Exploiting Symmetry to Study Solid Solutions and Disordered Crystalline Systems

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Very often minerals involve solid solutions characterized by disordered cation distributions. They challenge the quantum-mechanical approach because the inherent site disorder implies dealing with large low-symmetry supercells, where a multitude of atomic distributions (configurations) exists.

A methodological breakthrough was the recent development of a symmetry-adapted Monte Carlo (SA-MC) method [1,2] which overcomes the main flaws of standard MC and Metropolis algorithms. It exploits space symmetry (i) to partition the configurations in classes of equivalence (SICs), thus avoiding repetitions, and (ii) to assure a uniform draw probability for all SICs. This latter aspect is important because the most stable configurations usually correspond to “rare events”, namely low multiplicity SICs.

Results obtained by applying the SA-MC for a fully ab initio investigation of the hydrogrossular solid solution are presented [3]. The hydrogarnet substitution, $SiO_4 = H_4O_4$, yields 136 SICs in the primitive cell. Considering only the most stable configurations after structural relaxation, average geometrical features of the actual solid solution are closely approximated, while the excess enthalpy draws an asymmetric function of composition with two minima that can be associated to structures or compositions observed in nature.

Further examples of application of the SA-MC include the case studies of a Ca-Mg carbonate, and of soda-melilite $(Na,Ca)AlSi_2O_7$. They will serve to show efficient and effective strategies to achieve convergence on the calculated properties and to save as much computational effort as possible on the choice of the size of the supercell.

[1] S. Mustapha et al. J. Phys.: Condens. Matter, 25:105401, 2013. [2] Ph. D'Arco et al. J. Phys.: Condens. Matter, 25:355401, 2013.
[3] V. Lacivita et al. Am. Mineral., 100:2637–2649, 2015.