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High field multinuclear solid state NMR and first principle calculations in MgSO₄ polymorphs¹

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Abstract

A combination of solid state NMR and first principles calculations was applied to obtain ^{17}O , ^{25}Mg and ^{33}S NMR parameters for two polymorphs of anhydrous magnesium sulfate. Working at the very high magnetic field of 21.14 T results in a dramatic improvement of resolution through a reduction of effects of quadrupolar interactions and significant improvement in sensitivity. Experimental ^{25}Mg and ^{33}S spectra are dominated by quadrupolar interactions with the quadrupolar parameters unique for each polymorphs. In the case of ^{17}O , there is a substantial contribution of the chemical shift anisotropy. The use of multiple-quantum MAS (MQMAS) experiments allows the resolution of distinct oxygen species and assignment of signals in the experimental ^{17}O spectra. Chemical shielding constants and quadrupolar parameters for all three nuclei were calculated using plane wave pseudo-potential density functional theory as implemented in the CASTEP computational package. The calculated NMR parameters are in very good agreement with the experimental results and help in signal assignment of the ^{17}O spectra. The results suggest applicability of such a combined computational – experimental solid state NMR approach for the refinement of the crystallographic data.

Keywords: Multinuclear Solid State NMR, MgSO_4 polymorphs, ^{17}O , ^{25}Mg , ^{33}S , Chemical Shift Anisotropy, Electric Field Gradient, DFT Calculations.

Introduction

Recent developments in NMR instrumentation, especially ultrahigh field NMR magnets, combined with advances in computation of NMR parameters, significantly broadens the scope of Solid State NMR spectroscopy of materials. These advances are especially significant in studies concerned with low- γ , low natural abundance and quadrupolar nuclei.² Another modern development that makes SS NMR an even more powerful tool in materials research is Quantum Chemical Calculations of NMR parameters. The complicated nature of interactions in solid state NMR poses some serious challenges in the analysis of spectral data and the accurate extraction of shielding and quadrupolar parameters. Correct interpretation of the experimental spectra may require some elaborate quantum mechanical calculations and spectral simulations. First-principles calculations may well complement experimental data and help in interpretation and assignments of the spectra. Recent development of the gauge including projector augment wave (GIPAW)³ formalism, implemented within the CASTEP⁴ computational package, is particularly useful for solid state NMR. Several recent studies have demonstrated that highly accurate evaluation of SS NMR parameters is possible,⁵⁻⁹ with most examples coming from Earth sciences and silicates research. Thanks to the availability of more user-friendly quantum chemical software and advances in computational hardware, today this task can be accomplished as never before.

In the current study we explore a combination of experimental multinuclear Solid State (SS) NMR at very high magnetic field of 21.14 T with quantum-mechanical

computations to study two polymorphs of anhydrous magnesium sulphate. It is considered that magnesium sulfates are important planetary rock-forming materials in our solar system.^{10,11} Specifically, MgSO_4 is considered to be an important mineral in putative carbonatite lavas on Venus.¹⁰ In the outer solar system, MgSO_4 may well be the most important leachate from chondritic materials.¹¹ In many respects the importance of magnesium sulfates as a planetary mineral resembles those of magnesium ortho- and meta-silicates in the Earth's mantle, the latter being recently studied comprehensively with a combination of multinuclear SS NMR and first principles computations.⁹

Below about 800 K anhydrous magnesium sulfate is known to co-exist in two polymorphic forms. The α -phase can be grown from a solution of MgO in H_2SO_4 . The structure of the α -form is orthorhombic with space group $Cmcm$ ($Z = 4$) and unit-cell dimensions $a = 5.182 \text{ \AA}$, $b = 7.893 \text{ \AA}$, $c = 6.506 \text{ \AA}$.¹² The β - MgSO_4 can be formed either by thermal dehydration of MgSO_4 hydrates or by heating α - MgSO_4 to 868 K¹³ followed by quenching to room temperature. The structure of β -form is orthorhombic with space group $Pbnm$ and unit-cell dimensions $a = 4.742 \text{ \AA}$, $b = 8.575 \text{ \AA}$, $c = 6.699 \text{ \AA}$.¹⁴ After quenching, β - MgSO_4 persists in this form indefinitely. The polymorphs are structurally very similar and consist of edge-sharing MgO_6 octahedra arranged in infinite ribbons and cross-linked by sheets of pseudo-close-packed SO_4 tetrahedra. The latter, however, are oriented in α - and β -forms in different planes. The structural similarities and differences of α - and β -forms were considered in some detail in a recent neutron powder diffraction study.¹⁵ One needs to emphasise that due to the difficulties of growing single crystals of highly hygroscopic MgSO_4 , the earlier structures were solved from X-Ray powder data

and were later refined using powder neutron diffraction. The first single crystal study of β -MgSO₄ was published only in 2007, soon after the neutron powder diffraction refinement for both α - and β - polymorphs.¹⁶

MgSO₄ poses some serious solid state NMR challenges. All three nuclei are quadrupolar, and their SS NMR signals are broadened by quadrupolar interactions.^{17,18,19} Two of the three nuclei (²⁵Mg and ³³S) have very low gammas, and only one of them has a moderate natural abundance (²⁵Mg - 10%, ³³S - 0.75%, ¹⁷O - 0.037%).²⁰ The combination of the above results in a very poor NMR receptivity (see Table 1). In this work we report the results of a solid state NMR study using all three nuclei in the α - and β -forms of anhydrous magnesium sulfate at a magnetic field of 21 T. At this very high magnetic field the effects of the quadrupolar interactions are reduced significantly^{17,18} and the sensitivity and accuracy in determining the NMR parameters improve dramatically. We demonstrate that for all three nuclei the quadrupolar effects dominate the NMR spectra. A complete analysis of experimental SS NMR parameters has become possible with the use of the CASTEP^{3,4} computational package.

