# $^{47,49}$Ti NMR in Metals, Inorganics, and Gels

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Some recent progress in solid state $^{47,49}$Ti NMR is described and reviewed. The metallic-state work described covers metals such as hcp titanium, $TiB_2$, a number of intermetallics such as $TiAl_2$ and $TiAl_3$. The inorganic work covers the various titanium oxide based materials including the $TiO_2$ polymorphs, anatase, rutile and brookite. The gel work covers the evolution of crystalline titania from gels formed by hydrolysis of titanium isopropoxide. Some complementary data from $^{17}$O and $^{13}$ C NMR and powder X-ray diffraction is also included.

*Key words:* Titanium; NMR; Metals; Oxides; Gels.

## Introduction

Nuclear resonance investigations of Ti compounds using the nuclei $^{47,49}$Ti present experimental difficulties due to (i) two isotopes with different nuclear spin and low abundance ($^{47}$Ti, $I$ = 5/2, 7.3%; $^{49}$Ti, $I$ = 7/2, 5.5), (ii) moderately large quadrupole interaction ($C_q \cong e^qQ/h \sim 10$ MHz), accompanied by linewidths that exceed the bandwidth of the probe or the pulses used for excitation and detection, and (iii) low, almost identical magnetic moments: The gyromagnetic ratios are such that at a field of 9.4 T the frequencies of the two isotopes differ by 6 kHz, so that with a ratio of quadrupole moments of $^{49}Q/^{47}Q$ = 0.819, the spectrum from the central (1/2,–1/2) transition of $^{49}$Ti will be nested within that of the $^{47}$Ti.

Early $^{47,49}$Ti NMR investigations of non-cubic Ti compounds were a low temperature study of titanium metal [1] and single crystal rotation studies of rutile ($TiO_2$) [2] and $BaTiO_3$ [3]. Later MAS work is described by Dec et al. [4]. Spectra for the titanium oxide polymorphs were subsequently given [5, 6] and NMR spectra presented for various metals and intermetallics [6]. The unexpectedly narrow lineshape that characterises the dried gel, and its evolution on specimen annealing have been very recently recorded [7].

## Experimental Details

The spectrometer was a Bruker 400 MSL operating around 22.55 MHz in a nominal field of 9.4 T and using a probe with a transverse 10 mm coil. The pulse widths used were usually around 4 μs which gave an irradiation bandwidth of 250 kHz. The probe was estimated to have a rather higher bandwidth of 3 - 400 kHz. The transmitter (tuned) output was estimated to be of order 2 MHz. A two pulse echo sequence with phase cycling was used for detection; the pulse widths were a trade-off between echo detection efficiency and a desire for larger frequency coverage. The result of this trade-off was that, even with 250 kHz excitation, the frequency covered by the FT spectrum in many instances apertured only part of the (1/2, –1/2) lineshape of the isotope pair. For each aperture the spectrum was obtained by Fourier transforming the complete echo (effectively $-\infty < t < \infty$, followed by a magnitude calculation which then gives the true absorption lineshape. Between 200,000 and 500,000 scans were collected for each file, with recycle delays from 0.1 s to 0.5 s.

A sharply defined shift reference zero for each Ti isotope was provided by the cubic perovskite $SrTiO_3$. All spectra displayed here were obtained at room temperature. The preparation of the intermetallics, and

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Table 1. Parameters for Ti and Ti compounds.

| Compound | Structure | $^{49}C_q$ [a] (MHz) | $\eta$ | $K_{iso}/\delta_{iso}$ [b] (ppm) | $K_{ax}/\delta_{ax}$ (ppm) |
|---|---|---|---|---|---|
| Ti metal | hex | 9.25±0.01 | 0 | 2750±100 | 70±10 |
| $TiB_2$ | hex | 12.34±0.02 | 0 | ≈ 0 | –970±50 |
| $TiAl_3$ | tetrag | 14.39±0.02 | 0 | 2750±200 | 800±50 |
| $TiAl_2$ | orthorh | 8.5±0.1 | 0.7±0.05 | 3300±200 | nm |
| $TiO_2$ anatase | tetrag | 4.79±0.01 | 0 | –195±20 | nm |
| $TiO_2$ rutile | tetrag | 13.8±0.1 | 0.19±0.01 | ≈ 0 | nm |
| $TiO_2$ brookite | orthorh | < 13.9 | > 0 | ≈ 0 | nm |

