An assignment of the ^{23}Na MAS NMR spectrum of $Na_5P_3O_{10}\cdot 6H_2O$ using a general *ab initio* method

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A new assignment method based on the periodic *ab initio* calculation of ^{23}Na quadrupole coupling information using the CRYSTAL95 code is described and applied to the multi-site problem posed by $Na_5P_3O_{10}\cdot 6H_2O$.

Modern solid-state NMR techniques for non-integer quadrupolar nuclei, particularly those based on MAS NMR techniques, are now commonly used in the characterisation of a wide range of materials including simple inorganic salts and complexes, zeolites, catalysts, minerals and ceramics.[1] In the particular case of the ^{23}Na nucleus ($I = 3/2$) an extensive body of experimental information for the quadrupole parameters, that is the quadrupole coupling constant ($C_Q = e^2qQ/h$) and the asymmetry parameter (η), has now been established. The assignment of ^{23}Na spectra, however, still remains problematic even in cases for which a crystal structure is available. One approach has been to use classical electrostatic modelling methods, although these are not always reliable.[2] Here we describe an *ab initio* approach which is specifically designed to be used in a routine manner for assignment purposes. It is based on the CRYSTAL95 code.[3] This package performs *ab initio* calculations of the properties of periodic systems taking into account the symmetry of the crystal lattice to form crystalline orbitals from a linear combination of atomic orbitals.

The ability to assign quadrupole parameters to individual sodium sites in a known crystal structure is important. This is because the magnitudes of these parameters are directly related to the nature of the electronic charge distribution surrounding a given sodium site. A more detailed understanding of this relationship can provide information on the electronic structure of a solid as a whole. At a more practical level, the knowledge gained is useful for more complex assignment problems such as those associated with glassy and amorphous materials.

We have selected as an example the hydrate of pentasodium triphosphate, $Na_5P_3O_{10}\cdot 6H_2O$[4] since this material is recognised as presenting a particularly difficult assignment problem.[5] It crystallises in the triclinic space group $P\bar{1}$ with all atoms in general positions so that there are five different sodium sites with equal multiplicities.[6] The experimental ^{23}Na MAS NMR spectrum[7] is shown in Fig. 1 and, as expected, is complex with overlapping second-order quadrupolar lineshapes. Using our periodic *ab initio* approach we are able to provide a reasonable interpretation of this spectrum. In principle, MQMAS methods,[8] although experimentally demanding, could provide better spectral resolution and so comparison between the present work and any subsequent MQMAS investigation would be of direct interest.

We have used CRYSTAL95 to calculate the C_Q values for ^{23}Na for a wide range of sodium compounds with known crystal structures (19 in all involving 27 different sodium sites).[9] The Hartree–Fock calculations were based on the relatively small 3-21G molecular basis set of Pople and co-workers[10] and the basis sets for individual atoms were applied consistently across the whole range of compounds investigated. Only modest computer resources were required.[11] A key criterion was to obtain a good linear fit between calculated and experimental values of C_Q; exact agreement for each compound was not required. It can be noted that this approach is independent of the variability in the published values[12] of the nuclear quadrupole moment for ^{23}Na; in this work we use $Q = 0.1089 \times 10^{-28}$ m^2. For sodium, the 3-21G basis set was modified in the manner usually[3] adopted for alkali metal cations by replacing the valence orbitals by a single sp shell; we used an exponent of 0.18. Unmodified 3-21G basis sets were used for oxygen, sulfur and chlorine atoms, whereas some modifications to the values of the exponents for the outermost shells of hydrogen (0.183), nitrogen (0.273) and carbon (0.132) were required. In the case of aluminium, the outermost valence orbital of the 3-21G set is diffuse and this is known to cause convergence problems in periodic calculations.[3] Consequently, this orbital was removed giving a 3-2G set. The same modification of basis set was also found to be of benefit for silicon and phosphorus.

Fig. 2 shows a plot of experimental *versus* calculated C_Q values for ^{23}Na for all of the compounds that we have investigated.[13] The straight line in this figure represents the best linear fit to the data ($R^2 = 0.977$): the slope of the line is 0.979 ± 0.030 and the intercept is 0.084 ± 0.064 MHz. Since the sign of C_Q is usually not obtained in NMR experiments, it is assumed in Fig. 2 that the experimental value of C_Q takes the calculated sign. Overall we conclude that CRYSTAL95 calculations, based on the relatively simple 3-21G basis set, can calculate ^{23}Na C_Q values with sufficient accuracy to be useful for assignment purposes in multi-site problems.

