$  ions, the lack of splitting in the three planes in Fig. 2 indicates that the two orientations are not resolved and, thus, the principal axes of the  $g$  matrix must be close to the  $a$ ,  $b$ , and  $c^*$  directions.

The angular dependence in Fig. 2 is described by a spin Hamiltonian containing only an electron Zeeman term ( $H = \beta\mathbf{S} \cdot \mathbf{g} \cdot \mathbf{B}$ ). We write this spin-Hamiltonian as a  $2 \times 2$  matrix and use a least-squares fitting program to determine the three principal values of the  $g$  matrix. The 27 discrete points in Fig. 2, along with their corresponding microwave frequencies, were used as

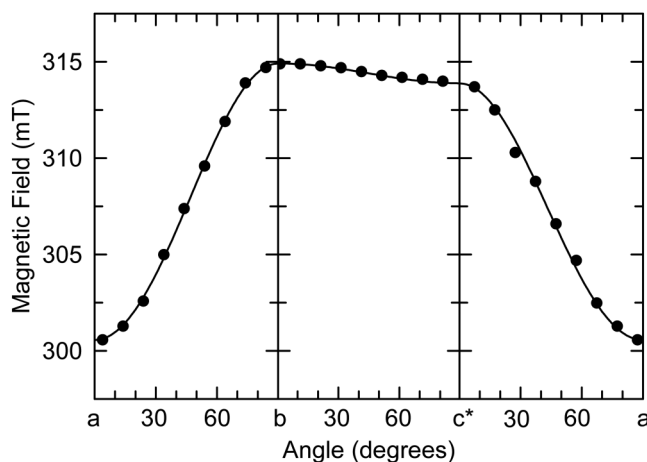


FIG. 2. Angular dependence of the EPR spectrum from  $\text{Ni}^{3+}$  ions. The direction of the magnetic field is rotated in three planes, from  $a$  to  $b$ ,  $b$  to  $c^*$ , and  $c^*$  to  $a$ . Discrete points are from the experiment. The solid lines were generated using the parameters in Table I.

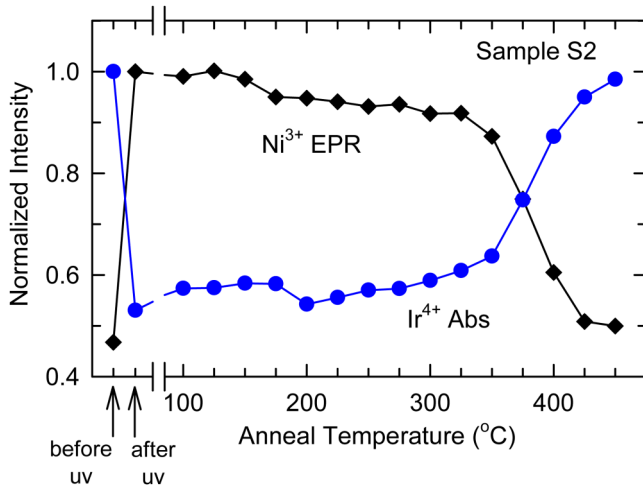
input data and the energy eigenvalues of the matrix were repeatedly calculated as the  $g$ -matrix parameters were systematically varied. At each step of the fitting process, the predicted line positions were compared to the measured positions. Best-fit values for the three principal  $g$  values are given in Table I. The solid curves in Fig. 2 were generated using these final parameters. Our  $g$  values for the  $\text{Ni}^{3+}$  ions in  $\beta\text{-Ga}_2\text{O}_3$  crystals are close to those reported for  $\text{Ni}^{3+}$  ions in  $\alpha\text{-Al}_2\text{O}_3$ .<sup>28,32</sup>

#### IV. (0/-) LEVEL OF Ni ACCEPTORS

As shown in Fig. 1, exposure to 275 nm light at room temperature increases the concentration of  $\text{Ni}^{3+}$  ions and decreases the concentration of  $\text{Ir}^{4+}$  ions. Subsequent heating in the dark restores their initial concentrations. The decay of the  $\text{Ni}^{3+}$  ions and the recovery of the  $\text{Ir}^{4+}$  ions were separately monitored with EPR and infrared absorption during a series of annealing steps above room temperature. These results are shown in Figs. 3 and 4. The Ni-doped crystal was initially exposed to 275 nm light at room temperature for 2 min. Then, after removing the light, the crystal was heated in  $25^\circ\text{C}$  steps from 100 to  $450^\circ\text{C}$ . The crystal was held at each higher temperature for 2 min and, after each step, an EPR spectrum of the  $\text{Ni}^{3+}$  ions was taken at 100 K and an

