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# The nature of oxygen exchange in $ZrW_2O_8$ revealed by two-dimensional solid-state $^{17}O$ NMR

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**$^{17}O$ magic angle spinning (MAS) NMR has been used to determine the nature of oxygen exchange in $ZrW_2O_8$. A highly effective isotopic labelling technique has been developed and 1D NMR and 2D exchange spectroscopy (EXSY) experiments have revealed that mutual exchange occurs between all oxygen sites, even at temperatures considerably below the α to β order–disorder phase transition.**

Cubic zirconium tungstate exhibits isotropic negative thermal expansion over an extremely wide temperature range (2–1050 K).[1] This property is of interest due to numerous potential technological applications.[2] It and other members of the $AM_2O_8$ family also show dynamic oxygen disorder at unusually low temperatures.[3,4,5] This disorder is understood to be responsible for an order–disorder phase transition observed at 175 °C[2] in which the space group symmetry changes from $P2_13$ to $Pa\bar{3}$.[6] Despite being the subject of much research, the specific mechanism of oxygen migration is currently unknown. We have used solid-state $^{17}O$ MAS NMR to determine the nature of oxygen mobility over a range of temperatures from 0 °C to 230 °C, and have performed 2D $^{17}O$ NMR experiments (EXSY[7]) to investigate the mechanism.

The structure of α-$ZrW_2O_8$ is shown in Fig. 1a.[6] It contains a network of corner-sharing octahedra and tetrahedra with a $W_2O_8$ unit, made up of a pair of $WO_4$ tetrahedra, along the main 3-fold axis of the cubic unit cell. In the high temperature β phase, the direction in which $WO_4$ tetrahedra point along the 3-fold axis becomes dynamically disordered (Fig. 1b).[6] The α to β phase transition therefore involves a formal inversion of the $W_2O_8$ groups.

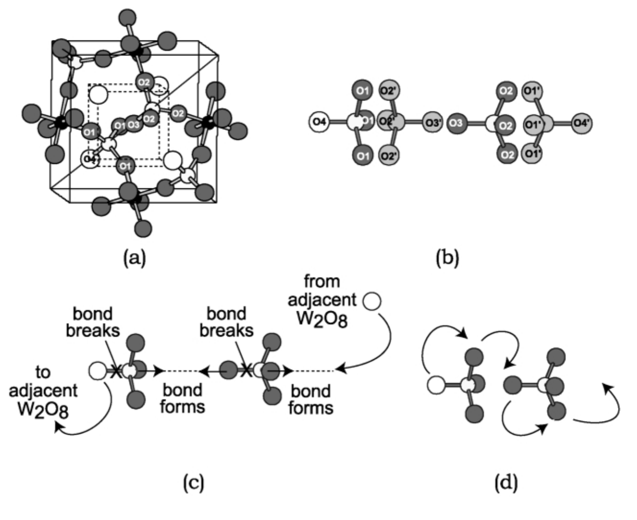

**Fig. 1** (a) Structure of cubic $ZrW_2O_8$, showing two-coordinate oxygen sites in grey and one-coordinate sites in white. (b) Ball and stick representation of the $W_2O_8$ group. For clarity tetrahedra have been displaced so that atoms do not overlap. The ratio of the numbers of O1:O2:O3:O4 sites is 3:3:1:1. Unprimed atomic sites are fully occupied in the ordered α phase; all sites are 50% occupied in the disordered β phase. (c), (d) Schematic diagrams showing two possible mechanisms of oxygen exchange.

Two feasible mechanisms can be proposed for this inversion, as illustrated in Fig. 1c–d. In one extreme view, one can envisage a "coupled $S_N2$" mechanism in which the formation of a W1–O3 bond leads to cleavage of the W1–O4 bond and a local inversion of tetrahedra (Fig. 1c). This process could occur in a cooperative way throughout the crystal or proceed *via* the local process of

$$4WO_4^{2-} \rightarrow W_2O_9^{6-} + W_2O_7^{2-}.$$

Alternatively, adjacent tetrahedra could rotate as a whole in a "ratchet" motion, causing mutual exchange between all oxygen sites (Fig. 1d).

$^{17}O$ NMR is an ideal technique to study these possibilities,[8,9] but has the drawback that the natural isotopic abundance of $^{17}O$, the only spin-active oxygen isotope, is just 0.037%. Enriched samples are therefore required for NMR experiments to be performed in a practical length of time.

