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Self-consistent interatomic potentials for oxides: A key to solid solution modelling

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Thermodynamic properties of various complex oxides and solid solutions can be calculated using static lattice energy minimization and lattice dynamics tools (e. g. Gale et al., 1997). Such calculations require a set of pre-determined empirical interatomic potentials. The potentials sets of Winkler et al. (1991) and Bush et al. (1994) include O(shell)-O(shell), cation(core)-O(shell) and O(core)-O(shell) interactions and permit resonably accurate description of structural, elastic and thermodynamic properties of many oxide minerals. Recent studies based on these and other similar potentials sets have revealed several problems, however. It was observed that potentials fitted to the properties of complex oxides are transferrable only within a group of structurally and chemically similar compounds. Similarly, the potentials, fitted to the properties of low-order systems (e.g. SiO_2, MgO, Al_2O_3), usually give poor results for complex oxides. These problems can be well understood considering the fact that complex oxides (e.g. Mg_2AlO_4 and Al_2SiO_5) contain pairs of unlike cations such as Al-Mg and Al-Si, which do not occur within simple oxides. As long as the potentials sets do not specify cation-cation interactions, a consistently accurate description of simple and complex oxides remains problematic.

We propose a set of empirical potentials for Si, Al, Mg, Ca, K, Na, Ti, and Zr oxides, which in addition to O(shell)-O(shell), cation(core)-O(shell) and O(core)-O(shell) terms, includes cation(core)-cation(core) interactions. We observe that with the new approach the properties of ternary and quaternary oxides can be described accurately with no additional adjustment of the potentials. Properties of various solid solutions can be calculated using a combination of the supercell formalism and the cluster variation method. Examples of such calculations are discussed.

References

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Magnetic and chemical ordering in the ilmenite-hematite solid solution: From lamellar magnetism to self reversals

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The ilmenite-hematite solid solution is one of the most important magnetic phases in nature. Unusual magnetic behaviour is often observed in intermediate compositions due to the interaction between cation ordering, magnetic ordering, and exsolution. This presentation describes how this interaction leads to the phenomenon of lamellar magnetism in slowly-cooled metamorphic rocks and the phenomenon of self-reversed remanent magnetization in rapidly-cooled volcanic rocks.

Metamorphic titanohematites from the Swedish Granulite Region carry an unusually strong and stable remanent magnetization, caused by the presence of exsolution microstructures at the nanometer scale. To provide insight into the effect of these precipitates on the bulk magnetic properties, we have performed a detailed series of Monte Carlo simulations, which successfully model the interaction between cation ordering, magnetic ordering, and exsolution in the ilmenite-hematite system. The simulations allow the magnetic transition in chemically heterogeneous systems to be studied. At low temperatures they predict an intergrowth of antiferromagnetic hematite and paramagnetic ilmenite. Despite the antiferromagnetic nature of the hematite component, the simulation cells as a whole are ferrimagnetic, with small but significant net magnetization associated with the interface between exsolved phases. Competition between chemical and magnetic interactions leads to a characteristic cation distribution at the interface, which ensures a local imbalance between the numbers of up and down magnetic spins. The interface moment acts as a defect moment of the antiferromagnetic hematite, and has both the magnitude, coercivity, and thermal stability required to explain the remanence properties of the metamorphic samples, thus establishing exsolved titanomagnetite as a potential carrier of strong remanence on Earth and other planets.

Intermediate samples cooled rapidly through the high-temperature cation ordering phase transition develop antiphase domains (APD's) with respect to the Fe-Ti distribution. These APD's are thought to be responsible for the phenomenon of self-reversed thermoremanent magnetization. A combination of neutron diffraction and Monte Carlo simulations are used to develop a self-consistent model for the origin of this phenomenon.