# Solid-State Oxygen-17 Nuclear Magnetic Resonance Spectroscopic Study of the Group II Oxides\*

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We have obtained the solid-state oxygen-17 nuclear magnetic resonance spectra of the group IIA and group IIB oxides (BeO, MgO, CaO, SrO, BaO, ZnO, CdO, and HgO) using high-field (8.45 and 11.7 T) static and "magic-angle" sample-spinning techniques. The results indicate a chemical-shift range of more than 600 ppm for the group II oxides, and a range of oxygen-17 nuclear quadrupole coupling constants  $(e^2qQ/h)$  from ~0 (CaO, SrO, BaO) to about 7 MHz (for HgO). The chemical shifts observed for the group IIA oxides are well fitted by an equation of the form  $\delta$  (ppm, from H<sub>2</sub>O) = 257r<sup>3</sup> (Å<sup>3</sup>) + 11, where r is the ionic radius of the metal cation. The  $e^2qQ/h$  values increase with increasing metal electronegativity and thus decrease on descending group IIA, but increase on descending group IIB. (a) 1985 Academic Press, Inc.

Recently, we reported the solid-state oxygen-17 nuclear magnetic resonance spectra of a variety of oxide and silicate phases (1, 2) by means of high-field observation of the central  $(\frac{1}{2}, -\frac{1}{2})$  transition of the spin  $I = \frac{5}{2}$  oxygen-17 nucleus. These results, and those reported in this article, represent part of a program aimed at determining the details of structure and bonding in a variety of technologically and geochemically interesting materials, such as zeolites and other catalysts, ceramics, glasses, and many mineral phases. To provide a basis for interpretation of results obtained on less well characterized, amorphous materials, we have now investigated the oxygen-17 NMR spectra of the group IIA (BeO, MgO, CaO, SrO, and BaO) and group IIB (ZnO, CdO, and HgO) oxides, and present our findings in this publication. Our results indicate an increase in the ionic nature of the M-O bond on descending group IIA, but a large increase in covalence on descending group IIB, as expected on the grounds of the Pauling electronegativities of the respective metallic elements, the total range of quadrupole coupling constants  $(e^2 qQ/h)$  varying from  $\sim 0$  to  $\sim 7$  MHz. The total range of oxygen-17 chemical shifts for the group II oxides is over 600 ppm, and a good correlation between metal-ion radius and oxygen-17 shift is observed, in accord with previous investigations. Oxygen-17 shifts become more deshielded with increase in metal-ion radius. These results should help form the basis for future studies of mixed oxide phases, whose structures are less well defined, and in addition, they may help provide new insights into the bonding which exists in the metal oxides themselves, by

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providing a new data base on oxygen-17 chemical shifts, quadrupole coupling constants, and their asymmetry parameters.

#### EXPERIMENTAL ASPECTS

All oxides (except HgO) were prepared by calcination of <sup>17</sup>O-labeled metal carbonates or hydroxides. Be<sup>17</sup>O, Ca<sup>17</sup>O, and Cd<sup>17</sup>O were prepared by first enriching K<sub>2</sub>CO<sub>3</sub> with <sup>17</sup>O by exchange in H<sub>2</sub><sup>17</sup>O at ~80°C for several days, then precipitating the metal carbonates by addition of BeCl<sub>2</sub>, CaCl<sub>2</sub>, or CdCl<sub>2</sub> in H<sub>2</sub><sup>17</sup>O, followed by washing and calcining. Mg(NO<sub>3</sub>)<sub>2</sub>, SrI<sub>2</sub> · 6H<sub>2</sub>O, Zn(NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O, and Hg(NO<sub>3</sub>)<sub>2</sub> were dissolved in H<sub>2</sub><sup>17</sup>O, then KOH in H<sub>2</sub><sup>17</sup>O was added to precipitate the respective hydroxides or hydrous oxides, which were subsequently washed and (except for HgO) calcined. Hg<sup>17</sup>O (yellow form) was dried over P<sub>4</sub>O<sub>10</sub> immediately after washing. BaO (unenriched) was obtained from Aldrich Chemical. H<sub>2</sub><sup>17</sup>O (30–40 at.% <sup>17</sup>O) was obtained from Merck Sharpe & Dohme (Montreal, Canada) or from Cambridge Isotope Laboratories (Cambridge, Mass.). All other reagents were of the highest purity commercially available, and were generally recrystallized and dried before use. All <sup>17</sup>O-labeled oxides had satisfactory elemental analyses, and X-ray powder diffraction data (obtained using a Rigaku-Miniflex (Danvers, Mass.) Model 2005 diffractometer).

