

Solid-state Scandium-45, Yttrium-89, and Lanthanum-139 Nuclear Magnetic Resonance Spectroscopy

A. R. Thompson and Eric Oldfield*

School of Chemical Sciences, University of Illinois, 505 South Matthews Avenue, Urbana, IL 61801, U.S.A.

We report the first observation of the solid-state nuclear magnetic resonance spectra of the group 3A elements (Sc, Y, and La) in a variety of inorganic solids, which yield chemical shift, and, where applicable, nuclear quadrupole coupling constant and electric field gradient tensor asymmetry parameter information.

The group 3A elements Sc, Y, and La are of considerable technological interest. For example, La^{3+} is a major constituent of 'rare-earth' modified Y-zeolites, of importance in hydrocarbon cracking,¹ and Y_2O_3 - and Sc_2O_3 -containing ceramics are topics of current interest.² Ways of studying the local structure and bonding of Sc, Y, and La are thus required,

and we report herein the first detailed study of the solid-state n.m.r. spectra of a series of 'model compounds.' Previously, Lutz and Oehler reported the solid state ^{139}La chemical shift and linewidth of LaB_6 , which appears however to be a particularly easy case, because of its high symmetry.³ A number of reports of the solution n.m.r. spectra of the group

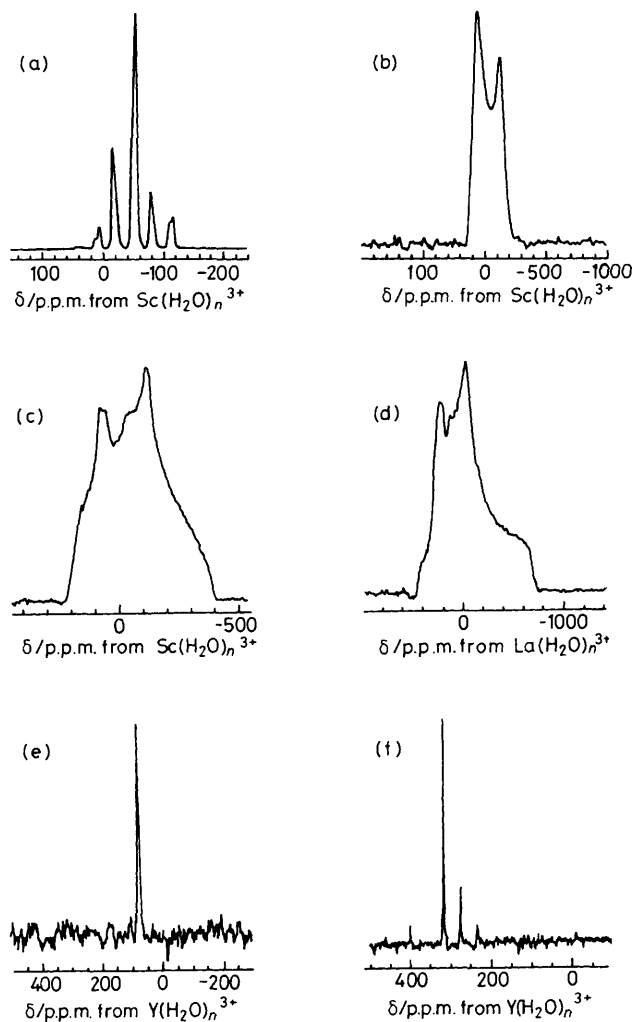


Figure 1. Representative ^{45}Sc , ^{89}Y , and ^{139}La static and m.a.s. n.m.r. spectra. Chemical shift and other simulation parameters are given in Table 1. The total times required per spectrum were as follows: (a), $\text{Sc}(\text{OAc})_3$, 5 min; (b), $\text{Sc}(\text{OAc})_3$, 8 h; (c), $\text{ScCl}_3 \cdot 6\text{H}_2\text{O}$, 13 min; (d), $\text{La}(\text{OAc})_3$, 2 h; (e), $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$, 12 h; and (f), Y_2O_3 , 20 h. All spectra were recorded at 8.45 T, except (b) which was at 3.52 T. (a), (e), and (f) were recorded with m.a.s.

3A elements have also appeared,⁴⁻⁶ but solution n.m.r. techniques are inadequate for a full characterization of solids, such as heterogeneous catalysts or ceramics.

All three nuclei have natural abundances in excess of 99.9%. ^{45}Sc and ^{139}La have $I = 7/2$, and resonate at 87.4 and 50.9 MHz, respectively, in a magnetic field strength of 8.45 Tesla (360 MHz ^1H resonance frequency). ^{89}Y has $I = 1/2$, but resonates at only 17.6 MHz, at 8.45 Tesla. All three nuclei are thus quite sensitive, in n.m.r. terms.

