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^{23}Na ^{27}Al ^{9}Be ^{29}Si SOLID STATE NMR STUDY OF TUGTUPITE

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ABSTRACT

The solid state NMR techniques of magic-angle spinning (MAS), dynamic-angle spinning (DAS) and double rotation (DOR) are used to study the local atomic environments in tugtupite, $Na_8[Al_2Be_2Si_8O_{24}](Cl,S)_2$. The structure is found to be exceptionally well ordered, with only one Si, Al, Na and Be environment. The quadrupolar parameters C_Q (quadrupolar coupling constant) and η (asymmetry parameter) of ^{23}Na and ^{27}Al were obtained by a comparison of a computer simulation of the MAS central transition lineshape at two different fields with experimental results. These results were verified in two ways: firstly, from the comparison of the observed difference in chemical shift of the same peak at two different fields with that calculated from the simulated results of C_Q and η, and secondly, from the comparison of the measured and calculated difference in position of the two peaks within the first set of spinning sidebands, which are due to the central transition and $\pm 1/2 \rightleftharpoons \pm 3/2$ satellite transition.

Keywords: nuclear magnetic resonance, magic-angle spinning, double rotation, dynamic-angle spinning, tugtupite, quadrupolar parameters.

SOMMAIRE

Les techniques de résonance magnétique nucléaire adaptées à l'état solide, par exemple la rotation à l'angle magique, la rotation à l'angle dynamique et la rotation double, ont été appliquées à l'étude des agencements locaux d'atomes dans la tugtupite, $Na_8[Al_2Be_2Si_8O_{24}](Cl,S)_2$. La structure donne toutes les indications d'un degré d'ordre exceptionnel, avec un seul milieu pour chacun des quatre cations, Si, Al, Na et Be. Nous avons obtenu les paramètres quadrupolaires C_Q (constante de couplage quadrupolaire) et η (paramètre d'assymétrie) de ^{23}Na et ^{27}Al par simulation sur ordinateur du profil de la transition centrale dans la rotation à angle magique à deux champs magnétiques différents, et par comparaison avec les résultats expérimentaux. Nous avons vérifié ces résultats de deux façons, d'abord en comparant la différence observée dans le déplacement chimique d'un même pic à deux champs différents, en comparaison avec le déplacement calculé à partir des simulations utilisant C_Q et η, et ensuite en comparant la différence mesurée et prédite dans la position des deux pics à l'intérieur de la première paire des satellites dus à la rotation, qui sont attribuées à la transition centrale et à la transition des satellites $\pm 1/2 \rightleftharpoons \pm 3/2$.

(Traduit par la Rédaction)

Mots-clés: résonance magnétique nucléaire, rotation à l'angle magique, rotation double, rotation à l'angle dynamique, tugtupite, paramètres quadrupolaires.

INTRODUCTION

Nuclear magnetic resonance (NMR) can be used to study local atomic environment in minerals. Recently, there have been significant advances in high-resolution solid state NMR, including stable high-speed magic-angle spinning (MAS) (Engelhardt & Michel 1987, Müller *et al.* 1981, Skibsted *et al.* 1991), double rotation (DOR) (Wu *et al.* 1990a, b) and dynamic-angle spinning (DAS) (Mueller *et al.* 1990, 1991). Each of these new techniques provides complementary information.

For spin-½ nuclei, such as ^{13}C, ^{29}Si, ^{19}F, broadening due to dipole–dipole interactions and chemical shift anisotropy (CSA) can be averaged or modulated by spinning the sample around an axis at an angle of 54.7° to the magnetic field (MAS), resulting in spectra with narrow lines. For nuclei with nonintegral spins greater than ½, such as ^{23}Na, ^{27}Al, ^{9}Be, ^{7}Li and ^{17}O, line-broadening due to second-order quadrupolar interactions cannot be completely averaged by MAS because the spatial part of the second-order quadrupolar interaction anisotropy has a factor of a fourth-

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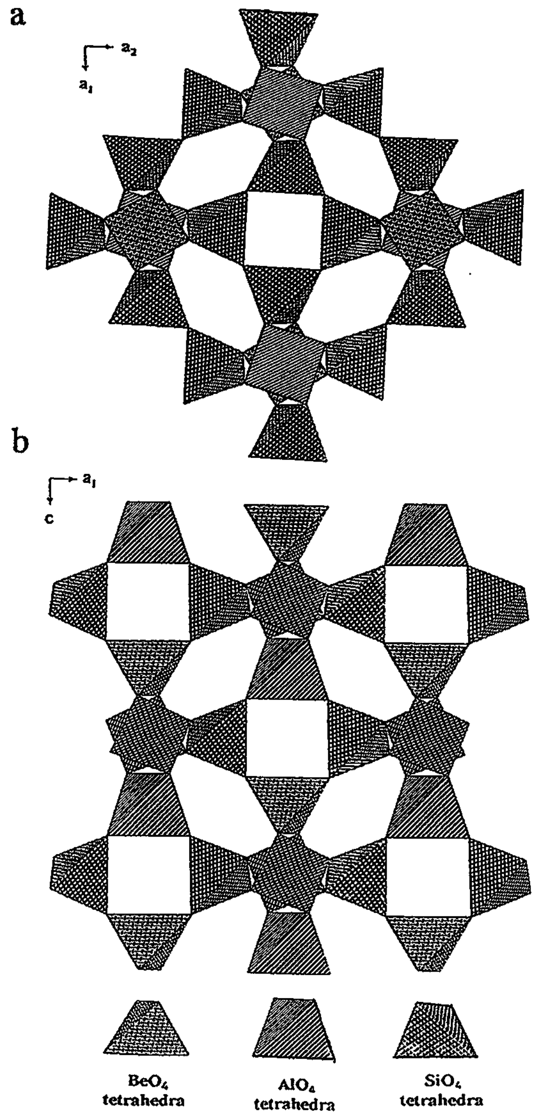

