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## Temperature-dependent nuclear magnetic resonance study of $^9\text{Be}$ in an alexandrite single crystal

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**Abstract.** Nuclear magnetic resonance (NMR) spectra of the  $^9\text{Be}$  nucleus in an alexandrite ( $\text{BeAl}_{2-x}\text{Cr}_x\text{O}_4$ ,  $x = 0.02$ ) single crystal, grown by the Czochralski method, have been investigated employing a Bruker FT NMR spectrometer. Two sets of NMR spectra for  $^9\text{Be}$  ( $I = 3/2$ ) were observed in the crystallographic planes. The principal  $X$  axis of the electric field gradient tensors for both is found to be along the crystallographic  $a$  axis. The principal  $Y$  and  $Z$  axes are located in the  $b$ - $c$  plane at about  $9^\circ$  from the crystallographic  $c$  and  $b$  axes, respectively. These results indicate that there are two magnetically inequivalent Be sites, but they are chemically equivalent. The temperature dependence of  $^9\text{Be}$  NMR spectra has been measured in the temperature range 120–440 K.  $e^2qQ/h$  for  $^9\text{Be}$  is found to increase linearly whereas  $\eta$  decreases with increasing temperature.

### 1. Introduction

Alexandrite ( $\text{BeAl}_2\text{O}_4:\text{Cr}^{3+}$ ) is a crystal which belongs to the chrysoberyl group of minerals ( $\text{BeAl}_2\text{O}_4$ ). Since natural alexandrite is a very attractive and expensive gemstone due to its rareness, there have been many attempts to synthesize this crystal. The first attempt to grow chrysoberyl crystals consisted mainly of melting a mixture of  $\text{BeO} + \text{Al}_2\text{O}_3$  in the presence of various mineralizers [1]. The growth of large single crystals by the Czochralski method made possible the first lasing of alexandrite in 1974 [2]. In recent years, alexandrite single crystals doped with Cr have been shown to be an excellent solid state tunable phonon-terminated laser host. This material possesses attractive laser characteristics, including room-temperature operation, flashlamp pumping, simple structure for devices, high power output and broad tunability and has wide potential applications for civilian, scientific and military uses [3, 4].  $^9\text{Be}$  NMR in a pure chrysoberyl single crystal has been studied with a wide-line NMR spectrometer before [5, 6].

In this work, NMR of the  $^9\text{Be}$  nucleus (100% natural abundance) in an alexandrite single crystal ( $\text{BeAl}_{2-x}\text{Cr}_x\text{O}_4$ ,  $x = 0.02$ ) has been investigated with an FT NMR spectrometer. The quadrupole coupling constant, the asymmetry parameter and the direction of the principal axes of the electric field gradient (EFG) tensor of the  $^9\text{Be}$  ( $I = 3/2$ ) are determined at room temperature. The temperature dependences of  $e^2qQ/h$  and  $\eta$  have also been measured in the temperature range 120–440 K. This temperature dependence of  $^9\text{Be}$  in alexandrite is a new result.

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## 2. Crystal structure

The crystal lattice of  $\text{BeAl}_2\text{O}_4$  belongs to the 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 [7]. The unit cell consists of four molecules and is comprised of eight aluminium ions in distorted octahedral sites and four beryllium ions in distorted tetrahedral sites formed with oxygen ions. The bond lengths of Be–O(1), Be–O(2) and Be–O(3) are 1.579  $\text{\AA}$ , 1.687  $\text{\AA}$  and 1.631  $\text{\AA}$ , respectively [8]. Four Be ions in the cage of distorted O tetrahedra lie at inversion symmetry sites known from the  $\text{BeAl}_2\text{O}_4$  crystal structure as shown in figure 1 [8].