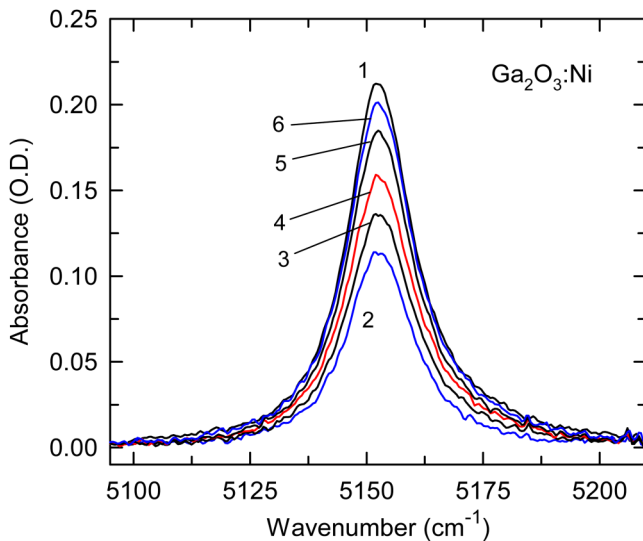
TABLE I. Spin-Hamiltonian parameters for  $\text{Ni}^{3+}$  ions in  $\beta\text{-Ga}_2\text{O}_3$ . Uncertainties are estimated to be  $\pm 0.002$  for the principal  $g$  values and  $\pm 3^\circ$  for the directions.

	Principal values	Principal-axis directions
<b>g matrix</b>		
$g_1$	2.131	$b$
$g_2$	2.138	$c^*$
$g_3$	2.233	$a$



**FIG. 3.** Thermal decay of neutral  $\text{Ni}^{3+}$  acceptors and thermal recovery of singly ionized  $\text{Ir}^{4+}$  donors in a Ni-doped  $\beta\text{-Ga}_2\text{O}_3$  crystal after an exposure to 275 nm light at room temperature. The EPR spectrum of the  $\text{Ni}^{3+}$  acceptors is monitored at 100 K, and the infrared absorption spectrum of the  $\text{Ir}^{4+}$  donors is monitored at room temperature.

infrared absorption spectrum of the  $\text{Ir}^{4+}$  ions was taken at room temperature. The  $\text{Ir}^{4+}$  infrared absorption band at  $5153\text{ cm}^{-1}$  was monitored (light propagated along the  $a$  direction with  $E\parallel b$ ). Figure 4 shows the  $\text{Ir}^{4+}$  absorption band before and after the



**FIG. 4.** Infrared absorption spectra, taken at room temperature, from  $\text{Ir}^{4+}$  ions in a Ni-doped  $\beta\text{-Ga}_2\text{O}_3$  crystal. Spectrum 1 was taken before exposure to 275 nm light. Spectrum 2 was taken after exposure to 275 nm light. Spectra 3, 4, 5, and 6 were taken after heating to 350, 375, 400, and 425 °C, respectively.

exposure to 275 nm light and at selected temperatures in the region where recovery occurs.

In Fig. 3, the thermal decay of the photoinduced  $\text{Ni}^{3+}$  ions occurs between 325 and 425 °C. We suggest that the responsible mechanism is the thermal excitation of electrons from the valence band to the neutral  $\text{Ni}^{3+}$  acceptors, with holes left in the valence band converting the  $\text{Ir}^{3+}$  ions formed by the light back to  $\text{Ir}^{4+}$  ions. An alternative explanation where an electron is thermally excited from the  $\text{Ir}^{3+}$  to the conduction band can be eliminated since the  $\text{Ir}^{3+/4+}$  level is near midgap<sup>8,45</sup> and temperatures above 750 °C would be required for thermal excitation of the electrons to the conduction band. An estimate of the activation energy describing the thermal decay of the neutral  $\text{Ni}^{3+}$  acceptors is obtained by using the approximation  $E \approx 25 kT_m$ ,<sup>46,47</sup>  $T_m$  is the temperature where half of the  $\text{Ni}^{3+}$  ions have decayed. A value of 375 °C (or 648 K) for  $T_m$  from Fig. 3 gives an activation energy of 1.40 eV for the Ni acceptors and places the (0/−) level 1.40 eV above the maximum of the valence band. The uncertainty in this value of  $E$  is estimated to be  $\pm 0.10$  eV.

