

Nuclear Quadrupole Interactions of ^{27}Al in Alexandrite Single Crystal *

T. H. Yeom^a, S. H. Choh^b, K. S. Hong^c, H. Y. Yeom^d, Y. H. Park^d, and Y. M. Yu^e

^a Department of Physics, Chongju University, Chongju 360-764, Korea

^b Department of Physics, Korea University, Seoul 136-701, Korea

^c Korea Basic Science Institute, Seoul Branch, Korea University Campus, Seoul 136-701, Korea

^d Department of Physics, Dankook University, Cheonan 330-180, Korea

^e Korea Research Institute of Chemical Technology, Taejeon 305-308, Korea

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In an alexandrite single crystal four sets of NMR spectra for ^{27}Al ($I=5/2$) were observed in the crystallographic ab, bc, and ca planes. The Al(I) center has four magnetically inequivalent Al sites, whereas the Al(II) center has two. The nuclear quadrupole coupling constant and asymmetry parameter of Al(I) and Al(II) in an alexandrite crystal were determined. Within the experimental accuracy, our parameters turned out to have the same values as those of a chrysoberyl crystal.

1. Introduction

Alexandrite ($\text{BeAl}_2\text{O}_4:\text{Cr}^{3+}$) is a crystal that belongs to the chrysoberyl (BeAl_2O_4) group of minerals. It has unique properties as a broadband solid state laser [1, 2]. Its attractive laser characteristics include room temperature operation, flashlamp pumping, simple structure for devices, high power output and broad tunability. NMR of ^9Be and ^{27}Al nuclei in chrysoberyl single crystals has been studied with a wide-line NMR spectrometer [3–5]. Forbes reported the result of Cr^{3+} electron paramagnetic resonance (EPR) in alexandrite crystal [6]. A temperature dependence NMR study of ^9Be [7] and a spin-lattice relaxation study of ^9Be and ^{27}Al [8] in an alexandrite single crystal have recently been reported. However, no information on the ^{27}Al NMR spectrum in alexandrite single crystal was given.

In this work, NMR of the ^{27}Al nuclei ($I=5/2$, natural abundance 100%) in an alexandrite single crystal ($\text{BeAl}_{2-x}\text{Cr}_x\text{O}_4$, $x=0.02$) has been investigated with a pulse NMR spectrometer.

2. Crystal Structure

The crystal structure of BeAl_2O_4 is orthorhombic (space group D_{2h}^{16}) with lattice parameters $a=5.4756\text{\AA}$,

$b=9.4041\text{\AA}$, and $c=4.4267\text{\AA}$ at room temperature [9]. The unit cell consists of four molecules and comprises eight aluminum ions in distorted octahedral sites and four beryllium ions in distorted tetrahedral sites formed with oxygen ions. The average bond lengths of Al(I)-O, Al(II)-O, and BeO are $1.890\text{\AA}$, $1.938\text{\AA}$, and $1.632\text{\AA}$, respectively [10]. The Al(II) octahedron is appreciably larger than that of Al(I). Al(I) occupies a set of inversion centers at $(0, 0, 0; 0, \frac{1}{2}, 0; \frac{1}{2}, 0, \frac{1}{2}; \frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, while the Al(II) sites at $\pm(x, \frac{1}{4}, z; \frac{1}{2}+x, \frac{1}{4}, \frac{1}{2}-z)$ possess mirror symmetry [10].

3. Experimental

Using the Czochralski method, alexandrite single crystals were grown at the Korea Research Institute of Chemical Technology [11] by melting a mixture of Al_2O_3 (99.995%, Sumitomo Chemical), Cr_2O_3 (99.99%, Institute of Nihon High Purity Chemical) and BeO (99.99%, Aldrich) powder. The crystallographic axes of the specimen were determined by the X-ray Laue method. The X-ray topography indicated that there was no twin domain structure in the alexandrite single crystal used in this NMR experiment. ^{27}Al NMR measurements were made with a Bruker FT NMR spectrometer (MSL200) in the Korea Basic Science Institute. The static magnetic field was 4.700 T, and the central ν_f frequency was set at $\omega_0/2\pi=52.140\text{ MHz}$. The free induction decay (FID) of ^{27}Al NMR was recorded with one pulse sequence, 8 scans, and a repetition time of 10 sec on the crystal-

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Reprint requests to Prof. S. H. Choh, Fax: 82 29 27 32 92.
E-mail: shchoh@kuccnx.korea.ac.kr.

