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First-principles energetics and structural relaxation of antigorite

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Abstract

We have investigated the antigorite $m = 17$ structure [$Mg_{48}Si_{34}O_{85}(OH)_{62}$] by density functional theory (DFT), with the aim to probe the method on such a large and low symmetry (*Pm*) system. We found a satisfactory match with the experiments using both LDA and GGA approximations to exchange-correlation, although the former performs slightly better here. Predicted cell constants are within 0.3% for LDA, and 0.5% for GGA, of the experimental values. Average atomic displacements after relaxation are within ~0.06 Å. All the fine structural details of antigorite are reproduced: apical Si-O bonds shorter than basal Si-O bonds; external Mg-O distances shorter than internal Mg-O distances; pronounced tetrahedral ditrigonal distortion. Where palpably biased bond distances were present in the experimental data because of disorder, theoretical methods promptly recover the structure into more reliable bond geometry. These findings let one envisage the employment of DFT calculations as a promising tool for refining or validating complex structures, whenever the experiments suffer of limitations due to the poor quality of the material being investigated.

As an additional benefit, we also compare the total energies of two competing models for the $m = 17$ antigorite structure, the one refined by Capitani and Mellini (2004) and that proposed by Dódony et al. (2002). We found the former more stable, both as published ($\Delta E = 1.1$ kJ/mol·atom^{-1}) and after full cell relaxation at constant volume ($\Delta E = 0.5$ kJ/mol·atom^{-1}).

Keywords: Antigorite, DFT, LDA, GGA