Phase transitions in disordered solids *via* hybrid Monte Carlo: the orthorhombic to cubic phase transition in (Mg,Mn)SiO_3 perovskite

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We show how a novel hybrid Monte Carlo simulation technique can be used to investigate the influence of high impurity or defect concentrations on phase transitions; impurity cations can have a much larger effect than that expected from a mean-field treatment or linear interpolation between end-member compounds.

We report a novel computational methodology for determining the phase stability of disordered inorganic materials and solid solutions. The motivation for this work is twofold. Firstly, although calculations have provided considerable insight into the thermodynamic and structural aspects of materials,[1] most have been limited to the study of solids with periodic, ordered structures. Secondly, a detailed understanding of the thermodynamics and phase stability of disordered solids is crucial for many areas of mineralogy and solid-state chemistry. For example, minerals often contain a large number of minor and trace element impurities, possibly disordered over several crystallographic sites, which may have dramatic effects on physical and chemical behavior and phase stability.

Supercell or *point* defect calculations have traditionally been used to investigate impurities in solid state materials. The clear limitations of these methods for systems with an appreciable impurity or defect content exclude studies of many naturally occurring minerals and ceramics of industrial importance. Accordingly, the principal objective of this work is to show how a modified hybrid Monte Carlo (HMC) technique can be used to study the effect of disorder on phase transitions in ionic solids and minerals. The HMC technique permits an efficient sampling of different configurations, takes explicit account both of ionic relaxation near impurity ions and thermal effects, and is readily extended to different ensembles. Our methods do not involve the use of an approximate parameterised Hamiltonian since the parameterisation of, for example, an Ising-type Hamiltonian becomes increasingly difficult beyond binary or pseudobinary mixtures and can average out local effects due to ion clustering and association. Moreover, such methods cannot readily be extended to include the effects of lattice vibrations and pressure.

Most Earth materials are solid solutions rather than pure end-members and an understanding of the effect of trace components is essential. Many properties of the deep Earth, such as electrical conductivity,[2] phase changes[3] and rheology are profoundly altered by the presence of impurities at concentrations of a few wt%, or less. The magnesium-rich silicate perovskite is thought to be the major constituent of the Earth's lower mantle and an understanding of its thermodynamic and physical behaviour is crucial for a wide range of geophysical and geochemical problems such as the convection and chemical differentiation of the mantle. Previous work[4] used constant-pressure molecular dynamics (MD) to demonstrate that at pressures above 10 GPa, orthorhombic $MgSiO_3$ undergoes a temperature induced phase transition to a cubic phase prior to melting, whereas at lower pressures the orthorhombic phase melts without any change of solid phase. The size difference between Mn^{2+} and Mg^{2+} is such that Mn–Mg mixing in silicates is expected to be quite non-ideal[5] and so here we investigate the effect of Mn, a minor element constituent of the Earth's mantle, on the high pressure orthorhombic–cubic phase transition. The potential model used within this study has been discussed previously;[6] we have employed the ionic model assigning charges of +1.2 for Mg and Mn, –1.2 for O and +2.4 for Si, and used the set of short-range potential parameters discussed in ref. 3.

The HMC approach we have developed is related to that used in the modelling of polymers and biomolecules.[7–9] The technique has been applied recently to such problems as the enthalpies of mixing of binary oxides[10] and non-convergent ordering of cations in olivine,[11] but not thus far to phase transitions. During one HMC cycle, one of three options is chosen at random, with equal probability. The first of these is a short NVE molecular dynamics (MD) simulation consisting of 15 steps and with a timestep of 1.5 fs. The length and timestep were chosen so as to allow efficient sampling of the different configurations. The last configuration is accepted or rejected by comparing its energy with the energy of the starting configuration and using the standard Metropolis algorithm.[12] If the last configuration is rejected, the original configuration is included in the statistical averaging of thermodynamic properties. In the second, which is only applicable to the solid solution, a short MD run follows a random exchange of Mg and Mn ions. Again, the difference in energy between the previous configuration and that immediately after the MD simulation is used in the Metropolis algorithm. At the start of each MD run, velocities are chosen anew at random from a Maxwellian distribution. The third option is a random change of the volume/shape of the box,[13] which again is accepted or rejected using the Metropolis algorithm. Enthalpy and structural data were averaged over a period of 50 000 cycles, prior to which an equilibration period of 50 000 cycles was undertaken. Results presented here are for a simulation cell containing 540 ions ($3 \times 3 \times 3$ unit cells).

