

Why use NMR?

Nuclear Magnetic Resonance (NMR) spectroscopy is a powerful technique that can probe the structure of solid materials and provides information on the local order of structures. This allows investigation of how nuclei in materials produce the unique properties the material exhibits. The Quadrupole interaction affects nuclei with spin greater than a half and is mainly an intramolecular effect. It arises due to the interaction between the quadrupole moment of the nucleus and the Electric Field Gradient (EFG) generated by the local electrons. This interaction dominates the NMR spectrum of certain nuclei and it must be accounted for when performing NMR on them. However, this effect provides key information on the unit cell of the compound and the local environment of the nucleus being studied. In this research nuclei with strong quadrupole effects are investigated to discover their role in the unique properties their compounds exhibit.



Lanthanum NMR

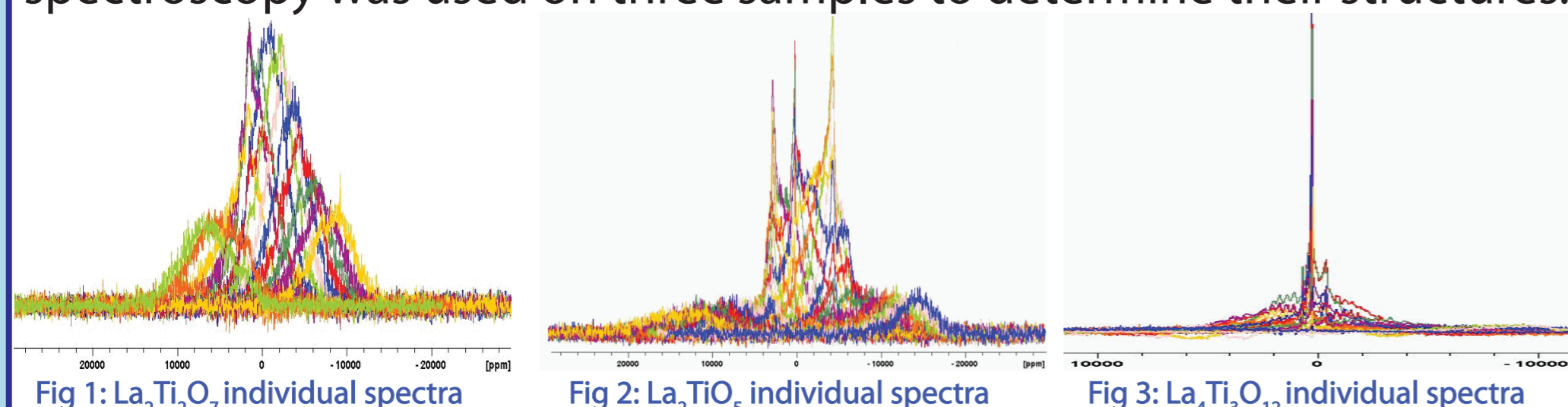
NMR spectroscopy on Lanthanum nuclei is hampered by the very broad peaks due to the large quadrupole moment. When you pulse the sample you record only a narrow section of the spectrum. This is overcome by using a method called Variable Offset Cumulative Spectroscopy (VOCS). This involves incrementing the pulse frequency and summing the recorded spectra as shown below.