FIG. 1. The structure of tugtupite. (a) Projection along the *c* axis; (b) projection along the *a* axis.

order polynomial function, and the magic angle of 54.7° is not a root of this polynomial function. To average the second-order quadrupolar interaction anisotropies to isotropic values, the powdered sample has to be spun around another angle besides the magic angle. The double-angle techniques of DOR and DAS are solutions to the problem of having to spin the sample around two axes at the same time.

Tugtupite, $Na_8[Al_2Be_2Si_8O_{24}](Cl,S)_2$, is a well-ordered cubic tectosilicate mineral that crystallizes in space group $I\bar{4}$ (Danø 1966). Si, Be and Al, in tetrahedral coordination with four oxygen atoms, form the framework of the structure (Fig. 1). There is a four-membered ring containing two Si, one Be and one Al atoms normal to the *a* axis, a four-membered ring containing four Si atoms perpendicular to the *c* axis, and a six-membered ring containing four Si, one Al and one Be atoms at the corners. Na and Cl are inside the cages, and the Cl atoms are either at the corners or the center of the unit cell. Na is in five-fold coordination with one Cl and four O atoms (Hassan & Grundy 1991).

From X-ray-diffraction results, it is not clear if there is any disorder of Si, Al and Be within the tetrahedral site. Different NMR techniques were used to study ^9Be, ^{23}Na, ^{27}Al and ^{29}Si nuclei in tugtupite in order to obtain the values of isotropic chemical shifts, C_Q and η, and to evaluate the degree of atomic order in the structure.

EXPERIMENTAL

Tugtupite from Ilímaussaq, Narssaq Kommune, South Greenland (Royal Ontario Museum sample number M32790) was finely ground prior to packing into the NMR rotors. It is from the same locality as the sample analyzed by Danø (1966). The NMR spectra were acquired using a Bruker AMX–500 console with an 8.4 T wide-bore magnet and an 11.7 T narrow-bore magnet.

MAS spectra were acquired at both fields using a high-speed MAS probe with 5-mm diameter rotors from Doty Scientific Ltd., spinning at an angle of 54.7° to the magnetic field. When acquiring spectra from nuclei with the spin quantum number $I > ½$, a long radio-frequency pulse will excite both the central and non-central (satellite) transitions. It has been shown (Samoson & Lippmaa 1983) that pulses shorter than $1/(2I+1)$ of the 90° pulse length will excite less than 5% of the satellite transitions. Only short pulses that satisfy this condition are used in these MAS experiments. The experimental parameters are listed in Table 1. MAS spectra for ^{23}Na were obtained at –35,

TABLE 1. MAS NMR EXPERIMENTAL PARAMETERS

	P_1 (μs)	D_1 (s)	Spectral Width (Hz)	Number of Scans	LB (Hz)	Spin Speed (kHz)	Larmor Frequency (MHz)
^{23}Na	0.4	2.0	20000	500	50	8.7	95.22
^{23}Na	0.4	1.0	125000	500	50	8.7	95.22
^{23}Na	0.4	2.0	20000	404	20	9.7	132.30
^{23}Na	0.4	1.0	125000	400	20	9.7	132.30
^{23}Na*	0.6	1.0	20000	300	50	6.0	132.30
^{27}Al	0.4	0.5	20000	600	10	8.7	93.80
^{27}Al	1.0	0.5	125000	904	20	8.7	93.80
^{27}Al	0.4	0.5	20000	547	10	9.7	130.32
^{27}Al	1.0	0.5	125000	800	10	9.7	130.32
^9Be	0.2	0.1	31250	5294	0	9.0	70.28
^{29}Si	2.0	30.0	10000	1235	30	7.1	99.35

D_1: relaxation delay between pulses; P_1: pulse length.
*: low-temperature experiments.

–52, –80 and –110°C at 132.3 MHz. The spectra were recorded with reference to $^{23}Na^{+}$ in a 0.1 M aqueous solution of NaCl, $^{27}Al(H_2O)_6$ in an aqueous solution of $AlCl_3$, $^{9}Be^{2+}$ in an aqueous solution of $Be(NO_3)_2$ solution, and ^{29}Si in tetramethylsilane (TMS).

In the DOR experiments, a 4-mm-diameter inner rotor spins at an angle of 30.6° to the magnetic field inside an outer rotor spinning at the magic angle. The ratio of the rates of spinning of the inner to outer rotors is approximately 5:1. The low rate of spinning, of less than 1200 Hz for the outer rotor, causes the spectra to be complicated by numerous spinning sidebands owing to the remaining quadrupolar and dipole–dipole interactions, and to chemical shift anisotropies. To simplify the spectra and to increase the signal-to-noise ratio, a synchronization method, described by Wu (Wu *et al.* 1990b, Xu & Sherriff 1993), was used to eliminate odd-numbered sidebands. Spectra recorded at different rates of spinning of the outer rotor can be used to distinguish the central bands from the spinning sidebands.