It is always of great interest to support known structural data obtained through X-ray or neutron diffraction methods with additional techniques. The use of a short-range order interaction technique such as NMR is expected to complement the existing structural data obtained through previous diffraction methods. As well, with the aid of computation, an attempt to distinguish polymorphs with the same chemical composition through SS-NMR can be accomplished. The possibility of assessing the structural details

in β -MgSO₄ obtained by two different diffraction techniques using SS-NMR in conjunction with *ab initio* calculations is another expected outcome of this work.

Experimental Part

Materials. Both MgSO₄ polymorphs studied in this work were synthesized as ¹⁷O enriched compounds. ¹⁷O enriched sulfuric acid was prepared by reacting sulfuryl chloride SO₂Cl₂ (Aldrich) with H₂¹⁷O (Cambridge Isotope Laboratories, Inc., 17.8% enrichment). The sulfuric acid obtained was added in about 20 mol. % excess to a small quantity (~ 0.3 g) of freshly calcined MgO (Aldrich) in a small Pt crucible and the slurry was left to evaporate over a hot plate (~ 300°C). After complete evaporation of the liquid sulphuric acid the crucible was put in an oven and kept there at a constant temperature of 450 °C overnight. The X-ray diffraction pattern of the resulting powder was that of α -MgSO₄.^{12,15} The β -phase of MgSO₄ was produced by heating the α -phase at 650°C.¹³ Because of the dilution of ¹⁷O in the course of synthesis, the final enrichment was estimated to be in the range of 5-7%.

NMR spectroscopy. All NMR measurements were performed on a Bruker Avance-II 900 MHz instrument (magnetic field of 21.14 T) at the National Ultrahigh Field NMR Facility for Solids in Ottawa. Larmor frequencies for ¹⁷O, ²⁵Mg and ³³S were 122.02, 55.1 and 69.09 MHz, respectively. Static powder spectra were obtained on a homebuilt 7 mm solenoid probe. A spin-echo pulse sequence optimized to reproduce accurately the powder line shapes²¹ and a QCPMG sequence²² were used in static experiments. Between 250 and 2000 scans were acquired for all nuclei with relaxation delays ranging from 10 to

40s. A Dual Frequency Sweep (DFS) sensitivity enhancing technique²³ was used in some of the experiments, particularly with ³³S. The optimal relaxation delays for each compound and nucleus were found from 3-4 short (16-32 scans) runs. The Magic Angle Spinning (MAS) experiments were performed using Bruker 4 mm (¹⁷O and ²⁵Mg) and 7 mm (³³S) MAS probes with dry nitrogen as a carrier gas. Two-dimensional MQMAS experiments on ¹⁷O were performed using phase-modulated split-*t*₁ pulse sequence^{24,25} with rotor synchronization. The spectra were externally referenced to neat H₂O (¹⁷O, δ = 0 ppm), 1M solution of Mg(NO₃)₂ (²⁵Mg, δ = 0 ppm), and 2M solution of Cs₂SO₄ (³³S, δ = 333.0 ppm from CS₂²⁶).

Spectral simulations. Analytical simulations of experimental spectra were carried out with the WSolids²⁷ and DMFit²⁸ simulation packages. In all simulations we first fitted the MAS spectra, which provided the isotropic chemical shifts δ_{iso} , quadrupolar constants C_Q and quadrupolar asymmetry parameter η_Q . These parameters were subsequently used in simulations of static powder pattern. Special attention was given to reproducing the spectral discontinuities and shoulders in fitting the spectra.

Quantum Chemical Calculations. All calculations were performed using the CASTEP⁴ density functional theory code using the GIPAW³ algorithm. The version used in this work is integrated within the Accelrys Materials Studios 4.4 suite. The computations use the generalized gradient approximation (GGA) and Perdew- Burke-Ernzerhof (PBE) functional,^{29,30} and the core –valence interactions were described by ultrasoft pseudopotentials.^{3(b)} Integrations over the Brillouin zone were done using a Monkhorst-Pack grid with a k-point spacings generally being less than 0.04 Å⁻¹.³¹ Crystallographic data used in the calculations were taken from the literature and the corresponded

references are given in the text. The calculations produce the absolute shielding tensor (σ), quadrupolar coupling constant C_Q and asymmetry η_Q . The later two parameters can be compared to the experimentally measured C_Q and η_Q directly. In the case of σ , however, some conversion needs to be done before comparing them with the experimentally measured chemical shifts. The isotropic chemical shift δ_{iso} relates to the isotropic shielding $\sigma_{iso}=1/3\text{Tr}\{\sigma\}$ as $\delta_{iso}=-(\sigma_{iso}-\sigma_{ref})$, where σ_{ref} is the isotropic shielding calculated on the reference material with well defined structure and known chemical shift. The references used for the nuclei studied in this work are as follows: For ^{25}Mg , the reference shielding obtained from a correlation of the calculated shielding constants and the experimental chemical shifts in numerous magnesium compounds, with $\sigma_{iso}=-1.072(\pm 0.036)\times\delta_{iso}+566.06(\pm 0.99)$.³² For ^{33}S , the reference shielding is again based on a correlation where $\sigma_{ref}(^{33}\text{S})=434.1$ ppm (updated data from Ref. 33). For ^{17}O , the chemical shielding was referenced to the well documented O1 site in forsterite as in Ref. 9, with $\sigma_{ref}(^{17}\text{O})$ value of 255.0 ppm.