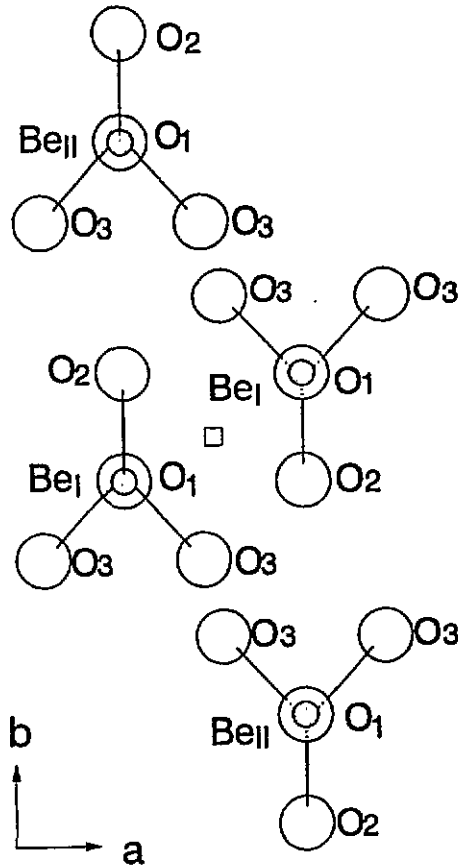


Figure 1. The chrysoberyl structure of Be–O tetrahedra projected on (001).

## 3. Experimental aspects

Alexandrite single crystals were grown by melting a mixture of  $\text{Al}_2\text{O}_3$  (purity, 99.995%; Sumitomo Chemical),  $\text{Cr}_2\text{O}_3$  (purity, 99.99%; Institute of Nihon High Purity Chemical) and BeO (purity, 99.99%; Aldrich) powder by the Czochralski method in KRICT [9]. The crystallographic axes of the specimen were determined by the x-ray Laue method.  $^9\text{Be}$  NMR

spectra, from an alexandrite single crystal of size approximately  $6.4\text{ mm} \times 6.8\text{ mm} \times 7.5\text{ mm}$ , were obtained with a Bruker MSL200 spectrometer at the Korea Basic Science Institute. The static magnetic field was 4.7 T and the central RF was set at  $\omega_0/2\pi = 28.104\text{ MHz}$ . The free induction decay (FID) of  $^9\text{Be}$  NMR was recorded with one pulse sequence, 16 scans and a repetition time of 5 s on the crystallographic  $a$ - $b$ ,  $b$ - $c$  and  $c$ - $a$  planes, respectively. The pulse length of  $3\ \mu\text{s}$  ( $90^\circ$  pulse) and a ringdown delay time of  $7\ \mu\text{s}$  were used to remove the after-pulse effect.

#### 4. Experimental results and analysis

Typical NMR spectra of  $^9\text{Be}$  in the sample at room temperature are shown in figure 2 curves (a)–(c), when the magnetic field is parallel to the crystallographic axes [100], [010] and [001], respectively. It is a Fourier transform of the FID for  $^9\text{Be}$  NMR. The spectrum consists of the central line and two equally spaced satellites. The linewidth of the central line is  $(\Delta\nu)_{\text{FWHM}} \simeq 2.6\text{ kHz}$ . The zero point of the  $x$  axis shows the resonance frequency, 28.104 MHz, of the bare  $^9\text{Be}$  nucleus. The resonance frequency is different for a nucleus embedded in bulk matter from that for a 'bare' nucleus. The origin of this frequency shift is due to the chemical shift [10]. Although  $\text{Cr}^{3+}$  impurity ions may play an important role in the spin–lattice relaxation of the nuclear spin system, their influence on the  $^9\text{Be}$  nuclear energy level is negligible [10]. Therefore, we dismiss the situation that paramagnetic ions of the sample crystal may cause the frequency shift.

