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ABSTRACT
Gallium oxide (β-Ga$_2$O$_3$) is a wide-bandgap compound semiconductor with a bandgap of ~4.9 eV that is currently considered promising for a wide range of applications ranging from transparent conducting electrodes to UV optoelectronic devices and power electronics. However, all of these applications require a reliable and precise control of electrical and optical properties of the material, which can be largely affected by impurities, such as transition metals commonly present during the growth. In this work, we employ electron paramagnetic resonance (EPR) spectroscopy to obtain EPR signatures of the 3d-transition metals Co$^{2+}$ and Cu$^{2+}$ in β-Ga$_2$O$_3$ bulk crystals and powders that were unknown so far. Furthermore, we show that both Co$^{2+}$ and Cu$^{2+}$ preferentially reside on the octahedral gallium lattice site.

β-Ga$_2$O$_3$ is a wide bandgap semiconductor that is attractive for various applications, including in power electronics, as transparent conductive electrodes, in solar-blind UV photodetectors and gas sensors, as well as for photoelectrochemical water splitting. For example, in the case of high-power electronics, β-Ga$_2$O$_3$ is predicted to outperform the current state-of-the-art technology based on GaN and SiC due to a higher breakdown field. Another significant advantage of β-Ga$_2$O$_3$ is that large bulk crystals can be grown by melt growth techniques, giving access to high quality and reasonably priced native substrates, which is essential for the fabrication of high-performance power devices. The key to the realization of device applications is to achieve control over conductivity by doping and mitigation of trap states, as most of the electronic properties of β-Ga$_2$O$_3$ are affected by the presence of dopants/contaminants and/or intrinsic defects. Here, transition metals (TMs) represent an important group of impurities, which are either unintentionally present during the growth or used as intentional dopants. These elements mostly introduce deep-level states in unintentionally present during the growth or used as intentional dopants. Thus, it is of crucial interest to understand the electronic structure of TMs and their interactions with intrinsic defects and impurities. Though spectroscopic signatures of several TMs, such as Fe, Cr, Mn, and Ti, have recently been obtained from electron paramagnetic resonance (EPR) studies, the electronic structure of other commonly present TMs, including Co and Cu, remains unknown so far. This has motivated the present study of TM signatures in undoped and cobalt doped β-Ga$_2$O$_3$ by employing EPR, as this technique is known to be among the most powerful and versatile experimental methods for nondestructive chemical identification and quantification of defects and impurities.

We used commercially available β-Ga$_2$O$_3$ powder from Sigma Aldrich and β-Ga$_2$O$_3$-Co bulk crystals. The β-Ga$_2$O$_3$ bulk crystals were grown by the Czochralski method from the melt (the Ga$_2$O$_3$ melting point is approximately 1800 °C) in an iridium crucible using Ga$_2$O$_3$ powder as a source material. A carbon dioxide containing growth atmosphere was used to control the temperature dependent...
Fermi level in the Ga$_2$O$_3$:Co crystal is lower than that in undoped Ga$_2$O$_3$ bulk crystals. The purity of the β-Ga$_2$O$_3$ powder is ≥99.99%, and we estimated that the Cu$^{2+}$ concentration in the powder is ~5 × 10$^{15}$ cm$^{-3}$. According to the performed X-ray diffraction (XRD) measurements, the β-Ga$_2$O$_3$ powder shows exclusive reflexes from β-Ga$_2$O$_3$, indicating that it has a very high phase purity (supplementary material). The samples were measured in an X-band resonator of a Bruker E500 spectrometer equipped with a He-gas flow cryostat for measurements with adjustable temperatures ranging from 5 K to 300 K in the dark. EPR spectra were analyzed using the following spin-Hamiltonian that includes an electron Zeeman term and a central hyperfine interaction term:

$$\mathcal{H} = \mu_B B g S + S A I.$$  

Here, S denotes the effective electron spin, I is the nuclear spin, and B is an external magnetic field. g and A are the electron g-tensor and the hyperfine interaction tensor, respectively, and $\mu_B$ is the Bohr magneton. Modeling of the EPR spectra was done using the Easyspin software package. Figure 1 depicts an EPR spectrum of a β-Ga$_2$O$_3$ bulk crystal measured at 6 K with an orientation of the external magnetic field parallel to the a’-axis of the crystal. The signal is centered around 105 mT and consists of one group of 8 equidistant lines (marked by the black rake), indicating that it stems from a paramagnetic center with an electron spin $S = \frac{1}{2}$ and a resolved hyperfine interaction involving a nuclear spin $I = 7/2$ with 100% natural abundance. The signal can be observed in the temperature range from 4 K to 40 K. In order to determine the full set of spin-Hamiltonian parameters given in Eq. (1), angular dependent EPR measurements were performed.