NMR spectra were obtained on "home-built" 8.45 and 11.7 T spectrometers using the methods described previously (1, 2). Pulse widths used on solid samples were 5–7  $\mu$ s (H<sub>2</sub>O reference 90° pulsewidth = 16–22  $\mu$ s). Chemical shifts are reported in ppm from external H<sub>2</sub>O, larger positive values correspond to low-field, high-frequency, paramagnetic, deshielded values ( $\delta$  scale). Accuracies are ±1 to ±2 ppm except for HgO, where the error may be as much as ±18 ppm.

## **RESULTS AND DISCUSSION**

We show in Fig. 1 the solid-state oxygen-17 "magic-angle" sample-spinning (MASS) NMR spectra of the group IIA oxides: BeO, MgO, CaO, SrO, and BaO. With the exception of BaO, all spectra were recorded at 11.7 T (corresponding to an oxygen-17 resonance frequency of 67.8 MHz), but spectra of BeO and MgO were also recorded at 8.45 T (corresponding to an oxygen-17 a resonance frequency of 48.8 MHz), their chemical shifts being identical (within experimental error) at the two magnetic field strengths. The spectrum of BaO was obtained at 8.45 T on a sample containing only natural abundance (0.037%) oxygen-17. The results of Fig. 1 illustrate two important points: First, increasing the radius of the metal ion, from Be<sup>2+</sup> (0.31 Å) to Mg<sup>2+</sup> (0.65 Å), to Ca<sup>2+</sup> (0.99 Å), to Sr<sup>2+</sup> (1.13 Å), to Ba<sup>2+</sup> (1.35 Å) (3), correlates with a very large deshielding of the oxygen-17 resonance, from 26 to 629 ppm downfield from H<sub>2</sub>O, a total range of some 603 ppm (Table 1).

Previous workers have found linear correlations between cation radius and anion chemical shift (2, 4-7). Our results yield a moderately good correlation between  $\delta$  and r (the correlation coefficient is 0.95 including Be<sup>2+</sup>, which has no p electrons, 0.98 without Be<sup>2+</sup>), but the results of log-log plots indicate that much better correlations are to be found between  $\delta$  and  $r^3$ , as follows (Fig. 2)

$$\delta = 257r^3 (\dot{A}^3) + 11.$$
<sup>[1]</sup>



FIG. 1. Oxygen-17 solid-state MASS NMR spectra of the group IIA oxides. (A) BeO, 8.45 T, 0.9 kHz MASS, 2352 scans, 30 s recycle time, 50 Hz line broadening. (B) MgO, 8.45 T, 0.9 kHz MASS, 284 scans, 30 s recycle time, 10 Hz line broadening. (C) CaO, 11.7 T, 4.5 kHz MASS, 60 scans, 30 s recycle time, 5 Hz line broadening. (D) SrO, 11.7 T, 4.1 kHz MASS, 1604 scans, 30 s recycle time, 10 Hz line broadening. (E) BaO, 8.45 T, 1.1 kHz MASS, 664 scans, 5 s recycle time, 10 Hz line broadening. The isotropic chemical shifts are indicated, and are in ppm from an external standard of tap water. The numerous sidebands present in (A) and (B) are due to the satellite transitions. Estimated errors are  $\pm 1$  to  $\pm 2$  ppm, depending on the linewidth and single-to-noise ratio.