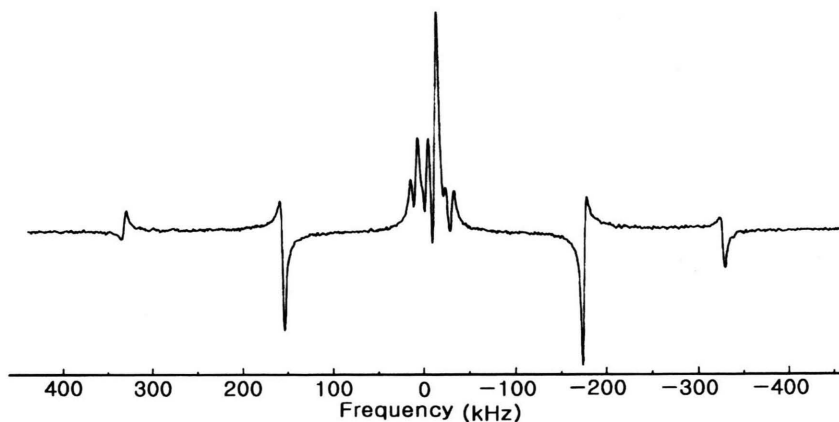


Fig. 1. Typical NMR spectrum of ^{27}Al in an alexandrite single crystal at room temperature, when the magnetic field is applied along the crystallographic [001] axis. The inner and outer satellite lines within ± 100 kHz are denoted Al(I) center, whereas there outside ± 100 kHz are denoted Al(II) center.

lographic *ab*-, *bc*-, and *ca*-planes, respectively. A pulse length of $1\ \mu\text{s}$ (about 30° pulse) and a ring down delay time of $7\ \mu\text{s}$ were used to remove the after-pulse effect. Rotation patterns of resonance lines for ^{27}Al in the crystallographic principal axes were obtained using NMR probe with a goniometer of $1/60$ degree accuracy.

A typical NMR spectrum of Al in alexandrite at room temperature for the magnetic field parallel to the crystallographic *c*-axis is shown in Figure 1. The spectrum consists of two sets of resonance lines, corresponding to the Al(I) and Al(II)-centers. The line width of the satellite line of the Al(II) center is $(\Delta\nu)_{\text{FWHM}} \approx 5.2\ \text{kHz}$. The four Al(II) centers in the unit cell give two sets of resonance lines for an arbitrary orientation of the magnetic field with respect to the crystallographic axes, whereas the four Al(I) centers give four sets of resonance lines. Therefore, all six sets of Al resonance lines were observed for an arbitrary orientation they gave 30 resonance lines. The six sets can be divided into two groups, assigned to the centers Al(I) and Al(II), which are related to the crystallographic symmetry of the crystal. The experimental resonance frequencies measured in the three crystallographic principal planes are plotted in Figs. 2, 3, and 4 with the open circles and triangles, which represent the two sets of resonance lines. The Al(I) and Al(II) centers contain four and two sets of resonance lines for an arbitrary orientation of magnetic field, respectively, defined as sites which arise from the chemically equivalent but magnetically inequivalent Al sites. These sets of Al(I) and Al(II) centers merged into one, respec-

tively, when the external magnetic field was orientated along a crystallographic axis (see Figs. 2, 3, and 4). These crossovers along a crystallographic axis are used to check the alignment of the crystal in the external magnetic field during each rotation. The resonance absorption spectra were observed after checking the crossover at intervals of 5° through the 180° rotation of the crystal.

The five-line structure (a central line, a pair of inner satellites, a pair of outer satellites) of each site for each center in Figs. 2, 3, and 4 is a result of the quadrupole interaction of the ^{27}Al nucleus. The central transition ($|1/2\rangle \leftrightarrow |-1/2\rangle$) is slightly shifted by the quadrupolar interaction, and the satellite transitions ($|5/2\rangle \leftrightarrow |3/2\rangle$, $|3/2\rangle \leftrightarrow |1/2\rangle$, $|-1/2\rangle \leftrightarrow |-3/2\rangle$, and $|-3/2\rangle \leftrightarrow |-5/2\rangle$) are very well separated from the central spectrum.

