A ^{6}Li and ^{7}Li MAS NMR Study of the Spinel-type Manganese Oxide $LiMn_2O_4$ and the Rock Salt-type Manganese Oxide Li_2MnO_3

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^{6}Li and ^{7}Li MAS NMR spectroscopy is used to identify distinct lithium sites in two paramagnetic manganese oxides: spinel-type $LiMn_2O_4$ and rock salt-type Li_2MnO_3.

In the solution NMR of paramagnetic compounds, narrow resonances are observed if the electronic relaxation times compared to the hyperfine coupling constant are sufficiently short. For paramagnetic solids if comparable conditions apply then, as Cheetham *et al.*[1] and Grey *et al.*[2] have recently shown, NMR resonances of nuclei can be observed and narrowed under magic angle spinning (MAS). For static powders the resonances are in general broad because of the angular dependence of the dipolar interaction between the nucleus and the electron, but under MAS the resonances narrow and appear as a wide spinning side-band manifold. While a large spinning side-band manifold may be inconvenient for observing resonances with small isotropic shifts, nuclei in paramagnetic compounds generally have large isotropic shifts as well, and resonances that would normally overlap in a diamagnetic compound can readily be resolved in a paramagnetic compound. The dominant contribution to the isotropic shift for a nucleus in a cubic environment is the Fermi contact shift,[3] although the pseudocontact shift, resulting from a dipolar interaction with the nucleus in a non-cubic environment, may also be significant in some paramagnetic solids.[4,5] Overall, the shift effects in a paramagnetic solid are similar to the action of shift reagents in solution NMR, and this has prompted Grey *et al.*[1] to refer to these nuclei in solids as 'paramagnetic shift probes'.

We have been using ^{6}Li and ^{7}Li solid-state NMR to examine the structure of the paramagnetic lithium spinel-type manganese oxides, since these solids have a number of commercial uses; as lithium ion selective detectors, lithium cathodes in batteries, and as lithium ion absorbers they may have commercial potential for mining lithium from sea and geothermal waters.

As part of our NMR studies of these compounds and a more comprehensive investigation of lithium manganese oxides, we have examined the ^{6}Li and ^{7}Li solid-state NMR of two stoichiometric oxides, the spinel-type manganese oxide, $LiMn_2O_4$, and the rock salt like manganese oxide, Li_2MnO_3.† Both compounds have structures that have been characterised by X-ray and neutron diffraction studies.[6–8] Li_2MnO_3 was included as part of this exploratory study as it can appear in various proportions in preparations of some of the spinel-type manganese oxides, especially if the oxides are heated above 400 °C.

Kanzaki *et al.*[9] have previously reported poorly resolved ^{7}Li MAS NMR spectra of Li_2MnO_3 and $LiMn_2O_4$ and assigned the large observed shifts to a Knight shift. This is not likely, however, as the compounds do not show metallic conductivity (Li_2MnO_3 is antiferromagnetic at low temperatures), and the NMR shifts are larger than that for metallic lithium and show an inverse temperature dependence.[10]

The ^{6}Li and ^{7}Li NMR‡ spectra of $LiMn_2O_4$ are shown in Fig. 1, and of Li_2MnO_3 in Fig. 2. An unusual feature of these spectra, but characteristic of paramagnetic solids, are the very large isotropic shifts of the resonances, 500–2000 ppm, whereas the normal isotropic shifts for lithium in diamagnetic compounds are usually only a few ppm, and resonances of chemically distinct lithiums are often unable to be resolved in the solid state.[11]

All the resonances are extremely broad having spinning side band manifold widths of several thousand ppm. It may be tempting to assign some of the line broadening to quadrupolar effects, since both ^{6}Li and ^{7}Li are quadrupolar nuclei. However, both the ^{6}Li and ^{7}Li spectra of the oxides show similar amounts of line broadening (in ppm), even though for ^{6}Li the quadrupolar coupling constant is two orders of magnitude smaller than that for ^{7}Li. In the absence of quadrupolar effects, the only other two interactions that can contribute to significant line broadening are electron-nucleus coupling, and magnetic susceptibility broadening.[12] The latter

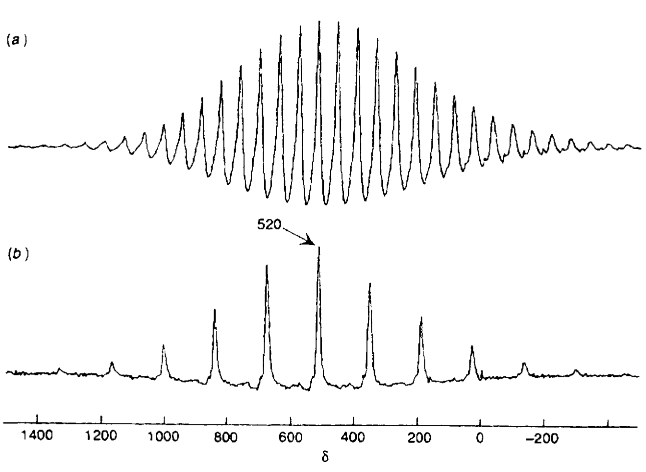

Fig. 1 (*a*) ^{7}Li MAS NMR spectrum of $LiMn_2O_4$ (spinning speed of 11.8 kHz) and (*b*) ^{6}Li MAS NMR of ^{6}Li enriched $LiMn_2O_4$ (spinning speed of 12.0 kHz). The centre band is marked on the ^{6}Li spectrum.

