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Study of nuclear quadrupole interactions and quadrupole Raman processes of ^{69}Ga and ^{71}Ga in a β-Ga_2O_3:Cr^{3+} single crystal

Tae Ho Yeom [a], Ae Ran Lim [b,*]

[a] Division of Applied Science, Cheongju University, Cheongju 360-764, Republic of Korea
[b] Department of Science Education, Jeonju University, Jeonju 560-759, Republic of Korea

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ABSTRACT

Nuclear magnetic resonance (NMR) data and the spin–lattice relaxation times, T_1, of ^{69}Ga and ^{71}Ga nuclei in a β-Ga_2O_3:Cr^{3+} single crystal were obtained using FT NMR spectrometry. Four sets of NMR spectra for ^{69}Ga ($I = 3/2$) and ^{71}Ga ($I = 3/2$) were obtained in the crystallographic planes. The ^{69}Ga and ^{71}Ga nuclei each had two chemically inequivalent Ga_I and Ga_{II} centers. Each of the ^{69}Ga and ^{71}Ga isotopes yielded two different central NMR resonance lines originating from Ga_I and Ga_{II} sites. The nuclear quadrupole coupling constants and asymmetry parameters of $^{69}Ga_I$, $^{69}Ga_{II}$, $^{71}Ga_I$, and $^{71}Ga_{II}$ centers in a β-Ga_2O_3:Cr^{3+} crystal were obtained. Analysis of the EFG tensor principal axes (PAs) for Ga nuclei and the ZFS tensor PAs for the Cr^{3+} ion confirmed that the Cr^{3+} paramagnetic impurity ion substitutes for the Ga^{3+} ion in the oxygen octahedron. In addition, the temperature dependencies of the ^{69}Ga and ^{71}Ga relaxation rates were consistent with Raman processes, as $T_1^{-1} \propto T^2$. Even though the Cr^{3+} impurities are paramagnetic, the relaxations were dominated by electric quadrupole interactions of the nuclear spins in the temperature range investigated.

1. Introduction

Transparent conducting oxides (TCOs) are key materials in state-of-the-art optoelectronics. TCOs are used in a variety of devices including flat-panel displays and solar energy conversion devices. Among the TCOs reported to date, gallium oxide (β-Ga_2O_3) has the widest band gap energy of 4.8 eV [1], is transparent from the visible into the UV region [2], and demonstrates thermal stability because of a high melting point [3]. Interest in β-Ga_2O_3 continues, because it is a relatively new material with a number of potential applications in optoelectronics and gas sensing. β-Ga_2O_3 may also be used as a host material in electroluminescent devices [4,5]. β-Ga_2O_3 is intrinsically an insulator with a band gap of 4.8 eV. The material becomes n-type semiconducting when synthesized under reducing conditions. The n-type semiconductivity is known to arise because of a slight oxygen deficit in the crystal lattice [6]. The electrical conductivity of β-Ga_2O_3 at elevated temperatures is markedly and reversibly altered in the presence of oxidizing or reducing gases.

β-Ga_2O_3 has a monoclinic crystal structure and belongs to the space group C_{2h}^3–$C2/m$ with lattice parameters $a = 1.2214$ nm, $b = 0.30371$ nm, and $c = 0.57981$ nm, and $\beta = 103.83°$ [7–9]. Melting points of $T_m = 1740$ °C [7,8] or 1807 °C [10] have been reported in the literature. The unit cell contains four Ga_2O_3 molecules. Two chemically distinguishable cationic sites are coordinated either tetrahedrally or octahedrally with oxygen ions. The crystal structure is a double chain of GaO_6 octahedra, Ga_I, arranged parallel to the *b*-axis of the lattice, which is connected by GaO_4 tetrahedra, Ga_{II}, as shown in Fig. 1. The crystal has two cleavage planes, perpendicular to the *a*- and *c*-axes, respectively.

A nuclear magnetic resonance (NMR) study of ^{69}Ga and ^{71}Ga nuclei in pure β-Ga_2O_3 single crystals grown by the Verneuil method [11] has been performed [12]. These studies, which disclosed all ^{69}Ga and ^{71}Ga resonances, yielded eight sets of NMR parameters; these eight sets of resonance lines originated from a twin structure. Also, electron paramagnetic resonance (EPR) studies of Cr^{3+} [13,14] in β-Ga_2O_3 single crystals have been reported.

