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Atomistic simulation of solid solutions with heterovalent substitutions

Y. G. Yu, V.L. Vinograd, and B. Winkler
Institute of geoscience, University of Frankfurt, Frankfurt am Main, Germany (yu@kristall.uni-frankfurt.de)

Recent studies have shown that the thermodynamic mixing properties in (A,B)R type solid-solutions, such as (Na,K)Cl, can be accurately predicted using effective pairwise interactions (EPI) derived from first principles calculations. An EPI is defined as the enthalpy change due to the intracrystalline reaction AA + BB = 2AB between pairs of atoms at a given distance. An efficient way to extract EPIs is by the double defect method (DDM), which takes into account all distinct atomic configurations in a supercell structure with the composition $(A_{m-2},B_2)R_m$, where m is the number of the exchangeable sites [1]. In this study, the DDM is extended to study solid solutions of (A,B)(C,D)R type, where mixing occurs over two Wyckoff positions. For example, in (Mg,Al)(Si,Al)O_3 perovskite Mg^{2+} and Si^{4+} are substituted simultaneously by two Al^{3+} cations. In this case the EPIs correspond to intracrystalline reactions of the three types: AA + BB =2AB, CC + DD = 2CD and AC + BD = AD + BC. We show that the EPIs can be computed from the total energies of the supercell structures with the compositions $(A_{m-2},B_2)\{C_{m-2},D_2\}R_m$, $\{A_{m-2},B_2\}(C_{m-2},D_2)R_m$ and $(A_{m-1},B_1)(C_{m-1},D_1)R_m$, respectively, where the curly brackets denote that a given Wyckoff position is occupied by a hybrid atom whose pseudopotential is constructed using the virtual crystal approximation [2]. The approach is used to predict the thermodynamics of mixing of $MgSiO_3$ and Al_2O_3 in perovskite and postperovskite at lower mantle pressures.

[1] V.L. Vinograd, M.H.F. Sluiter, and B. Winkler (2009) Subsolidus phase relations in the $CaCO_3$-$MgCO_3$ system predicted from the excess enthalpies of supercell structures with single and double defects. Physical Review B, 79:104201-9.

[2] B. Winkler, Ch. Pickard, V. Milman (2002) Applicability of a quantum mechanical 'virtual crystal approximation' to study Al/Si-disorder. Chemical Physics Letters, 362:266-270.