In the case of $Na_5P_3O_{10}\cdot 6H_2O$ the calculated values of the ^{23}Na C_Q for each of the five different sodium sites in the crystal structure are given in Table 1. These values provide a powerful starting point, along with the knowledge that the individual resonances must be of equal intensity, for the simulation of the experimental ^{23}Na MAS NMR spectrum shown in Fig. 1. The results of this simulation[15] are summarised in Table 1 and the simulated MAS NMR spectrum is compared with experiment in Fig. 1.

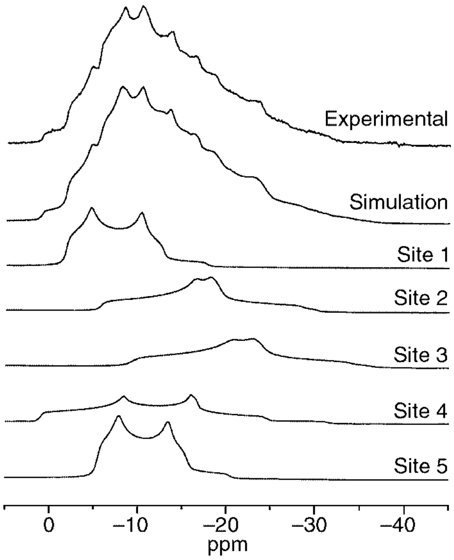

Fig. 1 Experimental (proton-decoupled) and simulated ^{23}Na MAS NMR spectrum of $Na_5P_3O_{10}\cdot 6H_2O$. Individual contributions to the simulated spectrum are also shown.

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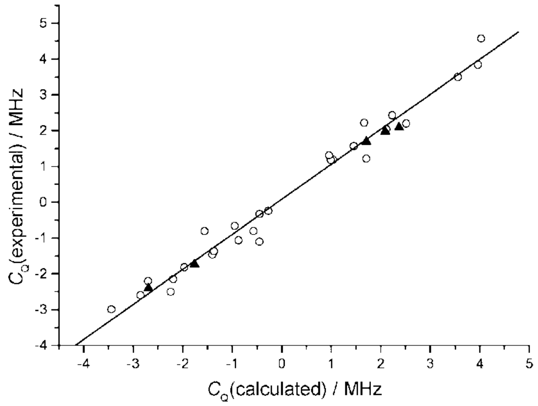

Fig. 2 A plot of experimental *versus* calculated ^{23}Na C_Q values for (i) sodium compounds involving oxyanions of silicon, sulfur, phosphorus, nitrogen, carbon, aluminium, chlorine and hydrogen (○) and (ii) the different sodium sites in $Na_5P_3O_{10}\cdot 6H_2O$ (▲): see Table 1.

Table 1 Information from both *ab initio* calculation and simulation of the experimental ^{23}Na MAS NMR spectrum for the different sodium sites in $Na_5P_3O_{10}\cdot 6H_2O$

	Calculation	Simulation			
Site[a]	^{23}Na C_Q/MHz	^{23}Na C_Q/MHz[b]	η	$\delta_{iso,cs}$(^{23}Na)[c]	Intensity[d]
1	−1.76	1.74	0.29	−0.55	0.21
2	2.09	1.97	0.85	−5.71	0.18
3	2.37	2.09	0.81	−9.09	0.19
4	−2.69	2.40	0.51	2.20	0.22
5	1.71	1.69	0.26	−4.20	0.21

[a] The labels correspond to those used in ref. 6. [b] The sign of these values cannot be determined from the ^{23}Na MAS NMR spectrum. [c] Isotropic chemical shift relative to external solid NaCl. [d] These values have been corrected using the method of Massiot *et al.*[14]

The assignment of the individual sodium sites (1–5) in Table 1 is based on the general linear relationship shown in Fig. 2; individual points corresponding to the assignment are plotted in this figure. The relatively small differences between the simulated ^{23}Na C_Q values does introduce some uncertainty into the assignment. Nonetheless, by using a consistent approach for all 5 sites we obtain, in the absence of any other information, a reasonable assignment. Potentially, the results also provide a very good starting point for a more detailed MQMAS investigation. It is worth noting that the sign of C_Q, if available experimentally, is an important assignment parameter; for example, in the present work it would resolve any ambiguity in the assignment of sodium sites 1 and 5.

In a wider context we have found the periodic *ab initio* approach described in this communication to be useful in a number of assignment problems in ^{23}Na solid-state NMR spectroscopy. In some cases it is sufficiently robust to indicate errors in published crystal structures.[16] In addition, we have found that it can be applied equally well to other widely-studied quadrupolar nuclei such as ^{17}O and ^{27}Al.

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Notes and references

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