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Quantum calculations of the electronic structure and NMR quadrupolar interaction parameters for tugtupite

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ABSTRACT

Tugtupite [$Na_8(Al_2Be_2Si_8O_{24})Cl_2$] is an extremely ordered mineral containing ^{27}Al, ^{23}Na, and ^{9}Be quadrupolar nuclei. The quadrupolar interaction parameters (QI), C_q and η, for these nuclei were calculated from the electronic structure by full-crystal linearized augmented plane-wave (FC LAPW) or ab initio molecular orbital (MO) calculations. The orientation of the EFG tensors, calculated using FC LAPW correspond with the crystallographic axes **a1**, **a2**, and **c**, and η at the Al site is equal to 0.00 as required by the symmetrical electron density distribution in the **a-c** planes. The electron density of states (DOS) shows the EFG to originate from the valence band of the *p-p*, *p-s* electrons. The agreement between the calculated QI values and experimental results for tugtupite shows that FC LAPW is very effective to evaluate the electronic structure of an ordered mineral, and aid in the interpretation of MAS NMR spectra.

The combination of computational efficiency and accuracy of ab initio cluster MO calculations were examined by using different cluster sizes, basis sets, theoretical levels, and charge backgrounds using the Gaussian 98W program. A small cluster embedded in a point charge background gave sufficiently accurate ^{27}Al EFG tensors, with much greater computational efficiency than with WIEN2k. The MO cluster calculation became closer to the experimental results as the number of atoms in the clusters increased, but the calculation cost increased as well. The point-charge background was found to contribute about 10% to the EFG. MO calculations, with B3LYP level and basis set 6-311G+d** for the cluster of two atom shells around the central Al nucleus, gave quadrupole interaction values within 13% of that found by the FC LAPW method using the WIEN2k program. Therefore, MO cluster calculations can provide a more efficient but less accurate alternative to FC LAPW for quantum calculations of mineral structures.