## Oxygen-17 Nuclear Magnetic Resonance Spectroscopic Study of the Lanthanide Oxides

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There is currently considerable interest in determining the electronic structures of the normal states of a variety of high-temperature oxide superconductors (and model systems) containing lanthanide ions, e.g.,  $Ln_{1.85}Ce_{0.15}CuO_4$  (Ln = Pr, Nd, and Sm) (1) and LnBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> (Ln = Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb, Lu) (2), and <sup>17</sup>O solid-state nuclear magnetic resonance spectroscopy has been shown to play a useful role in probing the spin susceptibilities of such systems (3-6). When paramagnetic lanthanide ions are present, e.g. Eu<sup>3+</sup> and Nd<sup>3+</sup>, it is instructive to assess their effects on the observed <sup>17</sup>O NMR spectra (7), and in this Note we report the chemical shifts for most of the simple lanthanide oxides, as a benchmark for further studies on the more complex mixed-metal (high- $T_c$ ) oxides.

<sup>17</sup>O-labeled lanthanide oxides were prepared by heating high-purity oxides in an <sup>17</sup>O<sub>2</sub> atmosphere as described previously ( $\delta$ ). X-ray diffraction powder patterns indicate that, except for Pr<sub>6</sub>O<sub>11</sub>, which had a minority phase of PrO<sub>2</sub>, all samples were single phase (9). Solid-state static and "magic-angle" sample-spinning (MASS) NMR spectra were obtained at 11.7 T (67.76 MHz) using a 5 mm MASS probe (Doty Scientific, Columbia, South Carolina) with either single-pulse or spin-echo excitation (10). Chemical shifts are reported relative to an external standard of tap water, using the convention that high-frequency, low-field, paramagnetic, or deshielded values are positive (International Union of Pure and Applied Chemistry  $\delta$  scale).

Table 1 shows the <sup>17</sup>O NMR chemical shifts of a series of lanthanide oxides. All compounds studied are cubic and have a single oxygen site, except for Nd<sub>2</sub>O<sub>3</sub> and La<sub>2</sub>O<sub>3</sub>, which are hexagonal, with two oxygen sites, assigned on the basis of their integrated intensities. The shifts of La<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>, Pr<sub>6</sub>O<sub>11</sub>, and Eu<sub>2</sub>O<sub>3</sub> have been reported previously (*11*, *12*). Figure 1 shows typical MASS NMR spectra of Sm<sub>2</sub>O<sub>3</sub>, Pr<sub>6</sub>O<sub>11</sub>, Eu<sub>2</sub>O<sub>3</sub>, and Yb<sub>2</sub>O<sub>3</sub>. High-resolution spectra of La<sub>2</sub>O<sub>3</sub>, Nd<sub>2</sub>O<sub>3</sub>, and Tm<sub>2</sub>O<sub>3</sub> were also obtained (data not shown). However, for Gd<sub>2</sub>O<sub>3</sub>, Nd<sub>2</sub>O<sub>3</sub>, Dy<sub>2</sub>O<sub>3</sub>, and Er<sub>2</sub>O<sub>3</sub>, spinning sidebands were much broader, and both static and MASS spectra were used to estimate the isotropic chemical shifts. The decreased resolution is attributed to short transverse relaxation times. For example, the *T*<sub>2</sub> values of Gd<sub>2</sub>O<sub>3</sub> and Er<sub>2</sub>O<sub>3</sub> are both ~90  $\mu$ s, and those of Eu<sub>2</sub>O<sub>3</sub> and Yb<sub>2</sub>O<sub>3</sub> are ~2 ms and 500  $\mu$ s, respectively. We were unable to observe the <sup>17</sup>O NMR spectrum of Ho<sub>2</sub>O<sub>3</sub>, due, we believe, to its extremely short

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### TABLE 1

of some Lanthanide Oxides <sup>a</sup>		
Oxide	Shift (ppm)	Uncertainty (ppm)
La <sub>2</sub> O <sub>3</sub>	$584,^{b} 467^{c} \approx 500^{d}$	±5
	584, <sup>b,e</sup> 467 <sup>c,e</sup>	
CeO <sub>2</sub>	877 <i>d</i>	±5
	878 <sup>e</sup>	
$Pr_6O_{11}$	2,190	$\pm 100$
	$2,150^{d}$	
$Nd_2O_3$	3,040, <sup>b</sup> 1,140 <sup>c</sup>	$\pm 400$
$Sm_2O_3$	10	$\pm 5$
Eu <sub>2</sub> O <sub>3</sub>	-3,290	$\pm 100$
	$-3,212^{d}$	
$Gd_2O_3$	-11,400 <sup>f</sup>	$\pm 1000$
$Dy_2O_3$	-8,800 <sup>f</sup>	$\pm 1500$
Er <sub>2</sub> O <sub>3</sub>	$-6,600^{f}$	$\pm 1000$
$Tm_2O_3$	-4,450	$\pm 200$
$Yb_2O_3$	-1,670	$\pm 100$
Lu <sub>2</sub> O <sub>3</sub>	305	±5

# Solid-State Oxygen-17 NMR Chemical Shifts

<sup>a</sup> In parts per million from an external standard of tap water (IUPAC  $\delta$  scale).

