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Probing the local structural environment of calcium by natural-abundance solid-state ^{43}Ca NMR

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New natural-abundance ^{43}Ca magic angle spinning (MAS) NMR data measured at high magnetic field (14.1 T) is presented for a range of crystalline calcium-containing binary and ternary inorganic compounds. The combination of high field, moderate MAS (up to 4.5 kHz), and large sample volume (a 9.5 mm diameter MAS rotor) means that a good signal-to-noise ratio can generally be obtained in a time ($\sim$12 h) that makes ^{43}Ca NMR a feasible approach for determining information about calcium siting in a wide range of materials of physical interest. This study greatly increases the number of ^{43}Ca NMR parameters determined for solid materials in the literature, extending reports to local nearest-neighbor coordinations to other than oxygen. These data show that the isotropic chemical shift range is >250 ppm and typically that the quadrupole interaction is <4 MHz. In ternary compounds where Ca is coordinated in the nearest-neighbor shell by only oxygen, the isotropic ^{43}Ca chemical shift correlates well to the mean Ca-O distance, consistent with the only previous study. In binary compounds the isotropic ^{43}Ca chemical shift does not appear to be correlated with the mean Ca-X bond length. The extension of natural-abundance ^{43}Ca MAS NMR studies to amorphous materials are reported by examining sol-gel prepared calcium silicate materials. The data show that in the initial amorphous mixture at lower temperatures (120–350°C) the calcium environment is more like that in the parent calcium nitrate than a silicate, and that further heat treatment causes very significant broadening of the calcium resonance. The implications of this observation for the use of natural-abundance ^{43}Ca MAS NMR structural studies of amorphous materials are examined.

I. INTRODUCTION

High-resolution solid-state NMR based around the magic angle spinning (MAS) technique has become an increasingly important probe method for many aspects of the physical sciences over the last two decades.[1] However, although there are NMR-active nuclei across almost all of the periodic table, a large majority of the NMR reports in the literature concern only a small fraction of the potentially accessible NMR-active nuclei. This imbalance results from many nuclei being regarded as "difficult" for routine observation. These difficulties include poor sensitivity through low natural-abundance, significant residual second-order quadrupole broadening effects, and long relaxation times.[1] These effects are exacerbated for nuclei with small magnetic dipole moments (which have been termed low γ because of their small gyromagnetic ratio). However, a range of potentially very important nuclei fall into this category of low-γ quadrupolar nuclei including ^{25}Mg, ^{33}S, ^{35,37}Cl, ^{43}Ca, ^{47,49}Ti, and ^{91}Zr.[1,2] In the last decade, considerable progress has been made in solid-state NMR investigations of these nuclei. The impetus for much of the progress in solid-state NMR, but especially for these low-γ nuclei, has been provided by the increased availability of higher magnetic fields (e.g., $\geqslant$14.1 T) with sufficient homogeneity for high resolution spectroscopy. Among the low-γ nuclei, solid-state ^{43}Ca NMR data are still relatively scarce, despite its importance in many scientifically and technologically significant solids such as glasses, cements, ceramics, minerals, superconductors, sol-gel materials, magnetic materials, and biomaterials. Experimental dif-

ficulties that have led to this scarcity of data include its low natural abundance of only 0.135%, its low gyromagnetic moment, and its possessing a quadrupole moment. In most solid-state NMR studies of quadrupole nuclei it is usually the central $(1/2, -1/2)$ transition that is observed where second-order quadrupole broadening becomes significant.[3] The inverse dependence of this second-order quadrupole effect on the Larmor frequency means it is a more significant broadening mechanism for low-γ nuclei (at a particular magnetic field). Although ^{43}Ca is a low-γ nucleus, its relatively high spin (7/2) and its quite small nuclear electric quadrupole moment mean that it should generally experience relatively small second-order quadrupole broadening of the central transition. For example, compared to ^{27}Al, which is commonly studied by solid-state NMR, in a site with the same structural distortion, ^{43}Ca would experience only 0.14 of the broadening of the central transition of ^{27}Al.[3] Nearly all the solid-state ^{43}Ca NMR studies published to date have been on expensive enriched (>50% ^{43}Ca) samples, and have included calcium acetate,[4] high-temperature ceramic superconductors, such as $(Bi,Pb)_2Sr_2CaCu_2O_{8+x}$,[5–7] sol-gel prepared calcium silicate materials,[8] and model crystalline compounds such as CaO, Ca(OH)$_2$, and CaCO$_3$.[9]

