American Mineralogist, Volume 92, pages 699–702, 2007

LETTER

Entropies of mixing and subsolidus phase relations of forsterite–fayalite (Mg_2SiO_4–Fe_2SiO_4) solid solution

EDGAR DACHS[1,*] AND CHARLES A. GEIGER[2]

[1]Fachbereich Materialwissenschaften, Universität Salzburg, Hellbrunnerstrasse 34, A-5020 Salzburg, Austria
[2]Institut für Geowissenschaften, Abteilung Mineralogie, Christian-Albrechts-Universität zu Kiel, D-24098 Kiel, Germany

ABSTRACT

The heat capacities of a series of synthetic forsterite (Fo)–fayalite (Fa), Mg_2SiO_4–Fe_2SiO_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 antiferromagentic 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 $W^{Ol}_{S,Mg\text{-}Fe} = -1.6$ J/(mol·K) one can calculate a value for the excess Gibbs free energy of mixing of $W^{Ol}_{G,Mg\text{-}Fe} = 6.9$ kJ/mol at 1000 K using the most recent solution calorimetric study of Kojitani and Akaogi (1994) on Fo-Fa olivine with $W^{Ol}_{H,Mg\text{-}Fe} = 5.3$ kJ/mol. This $W^{Ol}_{G,Mg\text{-}Fe}$ 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

INTRODUCTION

Olivine is an important mineral in mafic und ultramafic igneous and metamorphic rocks and it is the most abundant phase of Earth's upper mantle. Clearly, knowledge of its thermodynamic properties is crucial for undertaking many mineralogic, petrologic, geophysical, and meteoritic investigations. The *T-X* phase diagram at 1 atm for the Mg_2SiO_4–Fe_2SiO_4 system was one of the first, for a system containing a transition-metal cation, to be determined by experimental mineralogists (Bowen and Schairer 1935). Published results relevant to this present work are reviewed briefly (see Dachs et al. 2007 for a more extensive review).

CALORIMETRIC INVESTIGATIONS

Low-temperature adiabatic calorimetric (low-TAC) experiments were made by Robie et al. (1982a, 1982b) to determine the heat capacities of end-member fayalite and forsterite between 5 and 380 K and to derive their standard third-law entropies.

The enthalpies of mixing for Fe-Mg olivines were first measured by high-temperature solution calorimetry by Thierry et al. (1981) and Wood and Kleppa (1981). These two studies indicated ideality or small positive deviations with an asymmetry toward end-member fayalite for the enthalpy of mixing behavior. The most recent high-temperature solution calorimetric study of Kojitani and Akaogi (1994) on Fe-Mg olivine yielded $W^{Ol}_{H,Mg\text{-}Fe} = 5.3 \pm 1.7$ kJ/mol. Combining this W_H value with published data on the excess free energy of mixing (see below), these authors proposed a value of $W^{Ol}_{S,Mg\text{-}Fe} = 0.6 \pm 1.5$ J/(mol·K) to describe the entropy of mixing behavior.

PHASE EQUILIBRIUM AND COMPUTATIONAL THERMODYNAMIC STUDIES OF FE-MG OLIVINE

Many experimental phase equilibrium studies have been performed to investigate the thermodynamic mixing properties of Fe-Mg olivine (see Wiser and Wood 1991; von Seckendorff and O'Neill 1993 and references therein). In general, most of these studies concluded that the thermodynamic Gibbs free energy associated with Fe-Mg mixing in olivine is approximately ideal or is associated with small positive deviations from ideality. Sack and Ghiorso (1989), in their thermodynamic analysis of published experimental data, challenged this generally accepted view and suggested significant positive nonideality for the mixing behavior. They obtained a value of $W^{Ol}_{G,Mg\text{-}Fe} = 10.2 \pm 0.3$ kJ/mol. Von Seckendorff and O'Neill (1993) rejected this proposal