Boron NMR

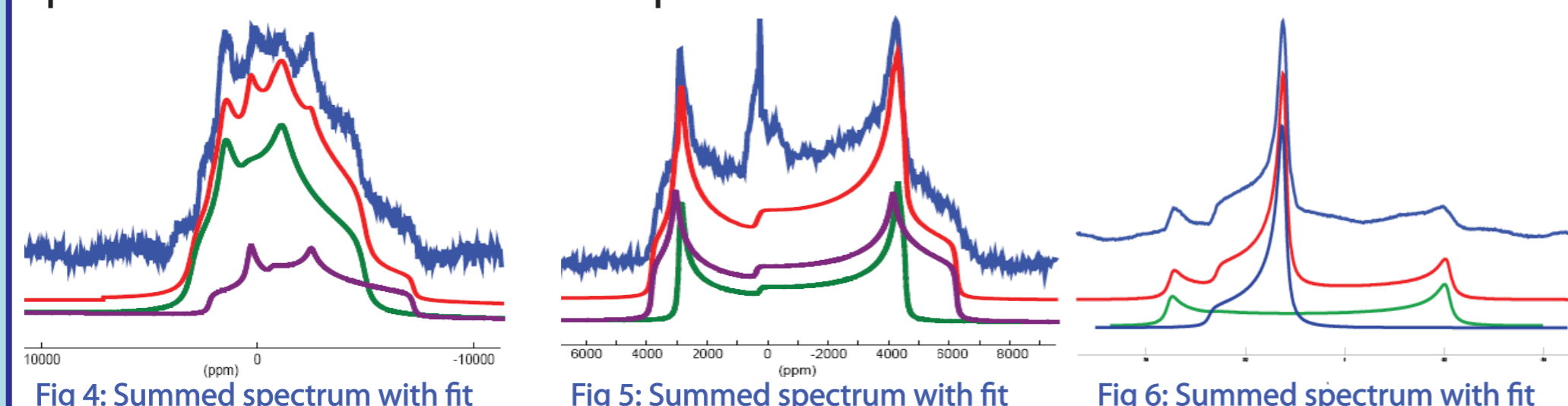
There are 2 isotopes of Boron that are sensitive to NMR spectroscopy. ^{11}B was chosen as the nucleus to study as it is 80% naturally abundant and has a gyromagnetic ratio roughly three times greater than ^{10}B . This makes it the preferred nucleus out of the two possibilities. ^{11}B is a highly sensitive nucleus for NMR and this makes it excellent for tracking a reaction such as the one shown below.

Lanthanum Results

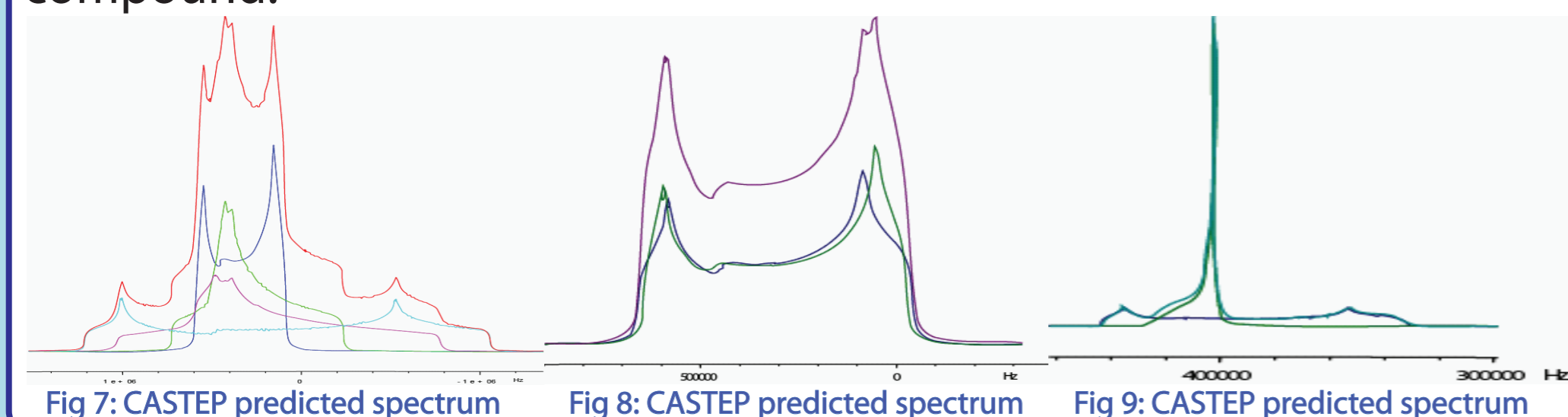
Compounds of the Lanthanide series of the periodic table exhibit the ability to withstand very large radiolytic doses. This is very important in the storage and immobilisation of nuclear waste. Little is understood about their structure however, and Lanthanum Titanates are believed to form structures similar to other compounds in the group. NMR spectroscopy was used on three samples to determine their structures.