The first natural-abundance ^{43}Ca solid-state NMR study was by Dupree *et al.* who investigated 12 calcium-containing crystalline inorganic samples, and found that the ^{43}Ca chemical shift covered $\sim$160 ppm, and the shift correlated well with the mean Ca-O distance of the first coordination shell of calcium within the same class of compounds (e.g., silicates,

carbonates, etc.).[10] This initial study was carried out at a magnetic field of only 8.45 T. Despite using a very large diameter rotor (14 mm) the signal-to-noise ratio was such that most of the lines were relatively featureless, making it difficult to extract useful quadrupolar interaction parameters. However, the potential high sensitivity of ^{43}Ca NMR to local structural detail was illustrated by the comparison of the polymorphs of $CaCO_3$, calcite, and aragonite. The resonances showed a shift difference of $\sim$50 ppm, with calcite giving a second-order quadrupole line shape under MAS, and aragonite showing measurable chemical shift anisotropy in the static spectrum.[10] Since this initial natural-abundance study the only other reports of ^{43}Ca at natural abundance have been from the calcium aluminates $CaAl_4O_7$ and $CaAl_{12}O_{19}$,[11] and $CaTiO_3$.[12] In the case of $CaAl_{12}O_{19}$ only a narrow resonance at -52.6 ppm was observed. In the other two cases distinct second-order quadrupole line shapes were observed with quadrupole coupling constants (χ_Q) of 3.5 and 2.15 MHz, and asymmetry parameters of 0.1 and 0.7 for $CaAl_4O_7$ and $CaTiO_3$, respectively.

All the ^{43}Ca NMR from diamagnetic, insulating solids to date has involved calcium environments where the local coordination is exclusively to oxygen. In this paper ^{43}Ca NMR data are presented for a range of inorganic compounds measured at the relatively high magnetic field for high resolution NMR of 14.1 T, including samples where calcium has halogens, group VI, IV, and III nonmetallic elements in the first coordination sphere. Ca-X bonds (X refers here to halogen, sulfur, oxygen, and other nonmetallic elements) in most calcium-containing inorganic compounds are ionic, which should generally give rise to small values of χ_Q. Hence line narrowing should be achieved at relatively modest MAS rates ($2-4$ kHz) so that large diameter sample rotors ($9.5-14$ mm) can be used which significantly alleviate the sensitivity problems, especially when combined with the higher magnetic fields used here compared to previous studies. These data considerably expand the number of calcium NMR parameters available, which places better constraints on the range of chemical shifts for calcium, tests the correlations to Ca-O bond lengths previously proposed, and develops a better understanding of how changes in the nearest-neighbor coordination affect the shift of calcium in solids. The signal-to-noise ratios obtained here show considerable improvement over most of the previous natural-abundance data, which enables the quadrupolar interaction parameters to be readily obtained from simulation of the spectra when they display a characteristic second-order quadrupolar lineshape. ^{43}Ca natural-abundance NMR data are also presented from amorphous solids by examination of sol-gel prepared calcium silicate samples. Many specialist techniques[1] are available to the solid-state NMR spectroscopist but to make the results of the work here as accessible as possible for the widest range of potential beneficiaries, data from simple one-pulse sequences are presented that can be readily implemented. ^{43}Ca NMR is potentially a very important physical probe that could be applied to a wide range of problems ranging from high-temperature superconductors to the calcium centers in biomolecules. The implications of these observations for the use of ^{43}Ca NMR to probe structure are discussed.

II. EXPERIMENTAL METHOD

Most of the samples examined here were either natural minerals or bought directly from commercial suppliers. X-ray diffraction patterns were collected, and all of these samples were determined to be single phase ($>$98%) except CaC_2, which appeared to be a mixture of phases/polymorphs. The sol-gel prepared $CaSiO_3$ samples were synthesized by adding small amounts of water and the stoichiometric quantity of $Ca(NO_3)_2$ sequentially to a tetraethylorthosilicate solution in anhydrous ethanol under acidic catalysis, stirring all the time. Various compositions $(CaO)_x(SiO_2)_{1-x}$ were examined with x in the range 0.3–0.5. After $5-10$ h of stirring the samples were aged and dried (70°C) for 4–6 days, and then heated at 120°C for $\sim$2 h. The samples were then successively heated to 350 and then 500°C.