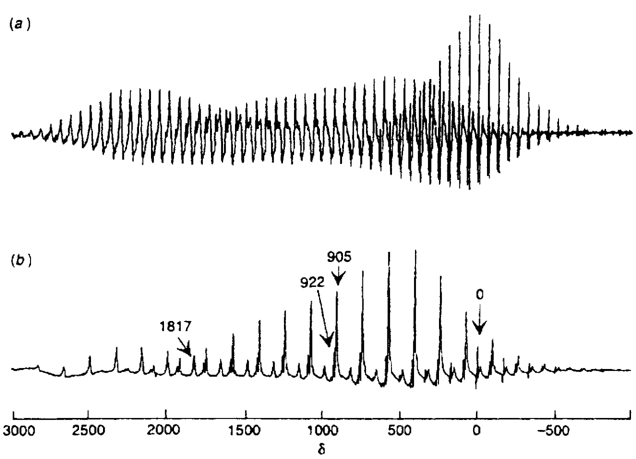

Fig. 2 (*a*) ^{7}Li MAS NMR spectrum of Li_2MnO_3 (spinning speed of 10.9 kHz) and (*b*) ^{6}Li MAS NMR of ^{6}Li enriched Li_2MnO_3 (spinning speed of 11.8 kHz). Both spectra have been resolution enhanced by applying a Lorentzian to Gaussian transformation to the FID. Centre bands are marked on the ^{6}Li spectrum.

effect is due to the paramagnetism of the small particles that form the powder. Grey *et al.* [13] have found that it is possible to remove the contribution from susceptibility broadening by matching the volume susceptibility of the solid with a surrounding solution containing paramagnetic ions. We found that both $LiMn_2O_4$ and Li_2MnO_3 had too high a volume susceptibility to match successfully with a saturated solution of erbium nitrate, and attempts to remove magnetic susceptibility broadening effects were not pursued further. We therefore report only the isotropic values.

Both the contact and pseudocontact shifts have an inverse temperature dependence. It was noted that an increase in spinning speed resulted in the isotropic shift moving to higher field. This puzzling observation was explained by an increase in temperature occurring due to frictional heating of the rotor at higher spinning speeds. Similar rotor heating has been noted by a number of other authors.[14–16]

Spectra of the ^6Li manganese oxides are preferred for determination of the isotropic shifts for a number of reasons. The line widths of the centre band of the ^6Li resonances are narrower (*ca.* 2000 Hz) than those of the ^7Li resonances (*ca.* 4000 Hz). There is less chance for the overlap of a spinning side band with an isotropic resonance in the ^6Li spectra, since the number of spinning side bands in ^6Li spectra are considerably smaller than in ^7Li spectra at similar rotor spinning speeds. Spectral widths are smaller in ^6Li spectra and this avoids the problems of spectral distortions seen in the ^7Li spectra.

For the ^6Li and ^7Li NMR spectra of $LiMn_2O_4$ (Fig. 1), there is a single spinning side band manifold centred on 520 ppm. This agrees with X-ray[6] and neutron diffraction studies[7] which show that lithium is in one type of tetrahedral site. For the ^6Li resolution-enhanced spectrum of Li_2MnO_3 [Fig. 2(*b*)], three spinning side band manifolds are observed at 905, 922 and 1817 ppm, but only two of these (905 and 1817 ppm) could be resolved in the ^7Li resolution-enhanced spectrum [Fig. 2(*a*)]. The ^6Li results are consistent with a single crystal study,[8] which found three unique octahedral lithium sites. For one of the sites (4h) there are four lithiums in the unit cell, while for the other two sites (2b and 2c) there are only two lithiums in the unit cell. The 4h site can therefore be assigned to the most intense spinning side band manifold, centred on 905 ppm.

The average bond length to the six adjacent oxygens in the 2c and 4h sites in Li_2MnO_3 is 210.2 pm, while that in the 2b site is only 205.9 pm. It is therefore tempting to suggest that the contact shift will be larger for the 2b site, while in the 2c and 4h sites the shift will be similar. We have therefore assigned the manifold at 1817 ppm to the 2b site and that at 922 ppm to the 2c site.

All spectra usually contain an additional sharp spinning side band manifold of variable intensity centred on 0 ppm [most clearly seen in Fig. 2(*a*)]. This band appears to be due to unreacted non-paramagnetic lithium salts which, nevertheless, are broadened by magnetic susceptibility effects from nearby lithium manganese oxide particles.

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Footnotes

† $LiMn_2O_4$ and Li_2MnO_3 were prepared by grinding Li_2CO_3 and β-MnO_2 in the mol. ratio of 1 : 2 and 2 : 1, respectively, in acetone to obtain homogenous mixtures. After the acetone was removed by filtration and drying the mixtures were heated to 850 °C. $LiMn_2O_4$ was isolated after 8 h and Li_2MnO_3 after 16 h of heating. ^6Li manganese oxides were prepared from the corresponding ^6Li enriched Li_2CO_3. The compounds were characterised by X-ray diffraction spectroscopy.

‡ Solid-state ^6Li and ^7Li NMR spectra were acquired on a Varian Unity 500 spectrometer. Samples were packed into 5 mm rotors and spun at speeds up to 13 kHz in a probe from Doty Scientific. Spectra were recorded using a single pulse experiment at 194 MHz and a spectral window of 1.6 MHz for ^7Li NMR, and at 74 MHz and a spectral window of 400 kHz for ^6Li NMR. Pulse repetition times were generally less than 0.1 s and the rf field was about 60 kHz. Pulse widths were 2 μs for ^7Li and 3 μs for ^6Li. Positions of the centre bands were determined by varying the spinning speed. Peaks were referenced with respect to solid LiCl.

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