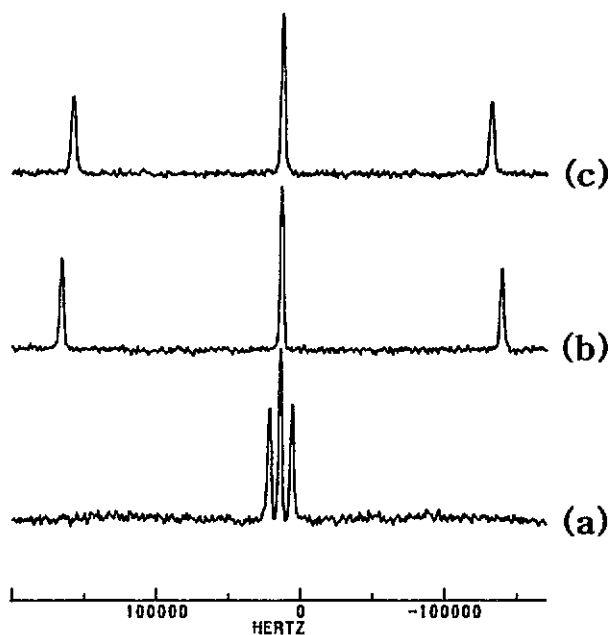


Figure 2. The NMR spectrum of  $^9\text{Be}$  in an alexandrite single crystal at room temperature. The magnetic field was applied along the crystallographic [100] axis (curve (a)), [010] axis (curve (b)) and [001] axis (curve (c)).

For rotation patterns in the  $a$ - $b$  and  $c$ - $a$  planes, only one set of resonance lines is recorded because of the superposition of two sets, but it was split by small deviations from the exact orientation. In fact, two sets of resonance lines are recorded in the  $b$ - $c$  plane as displayed in figure 3. Two sets of resonance spectra have nearly the same intensity. The zero point in figure 3 corresponds to the frequency 28 117.7 kHz. There are four Be ions per unit cell; two Be ions ( $\text{Be}_I$ ) and another two Be ions ( $\text{Be}_{II}$ ) lie at separate sites but are related to one inversion centre, respectively, as can be seen from figure 1. These two sets of lines originating from  $\text{Be}_I$  and  $\text{Be}_{II}$  ions are magnetically inequivalent sites. The inversion symmetry sites of Be ions are observed to be magnetically equivalent in NMR, which agrees with the known crystallography of  $\text{BeAl}_2\text{O}_4$  and  $^9\text{Be}$  NMR results. Two Be ions ( $\text{Be}_I$  or  $\text{Be}_{II}$ ) in the inversion symmetry sites always give one set of resonance signals.

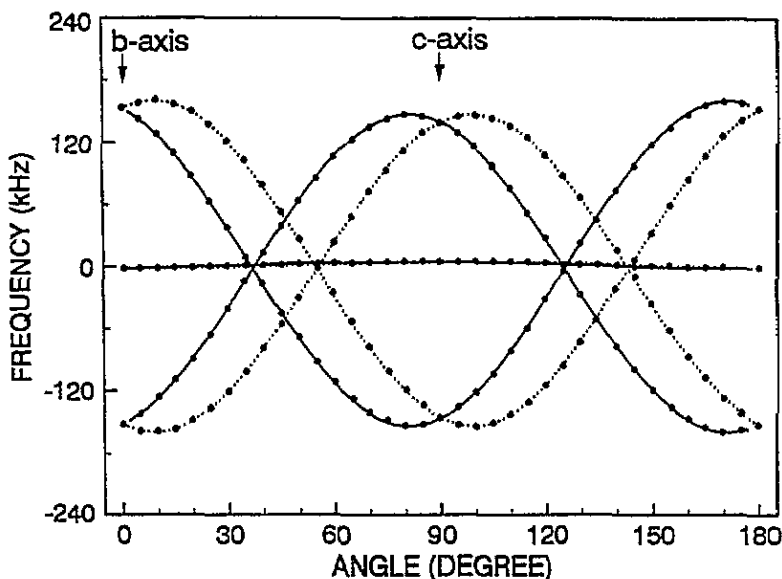


Figure 3. The rotation pattern of  $^9\text{Be}$  NMR spectra on the crystallographic  $b$ - $c$  plane.

Some crystals have a twin structure according to the growth conditions [11]. However, no indication of twin structure was found in our single crystal, as confirmed by x-ray topography. Therefore, two sets of resonance lines are definitely not from the twin structure.

The Hamiltonian to analyse the experimental results is the usual [10]

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

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

$$H_Q = \frac{e^2 q Q}{4I(2I-1)} [3I_Z^2 - I(I+1) + \frac{1}{2}\eta(I_+^2 + I_-^2)] \quad (2)$$

where  $e^2 q Q/h$  and  $\eta$  are the nuclear quadrupole coupling constant and the asymmetry parameter respectively. Conventionally  $X$ ,  $Y$  and  $Z$  are the principal axes of the EFG tensor with

$$eq = V_{ZZ} \quad \eta = \frac{V_{XX} - V_{YY}}{V_{ZZ}} \quad (3)$$

The parameters  $e^2qQ/h$  and  $\eta$  in equation (2) are determined using exact diagonalization of the spin-Hamiltonian matrices.