All ^{43}Ca solid-state NMR spectra of were acquired using a Chemagnetics-Varian CMX-600 spectrometer operating at a frequency of 40.39 MHz with a 9.5 mm Chemagnetics MAS probe using spinning speeds of 3.5–4.5 kHz. Spectra were acquired using a one-pulse acquire sequence with typically a pulse width of 3 μs ($<$90°). Acquisition delays of between 0.5 and 5 s were necessary to produce fully relaxed spectra. Between 4000 and 350 000 acquisitions were needed to obtain spectra with adequate signal-to-noise ratio, depending on the nature of the sample. Spectra of samples with narrow lines, such as CaS can be obtained within 1 to 2 h. Overnight acquisition was sufficient for most other samples, although for some materials like wollastonite, 2–3 days were required. The chemical shifts are quoted externally, relative to the accepted shift reference of saturated aqueous $CaCl_2$ solution. Spectral simulations were carried out using the DMFIT program.[13]

III. RESULTS

The samples investigated and the NMR parameters deduced from the resonances observed are listed in Table I, together with some of the compounds' structural parameters. Most samples gave relatively featureless spectra, as shown in Fig. 1. The lines are quite narrow for a low-γ quadrupole nucleus, with line widths typically in the range $400-800$ Hz. Some spectra displayed characteristic second-order quadrupolar line shapes, which are shown in Fig. 2 together with spectral simulations. In general, the signal-to-noise ratio was a considerable improvement on the lower-field (8.45 T) measurements. The peak position is the most readily measured parameter, and despite nearly all of these featureless lines showing some asymmetry they approximate quite well to Gaussian line shapes. For this set of materials, although second-order quadrupole effects are usually not sufficiently large to produce discernible second-order quadrupole line shapes, they can shift the observed peak position (δ_{peak}) away from the isotropic chemical shift (δ_{iso}). A better approximation to the isotropic chemical shift is to assume that the residual MAS linewidth is due to second-order quadrupole effects. Then an approximate correction to the peak position can be made via $\delta_{iso} = \delta_{peak} + 0.85$ (FWHM), where FWHM is full width at half maximum of the Gaussian in

TABLE I. ^{43}Ca solid-state NMR data of the samples studied here and their related parameters.

Samples	Coordination number[a] (CN)	Mean Ca-O Ca-X distance[a]	δ_{peak} (ppm)[b]	δ_{iso} (ppm)[b,c]	FWHM[b] (Hz)
CaSi$_2$	12	3.19	195.8	204.8	430
CaC$_2$	6	2.52		160.0	3940
			78.4	105.7	1300
CaO[d]	6	2.41	128	128	20
CaS	6	2.842	112.4	115.6	150
CaSe	6	2.958	107.4	113.2	280
CaH$_2$	9 (7+2)	2.434	93.8	101.1	350
CaBr$_2$	6	2.885	68.2	75.5	350
CaCl$_2$	6	2.745	53.1	56.0	140
CaF$_2$	8	2.366	−17.2	−9.4	370
CaB$_6$	11	3.057	−56.0	−41.3	700
CaWO$_4$	8	2.460	−11.7	−5.4	300
CaMoO$_4$	8	2.466	−13.2	−6.9	300
Ca(NO$_3$)$_2$·4H$_2$O	9	2.484	−23.6	−17.1	310
CaZrO$_3$	8	2.57		47.5	800
Ca(OH)$_2$	6	2.370		73.0	800
CaSiO$_3$[e]	6, 6, 7	2.399	−0.2	14.6	700
S50C50[f]			−20.1	−6.4	650
S50C50T3[f]			−20.2	−7.6	600
S70C30[f]			−9.9	−3.2	320

[a]The data were obtained from Ref. 14 and the Daresbury Laboratory CDS website.
[b]Errors: $\delta \pm 1–2$ ppm; FWHM $\pm 20–40$ Hz.
[c]δ_{iso} is taken as peak max +0.85 width except CaZrO$_3$ and Ca(OH)$_2$, which are taken from the simulation of the quadrupolar line shape.
[d]Data taken from Ref. 10.
[e]CaSiO$_3$ (β-wollastonite), the data were also from the above sources. Its structure consists of three Ca sites with coordination numbers of 6, 6, and 7 respectively. The value of Ca-O distance cited is the average of three sites.
[f]S50C50 is 50%SiO$_2$:50%CaO (molar ratio); S70C30 is 70%SiO$_2$:30%CaO; S50C50T3 is heated at 350°C for 1 h.

parts per million (ppm). For binary compounds in which calcium is coordinated by elements other than oxygen the chemical shift range is now over 250 ppm, greatly exceeding the 160 ppm observed when the local coordination was only to oxygen.[10] The relatively narrow linewidths typically observed here probably reflects two things: that the calcium environments are usually quite symmetric, and that the bonding to calcium is quite ionic, producing relatively small electric field gradients (exceptions to this are CaC$_2$ and CaB$_6$).

