Nuclear Quadrupole Resonance Studies in MICA*

S. Sengupta, S. Rhadakrishna, and R. A. Marino **

Department of Physics and Astronomy, Hunter College of CUNY New York, NY 10021, USA

Z. Naturforsch. **41 a,** 341 – 342 (1986); received August 2, 1985

Aluminum-27 NQR transitions were detected in Muscovite Mica at room temperature using double resonance by level crossing (DRLC) techniques. Three lines were observed with frequencies of 572.5, 1052.0, and 1624.5 kHz. These lines are assigned to the octahedrally coordinated site, $AlO_4(OH)_2$. The corresponding quadrupole coupling constant, e^2qQ/h, and asymmetry parameter, η, are 3554.8 kHz and 0.265, respectively. The remaining tetrahedrally coordinated sites, AlO_4, gave no discernible signal, perhaps due to the greater $^{27}Al-^{1}H$ distance.

Introduction

Aluminum-27, one of the most abundant isotopes in the Earth's crust, can be found commonly in rock-forming minerals where it plays a crucial role in the architecture of structural aluminosilicates. Although many techniques are available for structural studies of good crystalline material, there remains a need for well-developed probes of samples that lack long-range order. Magnetic resonance methods are well known to be applicable in such cases, and one of us earlier detailed the utility of ^{27}Al Nuclear Quadrupole Resonance (NQR) to structure and bonding studies, in particular when positional disorder may be present [1].

Aluminum-27 is 100% abundant, has spin $I = 5/2$ and an appreciable quadrupole moment. A database of quadrupole coupling constants, e^2qQ/h, obtained by single-crystal NMR studies, already exists and shows that values of e^2qQ/h fall in the low megahertz region, accessible by a variety or NQR techniques for polycrystalline samples. Representative examples are listed in Table 1. Inspection of this Table indicates that no immediately interpretable relation is evident between quadrupole coupling data and structural parameters like, for example, coordination number.

Naturally occurring mica has the formula $KAl_2(AlSi_3)O_{10}(OH,F)_2$ and exhibits disorder in the stacking of the silicate layers and in the distribution of the Aluminum atoms that interleave them. Therefore, mica can be an ideal sample for quadrupole resonance studies and further studies might reveal kinds and degree of disorder not obtainable

Table 1. Aluminum-27 quadrupole coupling data in some aluminosilicates obtained by single-crystal NMR. The quadrupole coupling constant, e^2qQ/h, and the dimensionless asymmetry parameter, η, are shown for each resolved site of coordination number N.

Mineral: formula	N	e^2qQ/h (MHz)	η	Reference
Albite: $NaAlSi_3O_8$	4	3.37		[5, 6]
	4	3.29	0.62	[7]
Andalusite: Al_2SiO_5	6	15.6	0.08	[8]
	5	5.9	0.7	
Anorthite: $CaAl_3Si_2O_8$	4	8.42	0.66	[9]
	4	2.66	0.66	
	4	7.25	0.76	
	4	6.81	0.65	
	4	6.30	0.88	
	4	5.44	0.42	
	4	4.90	0.75	
	4	4.32	0.53	
Corundum: α-Al_2O_3	6	2.39	0	[10]
Kyanite: Al_2SiO_5	6	10.04	0.27	[11]
	6	3.70	0.89	
	6	6.53	0.59	
	6	9.37	0.38	
Microcline: $KAlSi_3O_8$	4	3.22	0.21	[12]
Natrolite: $Na_2Al_2Si_3O_{10}$	4	1.66	0.50	[13]
Topaz: $Al_2SiO_4F_2$	6	1.67	0.38	[14]
	6	1.5918	0.704	[15]
	6	1.6506	0.501	[15]
Zoisite: $Ca_2AlSi_3O_{12}OH$	6	8.05	0.46	[16]
	6	18.50	0.16	

* Presented at the VIIIth International Symposium on Nuclear Quadrupole Resonance Spectroscopy, Darmstadt, July 22–26, 1985.

** Research supported by the US Department of Energy, and in part, by the National Institute of Health.

Reprint requests to Prof. R. A. Marino, Department of Physics and Astronomy, Hunter College of CUNY, New York, NY 10021, USA.

0340-4811 / 86 / 0100-0341 $ 01.30/0. – Please order a reprint rather than making your own copy.

by crystallographic means. In this work we present the NQR data for naturally occurring mica of excellent crystallinity obtained by the Double Resonance Level Crossing DRLC, technique [2, 3].

Experimental

The sample of Muscovite mica we used was obtained from World Scientific Company, and was claimed to have a low ratio of F^- ions to OH^- ions. The experiment was carried out at room temperature with a home-built DRLC spectrometer. The NQR search frequency was obtained from a remotely controlled PRD 7828 frequency synthesizer (Harris Corp.) amplified by an ENI 240L broadband power amplifier. An Arenberg pulsed rf oscillator model 6600 provides the 40 MHz transmitter pulses for proton NMR excitation. Proton free induction decay signals were then detected with a Matec 253 pre-amplifier and 625 broadband receiver, and captured with a Biomation transient recorder. The spectrometer is controlled and all timings are generated by an Imsai 8080 microcomputer with control software developed in-house. The steady magnetic field needed to polarize the protons is derived from a standard electromagnet which produces a stabilized magnetic field of about 1 Tesla.

Results

Table 2 summarizes our results for the room temperature NQR spectrum of Muscovite Mica.

Table 2. Aluminum-27 NQR data for Muscovite mica at room temperature.

Transition	Frequency kHz	e^2qQ/h kHz	η
1/2–3/2	572.5	3554.8	0.265
3/2–5/2	1052.0		
1/2–5/2	1624.5		

Since the highest of the three transitions observed is the sum of the lower two, we assumed that we detected all three possible transitions from a single site of spin $I = 5/2$. The values of the corresponding quadrupole coupling constant, e^2qQ/h, and asymmetry parameter, η, could then be computed from numerical tables, and are also shown in Table 2.

Crystallographic studies [4] have shown that there are three different aluminum sites in Muscovite Mica. One is octahedrally coordinated to four bridging oxygen atoms and to two hydroxyl groups, $AlO_4(OH)_2$. Both of the other two sites are tetrahedrally coordinated to four bridging oxygen atoms. The resulting AlO_4 groups play a structurally similar role to the SiO_4 tetrahedra in the architecture of this crystal. The single NQR site that we observed is then assigned to the octahedral site on the basis of its close proximity to hydroxyl protons. The argument rests on the fact that the sensitivity of the double resonance method we employed depends on the dipolar coupling with protons, which is considerably higher for the octahedral site. Because the foregoing argument is not conclusive, however, we consider the above assignment tentative at this time.

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