Careful packing of the sample in the DOR rotor and correct adjustment of the position of the inner rotor with respect to the outer rotor were needed to start the rotors spinning. It could be difficult to tell whether or not the inner rotor was spinning, especially at high speeds, and to maintain the speed for long owing to the critical balance of the inner and outer driving air pressure at spinning speed. Therefore, an MAS spectrum was obtained first to select the best parameters for acquisition during the DOR experiment and to make the duration of the DOR experiment as short as possible.

^{23}Na and ^{27}Al DOR spectra were acquired at a magnetic field of 8.4 T using a Bruker DOR probe, with an outer rotor spinning speed of 800 Hz. The delay between pulses was 2 s; short pulse-lengths of 2 μs were used for both ^{23}Na and ^{27}Al.

In a pure-phase absorption DAS experiment (Mueller *et al.* 1991), the rotor flips among three angles to allow the acquisition of the free induction decay (FID) to be at the magic angle. The time τ is incrementally increased between subsequent experiments. The Fourier Transformation of the acquired MAS FID gives the F_2 dimension of the two-dimensional plot, which contains both the isotropic and anisotropic second-order quadrupolar interactions. Fourier Transformation of equivalent points from spectra with different values of τ gives the F_1 dimension, which contains only isotropic interactions and can give separate peaks due to corresponding sites (Mueller *et al.* 1990). The projection of each of these peaks onto the F_2 dimension will result in normal MAS spectra, which can be used to obtain the quadrupolar interaction parameters by correlating the shape of each peak with the computer-simulated spectrum (Mueller *et al.* 1990, Zheng *et al.* 1991).

The DAS experiments were run at a magnetic field of 8.4 T using a DAS probe supplied by Doty Scientific Ltd. The sample was packed in a 5-mm rotor spun at 6.9 kHz around an axis capable of being flipped from 23° to 85° with respect to the magnetic field. In this experiment, the rotor was spun at 37.4° for time τ, flipped to 79.2° for another period τ then flipped to 54.7° while an FID was acquired. A 90° pulse was applied just before each rotor-flip in order to rotate the transverse magnetization to the *Z* axis to store it. Immediately after the flip, a 90° pulse with an opposite phase was used to recover the magnetization (Mueller *et al.* 1990). After the acquisition of the FID, the spinning axis was returned to 37.4°. Sixteen FIDs were recorded for each experiment, with 256 points being collected in the F_1 dimension and 512 in the F_2 dimension. The pulse lengths of 90°, measured at the three rotor-flip angles of 37.4°, 54.7° and 79.2°, were 3.8 μs, 2.1 μs and 2.0 μs, respectively. The time delay for switching between two angles was 50 ms. The duration of τ was increased by 2 μs between successive experiments. The relaxation delay between pulses was 3 s. A narrow spectral width of 20 000 Hz was chosen to just cover the frequency range containing the peaks in order to obtain sufficient resolution in the F_1 dimension and reduce the duration of the experiment.

The central transition line-shapes for nonintegral quadrupolar nuclei were simulated using a computer program modified after "SECQUAD" written by B. Power and R. E. Wasylishen (Power *et al.* 1990). In this simulation, spinning speeds were considered to be infinitely large, so that spinning sidebands did not need to be considered. The line-shapes were assumed to be only due to second-order quadrupolar interactions, as for noninteger quadrupolar nuclei, the central transitions are not affected by first-order quadrupolar interactions.

RESULTS AND DISCUSSION

^{29}Si

The ^{29}Si MAS spectrum has one narrow peak at –95.1 ppm, with a linewidth of 70 Hz (30 Hz line broadening) (Table 2, Fig. 2). This shows that ^{29}Si is

TABLE 2. NMR RESULTS, TUGTUPITE

	δ_{obs}* (ppm)	linewidth (Hz)		C_Q (MHz)	η	δ_{iso} (ppm)
^{29}Si MAS, 11.7 T	-95.1	70	lb=30			-95.1
^{9}Be MAS, 11.7 T	-2.1	22	lb=0			-2.1
^{23}Na MAS, 8.4 T	2.0	830	lb=50	1.27	0.48	6.8
^{23}Na MAS, 11.7 T	4.4	590	lb=20	1.27	0.48	6.9
^{23}Na DAS, 8.4 T	2.1	240	lb=20	1.27	0.48	6.9
^{23}Na DOR, 8.4 T	1.8	68	lb=10	1.27	0.48	6.6
^{27}Al MAS, 8.4 T	62.3	180	lb=10	1.70	0.19	64.2
^{27}Al MAS, 11.7 T	63.3	140	lb=20	1.70	0.19	64.2
^{27}Al DOR, 8.4 T	62.5	43	lb=10	1.70	0.19	64.4

*: δ_{obs}: the observed frequencies of the center of gravity of the central bands.