Second-order quadrupolar line shapes were observed in CaZrO$_3$, Ca(OH)$_2$ and possibly CaC$_2$. For CaC$_2$, the spectrum shows at least two overlapping resonances; one of them is very broad with FWHM $\sim$100 ppm. This spectrum was not simulated because x-ray diffraction showed the sample to be of relatively low purity so that the large width could be due to a spread of lines. In CaZrO$_3$ calcium is in a noncubic symmetry environment coordinated by a range of oxygens, with 5 different bond lengths for the 8 nearest oxygen neighbors.[15] The observed second-order quadrupolar line shape is associated with the larger electric field gradient caused by this environment. From the spectral simulation χ_Q=2.80±0.03 MHz and η=0.45±0.10. The ^{43}Ca line shape from Ca(OH)$_2$ has previously been reported from a sample enriched to 58% ^{43}Ca, but spectral analysis of the line shape was not attempted.[8] Spectral simulation of the line shape

from the natural-abundance sample recorded here produces χ_Q=2.83±0.03 MHz and η=0.20±0.10.

The linewidth for β-wollastonite is measured here as 700 Hz, which is approximately half the value measured at 8.45 T, indicating that second-order quadrupolar effects are the dominant cause of the linewidth in this case (the narrowing is a little greater than the expected factor of 1.67, which may indicate that the previous sample was also less well crystallized and therefore had some chemical shift dispersion effects as well). The resonance shows some features on the high-field side (Fig. 3), which may be associated with the different sites in the mineral. The chemical shifts of two sol-gel produced amorphous calcium silicate materials heated to 120°C are both significantly more negatively shifted than β-wollastonite (Fig. 3). The sample with 70% silica content gave a considerably narrower resonance than that from a 50% SiO$_2$ containing sample (Table I). These samples were heated successively to 350°C and then 500°C. After heating to 350°C the spectra from the samples were similar to those at the lower temperature. However, no calcium signal could be recorded even after averaging for 24 h for the samples heated to 500°C.

IV. DISCUSSION

For systems involving calcium bonded to only oxygen in the nearest-neighbor coordination sphere, the data reported
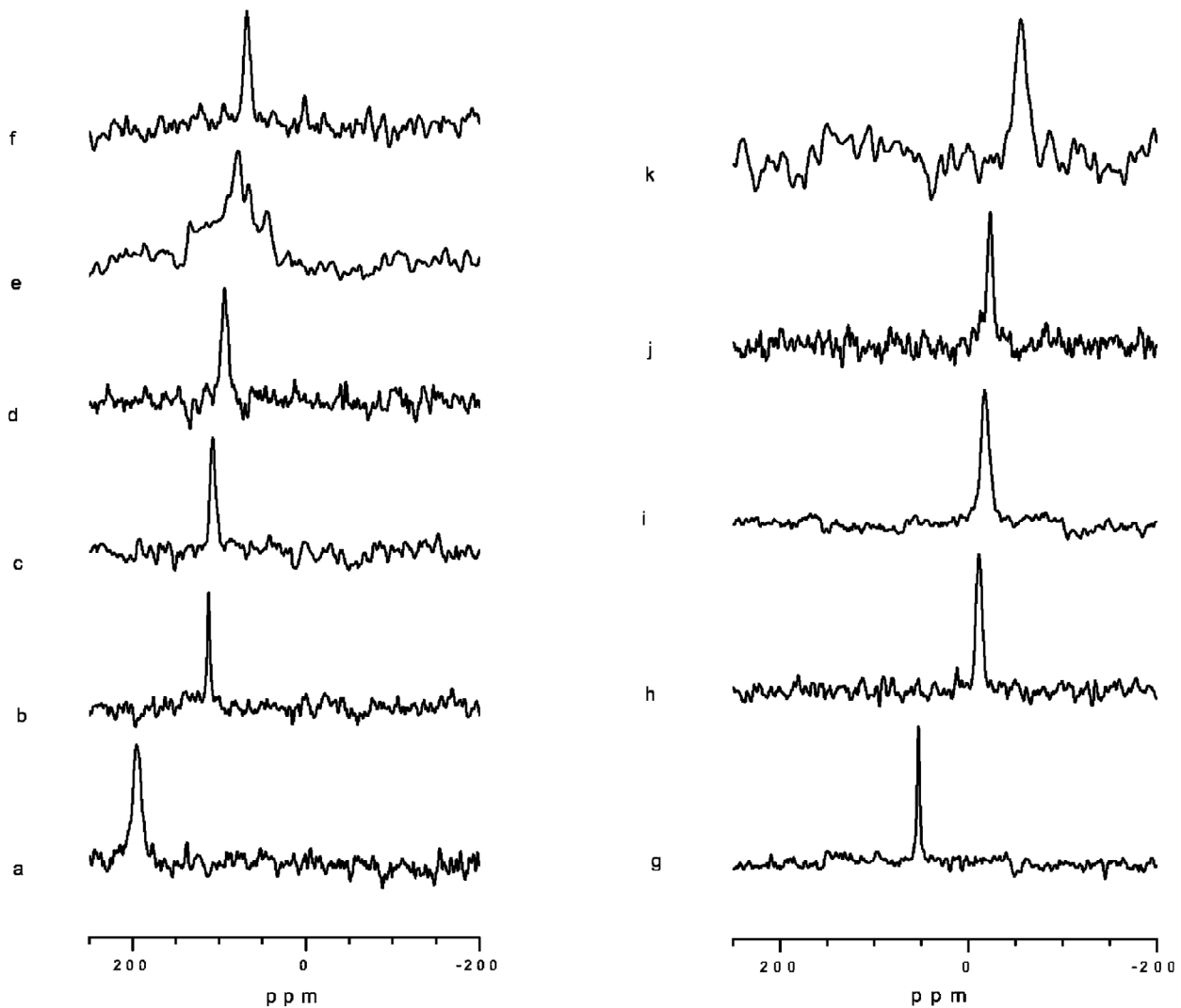
FIG. 1. ^{43}Ca MAS NMR spectra of eleven calcium inorganic compounds. (a) CaSi$_2$, (b) CaS, (c) CaSe, (d) CaH$_2$, (e) CaC$_2$, (f) CaBr$_2$, (g) CaCl$_2$, (h) CaWO$_4$, (i) CaF$_2$, (j) Ca(NO$_3$)$_2$·4H$_2$O, and (k) CaB$_6$.