Experimental Results and Discussion

Structural Details of System Studied

Table 2 shows the structural parameters for $\alpha\text{-MgSO}_4$ and both reported structures of $\beta\text{-MgSO}_4$ from the most recent reports.^{15,16} As can be seen in Table 2 the structures for the two polymorphs of MgSO_4 are somewhat similar, yet they do have significant differences. Both polymorphs crystallize with an orthorhombic lattice but $\alpha\text{-MgSO}_4$

crystallizes in space group *Cmcm* whereas β -MgSO₄ crystallizes in space group *Pbnm/Pnma*. The lattice volume is approximately the same for both polymorphs, yet the individual lattice parameters vary significantly. The site symmetry of the separate atoms in each cell is also quite different between the polymorphs. For Mg and S each polymorph has only one crystallographically unique site. The most significant differences between the two polymorphs is the number of crystallographically inequivalent oxygen sites. α -MgSO₄ has two unique oxygen sites with ratio 1:1, while β -MgSO₄ has three sites with ratio 2:1:1. When examining the two reported structures of β -MgSO₄, it can be seen that the differences between the two are quite small. It is therefore interesting to test whether the first principle calculations are capable to distinguish the differences and how accurately they can reproduce the experiment.

²⁵Mg Results

Although ²⁵Mg has the highest natural abundance of all the nuclei examined in this work, it also has the largest quadrupole moment and the smallest magnetogyric ratio. With this in mind, one may expect that the quadrupolar interactions would dominate the NMR spectra of ²⁵Mg in MgSO₄. The ²⁵Mg natural abundance SS-NMR spectra obtained at 21.1 T for α -MgSO₄ and β -MgSO₄ are shown in Figures 1 and 2. Both stationary and MAS spectra are shown obtained with Hahn Echo and QCPMG pulse sequences. The parameters extracted from the experimental spectra together with the CASTEP computational results can be found in Table 3. The quadrupolar interaction indeed dominates the experimental ²⁵Mg spectra with the magnitudes differing significantly for

α - and β -MgSO₄ polymorphs. In fact, the determined values $C_Q = 7.41 \pm 0.05$ MHz and $C_Q = 10.4 \pm 0.1$ MHz in α - and β -MgSO₄ respectively, are among the largest observed for magnesium salts, where typically $C_Q < 5$ MHz for ²⁵Mg.^{19,32,34-40} The quadrupolar asymmetry parameter, η_Q , is also quite different for the two the polymorphs. ²⁵Mg in α -MgSO₄ has an $\eta_Q = 0.35 \pm 0.02$ whereas that of β -MgSO₄ is practically equal to 1.0. With just the ²⁵Mg quadrupolar parameters alone it is possible to differentiate these two polymorphs based on the SS NMR spectra. The isotropic chemical shifts δ_{iso} for α - and β -MgSO₄ are -8.1 ± 1.0 ppm and 0.2 ± 2.0 ppm, respectively, which is well within the range of the shifts expected for a compound such as MgSO₄.³² Typically for octahedrally oxygen-coordinated Mg compounds the isotropic chemical shift ranges from ~ -10 ppm to ~ 10 ppm.^{32,34,40} Since the range of ²⁵Mg chemical shifts for oxygen-coordinated magnesium is relatively small, it is not surprising that the chemical shift anisotropy for ²⁵Mg in both α - and β -MgSO₄ is quite small. Considering the scale of the quadrupolar interactions for both polymorphs, the accuracy of the experimental ²⁵Mg CSA is rather low. The experimental values can found in Table 3. Due to a considerably larger magnitude of the quadrupolar interactions for β -MgSO₄, detection of the CSA is even more difficult, and only an estimate for the upper limit of the anisotropy σ_{aniso} is reported.

Data in Table 3 demonstrate very reasonable agreement between experimental and calculated ²⁵Mg NMR parameters. The isotropic chemical shift was predicted accurately for ²⁵Mg in α -MgSO₄ yet was slightly overestimated for both calculations in β -MgSO₄. CASTEP was also able to predict the scale of the ²⁵Mg CSA for both polymorphs, and the parameters match quite well with the experimental values for σ_{aniso} ,

η_{CSA} , and Euler angles α , β , and γ . The calculated quadrupolar parameters are also in good agreement with the experiment. Although the calculated quadrupolar coupling constant for both polymorphs was slightly overestimated, the prediction of η_Q , was good for both polymorphs. Looking at the two sets of calculated data for β -MgSO₄, one can see that the calculations for the NPD structure and the single crystal XRD structure produce somewhat different results. Notwithstanding, from the ²⁵Mg parameters alone it is difficult to conclude if one structure produced more accurate calculations than the other. The calculated isotropic shifts were overestimated in both cases, although the single crystal diffraction structure calculations produced a result closer to the measured shift of 0.2 ppm. The calculated quadrupolar coupling constants for the NPD and the XRD data are much the same, with both structures producing overestimated values of C_Q 's. In this case, though, the neutron powder diffraction structure calculation produced a C_Q closer to the measured value of 10.4 MHz. Once again, at this stage it is hard to discern if one structure more accurately represents the actual room temperature structure of β -MgSO₄.