[a] $^{49}C_q = 0.819 \times {}^{47}C_q$, [b] $K_{iso}/\delta_{iso}$ applies to metals/insulators, respectively.

the sources of the metals are given in [9]. The oxide based materials were prepared by powder ceramic techniques, and the titania gels were prepared by hydrolysis of titanium isopropoxide.

Values of the nuclear quadrupole coupling constant $C_q = e^2qQ/h$, asymmetry parameter $\eta$, and isotropic and anisotropic chemical shifts $\delta_{iso}$, $\delta_{ax}$ (Knight shifts $K_{iso}$, $K_{ax}$) are collected in Table 1. In cases where the lineshapes for $^{47}$Ti and $^{49}$Ti can be separately observed, the values of $^{47}C_q$ and $^{49}C_q$ can be independently (but redundantly) computed. The ratio of $^{49}Q/^{47}Q$ has been previously measured by an atomic beam technique [8]and confirmed by single crystal $BaTiO_3$ NMR measurements [3].

## Discussion

### *Metals*

Ti metal is hexagonal close-packed with Ti in an axially symmetric site. The $^{47,49}$Ti spectrum of Ti metal was first observed by field sweeping at 4 K [1]. The powder spectrum recorded in this manner is relatively noisy despite the large increase in the Boltzmann factor compared to working at room temperature. The efficiency of the FTNMR signal averaging is well illustrated by the high signal to noise obtainable at room temperature for the $^{47,49}$Ti (1/2,–1/2) lineshape shown in Figure 1 . Also shown in Fig. 1 are the satellite lineshapes for the ±(1/2, 3/2) satellites for $^{49}$Ti. The separation $\nu_q$ between them gives a true value for $C_q$, which, together with an estimate of the coupling constant ($C_q(2)$) obtained by a simulation of the ((1/2,–1/2) powder pattern, assuming only 2nd order quadrupole interaction, yields the Knight shift anisotropy $K_{ax}$, along with $K_{iso}$.

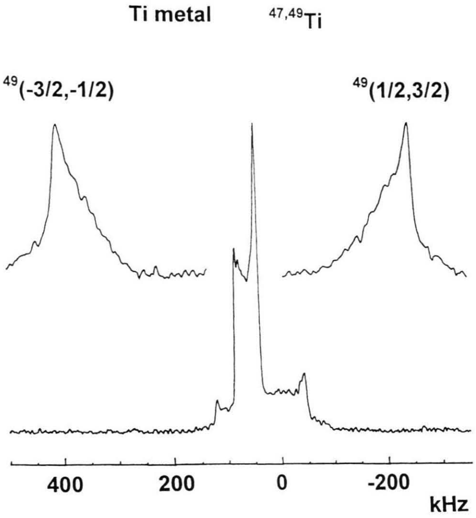

Fig. 1. Ti metal: $^{47,49}$Ti (1/2,–1/2) spectrum with $^{49}$Ti ±(1/2,3/2) spectrum superposed.

$$K_{ax} = 5\nu_q[\pm\nu'_q - \nu q]/\nu_L^2,$$

where $\nu_q = 3C_q/2I(2I-1)$, and $\nu_q$ and $\nu'_q$ are derived from $C_q$ and $C_q(2)$ respectively [6].