The spin–lattice relaxation times of nuclei in a crystal reflect crystal dynamics, such as nucleus–phonon interactions, and indicate how easily the excited state energy of the nuclear system can be transferred into the lattice. In the present study, the behavior of Ga in a β-Ga_2O_3:Cr^{3+} single crystal was explored using NMR and relaxation time measurements. To obtain detailed information on crystal dynamics, it was necessary to measure spin–lattice relaxation times, T_1, of constituent ^{69}Ga and ^{71}Ga nuclei.

In the present study, the NMR properties of ^{69}Ga and ^{71}Ga in a β-Ga_2O_3:Cr^{3+} single crystal were investigated using a Pulse NMR spectrometer. Four sets of Ga NMR spectra were obtained in the crystallographic planes at room temperature and analyzed using

* Corresponding author. Fax: +82 (0)63 220 2053.
E-mail addresses: aeranlim@hanmail.net, arlim@jj.ac.kr (A.R. Lim).

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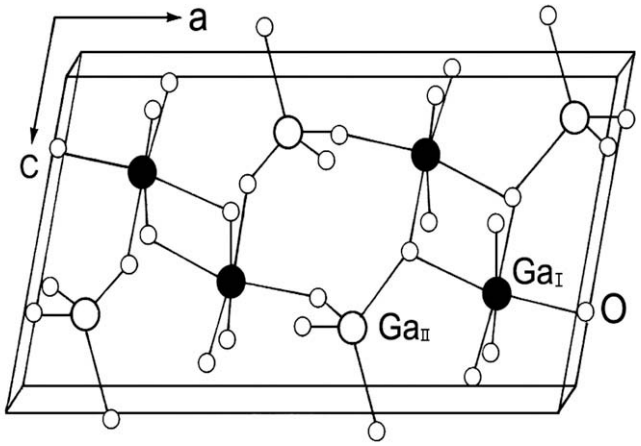

Fig. 1. Projection of the β-Ga_2O_3 single crystal unit cell structure onto the *ca*-plane.

the Zeman and nuclear quadrupole Hamiltonians. The quadrupole coupling constants (e^2qQ/h), asymmetry parameters (η), and directions of the principal tensor axes of electric field gradients (EFGs) of the ^{69}Ga and ^{71}Ga centers in the β-Ga_2O_3:Cr^{3+} single crystal were determined and compared with those of previous reports. In addition, the spin–lattice relaxation times, T_1, of both ^{69}Ga and ^{71}Ga nuclei were investigated in detail as a function of temperature. This work will enhance understanding of nuclear relaxation processes in the crystal.

2. Experimental

Single crystals of β-Ga_2O_3 doped with Cr^{3+} (0.05 mol%) were grown using a floating zone method [14]. Crystallographic axes were determined by the X-ray Laue approach. No twin domain structure was found by X-ray, NMR, or EPR. Ga NMR measurements were conducted using a Bruker FT NMR spectrometer (MSL 200 model) of the Korea Basic Science Institute. The static magnetic field was 4.7 T and central rf frequencies for ^{69}Ga and ^{71}Ga nuclei were set at $\omega_0/2\pi = 48.0372$ MHz and $\omega_0/2\pi = 61.0296$ MHz, respectively. The free induction decay (FID) of ^{69}Ga and ^{71}Ga NMR was recorded with a single pulse sequence, 5000 scans, and a repetition time of 0.5 s on each crystallographic plane. A pulse length of 1 μs (90° pulse) was used. For T_1 measurements, a π–t–$\pi/2$ inversion recovery pulse sequence was employed. The width of the π pulse was 2 μs for both ^{69}Ga and ^{71}Ga. Sample temperatures were maintained at constant values by controlling helium flow and heater current, with an accuracy of ±0.5 °C.

Typical NMR spectra of ^{69}Ga and ^{71}Ga in the β-Ga_2O_3:Cr^{3+} crystal in an arbitrary external magnetic field at room temperature are shown in Fig. 2(a) and (b), respectively. These spectra were obtained by Fourier transforming the FID of Ga ($I = 3/2$) NMR. Only central resonance lines are observed because of a large quadrupole interaction. The spectra of each of the ^{69}Ga and ^{71}Ga nuclei consist of two sets of resonance lines, denoted as Ga_I at the six-oxygen octahedron (Ga_I center) and Ga_{II} at the four-oxygen tetrahedron (Ga_{II} center). The resonance lines from ^{69}Ga at the octahedral site and ^{69}Ga at the tetrahedral site are designated the $^{69}Ga_I$ center and the $^{69}Ga_{II}$ center, respectively. The resonance lines from ^{71}Ga at the octahedral site and ^{71}Ga at the tetrahedral site are termed the $^{71}Ga_I$ center and the $^{71}Ga_{II}$ center, respectively. The central line widths of the $^{69}Ga_I$, $^{69}Ga_{II}$, $^{71}Ga_I$, and $^{71}Ga_{II}$ centers were $(\Delta\nu)_{FWHM} \approx 5.0$–$5.8$ kHz, depending on the direction of the applied field with respect to the crystallographic axes.