The CASTEP calculations also provide orientations of the CSA and EFG tensors for all atoms of interest. This is particularly useful for assisting in analyzing the fine structural details in a given material. For the case of magnesium in both polymorphs the crystallographically unique magnesium site is present in an octahedral environment of oxygen atoms. However, as can be seen in Table 2 the point group symmetry of Mg sites in MgSO₄ is far from perfectly octahedral. For α -MgSO₄ magnesium is present in C_{2h} symmetry and the relevant symmetry operations present at the magnesium site can be seen in Figure 1B. For this type of symmetry it has been shown that the principal

components of the symmetric part of the shielding tensor are independent of each other.^{41,42} Thus, one might not necessarily expect an axially symmetric shielding tensor with these restrictions on the principal components of the shielding tensor.⁴³ Indeed, looking at the shielding asymmetry parameter, η_{CSA} , for ^{25}Mg in $\alpha\text{-MgSO}_4$ shows a non-axially symmetric tensor with $\eta_{CSA} = 0.8 \pm 0.2$. A similar argument can be made for the axially symmetric nature of the EFG tensor.⁴⁴ In agreement, the quadrupolar asymmetry parameter for ^{25}Mg in $\alpha\text{-MgSO}_4$ shows a non-axially symmetric EFG tensor with $\eta_Q = 0.35 \pm 0.02$. Examination of the calculated tensors for ^{25}Mg in $\alpha\text{-MgSO}_4$ (Figure 1B) uncovers some interesting details. The largest calculated components of the EFG and CSA tensors, V_{33} and σ_{33} , both lie in the mirror plane through the magnesium atom. CASTEP also predicts that the V_{33} and σ_{33} components are coincident with the Euler angle $\beta = 0^\circ$, which is what is observed experimentally. The V_{33} and σ_{33} components also point directly towards one of the oxygen atoms that is part of the Mg-O pseudo-octahedron. Additionally, the V_{22} and σ_{11} components point along the C_2 proper rotation axis through the magnesium. The single unique Mg site in $\beta\text{-MgSO}_4$ is slightly different from that of $\alpha\text{-MgSO}_4$. In $\beta\text{-MgSO}_4$, Mg is present in a C_i site, which means one would again not expect an axially symmetric CSA or EFG tensor.⁴²⁻⁴⁴ Although the asymmetry parameter of the CSA tensor, η_{CSA} , could not be accurately measured due to the dominance of the EFG interaction, the quadrupolar asymmetry parameter is certainly not axially symmetric with $\eta_Q = 1.0$. The calculated EFG and CSA tensor orientations for Mg in $\beta\text{-MgSO}_4$ are shown in Fig. 2B. Since there is only a centre of inversion at the Mg site in $\beta\text{-MgSO}_4$ there is little to constrain the tensor orientations on the basis of symmetry. However, the largest component of the CSA tensor, σ_{33} , appears to point towards one of

the oxygen atoms of the Mg-O pseudo-octahedron. Although it might seem that V_{33} is pointing towards another of the oxygen atoms in the octahedron, the deviation is large enough that this might not necessarily be the case.

³³S Results

Sulfur-33 has a considerably lower natural abundance from that of ²⁵Mg making it quite a difficult nucleus to study. However, it has a larger magnetogyric ratio and smaller quadrupole moment than that of ²⁵Mg. As such, one might not expect the quadrupolar interaction to necessarily dominate the ³³S SS spectra as much as in the case of ²⁵Mg. The ³³S natural abundance SS-NMR spectra taken at 21.1 T for α - and β -MgSO₄ can be seen in Figures 3A and 3C. The NMR parameters extracted from the experimental spectra along with the calculations are summarized in Table 3. Indeed, the quadrupolar interactions do not dominate in the case of ³³S as they did for ²⁵Mg and CSA parameters could be reliably extracted (Table 3). The experimentally determined quadrupolar coupling constants were: $C_Q = 2.14 \pm 0.05$ MHz for ³³S in α -MgSO₄ and $C_Q = 2.00 \pm 0.05$ MHz for β -MgSO₄. Although the magnitude of the quadrupolar interaction is quite similar for both α - and β -MgSO₄, the asymmetry parameters η_Q are quite different. For α -MgSO₄ it is nearly completely asymmetric with $\eta_Q = 0.91 \pm 0.05$, whereas in β -MgSO₄ the ³³S EFG tensor deviates only slightly from being axially symmetric with $\eta_Q = 0.11 \pm 0.05$. This gives another distinctive characteristic for the two polymorphs. In terms of isotropic chemical shifts for ³³S sites in α - and β -MgSO₄ the values are very similar to each other with $\delta_{iso} = 313.1 \pm 0.5$ ppm for α -MgSO₄ and $\delta_{iso} = 316.8 \pm 0.5$ ppm for β -

MgSO₄. This is not surprising since the isotropic chemical shift range for ³³S in anhydrous sulfates is known to be quite narrow.^{19,33} At high magnetic fields the presence of the CSA potentially can complicate the spectra considerably. However, for the given case there is a discernable and measurable difference between the anisotropy in the sulfur sites of the two polymorphs. α -MgSO₄ has a larger chemical shielding anisotropy for ³³S than does β -MgSO₄, with $\sigma_{aniso} = -51.5 \pm 5.0$ ppm for ³³S α -MgSO₄ and $\sigma_{aniso} = -36.6 \pm 5.0$ ppm for ³³S in β -MgSO₄ (Table 3).

It is again of particular interest to compare the calculated NMR parameters to those obtained experimentally. It can be seen from Table 3 that overall agreement between ³³S experiments and calculations are very good. The CASTEP calculations for α -MgSO₄ reproduce quite well the isotropic chemical shift of sulfur. The quadrupolar coupling constant is only slightly underestimated and the asymmetry parameter is predicted very accurately. The magnitude of the anisotropy parameter, σ_{aniso} , was also accurately predicted for ³³S in α -MgSO₄, despite having an opposite sign (in Haeberlen convention,^{46,47} when the asymmetry η_{CSA} is close to 1 the reverse of the anisotropy sign is not uncommon). The calculated value for the asymmetry of the CSA, η_{CSA} , and the Euler angles, $\{\alpha, \beta, \gamma\}$ also match the experiment well. The CASTEP calculations reproduce the ³³S experimental results quite accurately for the β -polymorph too. The calculated isotropic chemical shift and the quadrupolar parameters match the experimental values well. The chemical shielding anisotropy is also predicted accurately in both magnitude and sign. When examining the calculated results for ³³S for the two reported structures of β -MgSO₄ a few notable differences can be seen. Both the