Spectra were recorded at either 3.52, 8.45, or 11.7 Tesla on 'home-built' spectrometers which are described elsewhere.⁷ For observation of the broadest resonances of scandium and lanthanum, a spin-echo sequence was used, to eliminate 'probe ringing'.⁸ ^{89}Y spectra were recorded using 'magic-

Table 1. Solid-state n.m.r. parameters for ^{45}Sc , ^{89}Y , and ^{139}La .

Compound	$(e^2qQ/h)/$ MHz ^a	η	Chemical shift (p.p.m.) ^b
$^{45}\text{Sc}(\text{OAc})_3$	5 ± 0.2	0 ± 0.05	-40 ± 5
$^{45}\text{ScCl}_3 \cdot 6\text{H}_2\text{O}$	14 ± 0.5	0.60 ± 0.05	-30 ± 40
$^{45}\text{Sc}(\text{NO}_3)_3 \cdot 2.5\text{H}_2\text{O}$	5.7 ± 0.2	0.90 ± 0.1	-10 ± 5
$^{45}\text{Sc}_2\text{O}_3$	15 ± 1	0.60 ± 0.20	0 ± 200
$^{89}\text{Y}(\text{OAc})_3$	—	—	45
$^{89}\text{YCl}_3 \cdot 6\text{H}_2\text{O}$	—	—	58
$^{89}\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	—	—	-55
$^{89}\text{Y}_2\text{O}_3$	—	—	$315,^c 270^d$
$^{89}\text{Y}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$	—	—	-50
$^{139}\text{La}(\text{OAc})_3$	11 ± 0.2	0.65 ± 0.05	-30 ± 50
$^{139}\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	21.5 ± 1	0.85 ± 0.05	-100 ± 100

^a Obtained via computer simulation. ^b With respect to 1 M external standards of the respective chlorides. ^c Resonance from one set of crystallographically distinct sites in cubic Y_2O_3 . ^d Resonance from the other crystallographically distinct site.

angle' sample spinning (m.a.s.) n.m.r. methods.⁷ Chemical shifts were referenced to external standards, of 1 M solutions of the appropriate chloride salts in water. Because of the extremely large linewidths, the ^{45}Sc and ^{139}La chemical shifts are only accurate to $ca \pm 5\%$ of the linewidth, while for ^{89}Y the errors are about ± 2 p.p.m. However, for ^{45}Sc and ^{139}La , the most important n.m.r. parameters are likely to be the nuclear quadrupole coupling constant (e^2qQ/h) and the asymmetry parameter of the electric field gradient tensor (η), which can be measured with some accuracy.

We show in Figure 1(a)–(d) representative ^{45}Sc and ^{139}La n.m.r. spectra. Figure 1(a) shows the 8.45 Tesla m.a.s. n.m.r. spectrum of $\text{Sc}(\text{OAc})_3$. Only the central ($1/2, -1/2$) transition is observed, and a complex sideband pattern is obtained. It is thus preferable to obtain a low-field spectrum [3.52 Tesla, Figure 1(b)] to determine e^2qQ/h and η , since the second-order quadrupolar broadening is much larger at low field, and a well resolved powder pattern lineshape may be recorded. The e^2qQ/h and η results of computer simulations of all experimental spectra are given in Table 1, together with the observed chemical shifts. For larger e^2qQ/h values, e.g. for $\text{ScCl}_3 \cdot 6\text{H}_2\text{O}$ [Figure 1(c)] or Sc_2O_3 , high-field static spectra are required in order to reduce the observed linewidths to manageable proportions.

We observed resonances from all the yttrium compounds studied, using single-pulse excitation and m.a.s. methods. Only a broad ($ca. 1$ kHz) resonance could be observed for static samples, owing presumably to dipolar interactions with protons (where present), or to chemical shift anisotropy effects (Y_2O_3). M.a.s. readily removes these interactions, and the resonances are narrowed to $ca. 30$ Hz. A typical result, for $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$, is shown in Figure 1(e). The only compound which had any noticeable chemical shift anisotropy was Y_2O_3 , but it was relatively small ($ca. 150$ p.p.m.), as shown in Figure 1(f). The Y_2O_3 resonance is also split by what appears to be crystallographic inequivalence.⁹ The total range of ^{89}Y shifts is quite large, some 370 p.p.m., with Y_2O_3 clearly the most deshielded.

Taken together, we believe these results demonstrate the practicality of obtaining solid-state n.m.r. spectra of the group 3A elements, ^{45}Sc , ^{89}Y , and ^{139}La , which should open up new areas for study in determining the structures of, for example, certain ceramics and zeolite catalysts.

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