Nuclear Magnetic Resonance of $^7$Li and $^{23}$Na in Zektzerite, NaLiZrSi$_6$O$_{15}$

Subrata Ghose$^1$, D. Brinkmann$^2$, and J. Roos$^2$

$^1$ Mineral Physics Group, Department of Geological Sciences, University of Washington, Seattle, WA 98195, USA
$^2$ Physik-Institut der Universität Zürich, Schönberggasse 9, CH-8001 Zürich, Switzerland

Abstract. The electric field gradient (EFG) tensors of $^7$Li and $^{23}$Na in a zektzerite, NaLiZrSi$_6$O$_{15}$ single crystal have been determined by the nuclear magnetic resonance technique. The quadrupole coupling constants, $e^2qQ/h$ and the asymmetry parameters, $\eta$, for $^7$Li are $119 \pm 5$ kHz, 0.05 and for $^{23}$Na $2.42 \pm 0.15$ MHz, 0.86 respectively. In both cases, the EFG tensors show the two-fold site-symmetries at the Li- and Na-sites. For $^7$Li, the magnitude of the quadrupole coupling constant and the principal axis of the EFG tensor reflect the large angular distortion of the [LiO$_4$] tetrahedron. The large quadrupole coupling constant of $^{23}$Na indicates a high degree of distortion of the Na coordination polyhedron.

Introduction

Zektzerite, NaLiZrSi$_6$O$_{15}$ occurs as stout prismatic crystals in microlitic cavities of the Golden Horn riebeckite-granite batholith, North Cascades, Washington. Its crystal structure consists of corrugated six-tetrahedral-repeat double silicate chains and tetrahedral-octahedral chains formed by alternating edge-sharing [LiO$_4$] and [ZrO$_6$] octahedra, giving rise to a three-dimensional network (Ghose and Wan 1978). The Na$^+$ ions occur in channels parallel to the a axis formed by five silicate tetrahedra and a [ZrO$_6$] octahedron (Fig. 1). This ten-coordinated sodium site (M1) is fully occupied, while another possible nine-coordinated sodium site (M2) is vacant in this structure. In two other compounds, synthetic Na$_2$Mg$_2$Si$_6$O$_{15}$ and emeleusite,.

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Fig. 1. A view of one half of the zektzerite crystal structure down the a axis; the second half is obtained by reflection across a mirror plane at $x=1/2$ passing through oxygen atoms O(7), O(9), and O(9), thereby doubling the silicate chain (after Ghose and Wan 1978)
Na$_2$LiFe$^{3+}$Si$_6$O$_{15}$, these sites are fully occupied (Cradwick and Taylor 1972; Johnson et al. 1978).

In zektzerite the sodium ion shows very strong anisotropic thermal vibration at room temperature. From structural considerations, we envisaged a possible migration of the sodium ions from the fully occupied M1 site to the vacant M2 site above a certain threshold temperature. Detailed x-ray refinements of the zektzerite structure as a function of temperature indicate that at 400°C the M1 site is fully occupied, while at 600°C the sodium ions begin to migrate from the M1 site to the M2 site (Ghose and Shaikh 1988, in preparation). Preliminary measurements of the nuclear spin-lattice relaxation times of $^7$Li and $^{23}$Na indicate high mobility of the sodium ions at high temperatures (D. Brinkmann and J. Roos 1981 unpublished data).

We have now determined the nuclear quadrupole coupling tensors for $^7$Li and $^{23}$Na in zektzerite, as a preliminary to more detailed measurements of the $^7$Li and $^{23}$Na spin-lattice relaxation times by the nuclear magnetic resonance technique to determine diffusion rates.

Theory

For an isolated nucleus of spin $I$ and magnetic moment $\mu = h I$ in an external magnetic field $H$, the Zeeman Hamiltonian or the interaction is given by (Cohen and Reif 1957):

$$\mathbf{H}_z = -\mu \cdot \mathbf{H} = -\gamma h I \cdot \mathbf{H},$$

where $\gamma$ is the gyromagnetic ratio of the nucleus and $h$ is the Planck's constant. There are $2I+1$ equally spaced Zeeman energy levels and the $2I$ transitions between adjacent levels would give rise to a single absorption at the Larmor frequency, $\nu = \gamma H / 2\pi$. For $I \geq 1$, the nucleus also has an electric quadrupole moment $eQ$. In a solid, the nucleus may be situated in a site where the surrounding charge distribution has less than cubic symmetry. Then there is an interaction $H_Q$ between the nuclear electric quadrupole moment $eQ$ and the (negative) electric field gradient (EFG), $\phi_{ij} = \partial^2 \phi / \partial q_i \partial q_j$, where $\phi$ is the electrostatic potential mostly due to the neighboring ions, $e$ is the electronic charge, and $q_i, q_j$ are the spatial coordinates. The total interaction is then $H_F + H_Q$. For the case $H_Q \ll H_F$, the $2I+1$ Zeeman energy levels are shifted slightly and the single absorption line is now split into $2I$ components.