calculated isotropic chemical shift and the quadrupolar coupling constant for the structure determined through single crystal X-ray diffraction reproduce the experimental parameters more accurately. The only parameter from the CASTEP calculations employing the neutron powder diffraction structure which matched the experiment more closely than that from the single crystal, was the quadrupolar asymmetry parameter, η_Q . Yet, the predicted η_Q from the single crystal structure is also well within experimental error of the experimental value. Altogether this suggests that the atomic coordinates obtained in a single crystal study of β -MgSO₄ are more accurate and reliable than those from the neutron powder diffraction study. Although it is not entirely correct to compare directly R-factors from the SC XRD and PND studies, we note that the single crystal XRD study of β -MgSO₄ reports R=0.017 [16], when the PND for the same polymorph resulted in R=0.036[15].

Further examination of the CASTEP calculations and structural features of sulfur in MgSO₄ shows some interesting details. Sulfur is, of course, in a tetrahedrally coordinated oxygen environment in the SO₄²⁻ anion. However, the symmetry present at the sulfur site is quite far from being perfectly tetrahedral. Table 2 and Figures 3B and 3D show the point group symmetry present at the sulfur site in α - and β -MgSO₄. Similar to the previous case of ²⁵Mg, it is interesting to examine the relationship, if any, between the local environment and the NMR parameters for ³³S, both experimental and calculated. For α -MgSO₄ (Figure 3B), symmetry of sulfur site is C_{2v}. For this type of symmetry there are three independent components of the symmetric part of the shielding tensor.^{41,42} So again one might not necessarily expect an axially symmetric shielding tensor with these

restrictions on the principal components of the shielding tensor.⁴¹ And indeed the experimental results for ^{33}S in $\alpha\text{-MgSO}_4$ show a non-axially symmetric shielding tensor with $\eta_{\text{CSA}} = 1.0 \pm 0.2$. A similar argument can be made for the case of the EFG tensor⁴⁴ and the experimentally determined quadrupolar asymmetry parameter is far from axially symmetric with $\eta_Q = 0.91 \pm 0.05$. Examining the calculated tensor orientations for $\alpha\text{-MgSO}_4$ in Figure 3B reveals some additional details. The largest component of the EFG tensor, V_{33} , is restricted to one of the mirror planes through the sulfur atom while σ_{33} lies in the other mirror plane. Additionally, V_{11} and σ_{22} are calculated to be along the C_2 proper rotation axis through the sulfur site. With these orientations the angle between the largest components of the EFG and CSA tensor, V_{33} and σ_{33} , is 90° , which is totally in agreement with experiment (Table 3). The situation for sulfur in $\beta\text{-MgSO}_4$ is quite different from that of $\alpha\text{-MgSO}_4$. The symmetry of the site is C_s with a mirror plane through the sulfur atom (Table 2 and Figure 3D). Thus, one would expect few restrictions on the number of independent components of the CSA and EFG tensors and axial symmetry generally should not be expected. The presence of sulfur on a mirror plane, however, requires that one component of each tensor to be perpendicular to the plane, and the others must be in the plane. This inflicts limitations on possible relative orientations of two tensors. Interestingly, though, the shielding tensor for $\beta\text{-MgSO}_4$ is predicted by CASTEP to be close to axially symmetric and is experimentally measured to be $\eta_{\text{CSA}} = 0.0 \pm 0.2$. The EFG tensor is also experimentally close to axially symmetric with $\eta_Q = 0.11 \pm 0.05$. Examining the calculated tensor orientations shows V_{33} is restricted to the mirror plane while σ_{33} is perpendicular to the plane. V_{33} also points to one of the oxygen atoms in the tetrahedron of the SO_4^{2-} group. This S-O axis may act as a pseudo- C_3

rotation axis in an SO_4^{2-} anion. This, together with very small differences in the S-O bond lengths in the ion, may explain nearly axially symmetric nature of the CSA and EFG tensors. Again, a 90° angle is predicted between V_{33} and σ_{33} and this is confirmed experimentally (Table 3).

^{17}O Results

The study of ^{17}O is known to be quite a challenge, in general, due to the extremely low natural abundance and quadrupolar nature of the nucleus. In this work the samples are slightly enriched in ^{17}O which significantly relaxes the sensitivity issues. Additionally, ^{17}O has a significantly larger magnetogyric ratio and a much smaller quadrupole moment from that of ^{25}Mg and ^{33}S . In magnesium sulfates, however, there is the additional problem of having multiple crystallographic sites for oxygen in both polymorphs studied.

The ^{17}O SS NMR spectra and spectral simulations for α - and β - MgSO_4 taken at 21.1 and 9.4 T can be seen in Figures 4 and 6, respectively. To aid in the assignment and extraction of spectral parameters for the multiple oxygen sites in each polymorph, MQMAS experiments were also performed and shown in Figures 5 and 7. The ^{17}O results for α - MgSO_4 are not as complicated as in the case of β - MgSO_4 since there are only 2 crystallographically unique oxygen sites in α - MgSO_4 . The 3Q MQMAS spectrum for α - MgSO_4 shows two clearly resolved unique oxygen sites. Measurements of the stationary powder samples at two different fields aided by the MAS data and combined with the

simulations allow for accurate extraction of parameters for both oxygen sites in α -MgSO₄. The ¹⁷O NMR parameters obtained for the two oxygen sites in α -MgSO₄ are in fact quite similar (Table 3). The isotropic chemical shifts differ only by about 3 ppm and the quadrupolar coupling constants are nearly identical. Despite the small differences, however, the numerous singularities in the spectra on Figure 4 can be resolved, aiding in the parameters evaluation. This example demonstrates the importance of using an ultrahigh field for obtaining the necessary resolution in studies of quadrupolar nuclei. The static experiments performed on α -MgSO₄ also show a measurable contribution of the CSA interaction. The extracted shielding anisotropy parameters are also listed in Table 3. The shielding asymmetry parameters for both sites are quite similar with $\eta_{CSA} = 0.18$ and $\eta_{CSA} = 0.15$. The anisotropy, on another hand, for one of the ¹⁷O sites at $\sigma_{aniso} = 128$ ppm is much larger than that for the other site with $\sigma_{aniso} = 77$ ppm, providing a means for a better assignment of the sites.