For $MgSiO_3$ we obtain very similar results using HMC to those of the MD study of Matsui and Price[4] with a calculated transition temperature of 3900 K at 20 GPa from the orthorhombic to the cubic phase. Fig. 1 shows the calculated variation of the lattice parameters for $Mg_{0.6}Mn_{0.4}SiO_3$ which shows that this compound also undergoes a similar phase transition at this pressure. From the calculated transition temperatures at 20 GPa for $Mg_xMn_{1-x}SiO_3$ (Fig. 2) as a function of composition x, it is clear that a linear extrapolation between the two end members, is a very poor approximation. For example, the phase transition for $Mg_{0.6}Mn_{0.4}SiO_3$ is at a much lower temperature (2500 ± 50 K) than the value of almost 3000 K predicted by a simple linear interpolation of transition temperature *vs.* composition. In this context it is worth noting that, unlike the transition temperature, the calculated volume as a function of composition displays only a small positive deviation from Vegards' law, since the *a* lattice parameter itself has a positive and the *b* and *c* lattice parameters a negative deviation. We have been unable to find any experimental data for comparison. An orthorhombic–cubic transition at high

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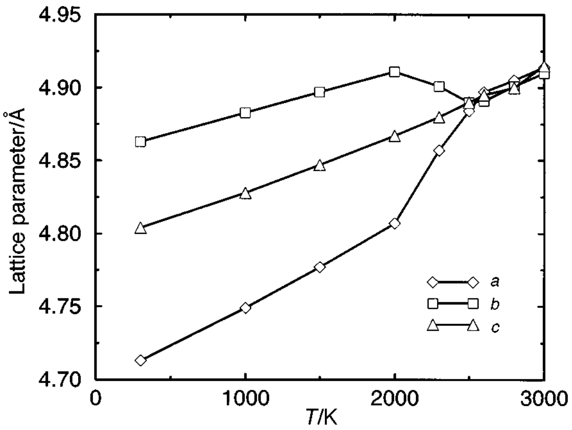

Fig. 1 Lattice parameters (Å) *vs.* T(K) at 20 GPa for $Mg_{0.6}Mn_{0.4}SiO_3$.

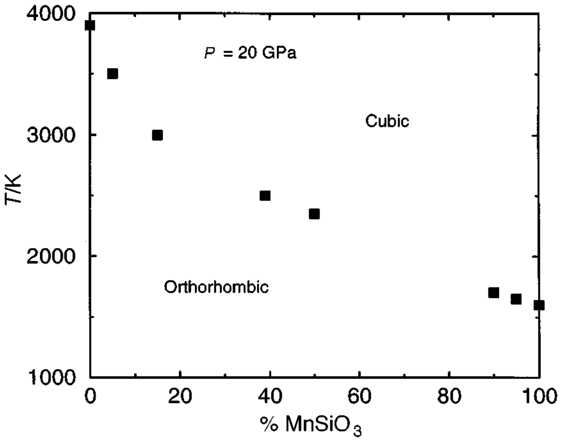

Fig. 2 Calculated orthorhombic–cubic transition temperature (K) at 20 GPa *vs.* composition.

pressure by the analogous compound (Mg,Fe)SiO_3, for which experimental evidence is currently contradictory,[14] would have important implications for the thermodynamic and compositional modelling of the Earth's mantle since thermodynamic data is often extrapolated from low pressures and temperatures and from the end-member compositions.

In summary, the HMC technique removes major limitations of the existing methods for the simulation of phase transitions in disordered solids, which restrict considerably the contact between experiment and theory. The methodology is general and readily applicable to a wide range of real rather than model, undefective systems. It is essential to take explicit account of ionic relaxation in each of the configurations without any averaging out of local effects. We envisage that that our new approach will add significantly to our understanding of the behaviour of complex systems at the atomic level, providing an important link between the microscopic and macroscopic behaviour of ceramics and minerals, and hope the present study will prompt new experimental investigations of the effects of trace impurities on high-pressure phase transitions.

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Notes and references

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