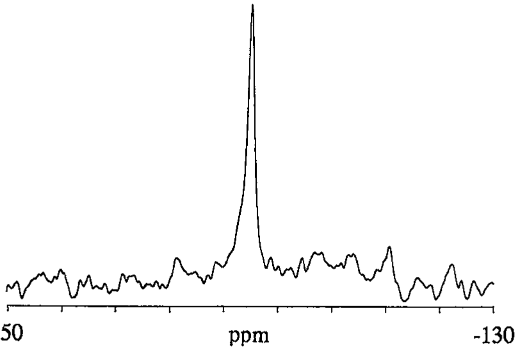

FIG. 2. ^{29}Si MAS spectrum of tugtupite at 11.7 T spinning at 7.1 kHz.

in a single site, which is tetrahedrally coordinated with one Al, one Be and two Si atoms. There is no Si–Al disorder among the tetrahedral sites (Fig. 1). Using the crystal-structure data of Hassan & Grundy (1991) and the empirical relationship derived by Sherriff *et al.* (1991), the peak position was calculated to be at –94.5 ppm.

^{9}*Be*

The MAS NMR spectrum gave one extremely narrow ^{9}Be peak at –2.1 ppm, with 22 Hz width at half peak-maximum (0 Hz line broadening) (Table 2, Fig. 3). ^{9}Be is therefore in a single symmetrical tetrahedral environment, with a small field-gradient and therefore quadrupolar interactions. The spinning sidebands indicate that C_Q is of the order of 9 kHz. The structure refinement from single-crystal X-ray-diffraction data shows that the site is very symmetrical, with the four Be–O bond lengths equal to 1.631(2) Å, four O–Be–O bond angles of 107.7(1)°, and two of 113.5(1)° (Hassan & Grundy 1991).

^{23}*Na*

There is one peak with two maxima in the ^{23}Na MAS spectra, at 95.2 and 132.3 MHz. DOR NMR was used to determine whether the two maxima are due to two Na peaks or to one peak with a quadrupolar shape. The DOR spectrum has a single peak at 1.8 ppm, with a peak width at half height of 68 Hz (10 Hz line broadening) (Table 2, Fig. 4), showing that there is one ^{23}Na environment in tugtupite.

For quadrupolar nuclei in a single site, the second moment of the central transition in MAS spectra will be inversely proportional to the strength of the magnetic field if the peak width is caused by the second-order quadrupolar interactions only (Freude *et al.* 1985). Therefore, by comparing the widths of MAS central transitions at different strengths of magnetic field, it is possible to determine if the line-shapes are caused only by second-order quadrupolar interaction anisotropy. For ^{23}Na, the ratio of the linewidths for the field strengths of 11.7 T and 8.4 T is 570:780 or 0.73 (Table 2). As this result is close to the ratio of the strengths of the magnetic field, 0.72, the ^{23}Na MAS line-shapes are considered to be caused solely by the second-order quadrupolar interactions.

The quadrupolar parameters, C_Q and η, were found by comparison of the MAS experimental results with computer simulations of the line-shape of the central transition. The quadrupolar parameters for C_Q, 1.27 MHz, and η, 0.48, were required to produce simulations with the same line-shapes as the experimental spectra recorded at both fields (Fig. 5).

To verify these parameters, the difference between the peak positions at the two fields was calculated in the following manner and compared to experimental results. For a quadrupolar nucleus, the center of gravity of a single MAS peak (δ_{obs}) is a resultant of the quadrupolar shift (δ_Q) and isotropic chemical shift (δ_{iso}).

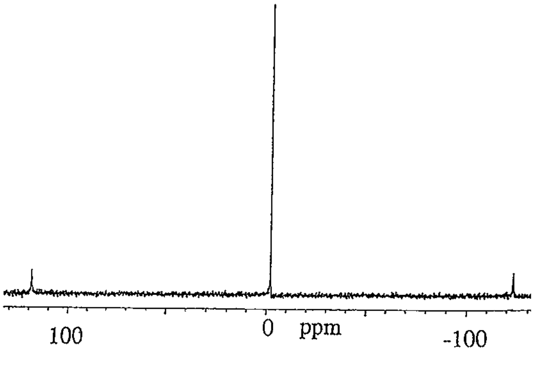

FIG. 3. ^{9}Be MAS spectrum of tugtupite at 11.7 T spinning at 9.0 kHz.

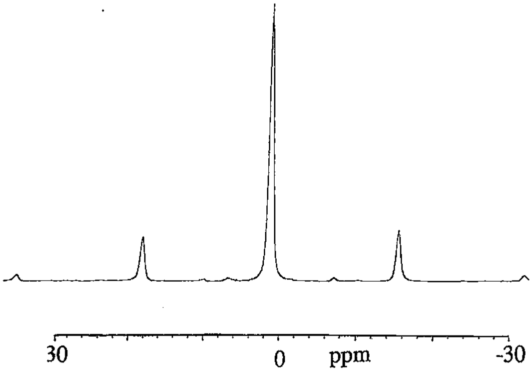

FIG. 4. ^{23}Na DOR spectrum of tugtupite at 8.4 T with the outer rotor spinning at 800 Hz.

