

**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  $\approx 15$  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  $\approx 40$  GPa.