The relationship  $E \approx 25 kT_m$  can also be used to obtain approximate activation energies from deep-level transient spectroscopy (DLTS) data. Here,  $T_m$  would correspond to the temperature of the DLTS peak. The  $\text{Fe}^{3+/2+}$  level in  $\beta\text{-Ga}_2\text{O}_3$ , better known as the E2 level, provides an example of the usefulness of this approximation. Ingebrigtsen *et al.*<sup>1</sup> found that the DLTS peak for the  $\text{Fe}^{3+/2+}$  acceptor level appears at 354 K. Using this value of  $T_m$  in the 25 kT approximation for  $E$  gives an activation energy of 0.763 eV, which is very close to the value of 0.78 eV that these investigators<sup>1</sup> obtained from a more detailed analysis.

Table II lists experimental values for the (0/−) levels of four acceptors in  $\beta\text{-Ga}_2\text{O}_3$  crystals. These results for the Mg, Zn, Cu, and Ni acceptors were obtained by using EPR to directly monitor the thermal decay of their photoinduced neutral charge states. The distinct advantage of using EPR for this purpose is the unambiguous identification of the specific acceptor being monitored, through unique  $g$  values and resolved hyperfine structure. Also, the fortuitous position of the  $\text{Ir}^{3+/4+}$  donor level near midgap helps when interpreting results. Values of (0/−) are included for Zn acceptors at the tetrahedral Ga(1) and octahedral Ga(2) sites. The other three acceptors in Table II are at the Ga(2) sites. For the neutral Mg and Zn acceptors, the hole is localized on an adjacent oxygen ion in the form of a small polaron.<sup>41,48–51</sup> In contrast, the

**TABLE II.** Experimental values, obtained from EPR, for the (0/−) levels of acceptors in  $\beta\text{-Ga}_2\text{O}_3$  crystals. These are the positions above the valence band. The results are given for Zn acceptors on the tetrahedral Ga(1) site and the octahedral Ga(2) site. The Cu value is for the isolated Cu(A) acceptors reported in Ref. 23.

Acceptor	(0/−) level (eV)	Reference
Mg	0.65	51
$\text{Zn}_{\text{Ga}(1)}$	0.78	41
$\text{Zn}_{\text{Ga}(2)}$	0.65	41
Cu	1.27	23
Ni	1.40	Present work

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deeper neutral Cu and Ni acceptors have the hole localized in a 3d orbital within the ion.<sup>23</sup>

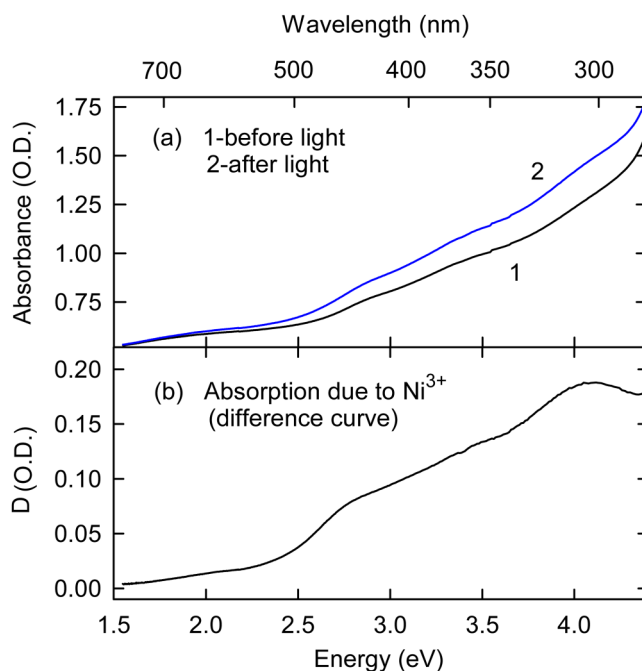
Support for the method used to obtain the acceptor values in Table II is provided by a recent experimental study of the electrical properties of Zn-doped Ga<sub>2</sub>O<sub>3</sub> thin films.<sup>52</sup> Hall effect measurements by these investigators indicate that the Zn-related acceptor-level ionization energy is 0.77 eV above the valence band maximum, in close agreement with the EPR results in Table II. We note that computational studies often predict very different values for (0/−) levels. For example, density functional theory (DFT) calculations, using the Heyd, Scuseria, and Ernzerhof (HSE) hybrid functional, place the (0/−) levels of the Zn<sub>Ga1</sub> and Zn<sub>Ga2</sub> acceptors more than 1.2 eV above the valence band maximum.<sup>36,53</sup> In an informative DFT study of acceptors in β-Ga<sub>2</sub>O<sub>3</sub>, Kyrtsos *et al.*<sup>54</sup> found that the PBE and HSE formalisms gave significantly different (0/−) values. For Zn acceptors, the generalized gradient approximation (GGA), as parameterized by Perdew, Burke, and Ernzerhof (PBE), predicted (0/−) values below the experimental results in Table II whereas the HSE hybrid functional gave values considerably above the experimental results.<sup>54</sup> Recently, Falletta and Pasquarello<sup>55</sup> described methods that address the many-body self-interaction when using DFT methods to model small polarons.