In the case of β -MgSO₄, there are 3 crystallographically inequivalent oxygen sites, making assignment somewhat more difficult. Indeed, the MQMAS spectrum of ¹⁷O in β -MgSO₄ was not able to completely resolve the 3 oxygen sites. Nevertheless, by fitting the high field 1D MAS and static experiments and examining the lower field data, reasonable estimates for the spectral parameters for all three oxygen sites still can be accomplished, as summarized in Table 3. It should be noted that the results obtained for ¹⁷O in β -MgSO₄ are similar to α -MgSO₄ in that the parameters for all sites are, in general, in the expected range and reasonably similar. Akin to the ²⁵Mg and ³³S results, the data obtained from ¹⁷O can be used in distinguishing the two polymorphs of MgSO₄.

One interesting observation in regard to the ^{17}O data, is that the singularities appear to be less resolved in the spectra obtained at the higher field. The main reason for this is an unfortunate interplay between the EFG and the CSA tensors. While the quadrupolar interactions clearly dominate the spectrum at 9.4T with a relatively small input from the CSA, the situation is altered at 21.1T. The dramatically reduced quadrupolar contribution together with an accordingly scaled up CSA, result in a strong overlap of singularities and contributions from several sites. One should also note, that although the stationary spectra at 21.1T appear visually broader than at 9.4 T, they actually span over much narrower spectral regions (i.e., compare the scales below the spectra).

The CASTEP-calculated NMR parameters for ^{17}O in both α - and β - MgSO_4 match the experimentally determined values quite well. The predicted quadrupolar coupling constants for all ^{17}O sites in both α - and β - MgSO_4 match the experimental values accurately. As well, the magnitude of the calculated shielding anisotropy is predicted correctly for all ^{17}O sites. The only seemingly large discrepancy between the calculated results and the experimental NMR parameters is the isotropic shift of the ^{17}O sites in α - and β - MgSO_4 . In all cases the calculated isotropic shift for ^{17}O is systematically lower than the experimentally determined value. The issue may be due to the shielding reference for ^{17}O used in this work, based on single point instead of a correlation reference as used in the case for ^{25}Mg and ^{33}S . Since the accurate prediction of ^{17}O NMR parameters is well documented,^{5,9} one might expect that if a correlation reference

produced on a large set of oxygen-containing compounds, the agreement between calculated isotropic shift and experimental isotropic shift would improve. From the ^{17}O calculations for $\beta\text{-MgSO}_4$ alone, it is somewhat difficult to conclude whether one structure provided more accurate NMR parameters than the other since the calculated parameters are rather similar. Still, by examining the calculated isotropic chemical shift it can be seen that the values obtained from the single crystal XRD structure provided a more accurate forecast of the experimental isotropic shifts.

Similar to ^{25}Mg and ^{33}S , a closer examination of the calculated results offers some interesting insights into the structural details of these MgSO_4 polymorphs. Since there are multiple oxygen sites, only the largest component of both the calculated EFG and CSA tensor are shown on Figures 5 and 7 to avoid figure complexity. The calculated tensor orientations at the both oxygen sites in $\alpha\text{-MgSO}_4$ are shown in Figure 5. Both oxygen sites in $\alpha\text{-MgSO}_4$ have C_s symmetry resulting in a single mirror plane through each atom. The V_{33} and σ_{33} components for both oxygen sites lie in their respective mirror planes. One oxygen site has both principal components pointed directly away from the sulfur atom with an Euler angle β of $\sim 10^\circ$, while the other oxygen site has V_{33} pointing directly away from the sulfur atom when the respective σ_{33} is pointing directly towards the sulfur resulting in an Euler angle β of $\sim 180^\circ$. This result accurately matches the experiment. Given the symmetry present at these oxygen sites one would not expect an axially symmetric EFG or CSA tensor.⁴¹⁻⁴⁴ Indeed, the experimental asymmetry parameters η_Q and η_{CSA} indicate the lack of axial symmetry for both tensors.

The calculated orientations for the main components of the EFG and CSA tensors in β -MgSO₄ are shown in Figure 7. As for the α -form, the principal components V_{33} and σ_{33} for the oxygen atoms that have C_s symmetry, lie in the mirror plane (O2 and O3, with corresponding V_{33}^2 , σ_{33}^2 and V_{33}^3 , σ_{33}^3). For both these oxygen atoms, the V_{33} and σ_{33} components also point directly towards the central sulfur atom with $\beta = \sim 5^\circ$ in an accord with the experiment (Table 3). For the oxygen site with symmetry C_1 the largest components of the EFG and CSA tensors are also almost coincident with $\beta = \sim 5^\circ$ similar to the other oxygen sites. In this case, however, V_{33} and σ_{33} point directly away from the central sulfur atom.

