Solid-state Magnesium-25 N.m.r. Spectroscopy

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Static and magic angle spinning n.m.r. spectra have been obtained from a selection of simple inorganic solids, demonstrating the utility of ^{25}Mg in structural investigations.

Multinuclear n.m.r. spectrometers having the capability of studying solids are becoming widespread, necessitating the evaluation and characterisation of more nuclei for their applicability to studies of solids. Magnesium is an important element whose study may be widely applied to problems in biological systems,[1] technologically important high temperature ceramics,[2] minerals,[3] and order-disorder phenomena.[4,5,6] ^{25}Mg is a 10% naturally abundant spin-5/2 nucleus with a small

Table 1. ^{25}Mg Room temperature chemical shifts and linewidths from some inorganic solids.

Compound	Crystal symmetry	Local co-ordination number of Mg	Technique	Isotropic chemical shift (w.r.t. 3 M $MgSO_4$)	F.W.H.M.[b]/Hz ± 10%
MgO	Cubic	6	M.a.s.	26 ± 1	50
$MgAl_2O_4$	Cubic	4	M.a.s.	52 ± 3	130
MgS	Cubic	6	M.a.s.	-3 ± 0.5	20
Mg_2Si	Cubic	4	M.a.s.	61 ± 0.5	30
$MgCl_2 \cdot nH_2O$	Monoclinic	6	Static	-2 ± 1	450
$MgSO_4 \cdot 6H_2O$	Monoclinic	6	M.a.s.	0 ± 15	1.5×10^3
$Mg(OH)_2$	Hexagonal	6	Static echo	10 ± 50	1.5×10^4
$Mg_2Si_3O_8$	Monoclinic	6	Static echo	0 ± 50[a]	1.4×10^4
Mg_3N_2	Hexagonal	4	Static echo	10 ± 100[a]	1.7×10^4
$Mg_3Al_2(SiO_4)_3$	Cubic	8	Static echo	0 ± 200[a]	4.5×10^4

[a] Peak position not the isotropic chemical shift. [b] Full width at half maximum.

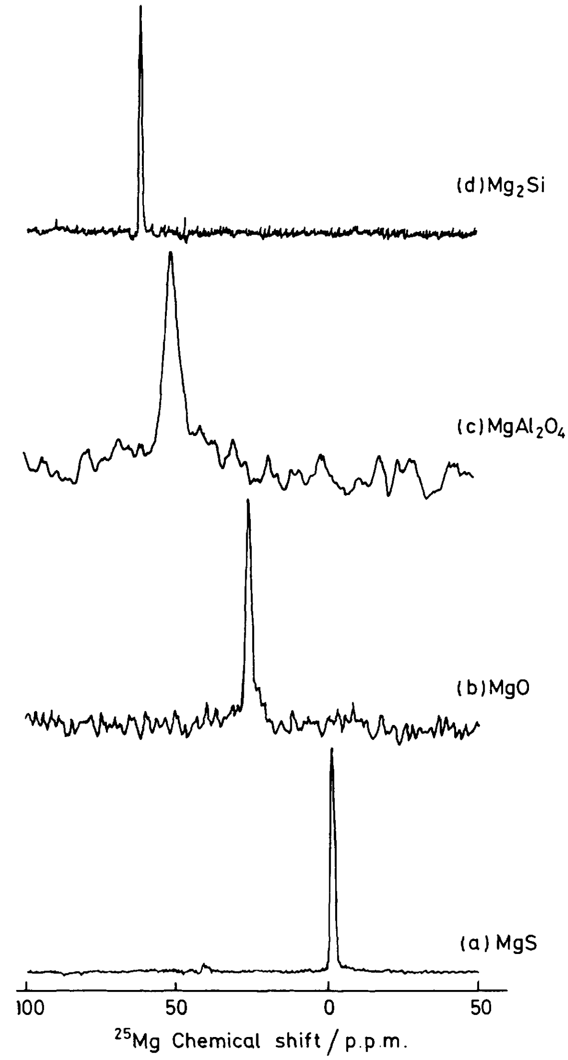

Figure 1. ^{25}Mg M.a.s.-n.m.r. spectra of (a) MgS, (b) MgO, (c) $MgAl_2O_4$, and (d) Mg_2Si. Reference is 3 M aq. $MgSO_4$.