Each spectrum was taken at 100kHz intervals, produced using a Hanh echo to avoid ringing. This is interference from the electronics used to produce the pulse, which discharge when you would be recording. The spectra are then summed to produce the blue line below.



The red line is the fitted spectra and the green and purple lines show the two sites that the Lanthanum nucleus occupies in the structures. These results are then compared to simulated spectrum produced using a program called CASTEP. This uses density functional theory (DFT) to produce a spectrum for a proposed cell structure of the compound.



Lanthanum Conclusions

Experimental results for the compounds La_2TiO_5 and $\text{La}_3\text{Ti}_4\text{O}_{12}$ show good agreement with the predicted spectra. This allows us to say with confidence they have the Orthorhombic and Rhombohedral cell structures. However, the results and the CASTEP predictions do not agree for $\text{La}_2\text{Ti}_2\text{O}_7$. Further work is required to determine its unit cell structure. This could be more DFT calculations using another program such as WEIN2K, as different programs use different methods to produce a theoretical spectra or a different technique such as XRD.

Boron Results

Alkali metal amino boranes are considered one of the best methods of storing Hydrogen for fuel cells. This research looks at the mechanism of H_2 release, via thermal decomposition, using Boron NMR spectroscopy. The theoretical reaction pathway is tested by taking samples from each stage and doing a simple one pulse NMR spectroscopy experiment on it. Only one of the initial reactants can be tested.

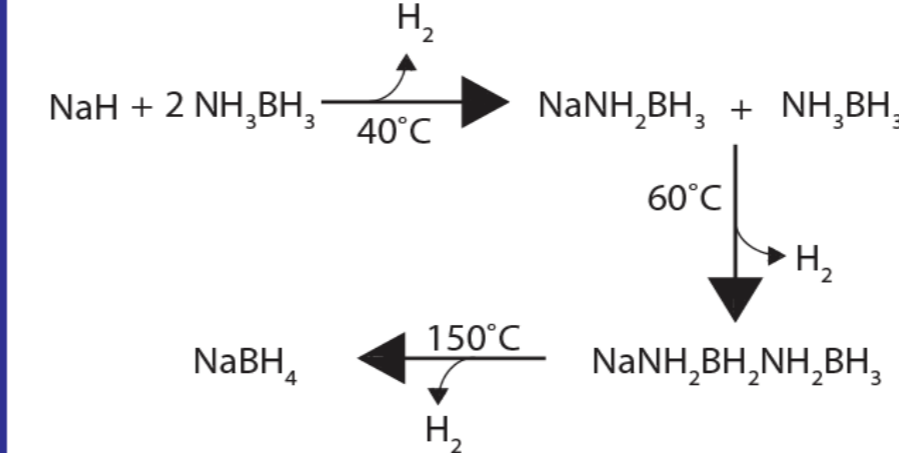


Fig 10: The proposed reaction chain

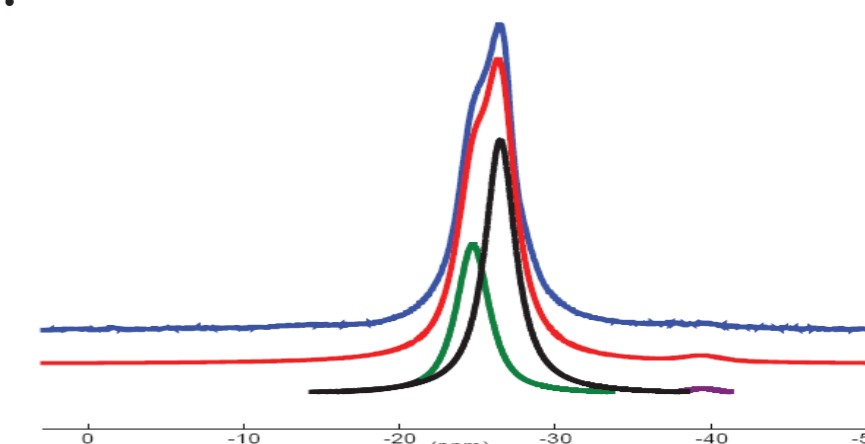


Fig 11: Initial reactant NH_3BH_3

At 40°C , the initial release of Hydrogen occurs and from the NMR it is clear a reaction has occurred. The Boron sites increase from the single, symmetric and anti-symmetric, site to 5. The 2 left sites (20 and 26ppm) are trigonal B_3 sites, the right hand two sites (-24 and -40ppm) are B_4 sites and the central site (0ppm) is an unwanted site of either BO or BN.

