27\text{Al} Double-Rotation NMR Study of \text{Al}_2\text{SiO}_5 Polymorph Minerals

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Abstract. 27\text{Al} double-rotation (DOR) NMR spectra of the alumino-silicate polymorph minerals, kyanite, sillimanite and andalusite, show separately resolved peaks, relating to the crystallographically non-equivalent sites. The isotropic chemical shifts are calculated from the observed peak positions and they correlate closely with those found previously by simulations of MAS NMR spectra. The intensities of the four non-equivalent sites in kyanite are found to have an exponential relationship with their corresponding quadrupolar coupling constants ($C_Q$).

1. Introduction

Quadrupolar interactions of nuclei with non-integral spin greater than 1/2, such as 27\text{Al}, 23\text{Na}, 17\text{O}, 9\text{Be} and 7\text{Li}, cause line-broadening and peak shifts in solid state NMR spectra, which can not be efficiently removed by fast MAS NMR even at high field [1, 2]. Variable Angle Spinning (VAS) [3] and Al nutation techniques [4] have also been applied to the problem, but neither gives completely satisfactory results [5]. Double angle techniques of double-rotation (DOR) [6] and dynamic angle spinning (DAS) [7] offer possible solutions to this problem.

The three alumino-silicate polymorphs kyanite, andalusite and sillimanite (\text{Al}_2\text{SiO}_5) are used by petrologists to determine the pressure and temperature of formation of rocks, due to their abundance in metamorphic rocks and their well characterized pressure and temperature ranges [8]. They are an interesting group of minerals to study using 27\text{Al} NMR as they have a variety of Al sites and coordinations. Each of the three mineral structures consists of a double chain of \text{AlO}_6 octahedra linked by \text{SiO}_4 tetrahedra. Additional linkages between the octahedral chains are formed by Al atoms in octahedral coordination in kyanite [9], in an irregular 5 fold coordination in andalusite [10] and in tetrahedral coordination in sillimanite [11]. Al is in four crystallographically non-equivalent octahedral sites in kyanite, in one
octahedral and one five-coordinate site in andalusite and in one octahedral and one tetrahedral site in sillimanite. They have been well characterized crystallographically and by single crystal [12] and MAS NMR [13-15].

One practical limitation of the DAS technique is the length of time required for flipping the stator between two angles, which we have found to be about 20 ms. Thus the DAS technique may only be applied to nuclei with spin lattice relaxation times greater than 0.5 seconds. Quadrupolar interactions provide the dominant relaxation mechanism for \(^{27}\)Al in solids. As this is extremely efficient, the relaxation time, which is typically of the order of tens of milliseconds, is too short for the DAS technique to be used [16]. The DOR probe does not have such a problem and can be used to obtain high resolution \(^{27}\)Al spectra. We here report the first double rotation (DOR) spectra of these polymorphs.

2. Experimental

Samples of the minerals kyanite (E 2912, from Pfitschthal, Tyrol), andalusite (BLS 218, from Minas Geraes, Brazil) and sillimanite (BLS 144, from Dil-lan, Mantana) were very finely ground prior to carefully packing them into the inner rotor.

The spectra were acquired on a Bruker AMX-500 console with an 8.42 T wide bore magnet. The construction of the Bruker DOR probe is similar to that discussed in detail by Wu et al. (1990) [6]. 2 \(\mu\)s pulse lengths were used, as the 90\(^\circ\) pulse length measured on 1 M \(\text{AlCl}_3 \cdot 6\text{H}_2\text{O}\) aqueous solution was 20 \(\mu\)s. The \(^{27}\)Al spectral reference was 1 M \(\text{AlCl}_3 \cdot 6\text{H}_2\text{O}\) solution. The spectra were Fourier Transformed with a line broadening of 10 Hz. Peak positions are accurate to ± 0.1 ppm.

Fig. 1. Pulse diagram for DOR NMR experiments: a experiment 1, \(VD\) set as 0 \(\mu\)s; b experiment 2, \(VD\) is half the period of rotation of the outer rotor.