gyromagnetic ratio resulting in a sensitivity of 0.74 compared to ^{29}Si. The second-order quadrupole broadening of the central transition ($\frac{1}{2} \rightarrow -\frac{1}{2}$) is ~9 times greater than for ^{27}Al in sites with the same electric field gradient in the same applied magnetic field. These factors have limited ^{25}Mg n.m.r. to a few solution-state studies of biological systems[1] and occasional single crystal[7] and powder studies.[8]

Here the results of some preliminary studies of some reagent grade, model solids are presented to ascertain the applicability of conventional ^{25} Mg n.m.r. techniques to the solid-state. The ^{25}Mg n.m.r. powder spectra were recorded on a Bruker MSL-360 spectrometer operating at 22.0 MHz (B_0 = 8.45 T). Single pulse spectra were accumulated using short pulses (2 μs, ~π/5) with (1—5) s pulse delays for (100—500) scans. Where appropriate magic angle spinning (m.a.s.)[9] spectra were recorded by spinning at (3—6) kHz in 5 mm zirconia rotors. Broad lines were acquired by using a 90°–τ–180° spin-echo sequence to overcome probe ringing distortions.[10,11] All spectra were referenced to an external standard of 3 M aqueous magnesium sulphate.

The results are summarised in Table 1 with some representative spectra shown in Figures 1 and 2. Although the electric field gradient is determined by the local site symmetry rather than the crystallographic symmetry these results indicate that the crystallographically cubic materials generally give narrow resonances. In contrast for most non-cubic materials there is a large increase in linewidth. For $MgSO_4{\cdot}6H_2O$ and $Mg(OH)_2$ the second-order quadrupole lineshape of the central transition can be distinguished (both static and spinning for $MgSO_4{\cdot}6H_2O$) allowing the quadrupole coupling constant (e^2qQ/h) to be deduced by spectral simulation as 1.6 MHz and 2.9 MHz respectively, both with an asymmetry parameter ~0. Both the static and m.a.s. spectra of the sulphate show second-order quadrupole structure with m.a.s. reducing the linewidth by (3—4) as expected for a quadrupole broadened line.[12] For other materials (*e.g.* Mg_3N_2) the quadrupole lineshape is obscured as it is convolved with other anisotropic broadenings (*e.g.* dipolar and chemical shift) so that e^2qQ/h and the isotropic chemical shift cannot be accurately deduced.

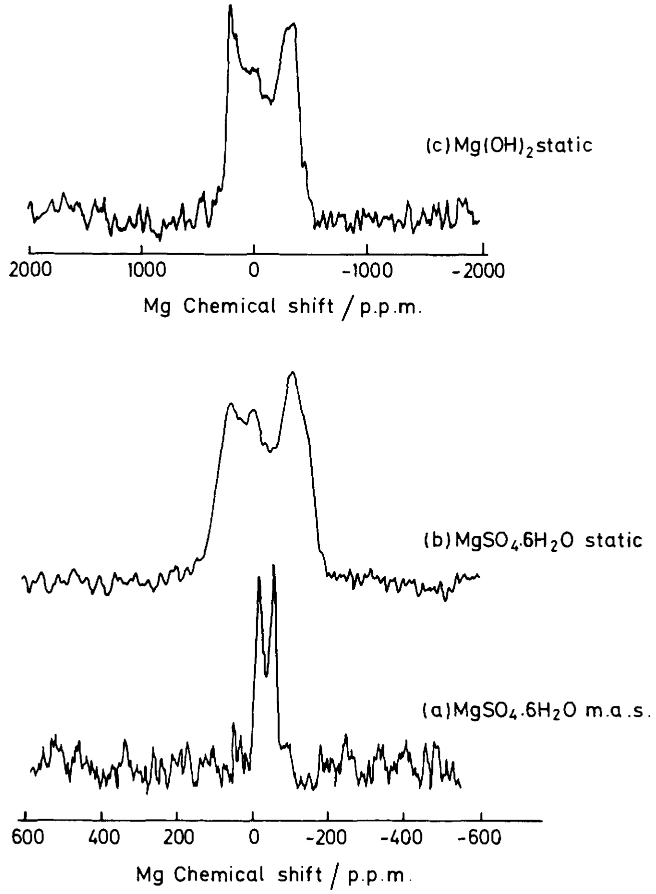

Figure 2. ^{25}Mg N.m.r. spectra of $MgSO_4.6H_2O$ (a) m.a.s. and (b) static echo, and (c) $Mg(OH)_2$ static echo. Reference is 3 M aq. $MgSO_4$.