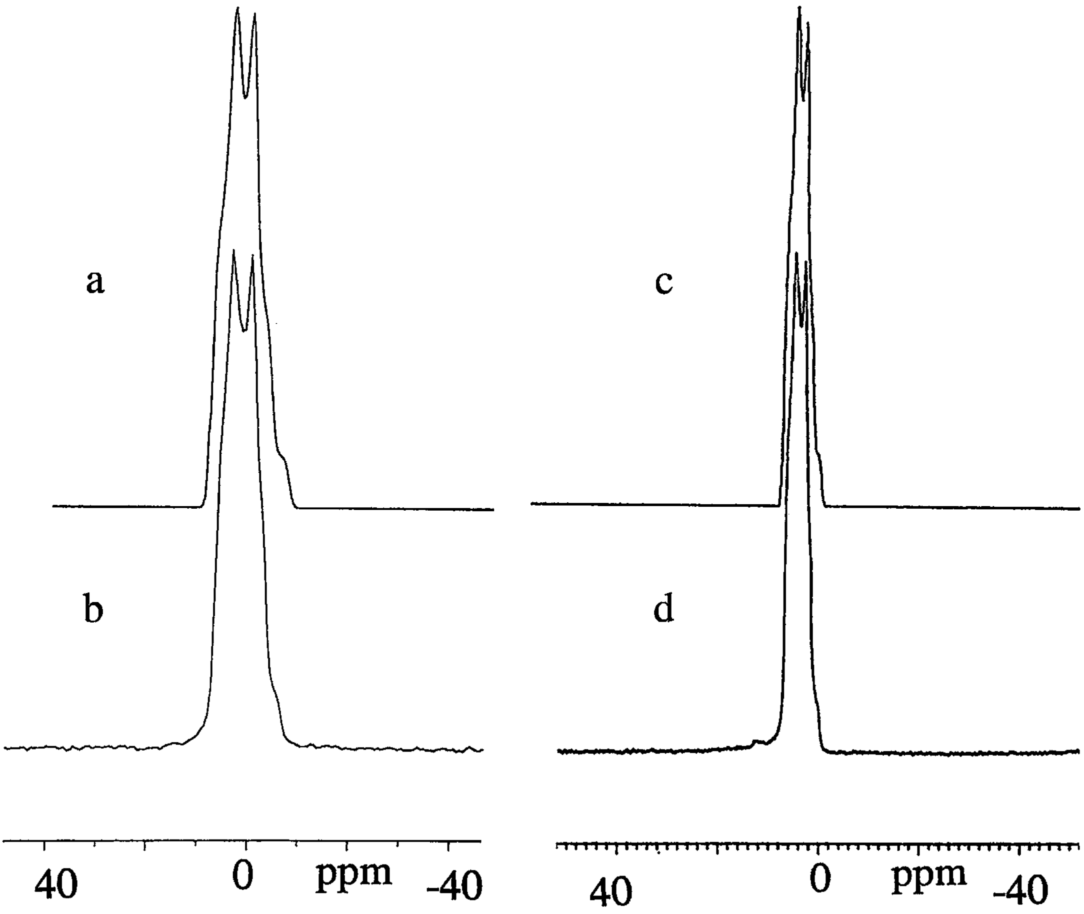

FIG. 5. ^{23}Na MAS spectra of tugtupite. (a) Simulated MAS spectrum at 8.4 T, (b) observed MAS spectrum at 8.4 T, (c) simulated MAS spectrum at 11.7 T, and (d) observed MAS spectrum at 11.7 T.

$$\delta_{obs} = \delta_Q + \delta_{iso} \tag{1}$$

For central transitions of a noninteger quadrupolar nucleus with spin I, the first-order quadrupolar shift is zero, and the second-order quadrupolar shift is given by:

$$\delta_{Q1,2} = -3{\cdot}10^6{\cdot}C^2{}_Q[I(I+1)-\tfrac{3}{4}](1 + \eta\tfrac{2}{3})/[40I^2(2I-1)^2\upsilon^2{}_{1,2}] \tag{2}$$

where $\upsilon_{1,2}$ is the Larmor frequency (MHz) at two different values of the magnetic field.

If one defines:

$$\Delta\delta_Q = \delta_{Q1} - \delta_{Q2} \tag{3}$$

$$\Delta\delta_{iso} = \delta_{iso1} - \delta_{iso2} \tag{4}$$

$$\Delta\delta_{obs} = \delta_{obs1} - \delta_{obs2} \tag{5}$$

Then

$$\Delta\delta_{obs} = \Delta\delta_{iso} + \Delta\delta_Q \tag{6}$$

As the isotropic chemical shifts are independent of the strength of the magnetic field, they will be the same in both fields, and $\Delta\delta_{iso}$ will be zero. Therefore,

$$\Delta\delta_{obs} = \Delta\delta_Q \tag{7}$$

If υ_1 is greater than υ_2, then from equation (2) and (3):

$$\Delta\delta_Q = -3[I(I+1)-\tfrac{3}{4}](1 + \eta\tfrac{2}{3})C^2{}_Q{\cdot}10^6(1/\upsilon_1^2-1/\upsilon_2^2)/[40I^2(2I-1)^2] \tag{8}$$

For ^{23}Na at the two field strengths of 8.4 T and 11.7 T, equation (8) becomes

$$\Delta\delta_Q = 1.329C^2{}_Q{\cdot}(1 + \eta\tfrac{2}{3})\text{ ppm} \tag{9}$$