## V. OPTICAL QUENCHING

After increasing the concentration of Ni<sup>3+</sup> ions with near-band-edge 275 nm light (as shown in Fig. 3), optical quenching of the photoinduced Ni<sup>3+</sup> ions was explored. Specifically, a search was made to find what wavelengths, if any, would return the Ni<sup>3+</sup> EPR signal to its initial lower intensity (i.e., convert the photoinduced Ni<sup>3+</sup> ions back to Ni<sup>2+</sup> ions). Exposure at room temperature to longer wavelengths (940, 850, 700, 633, and 594 nm) did not decrease the Ni<sup>3+</sup> EPR signal (monitored at 100 K), whereas shorter wavelengths (532 and 470 nm) brought the Ni<sup>3+</sup> EPR signal close to its initial intensity. This indicates a threshold for optical quenching of the photoinduced Ni<sup>3+</sup> ions near 2.2 eV. These results suggest that the primary optical quenching mechanism is the excitation of electrons from Ir<sup>3+</sup> ions to the conduction band<sup>8</sup> with their subsequent trapping at Ni<sup>3+</sup> ions to form Ni<sup>2+</sup> ions. [Note: The 2.2 eV threshold was also observed in similar experiments when we directly monitored the recovery of the infrared absorption signal from the Ir<sup>4+</sup> ions.] The excitation of electrons from the valence band directly to Ni<sup>3+</sup> ions with photons having energies near 1.4 eV is less probable, presumably because of a small optical cross section for this process.

## VI. PHOTOINDUCED OPTICAL ABSORPTION

Optical absorption spectra were obtained at room temperature from the Ni-doped β-Ga<sub>2</sub>O<sub>3</sub> crystal. Figure 5(a) shows the absorption curves taken before and immediately after an exposure at room temperature to 275 nm light. In these experiments, unpolarized light from the spectrophotometer propagated along the *a* direction and the optical path length (i.e., the thickness of the crystal) was 0.84 mm. The ultraviolet light produced an increase in absorption for wavelengths in the region between 550 and 280 nm. Figure 5(b) is the difference spectrum (“after light” minus “before light”). Two broad photoinduced bands are present, peaking near 442 nm



**FIG. 5.** Optical absorption spectra from a Ni-doped β-Ga<sub>2</sub>O<sub>3</sub> crystal, taken at room temperature with unpolarized light propagating along the *a* direction in the crystal. (a) Spectrum 1 was taken before exposure to 275 nm light, and spectrum 2 was taken after exposure to 275 nm light. (b) Difference spectrum (“after light” minus “before light”) showing absorption bands due to Ni<sup>3+</sup> acceptors.

and 4.09 eV (303 nm). We suggest that these two absorption features in Fig. 5(b) are the expected charge-transfer bands of the Ni<sup>3+</sup> ions. Their appearance in the difference spectrum is consistent with the light-induced increase in the intensity of the Ni<sup>3+</sup> EPR signal (see Fig. 3). They correspond to the 3.10 (400 nm) and 4.43 eV (280 nm) absorption bands assigned to Ni<sup>3+</sup> ions in α-Al<sub>2</sub>O<sub>3</sub> crystals.<sup>33,34</sup> Additional support comes from Y<sub>3</sub>Al<sub>5</sub>O<sub>15</sub> (YAG) crystals where a charge-transfer band from Ni<sup>3+</sup> ions appears at 420 nm.<sup>56</sup> Although expected to be weak for the concentration of Ni<sup>3+</sup> encountered in our β-Ga<sub>2</sub>O<sub>3</sub> crystal, absorption bands due to <sup>2</sup>E to <sup>2</sup>T internal transitions of the Ni<sup>3+</sup> ions may be present in the 2.5–4.5 eV region.<sup>57</sup>