A ^{25}Mg nuclear quadrupole resonance study of $MgCl_2{\cdot}6H_2O$ at 77 K measured e^2qQ/h = 1.477 MHz.[13] This corresponds to a static second-order quadrupole linewidth of ~ 140 p.p.m., much larger than the 20 p.p.m. measured on a sample of nominal composition $MgCl_2{\cdot}6H_2O$ as determined by *X*-ray diffraction in this study. Drying the sample at 140 °C for 6 days gave a peak at ~10 p.p.m. with a linewidth of ~1400 p.p.m., $MgCl_2{\cdot}nH_2O$ has an extensive range of hydration from 0—12 and e^2qQ/h is known to be sensitive to hydration state in other compounds such as $AlCl_3$.[14] Hence our narrow peak might be due to some minority hydration state. The effect of hydration will be the subject of further investigation. In MgO and $MgAl_2O_4$ the local co-ordination of magnesium is MgO_6 and MgO_4 respectively. The change is clearly indicated by the shift difference of ~26 p.p.m. between these units with the octahedron giving the more shielded environment as expected from electrostatic bond strength arguments.[15] This shift difference indicates a decrease in the chemical shift difference XO_6 and XO_4 units for ^{29}Si (~100 p.p.m.) to ^{27}Al (~50 p.p.m.) to ^{25}Mg (~25 p.p.m.) across the row of the Periodic Table towards the alkali metals which are known to have small shift ranges.

These results indicate that ^{25}Mg n.m.r. spectroscopy may yield useful structural information through the chemical shift or the quadrupole coupling constant provided these contributions can be disentangled. Since for second-order quadrupole broadened lines the resolution of different environments improves as the square of the applied magnetic field, ^{25}Mg will be still more attractive in larger fields especially when coupled with higher spinning speeds and other techniques such as cross-polarisation.[16]

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References

1 T. Drakenberg and S. Forsen, 'The Multinuclear Approach to N.M.R. Spectroscopy,' eds. J. B. Lambert and F. G. Riddell, Reidel, Dordrecht, 1982, pp. 329—342.
2 K. H. Jack, *J. Mater. Sci*, 1976, **11**, 1135.
3 R. J. Kirkpatrick, K. A. Smith, S. Schramm, G. Turner, and W. H. Yang, *Ann. Rev. Earth Planet. Sci.*, 1985, **12**, 29.
4 G. Gobbi, R. Christofferson, M. T. Othen, B. Miner, P. R. Buseck, G. J. Kennedy, and C. A. Fyfe, *Chem. Lett.*, 1985, 771.
5 B. J. Wood, R. J. Kirkpatrick, and B. Montez, *Am. Mineral.*, 1986, **71**, 999.
6 R. Dupree, M. H. Lewis, and M. E. Smith, *Phil. Mag. A.* 1986, **53**, L(17—20).
7 H. E. Bleich and A. G. Redfield, *J. Chem. Phys.*, 1977, **67**, 5040.
8 M. A. Fedotov and G. F. Gerasimova, *React. Kinet. Catal. Lett.*, 1983, **22**, 1977.
9 E. R. Andrew, *Int. Rev. Phys. Chem.*, 1981, **1**, 195.
10 I. P. Gerothanassis, *Prog. N.M.R. Spec.*, 1987, **19**, 267.
11 A. C. Kunwar, G. L. Turner, and E. Oldfield, *J. Magn. Reson.*, 1986, **69**, 124.
12 H. J. Behrens and B. Schnabel, *Physica B.*, 1982, **114**, 185.
13 Y. Hiyama, P. M. Woyciesjes, T. L. Brown, and D. A. Torchia, *J. Magn. Reson.*, 1987, **72**, 1.
14 R. A. Kinsey, PhD Thesis, University of Illinois, Urbana, 1984.
15 M. Magi, E. Lippmaa, A. Samoson, G. Engelhardt, and A.-R. Grimmer, *J. Phys. Chem.*, 1984, **88**, 1518.
16 I. E., Farnan, S. C. Kohn, and R. Dupree, *Geoch. Cosmochim. Acta*, 1987, **51**, 2869.