Highly enriched $ZrW_2O_8$ was prepared *via* the recently identified $ZrW_2O_8{\cdot}xH_2O$ phase.[10] 0.2 g of unlabelled $ZrW_2O_8$ was sealed under vacuum in a Pyrex glass ampoule with an excess of 0.2 g of 40% $^{17}O$ enriched water (Isotec). The sealed ampoule was heated to 240 °C for 21 days in a steel autoclave. Powder X-ray diffraction and thermogravimetric analysis of test samples confirmed that this procedure produces a hydrated material $ZrW_2O_8{\cdot}xH_2O$ ($x$ = ~0.5). The powder was then dehydrated under a dynamic vacuum for 2 hours at 240 °C. This technique produced a highly labelled and

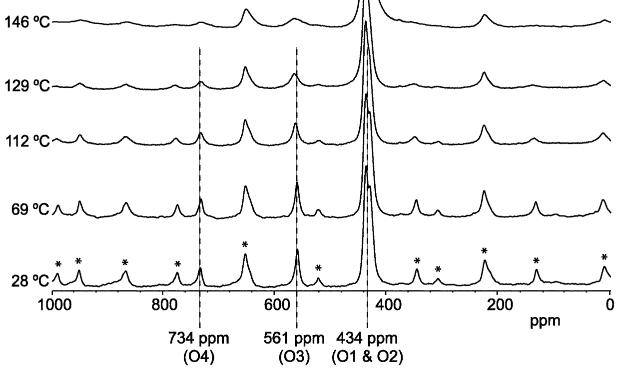

**Fig. 2** Variable temperature $^{17}O$ MAS spectra of $ZrW_2O_8$.† A MAS rate of 14.5 kHz was used throughout. Excitation pulse duration 2.0 μs. Pulse repetition times were between 3 s and 120 s depending on $T_1$. The number of transients per spectrum was varied between 32 and 1024 in order to maintain adequate signal-to-noise at each temperature. An exponential apodization of 100 Hz was applied to each spectrum.

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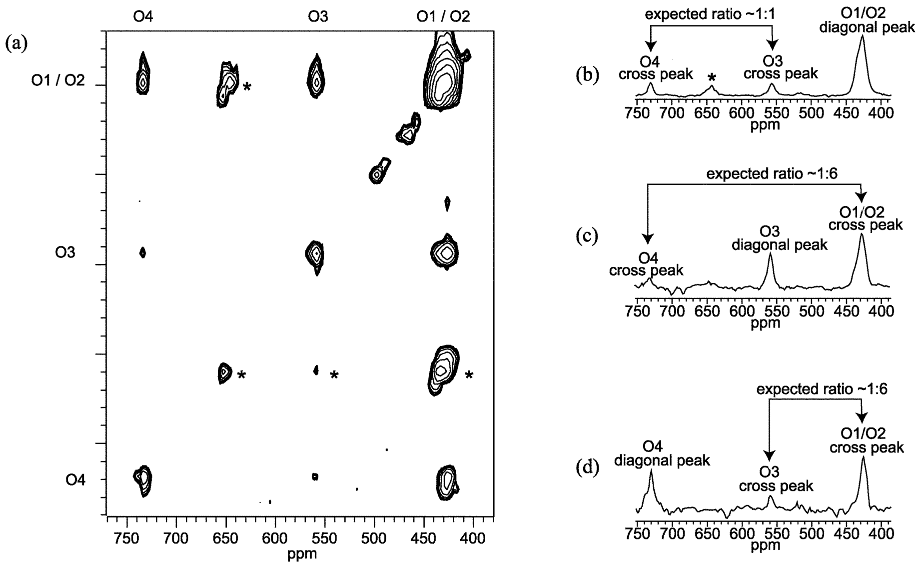

**Fig. 3** $^{17}O$ EXSY spectrum of $ZrW_2O_8$ at 57 °C†: (a) 2D spectrum; (b-d) Spectral slices through diagonal peaks for O1 and O2 (b), O3 (c), O4 (d). MAS rate of 14.5 kHz. 32 transients per increment, with 24 increments in $t_1$. Excitation pulse durations of 2.80 μs were used, with a dwell time in $t_2$ of 4.31 μs and a recycle delay of 90 s. The total experimental time was 38.4 hours. Linear prediction was used to extend the FID in the indirect dimension to 64 points, and 300 Hz exponential apodization was applied in both dimensions. Connecting arrows indicate integral ratios expected on the basis of equal probability exchange between sites.

pure sample of $ZrW_2O_8$, and was considerably more effective than previous attempts to produce labelled $ZrW_2O_8$ from pre-labelled oxides.