Conclusions

The present study has demonstrated that with the use of ultrahigh fields of 21.1 T previously unattractive nuclei such as ^{25}Mg , ^{33}S , and ^{17}O can be studied via SS NMR with relative ease. The α - and β - polymorphs of anhydrous magnesium sulfate were studied via SS-NMR on all the nuclei of material. The two polymorphs can be successfully distinguished and the spectra are in a complete accord with the crystal structures of the materials. For ^{25}Mg and ^{33}S simple 1D MAS experiments are all that is needed to distinguish between the polymorphs, whereas enrichment and 2D experiments were required for ^{17}O . With the aid of first principles calculations, fine structural details

and the relation of the EFG and CSA tensors were examined for all nuclei in both polymorphs. It was found that symmetry at the sites and character of the chemical bonds dictated specific tensor orientations. Another aspect of the study was to compare the recently reported crystal structures for β -MgSO₄. It was found that, at least for ³³S and ¹⁷O, the calculations performed on a structure from single crystal XRD reproduce the experimental parameters more accurately than the calculations using the structural data from the neutron powder diffraction. This work demonstrates how previously difficult NMR nuclei can now be successfully studied, assisting in a better understanding of materials nature. With the aid of first principles calculations, the information for each nuclei complements each other resulting in a detailed picture of the fine structural details.

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Figures Captions

Figure 1 Experimental and simulated ^{25}Mg spectra of $\alpha\text{-MgSO}_4$: A – stationary sample (both Hahn-Echo and QCPMG are shown), B - MAS (both Hahn-Echo and rotor-synchronized QCPMG are shown), and C - calculated orientations of the EFG and CSA tensors. Analytical simulations of the spectra were performed with WSolids²⁷ for stationary spectra and DMFit²⁸ for the MAS experiments.

Figure 2 Experimental and simulated ^{25}Mg spectra of $\beta\text{-MgSO}_4$: A – stationary sample with both Hahn-Echo and QCPMG experiments are shown, B – MAS at 16 kHz with rotor-synchronized QCPMG, and C - calculated orientations of the EFG and CSA tensors. Analytical simulations of the spectra were performed with WSolids²⁷ for stationary spectra and DMFit²⁸ for the MAS experiments, and included both quadrupolar interactions and the CSA.

Figure 3 Experimental and simulated ^{33}S spectra of $\alpha\text{-MgSO}_4$ (panel A) and $\beta\text{-MgSO}_4$ (panel C). Traces a', c' are the spectral simulations accounting only for quadrupolar interactions. Traces a'' and c'' are the fits that also include the CSA. The spectral fits to the MAS spectra account for quadrupolar interactions only. Panels B and D demonstrate the calculated orientations of the EFG and CSA tensors of sulfur nucleus in α - and β -polymorphs, respectively. Dotted vertical lines indicate positions of singularities in the spectra. Note the discrepancies between the simulations and the experiment when only quadrupolar interaction are considered (traces a' and c').

Figure 4 Experimental and simulated ^{17}O spectra of $\alpha\text{-MgSO}_4$ at 21.1T (panel A) and at 9.4T (panel B). Traces a', b' are the spectral simulations accounting only for quadrupolar interactions. Traces a'' and b'' are the fits that also include the CSA. The spectral fits to the MAS spectra account both for quadrupolar interactions and the CSA. Dotted vertical lines indicate positions of singularities in the spectra. For online color version, red (upper) traces in the simulated spectra correspond to the sums of the contributing individual sites, shown correspondingly in green, violet and black.

Figure 5 ^{17}O 3Q MQMAS spectrum of $\alpha\text{-MgSO}_4$ at 21.1T, and calculated orientations of the main components in the EFG and CSA tensors for two oxygen sites in the crystal.

Figure 6 Experimental and simulated ^{17}O spectra of $\beta\text{-MgSO}_4$ at 21.1T and at 9.4T. Traces a', b' are the spectral simulations accounting only for quadrupolar interactions. Traces a'' and b'' are the fits that also include the CSA. The spectral fits to the MAS spectra account both for quadrupolar interactions and the CSA. Dotted vertical lines indicate positions of singularities in the spectra. For online color version, red (upper) traces in the simulated spectra correspond to the sums of the contributing individual sites, shown correspondingly in green, violet and black.

Figure 7 ^{17}O 3Q MQMAS spectrum of $\beta\text{-MgSO}_4$ at 21.1T , and calculated orientations of the main principal components in the EFG and CSA tensors for the oxygen sites in the crystal. The components V_{33}^2 , σ_{33}^2 and V_{33}^3 , σ_{33}^3 lie along the O2-S and O3-S bonds, respectively, and all directed toward the sulfur atom.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Table 1. Magnetic resonance properties of nuclei in MgSO₄.²⁰

Isotope	Spin	Natural Abundance, %	Magnetogyric Ratio γ (10^7 rad T ⁻¹ s ⁻¹)	Larmor Frequency at 21.1T, MHz	Quadrupole moment, fm ²	Linewidth factor, l/fm ⁴	Receptivity (relative to ¹³ C)
¹⁷ O	5/2	0.037	-1.6388	122.02	-2.56	2.1	0.065
²⁵ Mg	5/2	10.00	2.0557	55.1	19.94	130	1.58
³³ S	3/2	0.76	-3.6281	69.09	-6.78	61	0.101

Table 2. Structural details of MgSO₄ polymorphs.