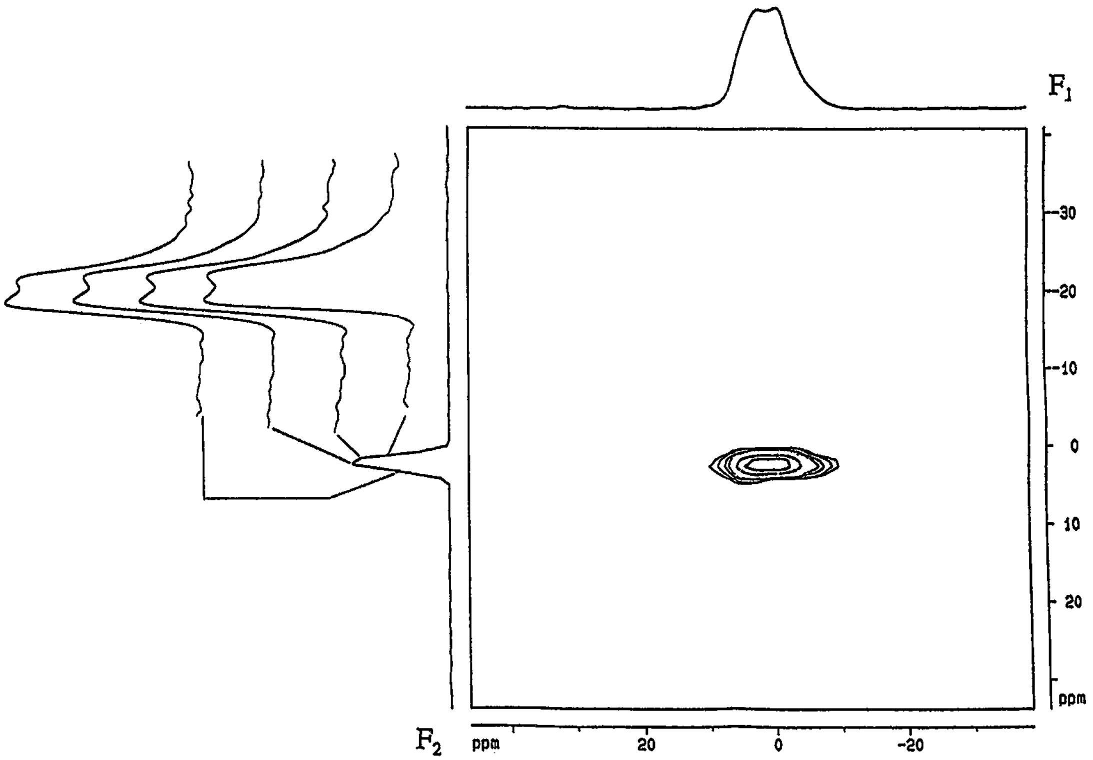

FIG. 6. Two-dimensional plot of ^{23}Na DAS spectrum of tugtupite at 8.4 T, with one-dimensional projections along the F_1 and F_2 axes, and projections of the four points of the F_1 peak onto the F_2 dimension.

By substituting the values of 1.27 for C_Q and of 0.48 for η, from the simulations of the MAS spectra, into expression (9), $\Delta\delta_Q$ was calculated to be 2.3 ppm. This compares favorably to the observed value of 2.4 ± 0.1 ppm.

The F_1 projection of the DAS spectrum showed only one ^{23}Na peak, with a linewidth of 240 Hz (20 Hz line broadening) (Table 2, Fig. 6). As the spectral width was 20 000 Hz and the number of points on F_1 was 256, the difference in frequency between two adjacent points was 78 Hz. There were only four points for the F_1 peak above the half-intensity of the peak. The projection of these four points on F_2 resulted in similar MAS spectra with the same line-shapes, but different intensities (Fig. 6). The shape of the peaks was found to be similar to that obtained in the MAS experiment (Fig. 5), though the resolution was lower. The computer simulation of these peaks gave the same values of C_Q and η as the MAS experiments. This finding shows that there is only one ^{23}Na site and no distribution of ^{23}Na chemical shift in tugtupite at room temperature.

^{23}Na MAS NMR spectra obtained at –35, –52, –80 and –110°C have exactly the same peak positions, line-shapes and linewidths as those measured at room temperature (Fig. 7). Therefore, there is no phase change affecting the Na site between +25°C and –110°C.

^{27}*Al*

The width of the ^{27}Al MAS peak at 130.3 MHz was found to be 140 Hz, which is relatively narrow for ^{27}Al in solids, indicating that the tetrahedrally coordinated Al site is very symmetrical, with a small gradient in electric field and, therefore, small ^{27}Al quadrupolar interactions. The structural refinement from single-crystal data (Hassan & Grundy 1991) shows this high symmetry, with four Al–O bond lengths of 1.748(2) Å, four O–Al–O angles of 109.0(1)° and two of 110.5(1)°.