The three-line structure in figure 2 is a result of the quadrupole interaction of the  $^9\text{Be}$  nucleus. The central transition ( $|1/2\rangle \leftrightarrow |-1/2\rangle$ ) is almost unshifted by the quadrupolar interaction, but the satellite transitions ( $|3/2\rangle \leftrightarrow |1/2\rangle$  and  $|-1/2\rangle \leftrightarrow |-3/2\rangle$ ) are well resolved from the central spectrum.

The rotation pattern of  $^9\text{Be}$  in the crystallographic  $b$ - $c$  plane is shown in figure 3 as full circles. The satellite resonance lines show an angular dependence. The maximum separation of the two sets of resonance frequencies due to the quadrupole interaction was observed when the magnetic field was applied along the  $b \pm 9^\circ$  ( $\pm 1^\circ$ ) directions, respectively, in the  $b$ - $c$  plane of the crystal and these directions were designated as the  $Z$  axis of the EFG tensor for two sets. The principal  $Y$  axis lies along the crystallographic  $c \pm 9^\circ$  ( $\pm 1^\circ$ ) directions, respectively, in the  $b$ - $c$  plane. The directions of Be-O(1) and Be-O(2) are roughly parallel to the crystallographic  $c$  and  $b$  axes, respectively, as shown in figure 1. The deviations of Be-O(1) and Be-O(2) directions are calculated to be about  $6^\circ$  from the crystallographic  $c$  and  $b$  axes, respectively, from the crystal structure [8]. These deviation angles of  $\pm 6^\circ$  are slightly smaller than the value of  $\pm(9 \pm 1)^\circ$  obtained from the NMR experiment.  $\text{Be}_I$  and  $\text{Be}_{II}$  give  $+9^\circ$  and  $-9^\circ$  deviation from the crystallographic  $b$  and  $c$  axes, respectively. According to our x-ray diffraction and NMR data, the assignments of  $a$  and  $b$  axes of chrysoberyl crystal in figure 2 of [6] are erroneous; they should be interchanged with each other.

From the fact that the resonance frequency of the central line is almost constant and the spacings between adjacent lines are equal, the first-order perturbation of  $H_Q$  with respect to  $H_Z$  may be sufficient for analysis. The parameters were determined by a least-squares fit to the experimental data and the simulation of resonance fields of  $^9\text{Be}$  on the  $b$ - $c$  plane is shown in figure 3 as solid and dotted lines. These lines fit the experimental data well. The nuclear quadrupole coupling constant and asymmetry parameter of  $^9\text{Be}$  in alexandrite crystal obtained are  $317.8 \pm 0.4$  kHz and  $0.904 \pm 0.002$ , respectively, at room temperature. These parameters turn out to be the same as those for  $^9\text{Be}$  in a pure chrysoberyl crystal [6]. The influence of the  $\text{Cr}^{3+}$  ion (0.02%) on the  $^9\text{Be}$  nucleus in alexandrite is negligible.

The temperature dependence of the  $^9\text{Be}$  NMR spectrum in alexandrite was also measured at 17 different temperatures in the range 120–440 K with the magnetic field parallel to the crystallographic  $c$ ,  $c + 9^\circ$ , and  $c + 81^\circ$  axes in the  $b$ - $c$  plane. The intensity of the resonance line is found to decrease as the temperature increases. While the central transition stays constant at the line position, the line spacings between the central and satellite lines are, however, found to increase as the temperature increases.

The temperature dependence of  $e^2qQ/h$  for the  $^9\text{Be}$  nucleus is shown in figure 4 as full circles. The value of  $e^2qQ/h$  was found to increase as a function of increasing temperature where the experimental data may be fitted with the linear equation  $e^2qQ/h = 317.8 + 2.2 \times 10^{-2}(T - T_r)$  kHz as represented by the solid line. Here,  $T$  (K) is the temperature and  $T_r$  (K) room temperature (300 K). The experimental error of  $\pm 0.4$  kHz for  $e^2qQ/h$  is mainly caused by reading the resonance line position from the NMR spectra. Generally,  $e^2qQ/h$  decreases as a function of increasing temperature in many substances; that is, the slope  $dv_Q/dT$  is negative [12, 13]. However,  $e^2qQ/h$  for  $^9\text{Be}$  in alexandrite increases as the temperature increases in contrast with the usual decreasing trend.