here, taken together with the data reported in Refs. 10–12 allow the influence of coordination number, and the correlation of δ_{iso} to Ca-O bond length to be better understood. In NMR δ_{iso} is often used to determine the coordination number of the nucleus under investigation. For nuclei such as silicon[1] and aluminum,[1,16] which tend to have well defined local (Si, Al)O$_n$ coordinations because of the much stronger covalent bonding, δ_{iso} provides direct, unequivocal assignment of the local units. For ^{29}Si and ^{27}Al it is well known that as the coordination number increases δ_{iso} becomes more negative.[1,16] For metals such as sodium and calcium the local oxygen coordination tends to be more diffuse than for these elements, and hence the ability to identify the coordination from δ_{iso} is weaker. For sodium, although the NaO$_5$ and NaO$_6$ shift ranges significantly overlap, the center of gravity of the NaO$_5$ range show the expected more positive shift than that for NaO$_6$.[17,18] Figure 4 shows the shift ranges associated with the CaO$_x$ units. It is clear that again the expected trend of decreasing shift with increasing coordination is certainly evident. From the data that have been recorded

there appears to be less overlap than for sodium, but in the region 10–30 ppm (Fig. 4) there are resonances from several different coordinations. If the ranges are considered with the next-nearest-neighbor element being the same, then the overlap decreases and the negative shift with increasing coordination number becomes clearer.

For sodium and calcium, correlations of δ_{iso} with the M-O bond length have been examined, with Dupree *et al.* considering these in detail for calcium. Again adding our data and the calcium aluminates from Ref. 11 these shift correlations are strong within particular groups (e.g., silicates) but are not limited to only the same kind of compounds, and can occur across different classes of compounds as well. The two lines shown in Fig. 5 are the correlations for the silicates/aluminates (upper in Fig. 5) and the second includes carbonates, tungstate, phosphate, nitrate, and molybdate. These two sets of data correlate well, with lines that are parallel to one another. Our data agree well with, and essentially confirms, the trend suggested by Dupree *et al.*, where the slopes of the correlations were found to be 280 ppm/Å.[10]
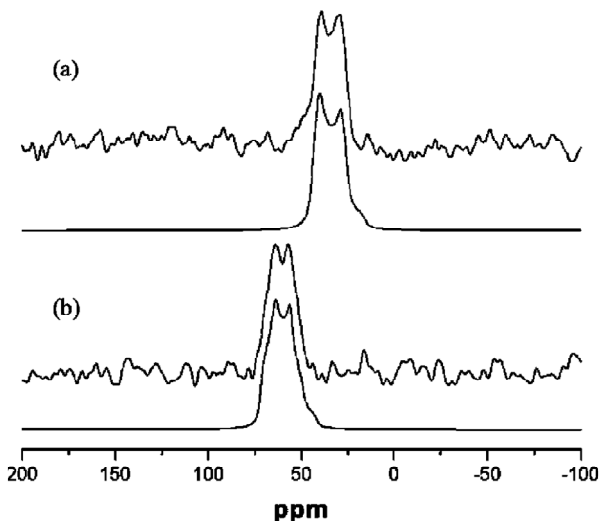
FIG. 2. ^{43}Ca MAS NMR spectra of (a) $CaZrO_3$ and (b) $Ca(OH)_2$ together with simulations of the line shapes directly below each spectrum.

