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Quantum-mechanical simulation of disordered systems: principles and applications to the Andradite-Grossular binary

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The increasing performances of computer hardware allow for the investigation at the quantum-mechanical ab initio level of complex systems, such as disordered structures and mineral solid solutions. In this context, symmetry can play a major role, permitting to largely reduce the set of structural configurations to be sampled for an accurate description of these systems.[1]
An efficient approach is here outlined, to generate a set of so-called symmetry independent configurations (SICs). It is based on a method of group algebra, known as the Pólya's enumeration theory,[2] and on an orderly generation algorithm.[3] Significant variables can be easily handled, such as composition, number of substituting species, and type of disorder (chemical/magnetic).
Relevant applications of this method can be found in the fields of materials science and geochemistry: non-stoichiometric oxides, magnetic materials, and mineral solid solutions. In this work, we present the investigation of the infrared (IR) vibrational spectrum of the Andradite-Grossular solid solution $Ca_3Fe_xAl_{2-x}Si_3O_{12}$.[4] IR frequencies and intensities have been computed on a symmetry-adapted subset of configurations, by using the B3LYP hybrid functional and an all electron Gaussian type basis set. Relationships have been established between these quantities and variables like structural parameters, chemical composition, short-range cation order. Results have been critically compared with those available in the literature.[5,6] Quantum-mechanical simulation proves to be a powerful tool for the study of complex disordered systems, able to provide complementary data that, combined with the experiments, can address significant problems, such as composition- and structural-order-dependent properties.

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