Figure 5 shows the temperature dependence of  $\eta$  which decreases as the temperature increases. The solid line is the linear fit of  $\eta$  with a linear equation  $\eta = 0.904 - 4.6 \times 10^{-5}(T - T_r)$ . The experimental error of  $\eta$  is 0.002.

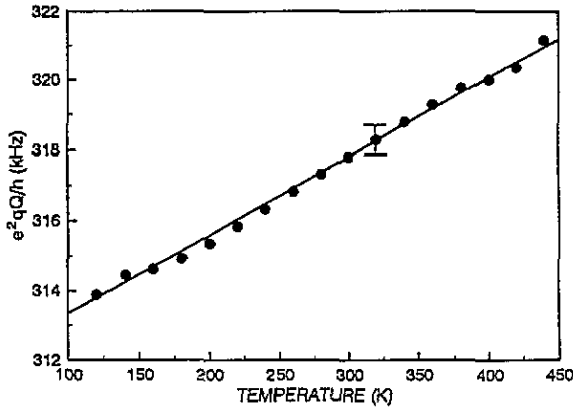


Figure 4. Temperature dependence of the nuclear quadrupole coupling constant  $e^2qQ/h$  for  $^9\text{Be}$  in alexandrite: ●, experimental data.

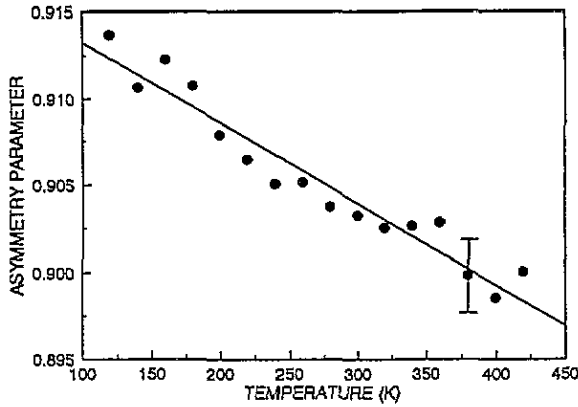


Figure 5. Temperature dependence of the asymmetry parameter  $\eta$  for  $^9\text{Be}$  in alexandrite: ●, experimental data.

## 5. Conclusion

Two sets of NMR spectra for  $^9\text{Be}$  are recorded in the crystallographic  $b$ - $c$  plane but they are reduced to one in the  $a$ - $b$  and  $a$ - $c$  planes. This shows that there are two chemically equivalent but magnetically inequivalent sites of Be in the alexandrite crystal. This is consistent with the crystallographic structure of pure  $\text{BeAl}_2\text{O}_4$  crystal showing inversion symmetry of  $\text{Be}_I$  and  $\text{Be}_{II}$ . The principal  $X$ ,  $Y$  and  $Z$  axes of the EFG tensor of the  $^9\text{Be}$  nucleus in the alexandrite single crystal are found to lie along the crystallographic  $-a$ ,  $c + 9^\circ$  and  $b + 9^\circ$  axes, respectively, for the  $\text{Be}_I$  site and  $-a$ ,  $c - 9^\circ$  and  $b - 9^\circ$  axes, respectively, for  $\text{Be}_{II}$ . The quadrupole coupling constant of  $^9\text{Be}$  in the alexandrite crystal increases as the temperature increases. However, the asymmetry parameter decreases with increasing temperature. The nuclear quadrupole coupling constant and asymmetry parameter obtained as functions of temperature for both  $^9\text{Be}_I$  and  $^9\text{Be}_{II}$  in the alexandrite crystal could be fitted by the linear equations  $e^2qQ/h = 317.8 + 2.2 \times 10^{-2}(T - T_r)$  kHz and  $\eta = 0.904 - 4.6 \times 10^{-5}(T - T_r)$ , respectively, in the temperature range 120–440 K.

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