Entropies of mixing and subsolidus phase relations of forsterite–fayalite (Mg$_2$SiO$_4$–Fe$_2$SiO$_4$) solid solution

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ABSTRACT

The heat capacities of a series of synthetic forsterite (Fo)–fayalite (Fa), Mg$_2$SiO$_4$–Fe$_2$SiO$_4$, olivines have been measured between 5 and 300 K on milligram-sized samples with the Physical Properties Measurement System (Quantum Design). The heat capacities for fayalite and fayalite-rich olivine are marked by a sharp lambda-type anomaly defining a transition from the paramagnetic to an antifer-romagentic state, which in the case of fayalite occurs at $T_N = 64.5$ K. In forsterite-rich compositions a feature in the C_P data around 25 K is observable and it could possibly be linked to a magnetic transition. Additionally, all Fe-bearing olivines show a Schottky-type anomaly. Excess heat capacities of mixing, ΔC_P^{xs}, for the various Fe-Mg olivine solid-solution compositions were calculated applying the equation $\Delta C_P^{xs} = C_P^{ss} - [(1 - X_{Fa}) C_P^{Fo} + X_{Fa} C_P^{Fa}]$ using fitted C_P polynomials for each composition. The calorimetric entropies at 298.15 K, S_{cal}, were determined by solving the C_P integral $s_{cal,298.15} = \int_0^{298.15} \frac{C_P}{T} dT$. If a symmetric Margules mixing model $\Delta S^{xs} = W_s \cdot X_{Fa}(1 - X_{Fa})$ is taken to describe the entropy of mixing behavior for the Fo-Fa binary, it yields an interaction parameter of $W_s = -1.6 \pm 1.7$ J/(mol·K) on a one-cation basis. The calorimetric data thus indicate ideal entropy of mixing behavior. Adopting, however, a value of $W_{S,Mg-Fe}^{Ol} = -1.6$ J/(mol·K) one can calculate a value for the excess Gibbs free energy of mixing of $W_{G,Mg-Fe}^{Ol} = 6.9$ kJ/mol at 1000 K using the most recent solution calorimetric study of Kojitani and Akaogi (1994) on Fo-Fa olivine with $W_{H,Mg-Fe}^{Ol} = 5.3$ kJ/mol. This $W_{G,Mg-Fe}^{Ol}$ value should be considered a maximum upper limit for thermodynamic nonideality. Using solely calorimetric data, the T-X phase diagram for the Fo-Fa binary is calculated at 1 bar and 50 kbar and compared to that obtained from a model-dependent thermodynamic analysis. The results suggest that exsolution in Fe-Mg olivine should only be possible in low-temperature environments depending on kinetic behavior.

Keywords: Calorimetry, forsterite–fayalite solid solution, thermodynamics, excess heat capacities and entropies, subsolidus phase relations, forsterite–fayalite solvus