* E-mail: edgar.dachs@sbg.ac.at

based on results from their experimental investigation. They constrained $W^{Ol}_{G,Mg\text{-}Fe}$ to be in the range 2 to 8 kJ/mol with a best-fit value of 5.5 ± 0.6 kJ/mol, but also stated that a value of $W^{Ol}_{G,Mg\text{-}Fe}$ = 3.7 ± 0.8 kJ/mol, as given by Wiser and Wood (1991), was consistent with their results. Using such a value, together with the calorimetric $W^{Ol}_{H,Mg\text{-}Fe}$ results, they proposed that excess entropies of mixing for the forsterite-fayalite solid solution should be small such that $W^{Ol}_{S,Mg\text{-}Fe}$ < 2 J/(mol·K). In a recent study related to the mixing properties of Fe-Mg olivine, O'Neill et al. (2003) presented a value of $W^{Ol}_{G,Mg\text{-}Fe}$ = 2.6 ± 0.5 kJ/mol that indicates only small deviations from thermodynamic ideality.

Goal of Investigation

Calorimetry is a powerful experimental method for determining thermodynamic mixing properties for C_P (S) and H (see Geiger 2001 for a review of silicate solid solutions), because it gives directly the mixing behavior of a solid solution. Further calorimetric measurements are needed to understand fully the thermodynamic properties of olivine, because the entropy of mixing behavior has not been measured directly and model-dependent calculations give conflicting results. In this paper, we present the low-temperature heat-capacity measurements between 5 and 300 K on forsterite–fayalite solid solutions using low-temperature heat-pulse calorimetry (Dachs and Bertoldi 2005; Dachs and Geiger 2006). This is a relatively new experimental method that allows for the measurement of samples weighing milligrams. Due to this technological advancement, we are able to investigate the nature of the heat capacity and entropy of mixing behavior of the Mg_2SiO_4–Fe_2SiO_4 olivine solid solution, using solely calorimetric data, for the first time.

Low-Temperature Calorimetric Methodology and Data Evaluation

Low-temperature heat capacities were measured with a commercially designed and built calorimeter [heat capacity option of the Physical Properties Measurement System (PPMS), constructed by Quantum Design] at Salzburg University. The measurements were performed at temperatures between 5 and 300 K on synthetic polycrystalline olivine whose characterization is described in detail in von Seckendorff and O'Neill (1993) and Dachs et al. (2007). Samples weighing between 20 and 48 mg and contained in hermetically sealed Al-containers were used for measurement. C_P data were collected at 50 different temperatures on cooling from 300 K with a logarithmic spacing, with C_P measured three times at each temperature. Further experimental details on the PPMS and our experimental method can be found in Dachs and Bertoldi (2005), Dachs and Geiger (2006), and Dachs et al. (2007).

A C_P-polynomial of the general form $C_P = k_0 + k_1T^{-0.5} + k_2T^{-2} + k_3T^{-3} + k_4T + k_5T^2 + k_6T^3$ was used to fit the measured molar C_P data. This empirical polynomial derives from that of Berman and Brown (1985) and includes additional terms, for example, to describe low-temperature C_P behavior (i.e., Debye T^3 behavior). The data for Mg-rich compositions (i.e., Fo, $Fo_{90}Fa_{10}$, $Fo_{70}Fa_{30}$, $Fo_{60}Fa_{40}$, $Fo_{50}Fa_{50}$) were divided into three separate temperature regions and the polynomial $C_P = k_0 + k_1T^{-0.5} + k_2T^{-2} + k_3T^{-3}$ was used for fitting the high-T portion of the data. The complete polynomial given above was used for the interval T = 5–35 K and the equation $C_P = k_2T^{-2} + k_4T + k_5T^2 + k_6T^3$ for the data in the interval T = 35–130 K. Iron-rich compositions (i.e., $Fo_{40}Fa_{60}$, $Fo_{30}Fa_{70}$, $Fo_{20}Fa_{80}$, $Fo_{10}Fa_{90}$, and Fa) all showed sharp C_P anomalies (see below) increasing in magnitude toward fayalite and therefore required a further splitting of the C_P data for fitting in this temperature region. Further discussion on the fitting procedure and the errors involved can be found in Dachs et al. (2007) and Dachs and Geiger (2006).