Here, the correlation coefficient is 0.99 when all data points are included. A similar relation also appears to hold for the group IIB elements whose spectra we discuss below. In that case, although only based on three data points, we find

$$\delta = 150r^3 \,(\text{\AA}^3) - 78.$$
[2]

The second interesting point about the results of Fig. 1 is that there is clearly a trend toward a decrease in the number and intensity of the spinning sidebands, which arise from the satellite  $(\pm \frac{1}{2}, \pm \frac{3}{2}; \pm \frac{3}{2}, \pm \frac{5}{2})$  transitions, on going down group IIA. This is especially evident in the slow-spin (~1 kHz) spectra of BeO and MgO vs CaO, SrO, and BaO, and implies a decrease in the value of the <sup>17</sup>O quadrupole coupling constant with decreasing electronegativity of the metal, as noted previously (2), due to the increased ionic nature of the M-O bond. For BeO, we can estimate from Fig. 1 that  $e^2 qQ/h$  is ~20 kHz, which correlates with the ~63% ionic nature of the Be-O bond (from the respective Pauling electronegativities), while for MgO we can estimate that  $e^2 qQ/h$  is ~14 kHz. For CaO, SrO, and BaO,  $e^2 qQ/h$  values are all ~0, which correlates with the  $\sim 80\%$  ionic nature of the Ca–O, Sr–O, and Ba–O bonds. These results also, of course, imply significant distortions of the cubic NaCl-type structure of MgO, and presumably of the wurtzite structure of BeO, and at present we cannot dissect the relative ionicity/distortion contributions in order to fully analyze the observed  $e^2qQ/$ h values. Such trends are even more pronounced in the group IIB species, as discussed below.

#### TABLE 1

Oxide	Chemical shift (ppm from H <sub>2</sub> O)	Quadrupole coupling constant (kHz)	Metal-ion radius (Å) <sup>a</sup>	
BeO	26	~20	0.31	
MgO	47	~14	0.65	
CaO	294	<5	0.99	
SrO	390	<5	1.13	
BaO	629	<5	1.35	
ZnO	-18	~130	0.74	
CdO				
200°C <sup>b</sup>	141	NM	0.97	
300°C <sup>b</sup>	81	NM	0.97	
550°C*	46	NM	0.97	
800°C*	51	NM	0.97	
900°C"	71	NM	0.97	
HgO	121	~7100	1.10	

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<sup>a</sup> Ref. (3).

<sup>b</sup> Calcination temperature: CdO from Cd(OH)<sub>2</sub>.

<sup>c</sup> Calcination temperature; CdO from CdCO<sub>3</sub>.

We show in Fig. 3 our results on the group IIB oxides: ZnO, CdO and HgO (yellow form). Figure 3A shows the 67.8 MHz (11.7 T) oxygen-17 MASS NMR spectrum of ZnO, which clearly indicates the central  $(\frac{1}{2}, -\frac{1}{2})$  transition at -18.4 ppm, together



FIG. 2. Plot of group II oxide oxygen-17 chemical shift versus the cube of the metal-ion radius. The straight line is the least-squares fit to the group IIA oxide data and the dashed line to the group IIB oxide data. A value of 60 ppm was used for CdO.



FIG. 3. Solid-state oxygen-17 NMR spectra of the group IIB oxides at 11.7 T (corresponding to an oxygen-17 resonance frequency of 67.8 MHz). (A) ZnO, 1.7 kHz MASS, 464 scans, 30 s recycle time, 5 Hz line broadening. (B) CdO (200° calcination temperature, prepared from Cd(OH)<sub>2</sub>), 6.1 kHz MASS, 1217 scans, 10 s recycle time, 200 Hz line broadening, (C) CdO (800° calcination temperature, prepared from Cd(OH)<sub>2</sub>), 4.2 kHz MASS, 3312 scans, 1 s recycle time, 100 Hz line broadening. (D) HgO (yellow form), static sample, 744 scans, 60 s recycle time, 500 Hz line broadening.