$TiB_2$ is hexagonal with the single crystallographically distinguishable Ti atom at an axially symmetric site. This material is a good metal like other transition metal borides. With a 250 kHz excitation bandwidth, only the central $^{49}$Ti (1/2,–1/2) transition is excited if the pattern is centrally irradiated. The singular edges of the $^{47}$Ti lineshape may be observed by moving the offset frequency appropriately, Figure 2. The magnitude of $K_{iso}$ is small (≈ 0) and very likely indicates an approximate cancellation of the positive s-contact and d-orbital terms with the negative d-core polarisation term in the total expression for the Knight shift. The satellite transitions ±(1/2,3/2) for $^{49}$Ti were separately observed and are also displayed in Figure 2. Their separation, $\nu_q$, may be used, as described above, to yield $^{49}C_q$, $K_{iso}$, and $K_{ax}$.

Note that the value of $K_{ax}$ is very much smaller for Ti metal than for $TiB_2$, perhaps reflecting the fortuitously low admixture of anisotropic 3d orbitals into the electron wavefunction centred on the Ti atom of hcp titanium.

$TiAl_3$ has a tetragonal structure. The unit cell is a fusion of two of the basic $L1_2$ units, from which many

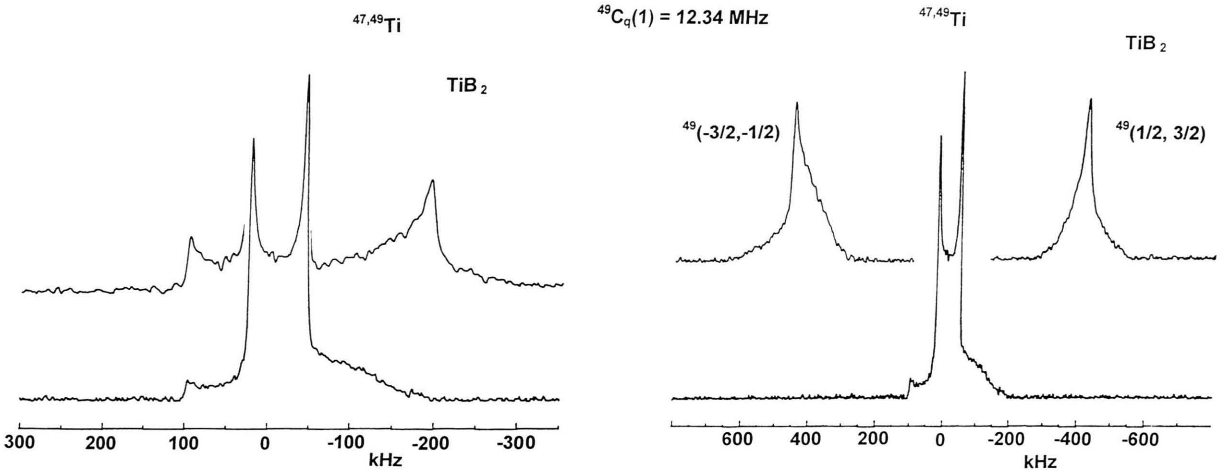

Fig. 2. $TiB_2$: (a) $^{49}$Ti (1/2,–1/2) spectrum with $^{47}$Ti superposed, and (b) with $^{49}$Ti ±(1/2,3/2) superposed.

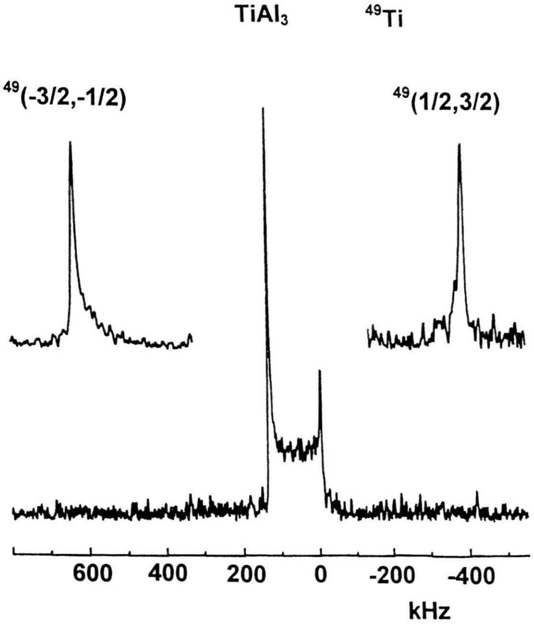

Fig. 3. $^{49}$Ti (1/2,–1/2) and (inset) ±(1/2,3/2) spectra of $TiAl_3$.