The calorimetric entropies at 298.15 K, $S_{cal,298.15}$, were determined by solving analytically and stepwise the C_P integral:

$$S_{cal,298.15} = \int_0^{298.15} \frac{C_P}{T} dT \quad (1)$$

The uncertainty in $S_{cal,298.15}$ was determined as described in Dachs and Geiger (2006).

Results

C_P and S_0 of end-member forsterite and fayalite

The PPMS C_P measurements on the olivine end-members fayalite and forsterite show good agreement with the data of Robie et al. (1982a, 1982b—see Dachs et al. 2007 for a detailed discussion). The standard third-law entropies, S_0, determined herein for forsterite and fayalite are in excellent agreement with literature data. For forsterite, S_0 obtained with the PPMS is 94.0 ± 0.1 J/(mol·K) (Table 1), compared to 94.1 ± 0.1 J/(mol·K) based on the low-TAC data of Robie et al. (1982b). The PPMS value for S_0 of fayalite is 151.4 ± 0.1 J/(mol·K), which is close to the value 151.0 ± 0.2 J/(mol·K) resulting from the low-TAC measurements of Robie et al. (1982a).

Excess heat capacities and entropies of mixing of forsterite–fayalite solid solutions

The heat capacities for fayalite and fayalite-rich olivines are marked by a sharp lambda-type anomaly marking a transition from the paramagnetic to an antiferromagentic state (Fig. 1). A weak feature in the C_P data around 25 K is observable in more forsterite-rich compositions and it could possibly be related to a magnetic effect. Additionally, all Fe-bearing olivines show a Schottky anomaly related to an electronic effect around 15 K (e.g., Gopal 1966). These aspects are treated fully in Dachs et al. (2007).

Excess heat capacities of mixing, ΔC_P^{xs}, for the various Fe-Mg olivine solid-solution compositions were calculated according to the equation

$$\Delta C_P^{xs} = C_P^{ss} - [(1 - X_{Fa})\, C_P^{Fo} + X_{Fa}\, C_P^{Fa}] \quad (2)$$

using the fitted C_P polynomials. The uncertainty in ΔC_P^{xs} was determined by propagating the error in the C_P measurements

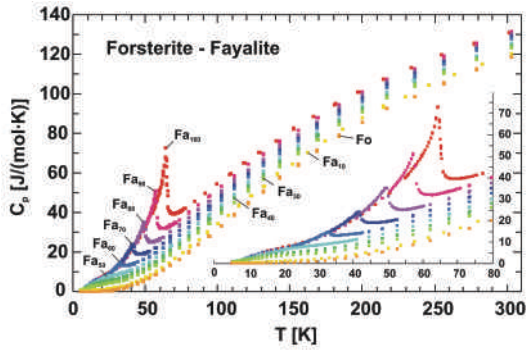

Figure 1. Measured heat capacities for end-member forsterite (Fo) and fayalite (Fa) and the solid-solution compositions $Fo_{10}Fa_{90}$, $Fo_{20}Fa_{80}$, $Fo_{30}Fa_{70}$, $Fo_{40}Fa_{60}$, $Fo_{50}Fa_{50}$, $Fo_{60}Fa_{40}$, $Fo_{70}Fa_{30}$, and $Fo_{90}Fa_{10}$ between 5 and 300 K. The paramagnetic-antiferromagnetic transition region is expanded in the inset and is clearly visible for the Fe-rich olivines fayalite, $Fo_{10}Fa_{90}$, $Fo_{20}Fa_{80}$, $Fo_{30}Fa_{70}$, and $Fo_{40}Fa_{60}$. The corresponding Neel temperatures, T_N, shift monotonically to lower values with decreasing Fe content in olivine. The uncertainty of the C_P data (i.e., 100 σ_{CP}/C_P) is smaller than the symbol size and amounts to ~0.5% at temperatures above, and to ~0.7% below T_N.

