First Principles Calculation of ^{17}O and ^{25}Mg NMR Shieldings in MgO at finite Temperature : (Ro)vibrational Effect in Solids.

S. Rossano,[1] F. Mauri,[2] C. J. Pickard, [3] and I. Farnan[4]

[1] *Lab. des géomatériaux, Univ. de Marne la Vallée, CNRS FRE2455*
5 Bd Descartes, Champs/Marne, 77454 Noisy-Champs cedex 2, France
[2] *Lab. de Minéralogie-Cristallographie, Univ. Pierre et Marie Curie*
4 place Jussieu, case postale 115, 75252 Paris cedex 05, France
[3] *TCM Group,Cavendish Laboratory*
Madingley Rd,Cambridge CB3 0HE, UK
[4] *Department of Earth Sciences, Univ. of Cambridge*
Downing Street, Cambridge, CB2 3EQ, UK

The temperature dependence of ^{17}O and ^{25}Mg NMR chemical shifts in solid MgO have been calculated using a first principles approach. Density functional theory, pseudopotentials, a plane-wave basis set, and periodic boundary conditions were used to describe both the motion of the nuclei and to compute the NMR chemical shifts. The chemical shifts were obtained using the gauge including projector augmented wave (GIPAW) method. In a crystalline solid, the temperature dependence is due to both (i) the variation of the averaged equilibrium structure, (ii) the fluctuation of the atoms around this structure. In MgO the equilibrium structure at each temperature is uniquely defined by the cubic lattice parameters, which we take from experiment. We evaluate the effect of the fluctuations within a quasiharmonic approximation. In particular, the dynamical matrix, defining the harmonic Hamiltonian, has been computed for each equilibrium volume. This harmonic Hamiltonian was used to generate nuclear configurations that obey quantum statistical mechanics. The chemical shifts were averaged over these nuclear configurations. The results reproduce the previously published experimental NMR data measured on MgO between room temperature and $1000°C$. It is shown that the chemical shift behavior with temperature cannot be explained by thermal expansion alone. Vibrational corrections due to the fluctuations of atoms around

their equilibrium position are crucial to reproduce the experimental results.