

s11.m2.o1 *Ab Initio* Simulations as a Tool in Mineral Crystallography. M. Catti, *Dipartimento di Scienza dei Materiali, Università di Milano Bicocca, via Cozzi 53, 20125 Milano, Italy.*

Keywords: theoretical models, crystal properties, minerals.

First-principles quantum-mechanical calculations are nowadays a quite powerful tool to obtain theoretical values of many crystal properties relevant for mineral physics. In particular, energetics and thermochemistry at low temperature and variable pressure, equation of state vs. pressure, elastic properties, and structural optimization are some examples of results related to phase stability and high-pressure behaviour of minerals [1].

Other fields of application, which are important for solid state kinetics, include the simulation of ion diffusion processes and defect chemistry, generally implemented by the use of supercell techniques.

Several *ab initio* methods and computer codes are available to calculate the mentioned properties in periodic systems (e.g., [2], [3]). In summary, most methods are based on the numerical solution of self-consistent-field (SCF) integral-differential equations whose unknowns are one-electron crystal orbitals, expanded in a suitable basis set of functions (one-electron approximation). The type of Hamiltonian used, determining the explicit form of the equations, may be based on Density Functional Theory (DFT) or on the Hartree-Fock (HF) approach; the basis set may be made of localized functions on atoms (atomic orbitals, LCAO scheme) or of delocalized plane waves (PW). Further, all electrons can be included explicitly in the SCF equations, or just the valence electrons, while the core contribution is taken into account by the pseudopotential scheme.

It is important to understand that, by combining the theoretical schemes outlined above in different ways, a number of distinct computational approaches arise, which may be more or less suited to a particular simulation task or crystal property one is interested in.

A number of examples of applications to problems relevant for mineral science are presented. Typically, the relative stability and structural properties of silica polymorphs, both at room and at high pressure, is one of the most instructive cases. Several calculations from different authors and by various computational approaches are available on this system, including both tetrahedral-Si and octahedral-Si based phases. This and other applications are discussed in detail.

s11.m2.o2 Atomistic modelling of the structure and reactivity of mineral surfaces. S.C. Parker, N.H. deLeeuw, D.J. Cooke and S.E. Redfern, *Department of Chemistry, University of Bath, Bath, BA2 7AY, U.K.*

Keywords: mineral surfaces simulation

Atomistic simulation techniques represent a powerful complementary tool for studying mineral surfaces. The aim of this presentation is to describe the recent progress in modelling the structure of oxide and mineral surfaces and in particular to review our attempts at studying the interaction and reactivity of water with the oxide and mineral surfaces. The basis of these techniques is to use the Born Model of Solids where simple parameterised analytical equations are employed to describe the interactions between atoms. Once these interatomic forces are specified energy minimisation and molecular dynamics techniques can now be applied to model mineral surfaces.

We will illustrate the scope of these simulation techniques by describing three examples. In the first example we consider the competitive adsorption between water and formic acid. The latter is chosen as a model for a surfactant head group. We show that for certain calcium containing minerals formic acid binds more strongly than water and yet for others the reverse is true. In the second example, we describe modelling studies of the interaction of cation additives with caelite surfaces and how this can be used to infer the effect of additives on step growth. The final section will describe recent work on the reactivity of water and mineral surfaces and will include a number of examples including aluminium and iron oxides. This shows that the reactivity is highly dependent on the surface structure and composition.

In summary, atomistic simulation is a useful tool for relating surface structure and reactivity and provides a good complement to experiment.

[1] M. Catti. Ch. 15 of "Microscopic Properties and Processes in Minerals", NATO-ASI Vol. 543, ed. by K. Wright and R. Catlow, Kluwer (1999)

[2] CRYSTAL98. V.R. Saunders, R. Dovesi, C. Roetti, M. Causà, N.M. Harrison, R. Orlando and C.M. Zicovich Wilson. University of Torino, Italy, and CLRC Daresbury Laboratory, U.K., 1999.

[3] WIEN97. P. Blaha, K. Schwarz and J. Luitz. Technical University of Vienna, Austria, 1997.