One peak has two maxima in the ^{27}Al MAS spectra recorded at both strengths of magnetic field (Table 2, Fig. 8). ^{27}Al DOR was used to determine whether this is due to two Al peaks or to one peak with a quadrupolar line-shape. The DOR spectrum has one symmet-

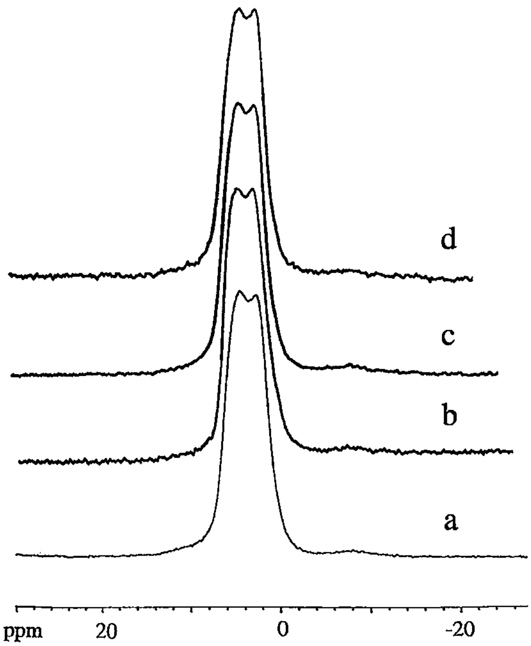

FIG. 7. ^{23}Na low-temperature MAS spectra of tugtupite at: (a) –35°C, (b) –52°C, (c) –80°C, and (d) –110°C.

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rical peak with a width at half maximum of only 43 Hz (line broadening of 10 Hz) (Table 2, Fig. 9), indicating that there is but one ^{27}Al environment in tugtupite.

The ratio of the widths of the ^{27}Al MAS peaks at 11.7 T and 8.4 T is 120:170, or 0.73 (Table 2), which is close to the ratio of the strengths of the magnetic fields, 0.72. This indicates that the linewidth is due mainly to the second-order quadrupolar interaction.

The quadrupolar parameters of 1.70 MHz for C_Q and of 0.19 for η were used to simulate the MAS spectra at the two field strengths (Fig. 8). These values

FIG. 8. ^{27}Al MAS spectra of tugtupite and simulations. (a) Simulation of MAS at 8.4 T, (b) spectrum at 8.4 T, (c) simulation of MAS at 11.7 T, and (d) spectrum at 11.7 T.

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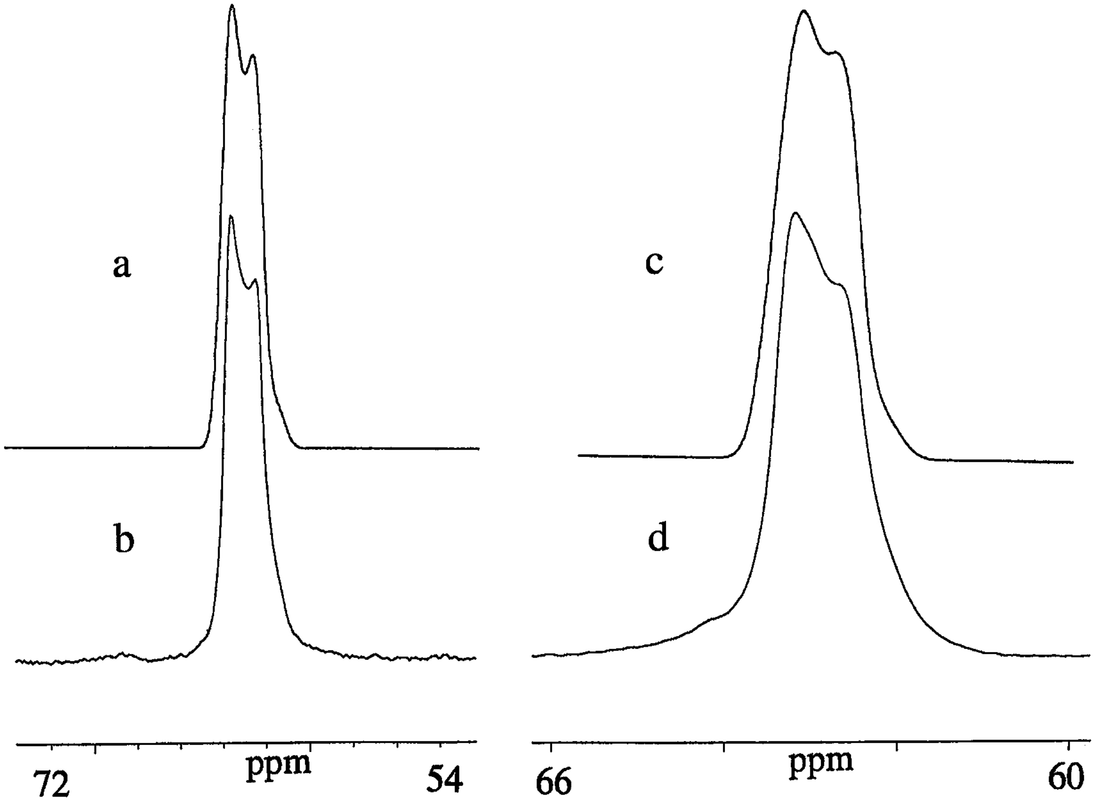

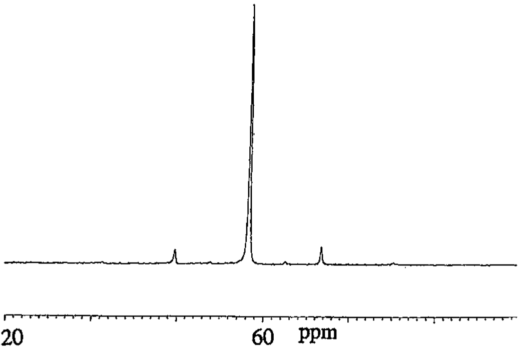

FIG. 9. ^{27}Al DOR spectrum of tugtupite at 8.43 T with outer rotor spinning at 800 Hz.

were verified by a comparison of the peak positions at the two fields. From equation (8) for ^{27}Al with a strength of the magnetic field of 11.7 T and 8.4 T:

$$\Delta\delta_Q = 0.328 \cdot C^2{}_Q \cdot (1 + \eta^{2/3}) \text{ ppm} \qquad (10)$$

Using values for C_Q of 1.70 MHz and for η of 0.19, $\Delta\delta_Q$ is found to be equal to 0.96 ppm. This is slightly higher than the measured difference between MAS chemical shifts obtained at the two magnetic field strengths of 0.8 ppm.

