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Oxygen-17 NMR in solids by dynamic-angle spinning and double rotation

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It is widely lamented that despite its unqualified success with spin-1/2 nuclei such as ^{13}C , ^{29}Si and ^{31}P , the popular NMR technique of magic-angle spinning (MAS) has experienced a somewhat restricted applicability among quadrupolar nuclei such as ^{17}O , ^{23}Na and ^{27}Al (refs 1–3). The resolution in the central ($1/2 \leftrightarrow -1/2$) transition of these non-integer quadrupolar spins under MAS is thought to be limited primarily by second-order quadrupolar broadening. Such effects of second-order spatial anisotropy cannot be eliminated by rotation about a fixed axis or by multiple-pulse techniques^{4,5}. More general mechanisms of sample reorientation (refs 6–8 and A. Samoson and A. Pines, manuscript in preparation) can, however, make high-resolution NMR of quadrupolar nuclei feasible. MAS is implemented by spinning a sample about a single axis so that second-rank spherical harmonics (which give rise to first-order broadening through anisotropy of electrical and magnetic interactions) are averaged away. But dynamic-angle-spinning (DAS) and double-rotation (DOR) NMR involve spinning around two axes, averaging away both the second- and fourth-rank spherical harmonics, which are responsible for second-order broadening. Here we present the application of these new techniques to ^{17}O in two minerals, cristobalite (SiO_2) and diopside ($\text{CaMgSi}_2\text{O}_6$). This work goes beyond previous results on ^{23}Na (ref. 8) by showing the first experimental results using DAS and by demonstrating the application of DOR to the resolution of distinct oxygen sites in an important class of oxide materials.

Both cristobalite and diopside have been studied by ^{17}O NMR using conventional sample-spinning techniques (ref. 9 and E.

Oldfield and R. J. Kirkpatrick, manuscript in preparation). Cristobalite is known to have a single crystallographically distinct oxygen site, with the oxygens arranged tetrahedrally about each silicon atom¹⁰. Crystalline diopside, shown in Fig. 1, contains three distinct oxygen sites¹¹ which give rise to overlapping MAS powder patterns even for high NMR magnetic fields (~ 10 tesla). E. Oldfield (personal communication) has pointed out that, under conditions of MAS, magnetic fields in excess of 25 tesla might be required to clearly resolve resonances from the three oxygen sites, as illustrated in Fig. 2.

In dynamic-angle spinning, the spinning axis is flipped from an angle θ_1 to an angle θ_2 after a given length of time. Figure 3 demonstrates the application of DAS to a sample of cristobalite enriched to 37% in ^{17}O . The experiment was performed at 54.25 MHz, allowing evolution for a time $t_1/2$ while the sample spun at 3,040 Hz around an axis inclined at $\theta_1 = 37.4^\circ$ and a further time $t_1/2 + t_2$ after the spinning axis had been flipped to

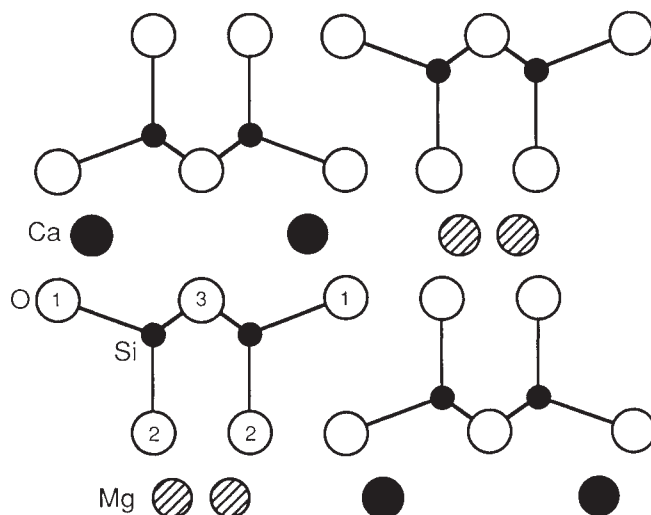


FIG. 1 Structure of diopside, $\text{CaMgSi}_2\text{O}_6$, viewed as a projection along the tetrahedral chains. Oxygen is represented by open circles with the three distinct sites labelled.