4. Experimental Results and Analysis

NMR spectra for ^{27}Al were observed in the crystallographic *ab*-, *bc*-, and *ca*-planes. There are eight Al ions per unit cell: four Al ions (Al(I)) at inversion centers and another four (Al(II)) at mirror centers lie at chemically inequivalent sites, as can be seen from the crystal structure. Six sets of Al NMR spectra in alexandrite were obtained for an arbitrary direction. It turned out that four sets of them originated from the Al(I) center and another two from the Al(II) center. However, four sets of resonance lines for the Al(I) center occurred in pairs with the open circles, when the

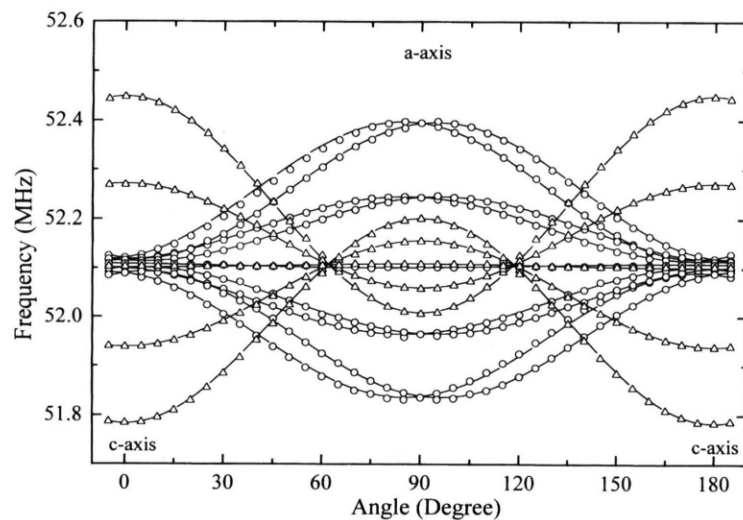
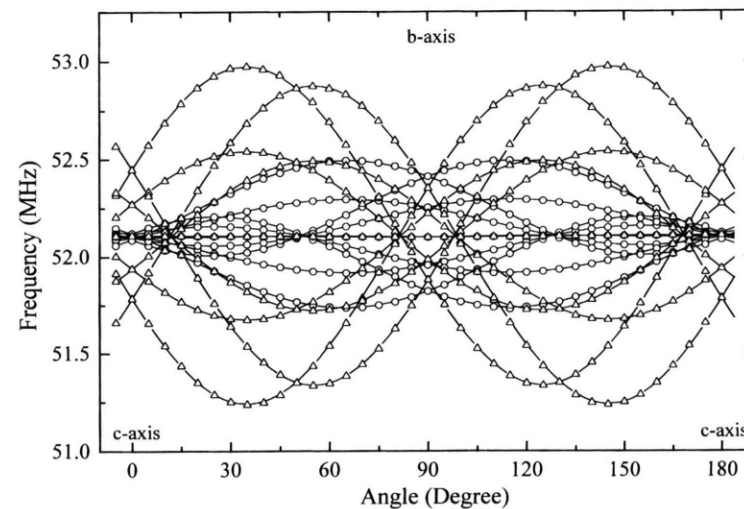
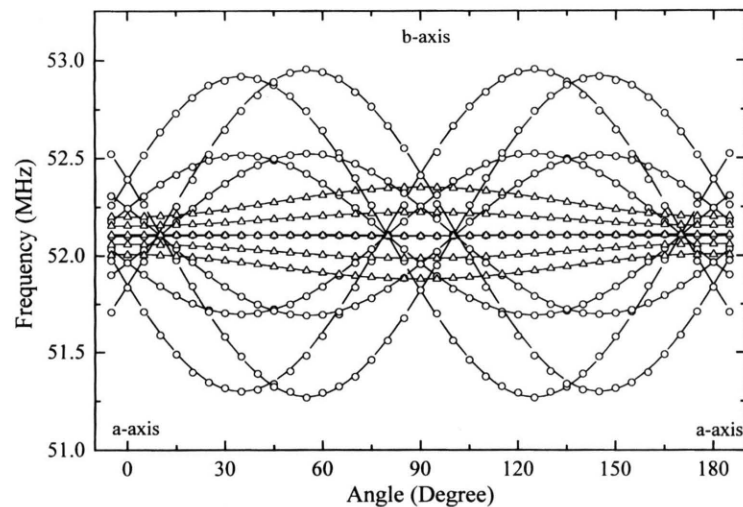