with a large number of spinning sidebands, which arise from the satellite transitions. Spectral simulation of a static spectrum of ZnO (data not shown) yields  $e^2 qQ/h = 130$  kHz. The increase of the <sup>17</sup>O  $e^2 qQ/h$  value in ZnO over that in BeO can be best rationalized by comparing their crystal structures. Both contain linked MO<sub>4</sub> tetrahedra, but the distortions from a perfect tetrahedron differ. If we define the deviation from a perfect tetrahedron as

$$D = \sum_{n=1}^{n} |109.5 - \theta_{\text{O-M-O}}|/n$$
 [3]

where 109.5 is the tetrahedral angle,  $\theta_{O-M-O}$  is the oxygen-cation-oxygen bond angle, and *n* is the total number of angles, we find that *D* is 1.35° for ZnO but only 0.5° for BeO (8, 9). It appears, therefore, for structurally similar oxides that  $e^2qQ/h$  values are a very sensitive measure of crystallographic distortion, which presumably arises in this case at least in part because of the increased covalence of ZnO over that of BeO.

Our results for CdO and HgO are far more complex. For CdO, the oxygen-17 MASS

NMR spectra are very dependent upon the detailed thermal history of the sample, since as Shatlock and Maciel have shown (10) the following reactions

$$CdO \rightarrow Cd(s) + \frac{1}{2}O_2(g)$$
 [4]

$$\operatorname{Cd}(s) \to \operatorname{Cd}(g)$$
 [5]

occur during the preparation of CdO (from CdCO<sub>3</sub> or Cd(OH)<sub>2</sub>), leading to a nonstoichiometric oxide (CdO-Cd). The amount of excess cadmium is typically a few hundredths of a percent (10), but being metallic, this leads to extensive spectral linebroadening and spectral shifts. We show in Figs. 3B,C oxygen-17 MASS NMR spectra of CdO formed by calcining Cd(OH)<sub>2</sub> in N<sub>2</sub> at 200 and 800°C, respectively. As discussed by Shatlock and Maciel, high-temperature calcination (in air) yields narrower line (cadmium-113) spectra, due to decreased Cd(O) levels.

To help correlate our <sup>17</sup>O NMR results with those of Shatlock and Maciel, we have obtained the <sup>113</sup>Cd NMR spectra of our Cd<sup>17</sup>O samples, using MASS NMR at 8.45 T (corresponding to a <sup>113</sup>Cd resonance frequency of 79.9 MHz), and we show in Fig. 4 and Table 2 <sup>17</sup>O and <sup>113</sup>Cd MASS NMR results on CdO samples prepared at 900°C (from CdCO<sub>3</sub>) and at 800°C (from Cd(OH)<sub>2</sub>). The <sup>17</sup>O spectra have chemical shifts and linewidths of 71, 10 ppm (900°C) and 51, 18 ppm (800°C), while the <sup>113</sup>Cd spectra exhibit shifts (in ppm from Cd(ClO<sub>4</sub>)<sub>2</sub> · 6H<sub>2</sub>O) and linewidths of 453, 35 ppm (900°C) and 364, 79 ppm (800°C). The <sup>113</sup>Cd results are in moderate accord with



FIG. 4. Oxygen-17 and cadmium-113 MASS NMR spectra of CdO samples. (A) Oxygen-17 MASS NMR spectrum of CdO (from 900° CdCO<sub>3</sub> calcination in N<sub>2</sub>) at 11.7 T, 4.2 kHz MASS, 3656 scans, 1 s recycle time, 20 Hz line broadening. (B) Oxygen-17 MASS NMR spectrum of CdO (from 800° Cd(OH)<sub>2</sub> calcination in N<sub>2</sub>) at 11.7 T, 4.2 kHz MASS, 3312 scans, 1 s recycle time, 100 Hz line broadening. (C) Cadmium-113 MASS NMR spectrum of CdO (sample from (A)) at 8.45 T, 3.3 kHz MASS, 4900 scans, 10 s recycle time, 100 Hz line broadening. (D) Cadmium-113 MASS NMR spectrum of CdO (sample from (B)) at 8.45 T, 3.0 kHz MASS, 3116 scans, 10 s recycle time, 100 Hz line broadening.