TABLE 1. Calorimetric entropies at 298.15 K ($S_{cal,298.15}$) for solid-solution members of the forsterite–fayalite join and excess entropies ($\Delta S^{xs}_{298.15}$) derived according to Equation 3

Entropy	Fayalite	$Fo_{10}Fa_{90}$	$Fo_{20}Fa_{80}$	$Fo_{30}Fa_{70}$	$Fo_{40}Fa_{60}$	$Fo_{50}Fa_{50}$	$Fo_{60}Fa_{40}$	$Fo_{70}Fa_{30}$	$Fo_{90}Fa_{10}$	Forsterite
$S_{cal,298.15}$ J/(mol·K)	151.4±0.1	144.9±0.1	138.9±0.1	134.2±0.1	128.9±0.1	121.7±0.1	116.1±0.1	110.8±0.1	99.5±0.1	94.0±0.1
$\Delta S^{xs}_{298.15}$ J/(mol·K)	0.00±0.60	–0.76±0.59	–1.01±0.59	–0.03±0.60	0.48±0.58	–1.04±0.58	–0.87±0.60	–0.39±0.59	–0.29±0.59	0.00±0.60

assuming an uncertainty in the mole fraction of the olivine composition of ± 0.01. ΔC_P^{xs} is plotted in Figure 2 as a function of temperature for each solid solution olivine. As a consequence of the magnetic phase transition and the Schottky anomaly, all fayalite-bearing olivines show a region of positive ΔC_P^{xs} at low temperatures with maxima at the Neel temperatures, T_N, and a maximal value of ~10 J/(mol·K) for $Fo_{10}Fa_{90}$ (Fig. 2a). Magnesium-rich compositions are characterized by having a smaller and broader maximum ΔC_P^{xs} at lower temperatures, i.e., about 20 K. At temperatures above T_N, in the case of Fe-rich olivines, ΔC_P^{xs} shows negative values with a sharp negative maximum at 64.5 K, corresponding to the magnetic transition in fayalite (Robie et al. 1982a). This negative maximum is strongest for $Fo_{10}Fa_{90}$ with a value of –35 J/(mol·K). It decreases monotonically with increasing Mg content in the olivine solid solutions. Above the T_N of fayalite, the absolute values of ΔC_P^{xs} decrease markedly and approach zero within 2σ uncertainty above 100 K.

The excess entropies for the forsterite–fayalite join at 298.15 K were calculated via the relation

$$\Delta S^{xs}_{298.15} = S^{ss}_{cal,298.15} - [(1 - X_{Fa})\, S^{Fo}_0 + X_{Fa}\, S^{Fa}_0]. \quad (3)$$

The results are listed in Table 1 and plotted in Figure 3[1]. Despite the measurable ΔC_P^{xs} occurring in solid-solution compositions, excess entropy of mixing behavior, which includes both positive and negative excess C_P contributions (see Dachs et al. 2007), largely cancels each other over the temperature interval from 0 to 300 K in Equation 1. If a symmetric Margules model $\Delta S^{xs} = W_s \cdot X_{Fa}\,(1 - X_{Fa})$ is taken to describe the data, it yields an interaction parameter of $W_s = -1.6 \pm 1.7$ J/(mol·K) (one-cation basis). Thus, the resulting ΔS^{xs} behavior is zero within 2σ-uncertainty at 298.15 K (Fig. 3).

DISCUSSION

The results of this study permit new insight into the thermodynamic mixing behavior of forsterite–fayalite solid solutions. Their entropies of mixing have been determined directly using calorimetry for the first time. In the case of Fe-Mg silicates thermodynamic behavior is complicated by Fe^{2+} because it gives rise to measurable electronic and magnetic contributions to the heat capacities of mixing. This aspect is important and mineralogical research along these lines is in its infancy. These aspects are discussed by Dachs et al. (2007) and are not directly relevant to the goal of this report.

