

First-principles calculations and ultrahigh-field multinuclear solid-state NMR in MgSO_4 polymorphs

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Developments in NMR instrumentation, especially ultrahigh-field NMR magnets, combined with advances in computation of NMR parameters, significantly broadened the scope of solid-state NMR of materials with low- γ , low natural abundance and quadrupolar nuclei.

Here we use a combination of ultrahigh-field NMR and first principles calculations (CASTEP) [1] to study ^{17}O , ^{25}Mg and ^{33}S NMR in polymorphs of anhydrous magnesium sulfate. Magnesium sulfates are believed to be an important planetary rock-forming materials in our solar system, particularly on Venus [2], as well as in the outer space [3]. Below about 800 K anhydrous magnesium sulfate is known to co-exist in two structurally similar polymorphs. Due to the difficulties of growing single crystals of highly hygroscopic MgSO_4 , the earlier structures were solved from X-Ray powder data [4] and were later refined using powder neutron diffraction [5]. First single crystal study for $\beta\text{-MgSO}_4$ was published only few years ago [6].

MgSO_4 poses some serious solid state NMR challenges. All three nuclei are quadrupolar, and their solid-state NMR signals broadened by the quadrupolar interactions. Two of the three nuclei (^{25}Mg and ^{33}S) have very low gammas, and only one of them have moderate natural abundance (^{25}Mg - 10%, ^{33}S - 0.75%, ^{17}O - 0.037%). A combination of all the above results in a very poor NMR receptivity.

In this work we performed solid-state NMR study on all three nuclei in α - and β -forms of anhydrous magnesium sulfate at a magnetic field of 21 T. At this magnetic field the effects of quadrupolar interactions are reduced significantly and the sensitivity and accuracy in determining the NMR parameters improve dramatically. For all three nuclei their spectra are dominated by the quadrupolar

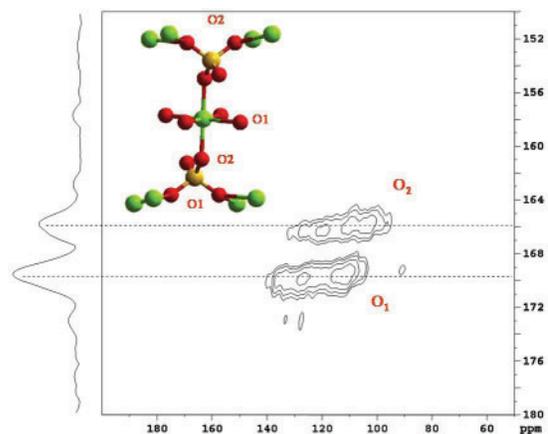


Figure 1: ^{17}O MQMAS NMR spectrum in $\alpha\text{-MgSO}_4$. Two oxygen sites can be accurately resolved.

effects, although in the cases of ^{17}O and ^{33}S there is a noticeable contribution from the CSA. We demonstrate that the results of the first principles calculation very accurately reproduce the experimental data and can be used as a structural assessment tool.

References

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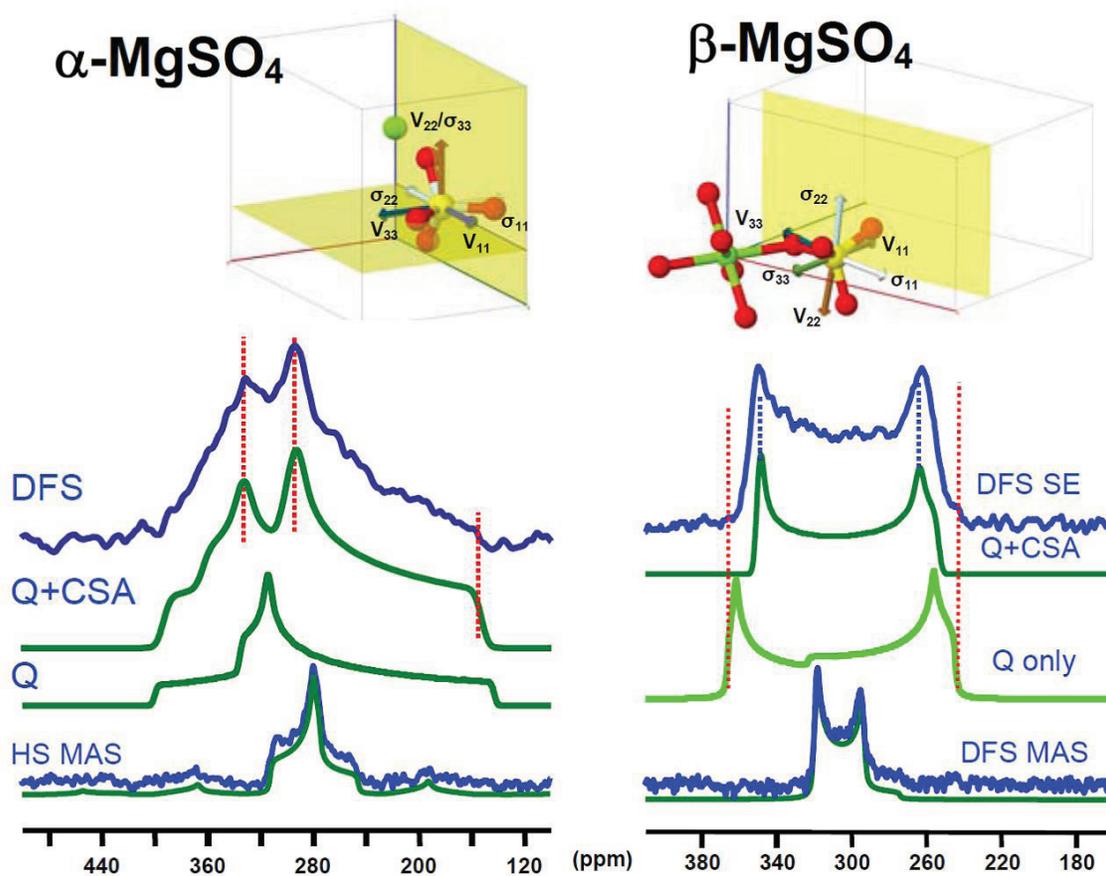


Figure 2: Solid-state ^{33}S NMR in α - and β - MgSO_4 . Combination of high magnetic field and signal enhancement techniques allows for reliable detection of the chemical shift anisotropy.