Source	Calcination temperature (°C)	Oxygen-17		Cadmium-113	
		Linewidth <sup>a</sup>	Chemical shift <sup>b</sup>	Linewidth <sup>a</sup>	Chemical shift <sup>c</sup>
Cd(OH <sub>2</sub> )	800	18	51	79	364
CdCO <sub>3</sub>	900	10	71	35	453

TABLE	2
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## Oxygen-17 and Cadmium-113 MASS NMR Spectral Parameters for CdO

" In parts per million.

<sup>b</sup> In parts per million from H<sub>2</sub>O.

<sup>c</sup> In parts per million from Cd(ClO<sub>4</sub>)<sub>2</sub> · 6H<sub>2</sub>O.

those reported previously, of 440, 117 ppm (800°C), given the differences in sample preparation and the great sensitivity to Cd(O). In any case, our results indicate that the <sup>17</sup>O linewidths are only about 25% of the <sup>113</sup>Cd linewidths (29% for CdO (900°C, CdCO<sub>3</sub>); 23% for CdO (800°C, Cd(OH<sub>2</sub>)), which we interpret as indicating inhomogeneously broadened lines *both* for <sup>17</sup>O and <sup>113</sup>Cd, due to the existence of a distribution of Cd(O) atoms in the CdO–Cd solid solution (*10*). Certainly, the linewidths observed cannot be due to the dominance of a bulk magnetic susceptibility broadening due to the cadmium metal atoms since then the <sup>17</sup>O and <sup>113</sup>Cd lines would have the same width (in ppm), or the <sup>17</sup>O lines would be even broader than the <sup>113</sup>Cd resonance, due to additional quadrupolar broadening contributions in the case of oxygen-17. We were unsuccessful in observing <sup>113</sup>Cd spectra for the other CdO samples, presumably because of their greatly increased width, due to increased Cd(O). Shatlock and Maciel (*10*) did observe such spectra, but our lines are expected to be about twice as broad (in hertz) due to the higher magnetic field strength we employed.

The results of Fig. 4 and Table 2 thus indicate that the true, isotropic shift of CdO (no Cd(O)) is  $\sim 60 \pm 10$  ppm. As anticipated, the increase in the ionic radius of Cd<sup>2+</sup> (0.97 Å) over that of Zn<sup>2+</sup> (0.74 Å) (3) correlates with a significant deshielding, Table 1, Fig. 2 and Eq. [2].

We show in Fig. 3D the static 67.8 MHz oxygen-17 NMR spectrum of HgO (yellow form). Our results with HgO are unusual for a group II oxide, but are consistent with the unique structure of this material, which contains Hg-O-Hg-O chains with only weak interchain interactions (11)



Thus, the structure of HgO differs radically from that of the highly symmetric NaCl, wurtzite, or zinc blend structures of the other group II oxides.

The large electronegativity of Hg ( $\sim$ 1.8 to 2.0, depending on the methods chosen to calculate EN) predicts a rather covalent bond, and using the empirical correlation developed previously (2), we can estimate an oxygen-17 quadrupole coupling constant of  $\sim$ 4.8–6.5 MHz. Thus, MASS NMR methods are expected to yield a complex series of spinning sidebands, and we thus chose to record static <sup>17</sup>O NMR spectra of HgO in order to obtain  $e^2 q Q/h$ ,  $\eta$  and  $\delta$  information, as shown in Fig. 3D. Computer simulation of the results of Fig. 3D, and of additional results obtained at 8.45 T (data not shown) yields  $e^2 qQ/h \approx 7.1$  MHz and  $\eta = 0.3$  at both field strengths, and  $\delta \sim 121$  $\pm$  18 ppm, the chemical shift being in accord with the deshielding expected due to increased ionic radius. The observed  $e^2 q Q/h$  is, however, about 10-50% greater than that predicted from the empirical correlation (2). There are a number of possible reasons for this. First, the correlation discussed in Ref. (2) contains points from a number of species which may engage in  $\pi$  backbonding with oxygen. However, bond lengths in HgO indicate that there are only single Hg–O bonds with sp hybridization (12), and for mercury the d orbitals are full, so there is no  $\pi$  backbonding, which leads to a larger O<sub>z</sub> imbalance, and thus a larger  $e^2 qQ/h$  value. If we assume  $sp^3$  hybridization at oxygen, we obtain  $e^2 qQ/h \sim 8.1$  MHz, using a Townes-Dailey approach. Then, however, assuming  $C_{2\nu}$  symmetry, we expect  $\eta \sim 1.0$ , whereas we observe  $\eta \sim 0.3$ . Thus, while predictions based on simple electronegativity differences do give reasonably accurate  $e^2 q Q/h$  predictions, the presence of additional effects, perhaps involving interchain interactions, clearly affect  $e^2 qQ/h$  and  $\eta$  values, so that much more detailed electric field gradient calculations need to be performed in the future to extract the maximum amount of information possible from the NMR results. Our results provide the experimental basis for such calculations.