Fig. 2. The rotation pattern of ^{27}Al NMR spectra on the crystallographic *ab*-plane. The experimental data of Al(I) and Al(II) centers are plotted with open circles and open triangles, respectively. The solid lines are the calculations of resonance lines with the parameters in Table 1.

Fig. 3. The rotation pattern of ^{27}Al NMR spectra on the crystallographic *bc*-plane. For further explanations cf. Figure 2.

Fig. 4. The rotation pattern of ^{27}Al NMR spectra on the crystallographic *ca*-plane. For further explanations cf. Figure 2.

magnetic field is rotated in a plane perpendicular to a crystallographic axis. These two sets of resonance lines overlap into one set when the magnetic field is parallel to a crystallographic axis (see Figures 2, 3, and 4). Two sets of resonance lines for Al(II) center overlap when the magnetic field is in the *ab*- and *ca*-planes, as can be seen in Figs. 2 and 4 with the open triangles, whereas they are split in the *bc*-plane, as shown in Figure 3. Two sets of resonance lines in the *bc*-plane also merge into one when the magnetic field is oriented along a crystallographic axis. From the crystal symmetry, the resonance lines at crystallographic axes can be predicted to overlap into one set.

Two magnetically inequivalent mirror sites for the Al(II)-center can be predicted from the crystallographic symmetry relationships of pure chrysoberyl. From the crystal symmetry and experimental rotation patterns with the open triangles, the direction of one of the principal EFG tensors is uniquely determined from the *ab*- and *ca*-planes, and the other is in the plane perpendicular to the *a*-axis. The maximum separation of the two sets of resonance frequencies, for two Al(II) sites, due to the quadrupole interaction was observed when the magnetic field was applied along the crystallographic $c \pm 35.0^\circ$ directions, respectively, in the *bc*-plane of the crystal, and these directions were designated as the *Z*-axis of the principal EFG tensor for two sets.

Some crystals have a twin structure depending on the crystal growth conditions [12]. However, no indication of twin structure was found in our single crystal, as confirmed by X-ray topography. Therefore, four sets of resonance lines in the crystallographic planes for $^{27}\text{Al(I)}$ and $^{27}\text{Al(II)}$ nuclei originate definitely not from the twin structure but from the crystal symmetry. The NMR spectra of the Al(I) and Al(II) centers were analyzed with the Hamiltonian as usual [13]:

$$H = H_Z + H_Q, \quad (1)$$

where H_Z is the Zeeman term and H_Q the nuclear electric quadrupole interaction. The Hamiltonian H_Q in the principal axes system of the EFG tensor is given by

$$H_Q = \frac{e^2qQ}{4I(2I-1)} \left\{ 3I_z^2 - I(I+1) + \frac{1}{2}\eta(I_+^2 + I_-^2) \right\}, \quad (2)$$

where e^2qQ/h and η are the nuclear quadrupole coupling constant and the asymmetry parameter, respectively.

The e^2qQ/h , η , and the directions of the EFG tensors for the Al(I) and Al(II) centers were determined

using the computer program (EPR/NMR version 6.0) with exact diagonalization of the Hamiltonian matrices. Here the "laboratory" axes used for the Hamiltonian analysis are labeled with the lower case *x*, *y*, *z*. These are chosen to coincide with the crystallographic axes *a*, *b*, and *c*. The principal axes of the EFG tensor are labeled with the upper case *X*, *Y*, *Z*. The set of input parameters is optimized using a nonlinear least-squares routine so as to minimize the weighted differences between the observed and calculated transition frequencies. A total number of 495 resonance line positions due to the quadrupolar interaction recorded in the three crystallographic planes are used to obtain a rigorous fit.

