

Ab-initio investigation of the thermodynamic stability of the magnesio-wüstite solid solution under Earth's lower mantle conditions

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Mg-wüstite, (Mg,Fe)O, is the second most abundant phase in the Earth's lower mantle. A profound understanding of the thermodynamic stability of this phase under deep mantle conditions is thus crucial for developing accurate models of the Earth's interior and the importance of drawing a complete picture of the stability fields of the Mg-wüstite solid solution, especially at high pressure/temperature regimes, is straightforward.

In the light of the above considerations, the present work has been undertaken where the thermochemical properties of the (Mg,Fe)O solid solution, over a wide PT range, have been modelled using mixing Helmholtz energy, $\Delta F(T,x)_{mixing}$. Calculations have been performed by means of cluster expansion, quantum mechanical and semi-empirical techniques.

Both high-spin (HS) and low-spin (LS) configurations of iron have been explored as a function of composition (x : molar fraction of FeO) over the MgO-FeO binary. Only the HS-model provides physically sound results at room pressure, yielding a correct trend of cell edge *versus* composition, whereas LS's issues are at variance with observations. Mixing Helmholtz energy has been parametrized by the following relationship $\Delta F(T,x)_{mixing} = x \times y \times [U(T)_0 + U(T)_1 \times (x-y) + U(T)_2 \times (x-y)^2]$, where $y=1-x$ and $U_j(T)$ are polynomials in T of the third order. $\Delta F(T,x)_{mixing}$ exhibits a quasi-symmetric behaviour and allows one to build the T - X phase relations diagram over the MgO-FeO join. On the basis of the HS-model including vibrational contribution to Helmholtz energy, a solid solution's critical temperature of some 950 K has been predicted, remarkably lower than olivine's and Mg-Fe-garnet's. All this points to a more difficult Mg-Fe mixing in periclase-like structure than olivine and garnet, which, in turn, provide more degrees of freedom for atomic relaxation. From $\Delta F(T,x)_{mixing}$, $\Delta H(T,x)_{mixing}$ and $\Delta S(T,x)_{mixing}$ have been derived, both exhibiting so modest a dependence on T as to be negligible. $\Delta H(T,x)_{mixing}$ and $\Delta S(T,x)_{mixing}$ exhibit quasi-regularity; either has been parametrized as $W \times x \times (1-x)$, obtaining $W_{H,Mg-Fe}$ and $W_{S,Mg-Fe}$ of 17.7 kJ/mol and 26.8 J/mol/K, respectively. $\Delta S(T,x)_{excess}$ has been estimated to be smaller than 0.5 J/mol/K in absolute. Moreover, it has been observed that the HS-configuration is stable and promote Mg-Fe solid solution up to ≈ 15 GPa better than LS does. At higher pressures, the LS-model becomes favourite and increasingly stabilizes (Mg,Fe)O upon rising P , whereas HS predicts ex-solving into the end members above ≈ 40 GPa.