Figure 2 shows EPR peak positions measured at 6 K as a function of the angle $\theta$ between B and the a’-axis for rotations around the crystallographic [010] axis (c) and the [001] axis (d). The crystal structure of β-Ga$_2$O$_3$ is displayed in Fig. 2(a). By fitting the experimental data given by the open circles by Eq. (1), we can determine the g-values as $g_a = 6.34 \pm 0.01$, $g_b = 3.37 \pm 0.01$, and $g_c = 2.0 \pm 0.01$, while the hyperfine interaction tensor is given by $|A_{ei}| = (550 \pm 10)$ MHz, $|A_{eb}| = (60 \pm 5)$ MHz, and $|A_{ec}| = (130 \pm 10)$ MHz. Here, the subscripts denote components of the g- and A-tensors that are parallel to the given crystallographic axes.

Let us now discuss the origin of this EPR signal. The only likely elements, which fulfill the criteria of the observed hyperfine interaction with a nucleus with $I = 7/2$ and 100% natural abundance, are scandium ($^{43}$Sc), vanadium ($^{51}$V), cobalt ($^{59}$Co), holmium ($^{165}$Ho), and tantalum ($^{181}$Ta). Sc$^{2+}$ has a 3d$^1$ electron configuration, $S = 1/2$, with $g = 1.94$ and $g_{||} = 1.98$ can be found in the literature. These values do not fit the experimental data and, therefore, scandium can be excluded as the chemical origin of the observed EPR signal. Vanadium has been observed by EPR in three different charge states, V$^{2+}$ in a 3d$^5$ electron configuration, V$^{3+}$ in a 3d$^4$ electron configuration, and V$^{4+}$ in a 3d$^3$ electron configuration. However, V$^{3+}$ can be excluded since it has the electron spin of $S = 1$, while V$^{2+}$ and V$^{4+}$ can be excluded due to their anisotropy and g-tensors of $g \sim 2$ and $g \sim 1.2$, respectively. Ho$^{2+}$ and Ho$^{3+}$ have both a very large hyperfine splitting and g-values, as observed by Boynt et al. and Shakurov et al.
The effective orbital g-factor $g_t$ equals $-3/2$ for the triplet orbital ground state with a fictitious angular momentum $l = 1$. The parameter $g_t$ is a measure of the distortion and is small as compared to unity. From the experimental $g_{\perp}$-value, the distortion parameter $a$ is calculated to be 0.12 using Eqs. (3) and (4). The obtained value is in agreement with the values for several cobalt salts.\(^{20}\) The $g$-factors roughly follow the relation
\[ g_t + 2g_{\perp} \approx 5g_0 - 2g_1 \approx 13.\]

In our case, the obtained value of 13.1 is indeed very close to the model. Cobalt on the tetrahedral gallium site is less likely as it is expected to have nearly isotropic $g$-values around 2.4.\(^{20}\) Therefore, the observed EPR signal can be assigned to Co$^{2+}$ located at the octahedral gallium site (0.62 Å lattice space). This position seems to be preferable as compared to the tetrahedral gallium site (0.477 Å lattice space), since it provides more space for the Co$^{2+}$ ion (0.75 Å ion radius) that has a larger ion radius as compared with the Ga$^{3+}$ ion with the radius of 0.62 Å. Also, the observed spin-Hamiltonian parameters are quite similar to those observed for Co$^{2+}$ on an octahedral lattice site in $\alpha$-Al$_2$O$_3$.\(^{26\text{a}}\)