Parameter	α -MgSO ₄ [XPD] ¹⁵	β -MgSO ₄ [NPD] ¹⁵	β -MgSO ₄ [SC XRD] ¹⁶
Lattice	Orthorhombic	Orthorhombic	Orthorhombic
a (Å)	5.1747	4.7460	8.5787
b (Å)	7.8756	8.5831	6.6953
c (Å)	6.4952	6.7093	4.7438
V (Å ³)	264.70	273.31	272.47
Z	6	4	4
Space Group	<i>Cmcm</i>	<i>Pbnm</i>	<i>Pnma</i>
Mg site symmetry	C _{2h}	C _i	C _i
S site symmetry	C _{2v}	C _s	C _s
O1 site symmetry	C _s	C _s	C ₁
O2 site symmetry	C _s	C _s	C _s
O3 site symmetry	-	C ₁	C _s

Table 3. Experimental and calculated ^{25}Mg , ^{33}S , and ^{17}O NMR parameters for MgSO_4 polymorphs.

Polymorph / Nucleus	NMR Parameters					
	$\delta_{\text{iso}}/\sigma_{\text{iso}}$ [$\delta_{\text{iso}}^{\text{calc}}$] ^c (ppm)	C_Q (MHz) ^d	η_Q ^e	$\Delta\sigma_{\text{aniso}}$ (ppm) ^f	η_{CSA} ^g	$\{\alpha, \beta, \gamma\}$ ^g (°)
<i>α-MgSO_4^a</i>						
^{25}Mg	-8.1 ± 1.0	7.41 ± 0.05	0.35 ± 0.02	19.5 ± 2.0	0.8 ± 0.2	{0, 0, 90}
CASTEP	576.45 [-10.4]	-8.89	0.45	17.36	0.45	{0, 0, 90}
^{33}S	313.1 ± 0.5	2.14 ± 0.05	0.91 ± 0.05	-51.5 ± 5	1.0 ± 0.2	{90, 90, 0}
CASTEP	118.81 [315.3]	-1.85	0.88	49.91	0.97	{90, 90, 180}
^{17}O (site1)	148.6 ± 0.3	8.24 ± 0.06	0.21 ± 0.05	77 ± 10	0.18 ± 0.1	{0, 10, 0}
(site2)	145.5 ± 0.3	8.25 ± 0.06	0.23 ± 0.05	128 ± 15	0.15 ± 0.1	{90, 180, 270}
CASTEP (site1)	108.77 [146.23]	-8.03	0.20	80.12	0.21	{0, 10, 0}
(site2)	111.31 [143.69]	-8.47	0.25	134.83	0.16	{90, 175, 270}
<i>β-MgSO_4</i>						
^{25}Mg	0.2 ± 3.0	10.4 ± 0.1	1.00 ± 0.05	< 35	-	-
CASTEP (NPD) ^a	579.59 [-13.53]	12.00	0.95	28.58	0.68	{270, 90, 180}
CASTEP (SCXRD) ^b	576.63 [-10.57]	12.54	0.91	28.25	0.74	{90, 90, 180}
^{33}S	316.8 ± 0.5	2.00 ± 0.05	0.11 ± 0.05	-37.6 ± 5	0.0 ± 0.2	{90, 175, 10}
CASTEP (NPD) ^a	126.88 [307.22]	-1.14	0.19	-34.30	0.04	{180, 90, 270}
CASTEP (SCXRD) ^b	120.89 [313.21]	-1.84	0.33	-40.24	0.14	{180, 90, 185}
^{17}O (site1)	145.3 ± 0.3	7.77 ± 0.07	0.16 ± 0.06	80 ± 20	0.25 ± 0.2	{-20, 5, 10}
(site2)	145.7 ± 0.3	8.40 ± 0.07	0.25 ± 0.05	115 ± 20	0.15 ± 0.2	{-90, 5, 10}
(site3)	146.6 ± 0.3	8.30 ± 0.07	0.20 ± 0.05	100 ± 20	0.10 ± 0.2	{90, 5, 90}
CASTEP (site1) (NPD) ^a	117.81 [137.19]	-7.94	0.18	97.47	0.20	{10, 5, 160}
(site2) (NPD) ^a	121.97 [133.03]	-8.00	0.23	109.88	0.06	{90, 5, 90}
(site3) (NPD) ^a	127.13 [127.87]	-7.89	0.29	111.98	0.12	{90, 5, 270}
CASTEP (site1) (SCXRD) ^b	115.91 [139.09]	-7.89	0.17	94.61	0.23	{190, 5, 160}
(site2) (SCXRD) ^b	115.44 [139.56]	-8.41	0.27	130.36	0.14	{90, 5, 270}
(site3) (SCXRD) ^b	114.55 [140.45]	-8.31	0.21	118.84	0.10	{270, 5, 90}

^a Calculations were performed on geometry optimized structures from NPD data.¹⁵ ^b Calculations were performed on geometry optimized structure from SC XRD data.¹⁶ ^c $\delta_{\text{iso}}^{\text{calc}}$ obtained as $\delta_{\text{iso}} = -(\sigma_{\text{iso}} - \sigma_{\text{ref}})$ with σ_{ref} defined in the experimental section. ^d Although the calculations produce the sign of the C_Q , only the magnitude can be obtained in our experiments. ^e η_Q defined as: $|V_{11} - V_{22}|/V_{33}$. ^f The Haeberlen convention^{45,46} is used in CASTEP with the anisotropy defined as $\sigma_{\text{aniso}} = \sigma_{33} - (\sigma_{11} + \sigma_{22})/2$. ^g Asymmetry parameter η_{CSA} is defined as $\eta = (\sigma_{22} - \sigma_{11})/(\sigma_{33} - \sigma_{\text{iso}})$. Principal components of the symmetric shielding tensor ordered as: $|\sigma_{33} - \sigma_{\text{iso}}| \geq |\sigma_{11} - \sigma_{\text{iso}}| \geq |\sigma_{22} - \sigma_{\text{iso}}|$. ^h α, β, γ – Euler angles defining the relative orientation of the CSA and EFG tensors.^{46,47} Accuracy is not expected to be better than $\pm 10^\circ$.