For nuclei with spin 5/2, such as ^{27}Al, the values of C_Q and η obtained from a simulation of the MAS spectra can be verified in a second way. The first pair of spinning sidebands can each be resolved into two peaks, due to the sidebands of the central transition and of the inner satellite $\pm 1/2 \rightleftharpoons \pm 3/2$ transitions. For nuclei with a spin of 5/2, these satellite transitions have small second moments and sufficient intensity to be observed. For nuclei with spin 3/2, such as ^{23}Na, the intensity of this transition is too small for observation of the sidebands (Samoson 1985). The difference in peak position between $\pm 1/2 \rightleftharpoons \pm 3/2$ and $+1/2 \rightleftharpoons -1/2$ transitions can be measured for the first pair of spinning sidebands. The second-order quadrupolar shift of non-central transitions can be expressed as:

$$\delta_Q = -3 \cdot 10^6 \cdot C^2{}_Q[I(I+1) - 9m(m-1) - 3] \\ (1+\eta^{2/3})/[40 \cdot \upsilon_0^2 I^2 (2I-1)^2] \qquad (11)$$

For a nuclear spin I of 5/2, the value of the difference in position between the $\pm 1/2 \rightleftharpoons \pm 3/2$ and the central $-1/2 \rightleftharpoons +1/2$ transition is:

$$\Delta\delta_Q = 27 \cdot 10^3 \cdot C_Q^2 (1 + \eta^{2/3})/(4 \cdot \upsilon_0^2) \qquad (12)$$

Substitution of the value of 1.70 MHz for C_Q and of 0.19 for η obtained from the simulation of MAS lineshapes gives:

$\Delta\delta_Q = 2.24$ ppm at 8.4 T magnetic field
$\Delta\delta_Q = 1.16$ ppm at 11.7 T magnetic field.

The measured differences were found to be

$\Delta\delta_{obs} = 2.5 \pm 0.2$ ppm at 8.4 T magnetic field
$\Delta\delta_{obs} = 1.2 \pm 0.2$ ppm at 11.7 T magnetic field.

COMPARISON OF MAS, DAS AND DOR TECHNIQUES TO OBTAIN PARAMETERS FROM QUADRUPOLAR NUCLEI OF MINERALS

MAS can efficiently average the broadening effects due to dipole–dipole interactions and chemical shift anisotropy, but not those from second-order quadrupolar interactions. As second-order quadrupolar interactions are inversely proportional to the strength of the magnetic field, the parameters C_Q and η can be calculated for simple spectra from the computer simulation of MAS spectra obtained at two strengths of the magnetic field. The isotropic chemical shift can be obtained by calculating the quadrupolar shift and subtracting that from the observed shift.

The length of time (40 ms) required for a flip of the rotor axis in DAS experiments confines its application to noninteger quadrupolar nuclei with relatively long T_1 relaxation times, such as ^{17}O, ^{23}Na and ^{87}Rb. DOR can be used for nuclei with much more rapid relaxation, as there is less limitation on the minimum time required for the acquisition of the free induction decay.

For DOR experiments, the outer rotor, which is at the magic angle, spins at only 1 kHz. This is not fast enough to average completely anisotropy in the chemical shift and dipole–dipole interactions greater than 1 kHz. In DAS experiments, the sample can spin at 14 kHz; as the acquisition is at the magic angle, this technique can be more efficient than DOR at averaging chemical shift anisotropy. The second dimension provided by the DAS experiment can provide site-by-site analysis of δ_{iso}, C_Q and η parameters in multisite systems that give overlapping peaks.

DOR is the most difficult experiment to perform technically, especially at high-speed spinning of the outer rotor, owing to the critical balance of the inner and outer rotor. In DOR experiments, short pulse-lengths can be used to excite only the center bands, which reduces the delay required for relaxation of nuclei between pulses, enhances the sensitivity of detection (Shaw 1976), and shortens the duration of the experiment. DAS experiments can take up to 14 hours in comparison to one hour for DOR experiments.

CONCLUSION

Si is in a single tetrahedrally coordinated site in tugtupite, and there is no Si–Al disorder. Be is in a single extremely symmetrical environment that has no measurable gradient in electric field. There is only one site for both ^{23}Na and ^{27}Al, with no distribution in ^{23}Na chemical shift. For ^{23}Na, δ_{iso}, C_Q and η were found to be 6.9 ppm, 1.27 MHz and 0.48, respectively. For ^{27}Al in a symmetrical tetrahedrally coordinated site, δ_{iso} is 64.2 ppm, C_Q is 1.70 MHz, and η is 0.19. These results were verified by comparison of the calculated and observed differences in chemical shift at two strengths of the magnetic field. There is no phase change involving Na between 23° and –110°C.

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