The information that solid-state NMR as a local probe of structure can add to conventional crystallography is well illustrated by comparing $CaZrO_3$ and $CaTiO_3$. These both have the $GdFeO_3$ structure type with space group *Pbnm*. X-ray diffraction data indicate that the zirconate is the more distorted structure with a $\sim$21% variation in the Ca-O bond lengths compared to only $\sim$13% in the titanate. This is mirrored in the larger ^{43}Ca χ_Q from the zirconate, and also the greater shift difference between the two distinct oxygen sites in the zirconate structure of 7 ppm compared to 4.6 ppm in the titanate.[19]

One of the most important pieces of new information presented here is the effect on the NMR parameters of ^{43}Ca of

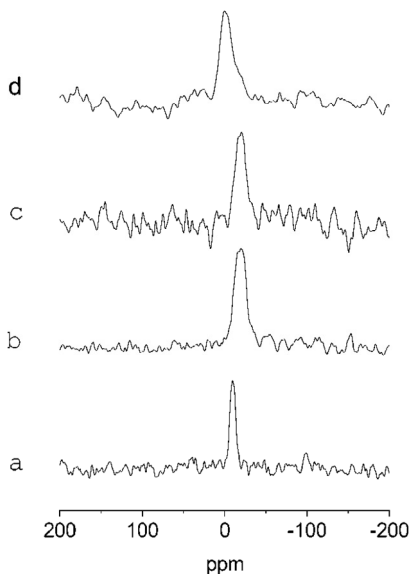FIG. 3. ^{43}Ca MAS NMR spectra of two sol-gel produced calcium silicate materials with (a) 70 mol% (S70C30) and (b) 50 mol% (S50C50) silica heated to 120°C, (c) S50C50 heated to 350°C, and (d) β-wollastonite.
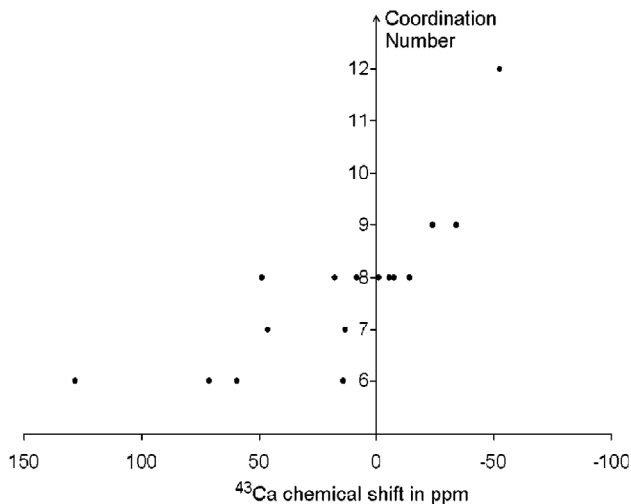

FIG. 4. The ^{43}Ca chemical shift vs Ca coordination number of oxygen-containing calcium inorganic compounds given in Table I, plus data from silicates, carbonates, oxides (Ref. 10), and aluminates (Ref. 11).