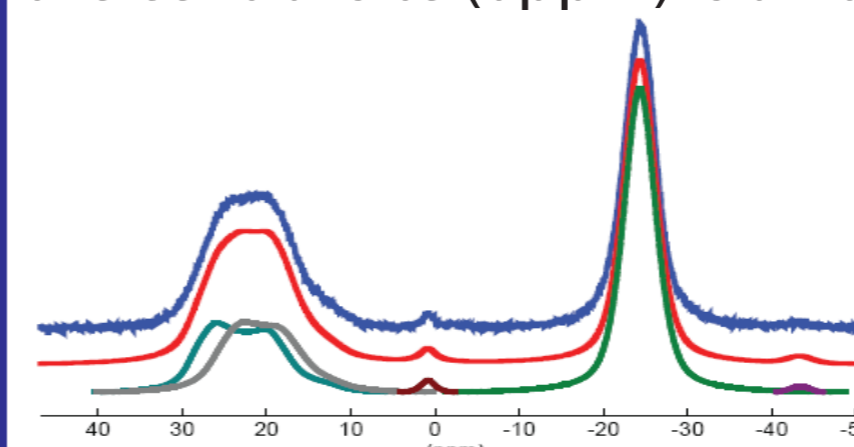


Fig 12: The first reaction products

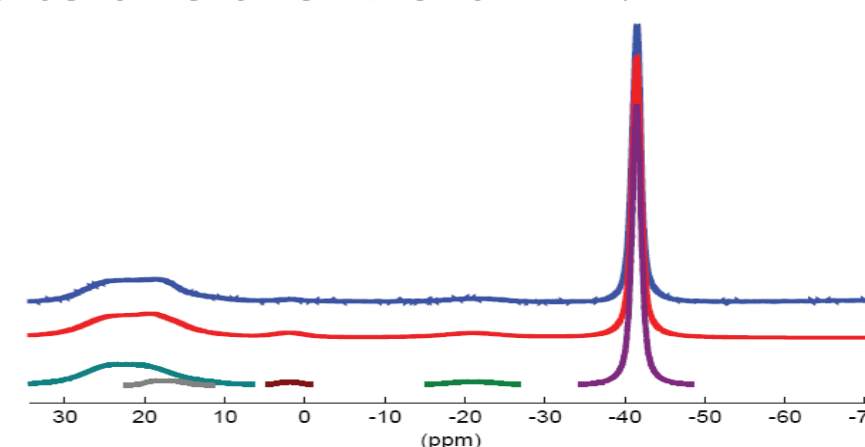


Fig 13: The second reaction products

At 60°C a second hydrogen releasing reaction occurs and there is a clear change in the occupation of the sites. The trigonal B_3 sites have decreased in number after this reaction and the tetrahedral B_4 sites have become rigidly symmetrical and shifted to 40ppm. The final reaction occurs as the sample is heated again to 150°C . With the release of more Hydrogen the second set of products is reduced to just a single final product of NaBH_4 . This site has a very narrow peak showing that it is highly symmetrical and rigid structure. The reaction pathway is complete at 150°C with all initial reactants having been used up.

Fig 14: The final reaction pathway product

Boron Conclusions

The proposed reaction chain is clearly not a complete one. In the second intermediate phase of the pathway there are clearly 5 sites present, as opposed to the 2 sites predicted. However, the final result is correct as the final spectra shows only the single NaBH peak. A few of the peaks are poorly resolved. Further work at higher fields would help to resolve these and allow better identification of the peaks. This would allow the theoretical reaction pathway to be made more accurate.