

## Prediction of NMR parameters by first-principles calculation: K-cymrite and polymorphs of $\text{AlPO}_4$

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NMR spectroscopy is a powerful technique to study the local structure of solid materials. The interpretation of NMR spectra is greatly facilitated by the development of (1) advanced NMR techniques that provide direct through-bond and through space atomic connectivity information, and (2) first principles calculations of NMR parameters. For the latter, thanks to the development of periodic first-principles methods (Pickard & Mauri, 2001), the calculation of NMR parameters (chemical shift, and quadrupolar coupling constant and electric field gradient (EFG) asymmetry parameter for quadrupolar nuclei, such as  $^{27}\text{Al}$ ) from crystal structures has become feasible. In this study, we have applied this technique to calculate the NMR parameters for K-cymrite ( $\text{KAlSi}_3\text{O}_8 \cdot \text{H}_2\text{O}$ ) that has a disordered Si/Al distribution and several  $\text{AlPO}_4$  polymorphs, and have compared them with the experimental data.

NMR parameters were calculated using GIPAW method (Pickard & Mauri, 2001) implemented in Quantum-ESPRESSO (Giannozzi et al., 2009). For  $\text{AlPO}_4$ -stishovite solid solution, a supercell of  $2 \times 2 \times 2$  was used, and 2 Si were replaced with Al and P. For K-cymrite, a supercell of  $2 \times 2 \times 1$  was used. Four different Al/Si disordered models were built.

For  $\text{AlPO}_4$ , 5 polymorphs including three recently discovered high-pressure phases were calculated. Their crystal structures,  $^{27}\text{Al}$  3Q MAS and  $^{31}\text{P}$  MAS NMR as well as other more advanced two-dimensional (2D) correlation NMR results have already been reported (Kanzaki et al., 2011; Kanzaki & Xue, 2012). The calculated chemical shifts of Al and P sites in these phases are within a few ppm from the observed ones. This further strengthened our previous site assignment of NMR peaks based on 2D correlation NMR experiments. We also calculated the chemical shift for  $\text{P}^{VI}$  in the  $\text{SiO}_2$ - $\text{AlPO}_4$  stishovite solid solution. The calculated chemical shift for  $\text{P}^{VI}$  is about 105 ppm more negative than that of  $\text{P}^{IV}$  site in cristobalite. A recent experimental NMR study of 1 wt%  $\text{AlPO}_4$  dissolved stishovite observed a peak about 130 ppm more negative than that of cristobalite, which was attributed to  $\text{P}^{VI}$  in stishovite (Stebbins et al., 2009). The general trend is consistent with our calculation, but there is a discrepancy of 25 ppm between the observed and calculated values. More detailed studies are necessary to resolve this discrepancy.

K-cymrite has a double-layered structure with Al/Si distributed in a single T site ( $\text{Q}^4$ ). Our  $^{29}\text{Si}$  MAS NMR revealed six peaks, although it has generally been assumed that a maximum of five peaks arising from different Si/Al distributions in the four next nearest T neighbors ( $n\text{Si}$ ,  $(4-n)\text{Al}$ , with  $n=0$  to 4) should occur for a single  $\text{Q}^4$  site (Xue and Kanzaki, 2012). We have shown from direct 2D J-coupling mediated  $^{29}\text{Si}$  NMR experiments that the  $\text{Si}(3\text{Si}1\text{Al})$  and  $\text{Si}(2\text{Si}2\text{Al})$  sites are each split into two peaks due to the existence of two populations of T-O-T angles ( $139^\circ$  and  $180^\circ$ ) (Xue and Kanzaki, 2012). In order to double-check this interpretation, the chemical shifts of  $\text{Si}(4\text{Si})$ ,  $\text{Si}(3\text{Si}1\text{Al})$  and  $\text{Si}(2\text{Si}2\text{Al})$  sites were calculated for K-cymrite. The calculated chemical shifts of  $\text{Si}(3\text{Si}1\text{Al})$  and  $\text{Si}(2\text{Si}2\text{Al})$  sites show two distributions for each site separated by about 2 ppm, consistent with our experimental observation. The relative shifts between  $\text{Si}(4\text{Si})$ ,  $\text{Si}(3\text{Si}1\text{Al})$  and  $\text{Si}(2\text{Si}2\text{Al})$  sites are also reproduced.

This study has thus demonstrated that first-principles calculation (GIPAW) of NMR parameters is a reliable mean to assist interpretation of NMR spectra for both ordered and disordered crystal structures.

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