transition metal aluminides are constructed [9]; a face centred cube with (say) Ti at the cube corners and Al at the face centres. There is a 4-fold axis at the Ti site which guarantees $\eta = 0$.The lineshape is characteristic for a site with second order quadrupole interaction and is due to $^{49}$Ti. The outer edges of the $^{47}$Ti lineshape are not excited at this offset frequency. The extremely sharply defined $^{49}$Ti singular edges displayed in Fig. 3 reflect the excellent crystallinity and high degree of atomic ordering in this intermetallic specimen. Similarly sharply defined $^{49}$T satellite transitions are also observed, yielding $^{49}C_q$, $K_{iso}$, and $K_{ax}$.

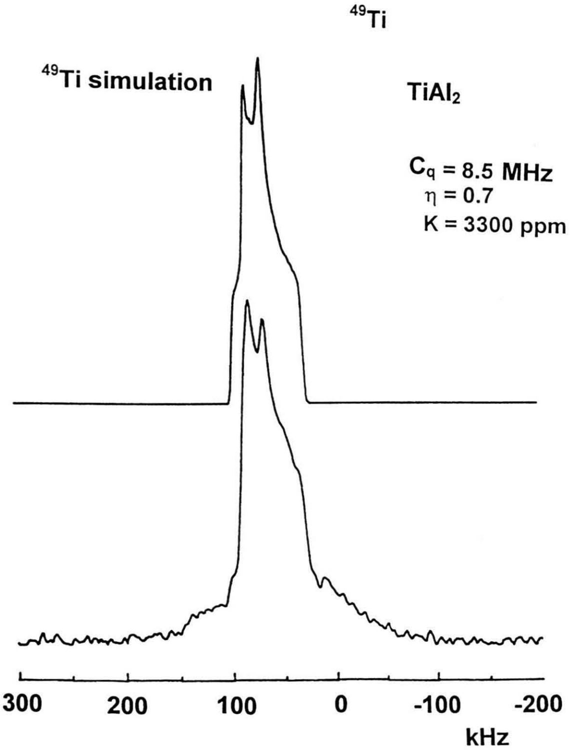

Fig. 4. $^{49}$Ti (1/2,–1/2) spectrum of $TiAl_2$, and $^{49}$Ti simulation.

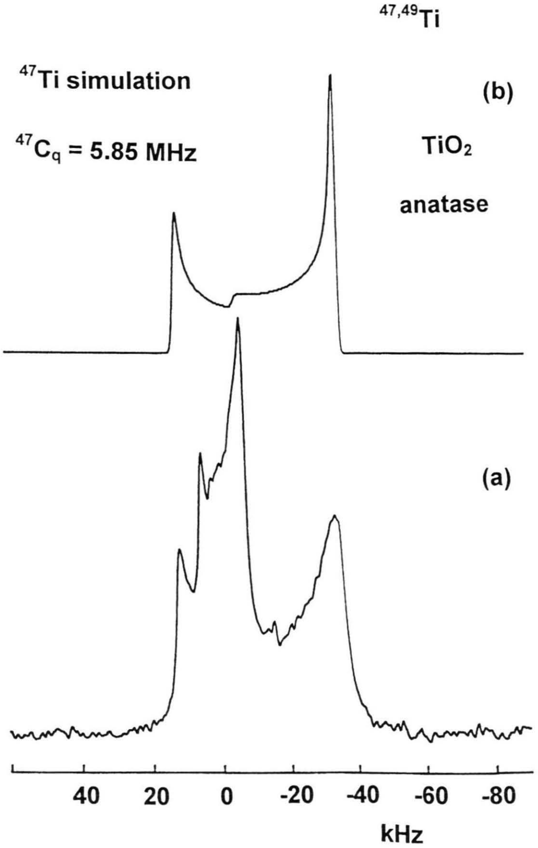

Fig. 5. (a) $^{47,49}$Ti (1/2,–1/2) spectrum of $TiO_2$ anatase, (b) $^{47}$Ti simulation.