changing the nature of its nearest neighbors. Considering the series of materials CaO, CaS, and CaSe calcium is sixfold coordinated in all these materials. The effect of decreasing the electronegativity of the attached atom means that the shift becomes less positive. The oxide has a well removed shift (which has the biggest electronegativity difference), whereas the shifts of the sulfide and the selenide are very similar, as are their electronegativities. Some of the materials have interesting coordinations such as CaB_6, which has a complex structure. As a group III (third column) element in the periodic table, boron is not a typical nonmetallic element with only a small electronegativity difference (ΔX) from calcium, and a smaller atomic radius. A feature of boron structural chemistry is its complexity. Most metal borides contain groups—chains, layers or networks of connected atoms. Calcium hexaboride may be described to a first approximation
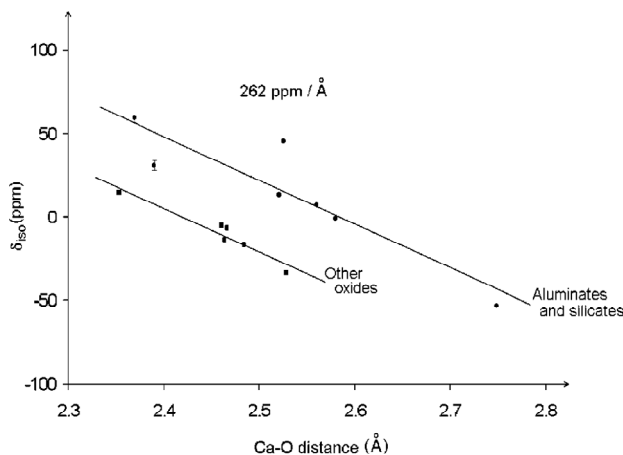

FIG. 5. The ^{43}Ca chemical shift correlation vs mean Ca-O distance of oxygen-containing calcium inorganic compounds given in Table I, plus data from silicates, carbonates, oxides (Ref. 10), and aluminates (Ref. 11).

as having metal and B_6^{2-} octahedral polymeric anions in a cesium chloride-type structure.[20] CaB_6 produces quite a negative shift in keeping with the higher coordination number of 11. CaC_2 has several different polymorphs,[21] and the spectrum shown in Fig. 1 is from a sample that is a mixture of polymorphs. Although the bonding between Ca^{2+} and C_2^{2-} is ionic, the bonding between carbon atoms is a covalent triple bond, and the configuration of the C_2^{2-} molecule is linear so that the nature of the bonding in this compound could produce the observed shift. Calcium silicide, which shows a distinctive shift at ~ 204 ppm, is at the opposite end of the shift scale compared to the expected shift of such a high coordination, as seen from the CaO_{12} unit. Again here the nature of the bonding in this compound could well be producing the observed shift.

Correlations of the shift of the binary compounds versus mean Ca-X distance in the first coordination sphere, as has been established for Ca-O, were examined. No obvious correlation between δ_{iso} and the mean of the Ca-X distance could be found, which is perhaps not surprising since this ignores shielding differences at calcium for Ca-X bonding caused by other effects. One important effect is the electronegativity difference between various Ca-X pairs, which will affect the electron density in the bonds and consequently the shielding of the calcium. Hence using either simply ΔX or the product of ΔX and the mean Ca-X distance can be examined for correlation with δ_{iso}. Good correlations can be obtained for limited ranges of compounds such as CaO, CaS, CaSe, and CaH_2 using this product, but when the bond involves a halogen the same correlation cannot be used.

The chemical shifts of two sol-gel prepared calcium silicate materials dried at $120\,°C$, with compositions $50\%\,CaO$: $50\%\,SiO_2$ and $30\%\,CaO$:$70\%\,SiO_2$ (molar ratio) peak at -20.1 ppm and -9.9 ppm, respectively. These (and their corresponding isotropic shift values) could be converted to Ca-O bond lengths using the correlation of Fig. 5. This would give Ca-O bond lengths of 2.7–2.9 Å, much longer than determined by diffraction from amorphous calcium silicates. However, the positions are very much closer to calcium nitrate, and if the other correlation line in Fig. 5 is used, then bond lengths 2.43–2.44 Å are obtained, much closer to the 2.35 Å determined by X-ray diffraction (XRD) in these gel materials.

Although analysis of the XRD can provide bond length information, there is certainly no unequivocal evidence as to the exact nature of the calcium environment in the initial gel (i.e., there are no distinct Bragg reflections from any phase). ^{17}O and ^{29}Si MAS NMR suggests that calcium does not enter the silicate network, but no information is provided about the nature of the calcium environment. Both the shift of the [43]Ca MAS NMR data and the inferred bond length provide strong evidence of a nitrate-like, rather than a silicate environment. It is likely that this phase is either very finely dispersed or is a surface layer since no direct XRD evidence of a calcium nitrate phase exists. In the initial room temperature formed gels the peak at -20.1 ppm (S50C50) is much broader than the -9.9 ppm peak (S70C30). A possible interpretation for the broader peak is that it consists of two components, one centered at -20 ppm with a very similar local environment to the nitrate and the other is centered at -10 ppm with possibly

some decrease of coordination number. Heating to $500\,°C$ will result in both nitrate breaking down and hydroxyls being lost, and the calcium being forced, from its charge balancing requirements, to interact more strongly with the silicate network. [43]Ca MAS NMR spectra were accumulated to follow the resulting changes in the calcium coordination. However, even after averaging for 24 h no signal could be observed. This is consistent with a previous study of sol-gel produced calcium silicates, enriched to 50 at.% calcium, from which again effectively no signal was observed.[9]