In the case of $\beta$-Ga$_2$O$_3$ powder, the EPR spectrum is found to be rather different as can be seen from Fig. 3(a). It now contains two groups of four EPR lines (indicated by the blue rakes) located at 280–304 and 320–350 mT, i.e., at $g$-values in the vicinity of 2.33 and 2.02. These $g$-values are characteristic for acceptor centers. The four lines are caused by a resolved hyperfine interaction with a nuclear spin $I = 3/2$. A close examination of the low field lines shows that they also contain a weaker set of four lines (indicated by the blue rakes), which cannot be resolved in the case of the second group at $g = 2.02$ due to low intensity and strong overlap with the more intense set. This suggests that the involved paramagnetic defect has two isotopes with the same nuclear spin $I = 3/2$. By comparing the signal intensities from both groups, the isotope ratio can be estimated. The calculation yields 70% (30%) for the signals marked by a black (blue) rake. The ratio of the line spacing within these sets implies that the ratio of nuclear magnetic moments between the two isotopes is 1.077. Figure 3(b) shows a simulated EPR powder spectrum of a defect with $I = 3/2$ with the following simulation parameters:

- 70% abundance: $g_{\sigma^+} = 2.33 \pm 0.01$, $g_{\sigma^-} = 2.29 \pm 0.01$, $g_b = 2.02 \pm 0.01$, and $|A| = (195 \pm 10)$ MHz,
- 30% abundance: $g_{\sigma^+} = 2.33 \pm 0.01$, $g_{\sigma^-} = 2.29 \pm 0.01$, $g_b = 2.02 \pm 0.01$, and $|A| = (210 \pm 10)$ MHz.

The simulations are in excellent agreement with the experimental data, justifying the proposed model.

Cu is the only element in the periodic table fulfilling the above criteria with the two isotopes $^{65}$Cu (69.2% natural abundance) and $^{63}$Cu (30.8% natural abundance). These isotopic abundances are in excellent agreement with the experimentally determined isotope ratio (70% and 30%). Also, the ratio of the observed hyperfine interaction
\[ \text{115} \text{MHz} = 1.077 \text{ is in excellent agreement with that of their nuclear magnetic moments}\]

\[ \frac{A^{65}_{\text{Cu}}}{A^{63}_{\text{Cu}}} = 1.077 \]

There are three possible charge states for Cu located on a gallium lattice site, namely, Cu\(^{+}\) with a 3d\(^{10}\) electron configuration and S = 0, Cu\(^{2+}\) with a 3d\(^{9}\) electron configuration and S = 1/2, and Cu\(^{3+}\) with a 3d\(^{8}\) electron configuration and S = 1. Since the detected EPR signal stems from the paramagnetic center with S = 1/2, it must be related to Cu\(^{2+}\). One possible location for the Cu\(^{2+}\) ion is the tetrahedral gallium position. However, in this case, the g-values should be similar to the g-values of Cu\(^{2+}\) in GaN\(_3\) or in ZnO\(_3\) (g\(_{\perp}\) \(\leq 0.7\) and g\(_{\parallel}\) \(\sim 1.5\)) that are very different from the g-values observed for the center here. On the other hand, Cu\(^{2+}\) is located at the octahedral lattice site in other materials shows g-values (g\(_{\perp}\) \(\sim 2.4\) and g\(_{\parallel}\) \(\sim 2.1\)), with g\(_{\parallel}\) corresponding to g\(_{e}\)) very similar to the ones obtained from the experimental data, see, e.g., Abragam and Bleaney (3d\(^{9}\) Cu\(^{2+}\) in an octahedral field)\(^{30}\) or Keeble et al. (Cu\(^{2+}\) in PbTiO\(_3\)).\(^{32}\) Thus, the observed signal can be assigned to Cu\(^{2+}\) located on the octahedral gallium site.

In conclusion, we have employed EPR spectroscopy to investigate the electronic structure and geometric arrangement of cobalt and copper in \(\beta\)-Ga\(_2\)O\(_3\). We show that both Co and Cu are present in undoped \(\beta\)-Ga\(_2\)O\(_3\) in the 2+ charge state in the 3d\(^{3}\) and 3d\(^{9}\) electronic configurations, respectively. Detailed angular-dependent EPR measurements yielded accurate spin Hamiltonian parameters, such as the g-tensor and the hyperfine interaction tensor, of the Co\(^{2+}\) and Cu\(^{2+}\) centers. The obtained parameters provide signatures of these TMs that can be used for their identification. Owing to their large ionic radii, both of these impurities preferentially occupy the octahedral Ga (II) lattice site, i.e., having the same lattice configuration as other TMs in \(\beta\)-Ga\(_2\)O\(_3\).

See the supplementary material for XRD measurements of the \(\beta\)-Ga\(_2\)O\(_3\) powder.

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