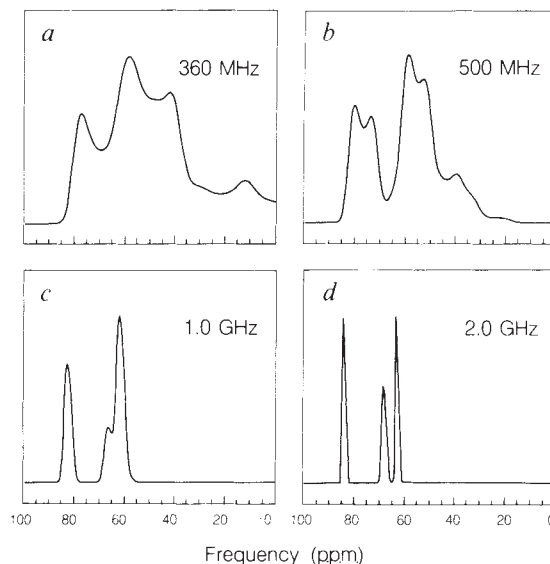


FIG. 2 Simulations of ^{17}O magic-angle-spinning spectra for diopside at magnetic fields (8.4–47 tesla) corresponding to proton NMR frequencies of 360 to 2,000 MHz (E. Oldfield, personal communication).

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an angle of $\theta_2 = 79.2^\circ$ (ref. 6). During the axis flip (~ 35 ms), magnetization is stored along the magnetic field^{12,13}. Phase-cycling followed by Fourier transformation yields a two-dimensional plot with the ω_1 frequency axis corresponding to a DAS spectrum devoid of second-order quadrupolar broadening. A further DAS experiment with the sample spinning at 2,460 Hz identifies a single centre-band of linewidth ~ 200 Hz, two orders of magnitude narrower than the central transition of ^{17}O in a static sample of cristobalite.

In the double-rotation experiment the sample is spun around two axes inclined at angles corresponding to zeros of the second and fourth Legendre polynomials, $\theta^{(2)} = 54.7^\circ$ and $\theta^{(4)} = 30.6^\circ$ respectively. Rapid sample rotation about these 'magic angles' results in removal of first-order ($\theta^{(2)}$) and second-order ($\theta^{(4)}$) broadening. For a sample of diopside enriched to 20% in ^{17}O , the MAS spectrum in Fig. 4a collapses under DOR, using a new Berkeley-Tallinn (BETA) double rotor (Y. Wu, A. Samoson and A. Pines, manuscript in preparation), at an excitation frequency of 54.25 MHz to three resolved peaks of linewidth ~ 100 Hz (Fig. 4b, c). The ^{17}O peaks in Fig. 4b, c are easily assigned to the three sites of diopside shown in Fig. 1.