We defined five directions as follows: *a*, *b*, *c*, *a**, and *c**. The first three directions are those of the principal crystallographic axes, and the last two are perpendicular to the *bc*-plane and *ab*-plane,

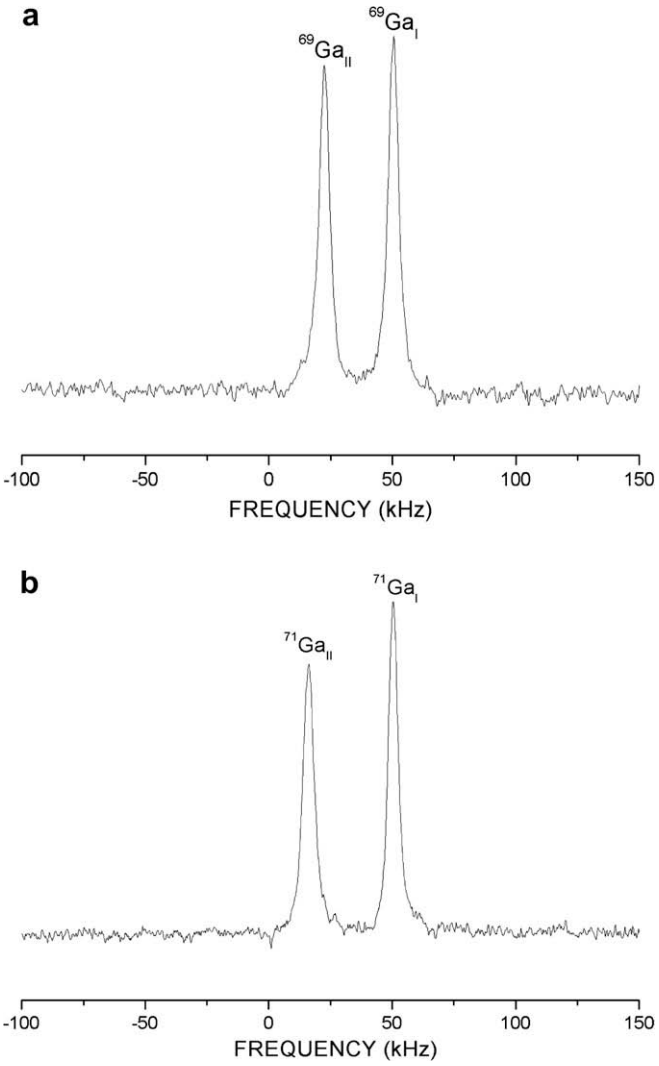

Fig. 2. Typical NMR absorption spectra of (a) ^{69}Ga and (b) ^{71}Ga nuclei in a β-Ga_2O_3:Cr^{3+} single crystal at room temperature.

respectively. The resonance absorption spectra of ^{69}Ga and ^{71}Ga nuclei in the β-Ga_2O_3:Cr^{3+} crystal were observed at intervals of 10° as the crystal was rotated through 180°. The experimental resonance frequencies of ^{69}Ga and ^{71}Ga nuclei measured on the crystallographic *ba***b*- and *bc***b*-planes are plotted in Figs. 3 and 4 as closed circles and closed rectangles, respectively, together with other data calculated as described below.

The resonance frequencies changed during crystal rotation with respect to the magnetic field. To obtain the actual Ga NMR frequencies in Figs. 3 and 4, 48.0372 MHz and 61.0294 MHz should be added to the frequencies in the graphs for ^{69}Ga and ^{71}Ga, respectively. The rotational angles in Figs. 3 and 4 are with reference to the crystallographic *b*-axis. We tried to adjust crystal mounting so that NMR spectral extrema along the *b*-axis in the *ba***b*- and *bc***b*-planes coincided. The crystallographic data show that the *b*-axis is parallel to the monoclinic direction of the crystal, consistent with previous reports [3,9].

3. Analysis and discussion

3.1. e^2qQ/h and η of ^{69}Ga and ^{71}Ga nuclei

NMR spectra of ^{69}Ga ($I = 3/2$, natural abundance 60.4%) and ^{71}Ga ($I = 3/2$, natural abundance 39.6%) centers were analyzed with the