$^{17}O$ NMR experiments on $ZrW_2O_8$ were carried out using a Varian InfinityPlus 500 spectrometer operating at a $^{17}O$ Larmor frequency of 67.78 MHz, with a Chemagnetics 4.0 mm MAS probe. All spectra were referenced to $H_2O$ at 0 ppm.

A simple hydration–dehydration mechanism without further site exchange might be expected to preferentially enrich O4. In fact the peak intensity ratios (Fig. 2) are similar to those observed for a sample prepared from enriched precursor oxides, where equal labelling of all sites would be expected, providing indirect support for full exchange between all oxygen sites at 240 °C. 1D spectra were recorded at temperatures from 28 to 229 °C†. As the material is warmed, peaks first broaden and then begin to coalesce (Fig. 2), the chemical shift of the single broad centreband peak at 229 °C tending towards the weighted mean of all those observed at low temperature (487 ppm). This indicates that all sites are involved in exchange at high temperature. At low temperatures, the broadening of the peaks implies that exchange is occurring, but does not give information as to which sites are interchanging.

In order to confirm the nature of the exchange process below the phase transition temperature, two-dimensional exchange spectroscopy ($^{17}O$ EXSY) was used. An off-diagonal cross peak in an EXSY spectrum implies exchange between two different chemical sites on the timescale of the mixing time, in this case 50 ms (Fig. 3). No cross peaks were observed in a control experiment with a 1 ms mixing time. Only a limited number of $t_1$ increments were needed, since only modest resolution in the indirect dimension is required to observe the presence of cross-correlation peaks.

The 2D EXSY spectrum (Fig. 3a) shows correlations between all oxygen sites, indicating that the low-temperature exchange mechanism involves mutual exchange between all oxygen environments. Furthermore, the ratios of the cross peak integrals in the spectral slices (Fig. 3b–d) are consistent with the probabilities expected if full scrambling occurs during the mixing time.

The results obtained are consistent with the “ratcheting” model involving whole rotations of intact $WO_4$ groups. If the “$S_N2$” mechanism were in operation, then cross peaks would be observed only between O1 and O2. Although O3 and O4 are physically moving, they remain in the same type of environment before and after the motion, albeit bonded to different tungsten atoms.

We have shown that a process involving complete exchange of all oxygen sites is in operation both above and below the phase transition. This exchange is consistent with powder diffraction data.[3,4] Further quantitative experiments are in progress to probe the kinetics of exchange, and to follow the variation of chemical shift of O3, which is found to change more rapidly with temperature than other oxygen sites.

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## Notes and references

† $^{207}Pb$ NMR of $Pb(NO_3)_2$ was used for the temperature calibration.[11]

1 T. A. Mary, J. S. O. Evans, T. Vogt and A. W. Sleight, *Science*, 1996, **272**, 90.
2 J. S. O. Evans, *J. Chem. Soc., Dalton Trans.*, 1999, 3317.
3 J. S. O. Evans, T. A. Mary, T. Vogt, M. A. Subramanian and A. W. Sleight, *Chem. Mater.*, 1996, **8**, 2809.
4 S. Allen and J. S. O. Evans, *J. Mater. Chem.*, 2004, **14**, 151.
5 S. Allen and J. S. O. Evans, *Phys. Rev. B: Condens. Matter*, 2003, **68**, 134101.
6 J. S. O. Evans, W. I. F. David and A. W. Sleight, *Acta Cryst. B*, 1999, **55**, 333.
7 K. G. Orrell, in “Encyclopedia of Nuclear Magnetic Resonance”, eds. R. K. Harris and D. M. Grant, Wiley, Chichester, 1996, **Vol. 8**, p. 4850.
8 N. Kim and C. P. Grey, *Science*, 2002, **297**, 1317.
9 J. F. Stebbins, *Science*, 2002, **297**, 1285.
10 N. Duan, U. Kameswari and A. W. Sleight, *J. Am. Chem. Soc.*, 1999, **121**, 10432.
11 A. Bielecki and D. P. Burum, *J. Magn. Reson., Ser. A.*, 1995, **116**, 215.