Additional defects are also contributing to the optical absorption spectra in Fig. 5(a). Spectrum 1 (before light) is expected to have broad absorption bands peaking near 428 and 356 nm from Ir<sup>4+</sup> ions<sup>23,36,58</sup> and a broad absorption band peaking near 370 nm from Ni<sup>2+</sup> ions. Support for this latter assertion comes from the report by Galazka *et al.*<sup>59</sup> of a broad optical absorption band peaking near 370 nm in an as-grown β-Ga<sub>2</sub>O<sub>3</sub> crystal doped with Ni<sup>2+</sup> ions. In α-Al<sub>2</sub>O<sub>3</sub> crystals, a Ni<sup>2+</sup> absorption band peaks near 400 nm.<sup>33</sup> In spectrum 1, these bands from Ir<sup>4+</sup>, Ni<sup>2+</sup>, and the initially present Ni<sup>3+</sup> ions combine to produce a steadily increasing absorption as the band edge is approached (charge-transfer bands from Fe<sup>3+</sup> ions may also be present). The absorption features associated with the Ir<sup>4+</sup> and Ni<sup>2+</sup> ions in spectrum 1 decrease in



intensity when the crystal is exposed to the 275 nm light and the  $\text{Ni}^{3+}$  bands grow and become more prominent. In spectrum 2 (after light) and, thus, in the difference spectrum in Fig. 5(b), there are small unresolved contributions from photoinduced  $\text{Cu}^{3+}$  bands peaking between 500 and 350 nm, as EPR shows that unintentional Cu is present in our Ni-doped crystal.<sup>23</sup>

## VII. SUMMARY

Electron paramagnetic resonance (EPR) and optical absorption have been used to identify and characterize neutral  $\text{Ni}^{3+}$  ( $3d^7$ ) acceptors in a  $\beta\text{-Ga}_2\text{O}_3$  crystal grown by the Czochralski method. These ions have a low-spin  $S = 1/2$  ground state. A  $g$  matrix (with principal values near 2.2) is extracted from the angular dependence of their EPR spectrum. Charge-transfer bands of the  $\text{Ni}^{3+}$  ions peak near 303 and 442 nm. At room temperature, 275 nm light moves electrons from singly ionized  $\text{Ni}^{2+}$  ( $3d^8$ ) acceptors to singly ionized  $\text{Ir}^{4+}$  ( $5d^5$ ) donors. Subsequent heating above 375 °C restores the initial concentration of  $\text{Ni}^{2+}$  ions when the photoinduced  $\text{Ni}^{3+}$  neutral acceptors thermally decay by hole release. This recovery temperature for the  $\text{Ni}^{3+}$  ions places the (0/-) level of the Ni acceptors in  $\beta\text{-Ga}_2\text{O}_3$  at approximately 1.40 eV above the maximum of the valence band.

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## AUTHOR DECLARATIONS

### Conflict of Interest

The authors have no conflicts to disclose.

### Author Contributions

**T. D. Gustafson:** Conceptualization (equal); Data curation (equal); Formal analysis (equal); Investigation (equal); Writing – review & editing (equal). **N. C. Giles:** Conceptualization (equal); Funding acquisition (equal); Investigation (equal); Resources (equal); Visualization (equal); Writing – review & editing (equal). **B. C. Holloway:** Conceptualization (equal); Investigation (supporting); Writing – review & editing (equal). **J. Jesenovc:** Conceptualization (equal); Investigation (equal); Writing – review & editing (equal). **B. L. Dutton:** Conceptualization (equal); Investigation (equal); Writing – review & editing (equal). **J. S. McCloy:** Conceptualization (equal); Funding acquisition (equal); Resources (equal); Writing – review & editing (equal). **M. D. McCluskey:** Conceptualization (equal); Funding acquisition (equal); Resources (equal); Writing – review & editing (equal). **L. E. Halliburton:** Conceptualization (equal); Formal analysis (equal); Writing – original draft (lead); Writing – review & editing (equal).

## DATA AVAILABILITY

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

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