The lack of observable signal needs to be carefully considered. An initial suggestion could be that given the quadrupole nature of [43]Ca, then in the highly disordered state the calcium site becomes much more distorted causing a much larger quadrupole interaction broadening the spectrum. Although this explanation cannot be ruled out, the data that have been accumulated from *all* the crystalline materials indicates that χ_Q is usually small, and the maximum value of χ_Q is ~ 3.5 MHz. This would *not* cause sufficient broadening to lose the resonance. However, an alternative explanation is possible, in the light of the observations presented here. It can be seen that even for the same type of nearest neighbor (e.g., oxygens) that the shift range for similar coordinations can be quite large (e.g., for $CaO_6 > 110$ ppm). Hence if there was a range of distortions of a particular coordination, and even a varying coordination number, then the broadening in the gel, as the calcium begins to interact with the silicate, could be due to chemical shift dispersion. If this were the main cause of the broadening (and all the evidence points to this being true), then the studies that have been carried out at 11.7 and 14.1 T could be at too high a magnetic field for these particular materials. It might be that lower fields are better, although Boltzmann factor sensitivity will then be worse. From the data that have now been collected from crystalline compounds the linewidth due to second-order quadrupole effects, and hence the minimum applied magnetic field that would still allow narrowing with large sample volume rotors, can be estimated.[1,3] Even being pessimistic taking the largest χ_Q measured in crystalline compounds, this would still readily narrow under 4.5 kHz MAS at 4.7 T. Such a field would strongly suppress chemical shift dispersion effects. To enhance sensitivity isotopic enrichment could be used, but to make the technique generally applicable, work on natural-abundance samples is preferred. Recently, several schemes have been developed for enhancing the signal from non-integer spin nuclei, including fast amplitude modulation sequences that produce an enhancement in amplitude of at least 3 for the central transition of a spin-7/2 nucleus,[22] and echo trains (e.g., the Quadrupole Carr-Purcell-Meiboom-Gill (QCPMG) sequence).[23,24] It can certainly be envisaged that further enhancement could be achieved through combining these approaches, and would require only one enriched sample to allow accurate optimization of these sequences for calcium. In the future one could also envisage the development of cryoprobes for solid-state NMR (as have made a huge impact on liquid-state NMR) and the reduced noise from cooled electronics could produce spectacular increases in sensitivity. This work has shown that high magnetic fields allow natural-abundance [43]Ca solid-state NMR studies of crystalline materials to be carried out using very

simple pulse sequences. For amorphous solids further technique development is required, but there are certainly some grounds for optimism. All of this suggests that even at natural abundance, ^{43}Ca NMR studies of solids in a wide range of materials of interest in physics, chemistry, and biology will become much more commonplace.

V. CONCLUSIONS

Natural-abundance ^{43}Ca MAS NMR data measured at a relatively high magnetic field of 14.1 T show that a good signal-to-noise ratio can be obtained from a large range of crystalline inorganic compounds. When the nature of the nearest neighbor is varied, a chemical shift range of >250 ppm is observed. Relatively narrow resonances are usually observed from crystalline materials, with only a few cases exhibiting second-order quadrupolar line shapes. This data indicate that for inorganic ionic (or oxo salt) compounds, calcium sites have $\chi_Q < 4$ MHz. When oxygen is the nearest neighbor of calcium, the isotropic chemical shift is correlated with the mean Ca-O distance, consistent with a previous study. The shift correlation extends over a wide range of compounds with the shift changing by 280 ppm/Å.

This study extends the calcium shifts to a much wider range of nearest-neighbor coordinations and some effects could be correlated with the electronegativity difference, but no general correlation could be found to include all binary compounds. The halogens gave very different trends compared to, for example, CaO and CaS. In sol-gel prepared calcium silicate materials ^{43}Ca MAS NMR spectra could be obtained for samples heated at 120 and 350°C, with the spectra suggesting that at this stage the calcium remains in an environment similar to the initial calcium nitrate. Heating to higher temperatures causes the samples to become more disordered and no calcium signal is observed. It is suggested here that it is probably chemical shift dispersion and not an increased quadrupole interaction that causes the large increase in linewidth in the amorphous state.

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