The final best fit of the e^2qQ/h and η in alexandrite crystal is listed in Table 1 together with those previously reported [4]. In this previous report, however, outer satellite lines ($|5/2\rangle \leftrightarrow |3/2\rangle$ and $|-3/2\rangle \leftrightarrow |-5/2\rangle$) could not be observed for chrysoberyl crystal because of impurities and imperfections. The obtained nuclear quadrupole coupling constants and asymmetry parameters of aluminium in alexandrite single crystal are 2.864 MHz and 0.936 for the Al(I) center and 2.861 MHz and 0.762 for the Al(II) center at room temperature. Our parameters, with better accuracy in alexandrite crystal, turn out to have the same values as those of Al in a pure chrysoberyl crystal [4] within experimental accuracy. It turns out that the doped Cr^{3+} ions do not influence the quadrupole interaction of the Al nuclei in alexandrite single crystal ($\text{BeAl}_{2-x}\text{Cr}_x\text{O}_4$, $x=0.02$). The principal axes of the EFG tensors for Al(I) and Al(II) centers are shown in Table 2. The orientation of the EFG principal axes

Table 1. The nuclear quadrupole coupling constants and asymmetry parameters of Al(I) and Al(II) centers.

	Al(I) center	Al(II) center	
e^2qQ/h	2.864 ± 0.003 MHz	2.861 ± 0.003 MHz	present study [4]
η	0.936 ± 0.002	0.762 ± 0.002	
	2.850 ± 0.015 MHz	2.846 ± 0.015 MHz	
	0.94 ± 0.02	0.76 ± 0.02	

Table 2. The orientation of the EFG tensor of Al(I) and Al(II) centers. A_{xy} is the angle between the laboratory *x*-axis and the principal *Y*-axis of the EFG tensor.

Al(I) center	Al(II) center
$A_{ij} = \begin{pmatrix} 102.3 & 36.5 & 56.3 \\ 92.3 & 125.1 & 35.2 \\ 12.5 & 81.3 & 81.1 \end{pmatrix}$	$A_{ij} = \begin{pmatrix} 0.0 & 90.0 & 90.0 \\ 90.0 & 35.0 & 55.0 \\ 90.0 & 125.0 & 35.0 \end{pmatrix}$

system (X, Y, Z) with respect to the laboratory axes system (x, y, z) is described for each center by a matrix of angles A_{ij} after conversion of direction cosines obtained from computer calculation. The orientation of the other three sites for Al(I) center and one site for Al(II) center is then obtained from the symmetry operations which produce the other sites of each center in the unit cell. The simulations of the resonance frequencies for the Al(I) and Al(II) centers are performed with the parameters in Table 1, and the simulations of rotation patterns in the ab -, bc -, and ca -planes are shown in Figs. 2, 3, and 4 with solid lines. These lines fit the experimental data well.

5. Conclusion

For any arbitrary orientation of the magnetic field with respect to the crystalline axes, four sets of resonance lines for the Al(I) center were observed, corresponding to the four positions of the inversion sites in the unit cell. When the magnetic field is rotated in a plane perpendicular to a crystallographic axis, the resonance lines occurred in pairs, and when the magnetic field is parallel to a crystallographic axis, the resonance lines merge into one. Two sets of resonance lines

for Al(II) center at mirror site were observed. The mirror site resonance lines remained magnetically equivalent for rotations in the ab - and ca -planes; however, the resonance lines were split into pairs for rotation in the bc -plane. The two sets of lines in the bc -plane also overlapped into one set.

The e^2qQ/h and η are 2.864 ± 0.003 MHz and 0.936 ± 0.002 for Al(I) center and 2.861 ± 0.003 MHz and 0.762 ± 0.002 for Al(II) center. This means that V_{zz} are equivalent for the two centers, whereas V_{xx} and V_{yy} are different. The principal X, Y , and Z axis of the EFG tensor for Al(II) center are found to be along the crystallographic $a, b + 35.0^\circ$, and $c + 35.0^\circ$ in the bc -plane, respectively. These values of two Al centers in an alexandrite single crystal, through with higher accuracy, are the same within experimental accuracy as those in a chrysoberyl crystal [4].

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