$TiAl_2$ has the orthorhombic HfGa2 structure which represents a further, more elaborate stacking variant of the basic L12 unit [9]. The point symmetry of the single Ti site is 2 mm, entailing $\eta > 0$. The observed lineshape in Fig. 4 suggests that only the $^{49}$Ti spectrum was recorded in the 250 kHz frequency range excited by the 4 µsec pulses. The wings observed on either side of the well defined line are the incompletely excited high and low frequency edges of the $^{47}$Ti lineshape. The simulation for $^{49}C_q$ was made for 2nd order quadrupole interactions only.

*Oxides*

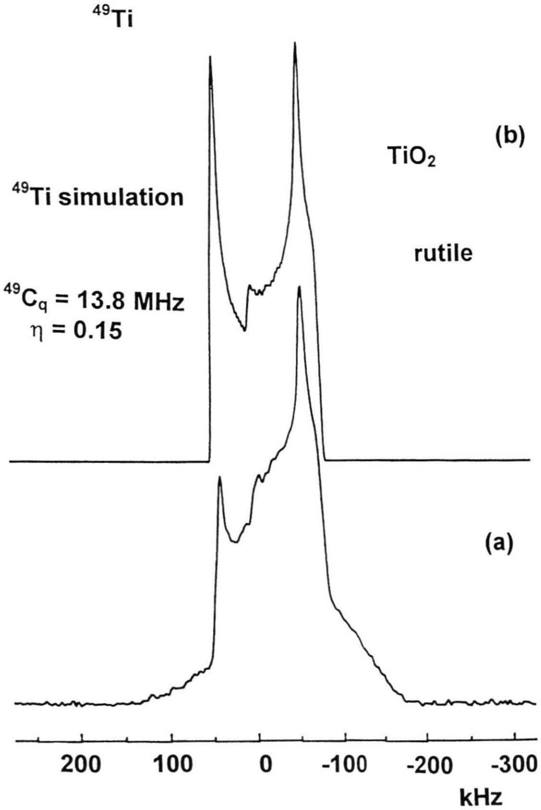

Fig. 6. (a) $^{49}$Ti (1/2,–1/2) spectrum of $TiO_2$ rutile, (b) $^{49}$Ti simulation (correction: $\eta = 0.19$).

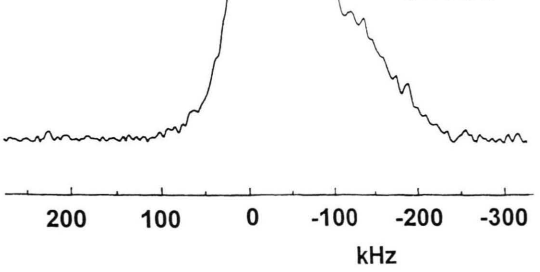

Fig. 7. $^{47,49}$Ti (1/2,–1/2) spectrum of $TiO_2$ brookite.

$TiO_2$ anatase has a tetragonal structure with Ti in a site with a 4-fold axis which gives $\eta =$ and entails sharply defined edge singularities for the second order quadrupolar perturbed Ti line shapes. The relatively small value for the line width of the superposed $^{47,49}$Ti spectra (ca. 50 kHz) together with the 250 kHz irradiation width, allows the central transition for both isotopes to be accurately recorded (Figure 5).