The results we have presented above are of interest for a number of reasons. First, they indicate that the range of <sup>17</sup>O chemical shifts of the group II oxides is extremely large, over 600 ppm, so it should be possible to readily detect small domains of alkaline earth oxides, if they exist, in more complex materials, such as some ceramics. Both the group IIA and group IIB chemical shifts are shown empirically to depend linearly on  $r^3$ , where r in the radius of the metal cation. The significance of this correlation is not immediately obvious, and the  $r^3$  dependence is probably fortuitous since different exponents are found in other systems, such as the alkaline earth silicates (unpublished results). Our results with the group II oxides do, however, parallel those found previously by others with the isoelectronic group IA fluorides, in which there is a monotonic deshielding of the <sup>19</sup>F resonance with increasing cation radius (13). The second interesting feature of our results in that the observed  $e^2 q Q/h$  values are in general agreement with those predicted on the basis of the electronegativity considerations discussed previously (2). For the more ionic systems, small increases in covalence (based on electronegativity differences) lead to increased deviation from tetrahedral bond angles for the respective MO<sub>4</sub> units, a trend which reaches its limit in the ribbon-like HgO structure.

Note added in proof: The <sup>17</sup>O chemical shifts for MgO, CaO and BaO are in accord with those given by Maciel *et al.* (Abstract II-B-14, 25th Experimental NMR Conference, Wilmington, Delaware, April 8-12, 1984).

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## REFERENCES

- 1. S. SCHRAMM, R. J. KIRKPATRICK, AND E. OLDFIELD, J. Am. Chem. Soc. 105, 2483 (1983).
- 2. S. SCHRAMM AND E. OLDFIELD, J. Am. Chem. Soc. 106, 2502 (1984).
- 3. J. E. HUHEEY, "Inorganic Chemistry," p. 73, Harper & Row, New York, 1972.
- 4. Q. ZH. GUO AND R. E. J. SEARS, J. Magn. Reson. 57, 143 (1984).
- 5. R. E. J. SEARS, J. Chem. Phys. 72, 2888 (1980).
- 6. R. E. J. SEARS, J. Chem. Phys. 76, 5651 (1982).
- 7. R. E. J. SEARS, J. Chem. Phys. 59, 973 (1973).
- 8. S. C. ABRAHAMS AND J. L. BERNSTEIN, Acta Crystallogr. Sect. B 25, 1233 (1969).
- 9. G. A. JEFFFREY, G. S. PARRY, AND R. L. MOZZI, J. Chem. Phys. 25, 1024 (1956).
- 10. M. P. SHATLOCK AND G. E. MACIEL, J. Chem. Phys. 81, 895 (1984).
- 11. K. AURIVILLIUS, Acta Chem. Scand. 18, 1305 (1964).
- 12. K. AURIVILLIUS, Acta Chem. Scand. 10, 852 (1956).
- 13. R. E. J. SEARS, J. Chem. Phys. 59, 5213 (1973).