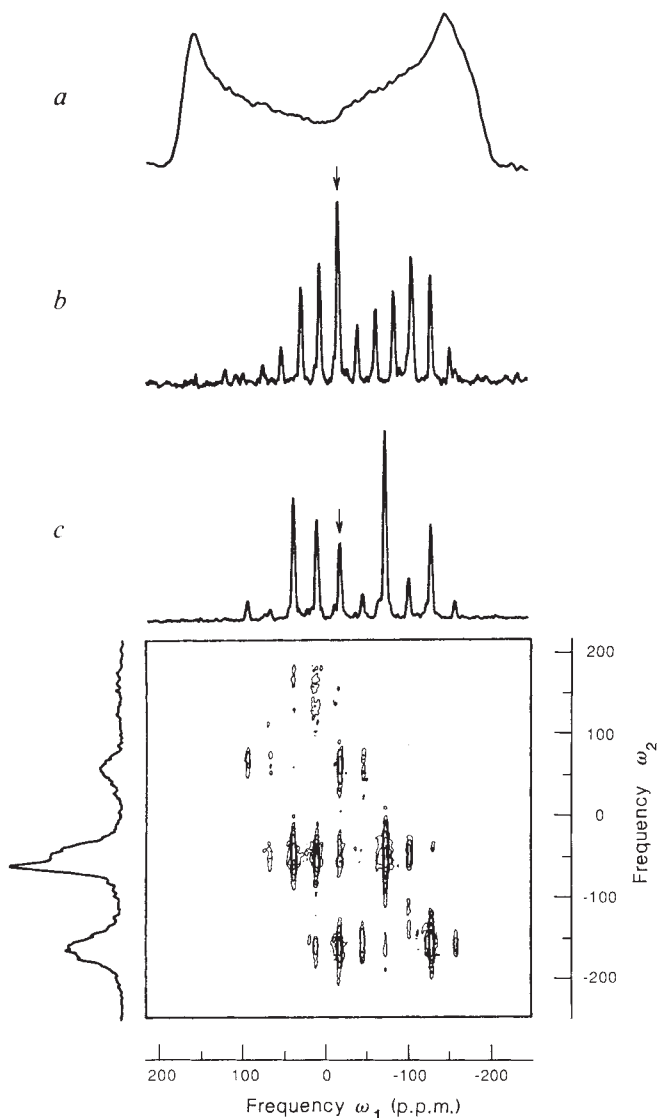


FIG. 3 NMR spectra of ^{17}O in cristobalite, SiO_2 , with a static sample (a), and under conditions of dynamic-angle spinning (DAS) at 2,460 Hz (b) and 3,040 Hz (c), showing a single centre-band peak of linewidth ~ 200 Hz. The vertical frequency axis (ω_2) in the two-dimensional spectrum corresponds to the sample spinning at an angle of $\theta_2 = 79.2^\circ$. Isotropic-shift scale referenced to H_2^{17}O .

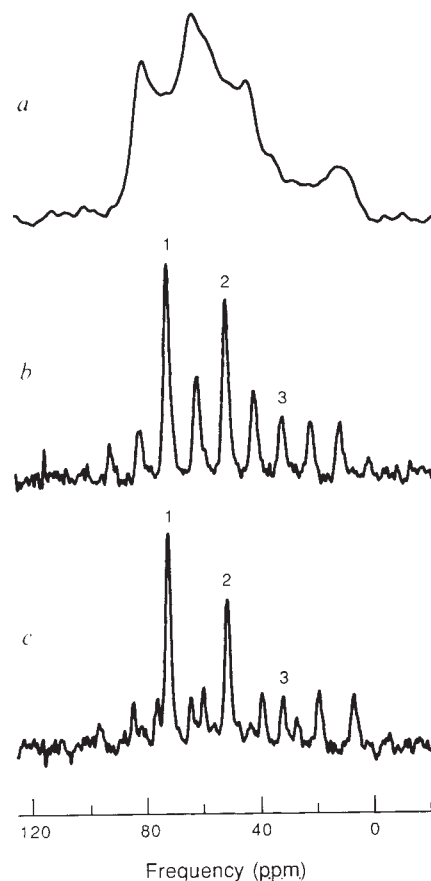


FIG. 4 NMR spectra of ^{17}O in a sample of diopside, $\text{CaMgSi}_2\text{O}_6$, under conditions of magic-angle spinning (MAS) (a), and in response to double rotation (DOR) with the outer rotor spinning at 540 Hz (b) and 680 Hz (c). The isotropic centre-band peaks correspond to the numbered oxygen sites in Fig. 1. Isotropic-shift scale referenced to H_2^{17}O .

Thus DAS and DOR do indeed seem to provide much enhanced resolution of isotropic chemical and second-order shifts for quadrupolar nuclei such as ^{17}O . We anticipate that, together with zero-field and SQUID magnetic resonance^{14,15}, these NMR techniques will contribute to the understanding of microstructural oxygen environments in solids and should constitute invaluable tools in the study of oxide materials in, for example, mineralogy, catalysis and high-temperature superconductivity. □

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