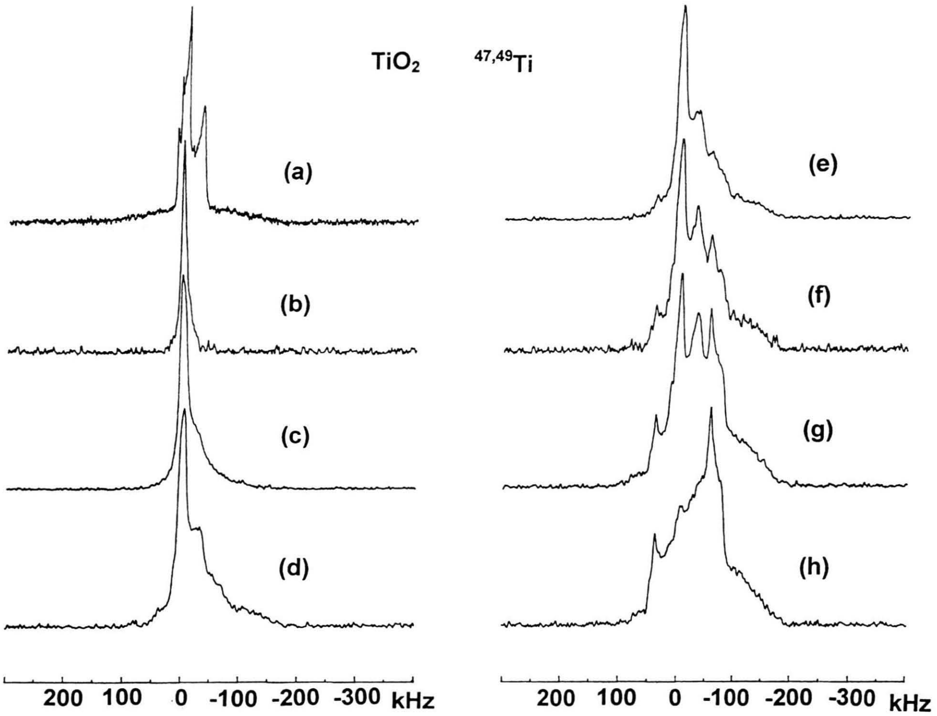

Fig. 8. $^{47,49}$Ti lineshapes for crystalline $TiO_2$ (anatase) and $TiO_2$ gel annealed at 200, 500, 520, 550, 580, 600, and 670 °C.

The powder spectrum from $TiO_2$ rutile (Fig. 6) has a considerably broader frequency spread (due to larger $C_q$) than for anatase, and, for central irradiation, only the $^{49}$Ti spectrum is excited here. The singular edges of the $^{47}$Ti spectrum can be observed by shifting the offset frequency. Note that the structure is body centred tetragonal and that the point symmetry at the Ti site allows a non-zero $\eta$. The spectrum can be fitted well for $C_q$ and $\eta$ by the single crystal NMR data [2].

The spectrum from $TiO_2$ brookite (Fig. 7) is less well defined than the other two polymorphs. Although the crystallographic order is excellent in this geological specimen, elemental analysis (EDAX) reveals the presence of Fe which would be expected to magnetically broaden the NMR spectrum. A pure synthetic brookite prepared by a sol-gel synthesis [10], offers hope for a more detailed spectrum with sufficient detail to allow a meaningful simulation for $C_q$ or $\eta$. There is only one Ti site, as in anatase and rutile, and the orthorhombic symmetry entails a finite asymmetry.

### *Titania Gel Evolution to Crystalline State*

The $^{47,49}$ Ti NMR spectra from selected annealing stages of a gel prepared by alkoxide hydrolysis are displayed in Figure 8. Because it is a component of the intermediate stages of annealing, a clear spectrum from a separate specimen of crystalline anatase is included as a reference in the top left hand frame. The subsequent spectra are identified in the figure by their annealing temperature. A surprising feature is the observation of a narrow, rather asymmetric resonance for the damp dry state, which remains, essentially unchanged, on annealing at temperatures of approximately 200 °C. The lineshape is comparable in width and general appearance to that from polycrystalline $^{47,49}$Ti in $BaTiO_3$ and $CaTiO_3$ [6], where X-ray determined structures show small distortions (orthorhombic and tetragonal, respectively) of the $TiO_6$ regular octahedral oxygen coordination that occurs in the cubic perovskite phase (e. g. $SrTiO_3$). The nuclear quadrupole coupling at the Ti site (which can be determined precisely for single crystal $BaTiO_3$) in both

