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A low-temperature calorimetric study of synthetic (forsterite + fayalite) $\{(Mg_2SiO_4 + Fe_2SiO_4)\}$ solid solutions: An analysis of vibrational, magnetic, and electronic contributions to the molar heat capacity and entropy of mixing

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Abstract

The molar heat capacities ($C_{p,\mathrm{m}}$) of a series of synthetic forsterite (Fo)–fayalite (Fa), ($Mg_2SiO_4 + Fe_2SiO_4$), olivines have been measured between 5 K and 300 K on milligram-sized samples with the Physical Properties Measurement System (Quantum Design®). Sharp, λ-type heat capacity anomalies are observed in the Fe-rich compositions fayalite, $Fo_{10}Fa_{90}$, $Fo_{20}Fa_{80}$, $Fo_{30}Fa_{70}$, and $Fo_{40}Fa_{60}$. The corresponding Neel temperatures T_N decrease linearly from 64.5 K in fayalite to 32.8 K in $Fo_{40}Fa_{60}$ following the relationship $T_\mathrm{N} = 79.02 \cdot x_\mathrm{Fa} - 14.07$. $Fo_{50}Fa_{50}$ and Mg-richer olivines show weak broad features in the heat capacity data around 15 K to 20 K that decrease in magnitude with increasing forsterite content. In order to derive and separate molar electronic, magnetic and vibrational heat capacity contributions, $C_\mathrm{el,m}$, $C_\mathrm{mag,m}$, and $C_\mathrm{vib,m}$ from the experimental heat capacities ($C_\mathrm{tot,m}$), we used a single-parametric phonon dispersion model to calculate $C_\mathrm{vib,m}$ for the solid-solution members and fayalite. The $C_\mathrm{el,m} + C_\mathrm{mag,m}(= C_\mathrm{tot,m} - C_\mathrm{vib,m})$ contributions were fit to expressions describing a Schottky-type electronic anomaly and a paramagnetic–antiferromagnetic transition. For $Fo_{50}Fa_{50}$ and Mg-richer olivines, our analysis of $C_\mathrm{tot,m}$ shows that also these compositions have a $C_\mathrm{mag,m}$ contribution with a maximum around 25 K. Decomposition of the molar excess heat capacity $C^\mathrm{E}_{p,\mathrm{m}}$ into electronic, magnetic and vibrational contributions yields the largest absolute values for $C^\mathrm{E}_\mathrm{mag,m}$. Molar excess entropies of mixing S^E_m at $T = 298.15$ K were also calculated from the heat capacity data. Despite considerable $C^\mathrm{E}_\mathrm{mag,m}$, the molar magnetic excess entropy at $T = 298.15$ K $S^\mathrm{E}_\mathrm{mag,m}(298.15\ \mathrm{K})$ is only weakly negative for the solid solution ($1.7\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ to $2.7\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$), because positive and negative contributions of $C^\mathrm{E}_\mathrm{mag,m}/T$ as a function of temperature largely cancel each other between 0 K and 298.15 K. The molar electronic excess heat capacity $C^\mathrm{E}_\mathrm{el,m}$ is positive for all temperatures and compositions, $S^\mathrm{E}_\mathrm{el,m}(298.15\ \mathrm{K})$ thus shows a positive contribution with a maximum of $0.8\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ for $Fo_{50}Fa_{50}$. The molar vibrational excess entropy $S^\mathrm{E}_\mathrm{vib,m}(298.15\ \mathrm{K})$ is also slightly positive for most members (maximum of $1.0\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ for $Fo_{40}Fa_{60}$). The resulting overall molar excess entropy, $S^\mathrm{E}_\mathrm{tot,m}(298.15\ \mathrm{K}) = S^\mathrm{E}_\mathrm{vib,m}(298.15\ \mathrm{K}) + S^\mathrm{E}_\mathrm{el,m}(298.15\ \mathrm{K}) + S^\mathrm{E}_\mathrm{mag,m}(298.15\ \mathrm{K})$ along the (forsterite + fayalite) join is weakly negative within 2σ-uncertainty. Smoothed values of the molar heat capacity $C_{p,\mathrm{m}}$, the molar entropies $\Delta_0^T S_\mathrm{m}$, molar enthalpies $\Delta_0^T H_\mathrm{m}$, and the molar Planck function Φ_m have been tabulated at selected temperatures for all olivine compositions.

Keywords: Low-temperature heat capacity; Vibrational, electronic, and magnetic contributions to heat capacity; Entropy of mixing behaviour; Olivine; Solid solution behaviour; (Forsterite + fayalite)

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1. Introduction

Orthosilicate olivine in the system ($Mg_2SiO_4 + Fe_2SiO_4$) {(forsterite + fayalite)} is a major phase in the solar system. It occurs in several types of meteorites and also on various planets and their moons. On Earth, Fe–Mg olivine is the most abundant phase of Earth's upper mantle and an important mineral in mafic and ultramafic igneous and metamorphic rocks. Knowledge of its thermodynamic properties is crucial for undertaking many mineralogical, petrological and geophysical investigations. The T–x phase diagram at ambient pressure for the ($Mg_2SiO_4 + Fe_2SiO_4$) system was among the first of a transition metal bearing solid-solution mineral to be determined by experimental mineralogists (Bowen and Schairer [1]). Since that time, there have been a large number of experimental phase equilibrium and calorimetric studies undertaken in order to obtain a better description of the phase relations and thermodynamic properties of ($Mg_2SiO_4 + Fe_2SiO_4$) olivines. In addition, a large number of studies exist on olivine's structural and crystal-chemical properties, as well as on its vibrational spectroscopic and lattice-dynamical behaviour. Because of the presence of Fe^{2+}, magnetic and electronic properties have also been studied rather intensively. The point has been reached where it is now possible to begin investigating the (forsterite + fayalite) system in its entirety and to address the question on how the micro- and nanoscopic-scale properties control the macroscopic properties, such as the various thermodynamic functions. Published results relevant to the present work are briefly reviewed.