Both $^7$Li and $^{23}$Na nuclei have spin $I = 3/2$; the values of $\gamma$ are 13.96 and 7.076 kHz/Gauss respectively. There are $2I = 3$ absorption lines: the central component, $m = 1/2$ to $-1/2$, with frequency $\nu_c$, not very different from the Zeeman frequency $\nu_0$, and a pair of satellites, $m = \pm 1/2$ to $\pm 3/2$, with frequencies $\nu'$ and $\nu''$ almost equally spaced above and below the Zeeman frequency $\nu_0$. These resonance frequencies were measured as the crystal was rotated about an axis perpendicular to the magnetic field. The EFG tensor components may be determined from several rotation patterns. Because of the orthorhombic symmetry of zektzerite with space group Cmca (Ghose and Wan 1978), the axes of rotation are chosen to be the crystallographic $a$, $b$ and $c$-axes. The components of the EFG tensor in the crystallographic axes system $(i,j = a,b,c)$ may be then obtained by standard procedures (Volkoff et al. 1952; Volkoff 1953). These components form a symmetric $3 \times 3$ matrix and the sum of the diagonal elements $\psi_{aa} + \psi_{bb} + \psi_{cc}$ is zero. By matrix diagonalization, the eigenvalues $V_{xx}, V_{yy}, V_{zz}$ and the eigenvectors, i.e., the principal values of the coupling tensor $(V_{xx} + V_{yy} + V_{zz} = 0)$ and the direction cosines of the principal axes $X, Y, Z$ may be obtained. Following the standard conventions of Cohen and Reif (1957), we choose $|V_{xx}| \geq |V_{yy}| \geq |V_{zz}|$. The quadrupole coupling constant is defined as $e^2 q Q / h = |V_{zz}|$ and the asymmetry parameter is defined as $\eta = (V_{xx} - V_{yy}) / V_{zz}, 0 \leq \eta \leq 1$. Since only the relative signs of EFG are known, the magnitude of the coupling constant may be determined from the experimental data; however there is an ambiguity in the sign.

Crystal Data and Experimental

Zektzerite is orthorhombic, space group Cmca, with unit cell dimensions: $a = 14.330(2), \quad b = 17.354(2), \quad c = 10.164(2)$ Å; $Z = 8$. A stout prismatic crystal ($5 \times 6 \times 8 \times$ mm) bounded by crystal planes {011}, {010}, {001} and cleavage planes {100} was used for the NMR experiments. These crystal planes were used to orient the crystal in the magnetic field on a single-axis goniometer. The accuracy of the crystal setting is estimated to be $\pm 2^\circ$.

The NMR signals were recorded at room temperature near 7.5 MHz using a crossed coil spectrometer of the Bloch type and a field-regulated electromagnet with Hall effect probe. The magnetic field was calibrated using LiNO$_3$ and NaCl in solution as standards. The differentiated $^7$Li and $^{23}$Na signals were recorded in the dispersion mode by varying the magnetic field. Two rotation patterns of the crystal around $a$ and $b$ axes were obtained. Since the point symmetries at the Li and Na sites are $2i || a$ and $2i || b$ respectively, these two rotation patterns were sufficient to characterize the electric field gradient tensors completely.

Results

(a) $^7$Li

For $^7$Li in zektzerite, the satellite pairs are readily observed. A typical spectrum is shown in Fig. 2a. The line width is $\sim 3$ G. The rotation pattern about the crystallographic $a$-axis is shown in Fig. 3, where the angle $\theta$ is measured from the $c$-axis. The pair separation in Gauss may be converted to frequency by multiplication with $\gamma / 2\pi = 1.655$ kHz/

\[\text{Fig. 2.} \quad \text{a Li NMR spectra in zektzerite; \textbf{H} at 30^\circ from c axis in the } \text{bc plane; b $^{23}$Na NMR spectra in zektzerite; \textbf{H} at 60^\circ from c axis in the } \text{bc plane}\]