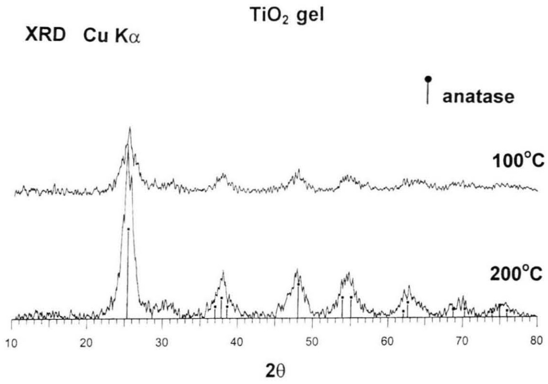

Fig. 9. XRD scans of $TiO_2$ gels annealed at 100 °C (upper trace) and 200 °C (lower trace).

these materials is less than that for anatase, but the intrinsic linewidth for both isotopes must be greater than their Larmor frequency separation of 6 kHz (at 9.4 T), leading to a lineshape which is isotopically unresolved, but skewed to low frequencies. It is apparent from the 200 °C gel linewidth that the distortion from cubic is also less than that from crystalline anatase, but that the gel peak has a shift value very close to the centroid of the sharp $^{49}$Ti component of the anatase spectrum.

On the other hand it was noted that the 100 °C and 200 °C anneals of the gel yielded powder XRD spectra characterised by broad lines centred at the crystalline anatase $2\theta$ values (Figure 9). The obvious interpretation is that the samples are nanocrystalline anatase. (They are clearly distinguishable from XRD traces from crystalline rutile and brookite specimens.) The above observations are compatible if, in the 100 °C and 200 °C gels (at least), the Ti atoms have large amplitude oscillations with vibrational frequencies fast on the time scale of the nuclear quadrupole interaction frequencies $^{47,49}\nu_q \sim 5$ MHz, but with a period slow compared to the time ($\sim 10^{-12}$ sec) for the X-ray photon to traverse the specimen. This would allow a partial motional averaging of the nuclear quadrupole interaction for crystalline anatase.

It should be noted that a previous study [11] has shown, using $^{17}$O MAS NMR and $^{13}$C CPMAS, that in a $TiO_2$ gel preparation (also via alkoxide hydrolysis) there were initially observed in the as-dried gel two broad $^{17}$O lines at 514 ppm and 368 ppm, corresponding to the presence of $OTi_3$ and $OTi_4$ groups. It may be noted that all three $TiO_2$ polytypes, anatase, rutile and brookite possess the oxygen coordination $OTi_3$. On annealing the gel in stages up to 300 °C, the $OTi_3$ $^{17}$O line sharpened considerably and the shift moved to that for anatase. The line at 368 ppm from the $OTi_4$ component (due to a polyoxyalkoxide species [12] present because of incomplete hydrolysis in the preparation, which, for economic reasons, used a severely limited amount of $^{17}$O enriched water) correspondingly diminished in intensity and disappeared at 300 °C along with the $^{13}$C spectrum for the alkoxide. In the gel preparation for the present $^{47,49}$Ti study the hydrolysis was complete.

For the 500 °C gel the line has broadened, so that the base has a width approaching that of anatase. The lineshape, now with a more prominent low frequency shoulder, is beginning to resemble a heavily smeared version of anatase. However as the gel is further annealed towards 600 °C, peaks begin to appear that can be identified by their shift values as belonging to both anatase and rutile $^{47,49}$Ti spectra. At 670 °C only well crystallised rutile was present, judging by the sharpness of the spectral features. Further annealing to 700°C and above did not appreciably further sharpen the rutile lineshape.

It can also be seen from the lineshape smearing that the anatase crystallites present in gels annealed at 600°C and below were not particularly well ordered. Note that almost as soon as the spectrum had developed recognisable anatase features it was also developing rutile features, and that anatase and rutile coexisted in the specimen for at least 100 °C. This is interpreted as indicating an inhomogeneity in the specimen, and that these two polmorphs were developing in spatially separate regions.

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