1.1. Review of previous studies

1.1.1. Crystal chemistry and structural state as well as the nature of defects

Numerous studies, both diffraction and spectroscopic, have been undertaken to describe the crystal chemistry of Mg–Fe olivines (see review by Brown [2] and subsequent work [3–5]). Olivine, M_2SiO_4, with $M = Fe^{2+}$(fayalite) and Mg (forsterite), is orthorhombic with space group *Pbnm*, and has 4 formula units per unit cell (figure 1). The $M2$, Si, O1 and O2 atoms are located on mirror planes and have C_s (C1h) point symmetry. The $M1$ cation is located at the origin of the unit cell and has C_i (S2) point symmetry, while O3 and O4 occupy general positions of C_1 symmetry.

One important aspect of crystal-chemical studies was a determination of the nature of the long-range Mg–Fe distribution over the two $M1$ and $M2$ octahedral sites. From the results obtained at ambient conditions, it can be concluded that Fe^{2+} and Mg are approximately disordered over $M1$ and $M2$, or that Fe^{2+} shows a slight preference for the smaller $M1$ site. However, in forsterite-rich compositions ($Fo_{80}Fa_{20}$ to $Fo_{92}Fa_8$), Mg may show a slight preference for $M1$ [3]. This view of ordering behaviour in olivine has been complicated following recent *in situ* high-temperature neutron diffraction investigations. Artioli *et al.* [6] determined the partitioning behaviour of Fe^{2+} and Mg in a natural single-crystal olivine of composition $Fo_{88}Fa_{12}$ between 298 K and 1333 K. The behaviour can be described by the cation partition coefficient (K_D) for the intracrystalline exchange reaction $Fe_{M2} + Mg_{M1} = Fe_{M1} + Mg_{M2}$:

$$K_D = [(Fe_{M1} \cdot Mg_{M2})/(Fe_{M2} \cdot Mg_{M1})], \qquad (1)$$

where the Fe and Mg represent the mole fractions of these atoms on the two M sites. Between room temperature and about 1153 K $K_D \geqslant 1$, but above 1173 K a reversal in the ordering behaviour occurs and $K_D < 0.7$ [6]. Rinaldi *et al.* [7] made further neutron-diffraction measurements on two olivine single crystals of composition $Fo_{88}Fa_{12}$ and $Fo_{90}Fa_{10}$ and argued that above 1173 K Fe^{2+} progressively partitions into the $M2$ site and that $K_D \approx 0.2$ at 1573 K. Redfern *et al.* [8] deduced similar ordering behaviour from powder neutron diffraction measurements on a synthetic $Fo_{50}Fa_{50}$ sample. The variation in the long-range ordering state was attributed to a change in the vibrational properties of the cations on the $M1$ and $M2$ sites [6]. It was proposed that an increase in vibrational entropy, as described by the diffraction-determined atomic displacement parameters, could counter the decrease in configurational entropy associated with increased ordering, and could be the main driving force for greater cation ordering at high temperature. Morozov *et al.* [5] studied the state of order in a synthetic olivine of composition $Fo_{50}Fa_{50}$ using ^{57}Fe Mössbauer spectroscopy. Their results showed a slight preference for Fe^{2+} on $M1$ relative to $M2$ from 773 K to 1073 K and their K_D behaviour was in direct contrast to the *in situ* diffraction results of [8]. With regard to the possible occurrence of short-range Fe–Mg cation order in olivine solid solutions, there are no studies to date to the best of our knowledge.

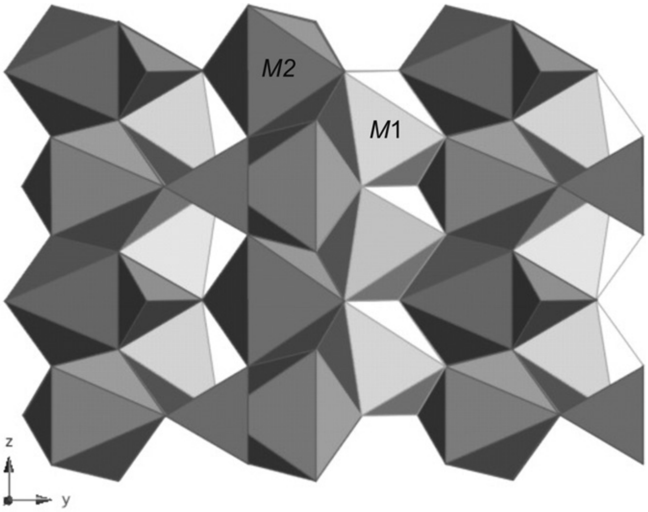

FIGURE 1. Polyhedral model of the olivine structure consisting of SiO_4 tetrahedra and $M1$ (light shaded) and $M2$ (dark shaded) octahedra projected onto (1 0 0).