<sup>b</sup> Tetrahedrally coordinated site.

<sup>c</sup> Octahedrally coordinated site.

<sup>f</sup>Estimated from static spectra.

 $T_2$ . For some oxides we also observed a small spinning-rate dependence of the isotropic shift, similar to that reported by Hayashi and Hayamizu (13) for cuprous halides and some inorganic phosphates, which also contributes to the uncertainties given in Table 1.

The paramagnetic shifts observed consist of two components: a through-bond contact shift and a through-space dipolar shift (14). For the contact shift, the change in the effective magnetic field,  $\Delta H$ , at the NMR nucleus, due to the unpaired f electrons is (14)

$$\left(\frac{\Delta H}{H}\right)_{mn}^{\text{con}} = \mathbf{a} \, \frac{\langle S_z \rangle_m}{g_n \beta_n H},\tag{1}$$

where **a** is the hyperfine interaction constant,  $\langle S_z \rangle$  is the averaged spin moment, and m and n represent the lanthanide ion and the NMR-observed nucleus, respectively. Golding and Halton (15) have calculated  $\langle S_z \rangle$  using second-order perturbation theory, and we show in Fig. 2 the relationship between the <sup>17</sup>O chemical shift of each of the lanthanide oxides (Table 1) and  $\langle S_z \rangle$  (15), together with, for comparison, corresponding shifts of H<sub>2</sub><sup>17</sup>O in aqueous lanthanide ion solutions, reported by Lewis et

<sup>&</sup>lt;sup>d</sup> Ref. (11).

e Ref. (12).



FIG. 1. <sup>17</sup>O MASS NMR spectra of some lanthanide oxides acquired at 11.7 T (67.76 MHz). (a)  $Pr_6O_{11}$ , (b)  $Eu_2O_3$ , (c)  $Sm_2O_3$ , (d)  $Yb_2O_3$ . A single-pulse technique and spinning speed of 9 kHz were used for  $Pr_6O_{11}$  and  $Sm_2O_3$ . A spin-echo experiment with a spinning speed of 14.5 kHz was used for  $Eu_2O_3$  and  $Yb_2O_3$ .

*al.* (16). For Nd<sub>2</sub>O<sub>3</sub> and La<sub>2</sub>O<sub>3</sub>, only the shift of the tetrahedrally coordinated oxygen site is included. The linear relationship between the average spin moments and the <sup>17</sup>O NMR shifts of the Ln<sup>3+</sup> ion containing aqueous solutions and those of the oxides indicates a common origin and confirms that the solid-state shifts are the result of the contact interaction (15, 16). Similar results for several lanthanide salts have been reported previously and show similar trends (17–19).

Assuming **a** is constant amongst the lanthanide oxides, by using the slope of  $\langle S_z \rangle$  versus the solid-state <sup>17</sup>O NMR chemical shifts, we find a value of -2.7 MHz for **a**, corresponding to a hyperfine field ( $H_{\rm h\,f} = \mathbf{a}/g_n\beta_n$ ) of 4.74 kOe. The magnitude of the hyperfine field is between that observed in the lanthanide phosphides [LnP, ~16 kOe; Ref. (18)] and the more dilute lanthanide fluorides [LnF<sub>3</sub>, ~1.5 kOe; Ref. (18)]. The positive sign of  $H_{\rm h\,f}$  is consistent with the general antiparallel spin transference to nearest neighbors seen with the 4f systems (18).

The results that we have shown above are in general accord with the shifts and linewidths observed in the oxide superconductors  $EuBa_2Cu_3O_7$  (7) and  $Nd_{1.85}Ce_{0.15}CuO_4$  (unpublished results). In  $EuBa_2Cu_3O_7$  (7), we find a 1000 ppm shift to lower frequency for the  $CuO_2$  planar oxygen with respect to that of  $YBa_2Cu_3O_7$ .





FIG. 2. Plots of the <sup>17</sup>O NMR chemical shifts for solid lanthanide oxides ( $\bullet$ , left), and H<sub>2</sub> <sup>17</sup>O in aqueous lanthanide ion solutions [O, right; from Ref. (16)], as a function of  $\langle S_z \rangle$ , the calculated spin moment [Ref. (15)]. The straight line is a best fit to the lanthanide oxide data and was used to calculate the hyperfine coupling constant, **a** (see text).

In Nd<sub>1.85</sub>Ce<sub>0.15</sub>CuO<sub>4</sub>, there is an overall line broadening, as with Nd<sub>2</sub>O<sub>3</sub>, with the center of gravity of the broad peak being shifted by  $\approx 1500$  ppm to higher frequency from that seen in the lanthanum cuprates (11), both results being due, we believe, to the contact interaction.

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