Excess entropies of mixing for Fe-Mg olivines, as calculated from the C_P data, are zero within the error of the experimental

[1] Deposit item AM-07-016, Figure 3. Deposit items are available two ways: For a paper copy contact the Business Office of the Mineralogical Society of America (see inside front cover of recent issue) for price information. For an electronic copy visit the MSA web site at http://www.minsocam.org, go to the American Mineralogist Contents, find the table of contents for the specific volume/issue wanted, and then click on the deposit link there.

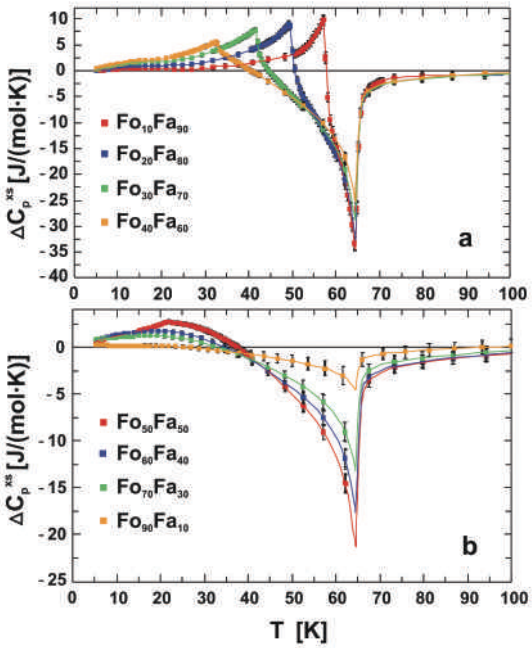

FIGURE 2. Excess heat capacities, ΔC_P^{xs}, as function of temperature between 0 and 100 K for olivine compositions: (**a**) $Fo_{10}Fa_{90}$, $Fo_{20}Fa_{80}$, $Fo_{30}Fa_{70}$, and $Fo_{40}Fa_{60}$; (**b**) $Fo_{50}Fa_{50}$, $Fo_{60}Fa_{40}$, $Fo_{70}Fa_{30}$, and $Fo_{90}Fa_{10}$. Error bars are ±2σ.

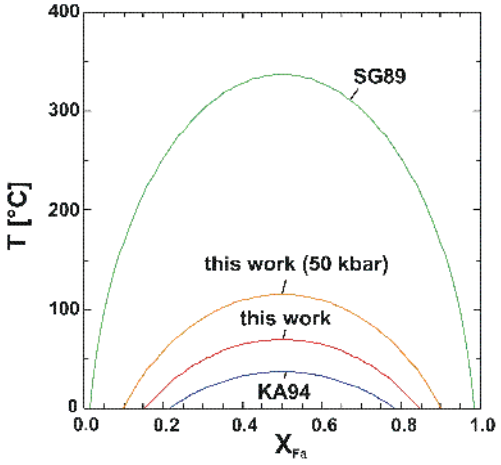

FIGURE 4. *T-X* phase diagram for the forsterite–fayalite join at subsolidus conditions and $P = 1$ bar and 50 kbar. The two solvi with critical temperatures <100 °C are obtained using the $W^{Ol}_{H,Mg\text{-}Fe} = 5.3 \pm 1.7$ kJ/mol term of Kojitani and Akaogi (1994) and $W^{Ol}_{S,Mg\text{-}Fe} = -1.6$ and 0.0 J/(mol·K) values (labeled "this work" and "KA94" and based on a one-cation basis). The solvus labeled "SG89" with a critical temperature of ~340 °C is computed using the term of $W^{Ol}_{G,Mg\text{-}Fe} = 10.2 \pm 0.3$ kJ/mol (Sack and Ghiorso 1989). The solvus labeled "this work (50 kbar)" was calculated with the same $W^{Ol}_{H,Mg\text{-}Fe}$ and $W^{Ol}_{S,Mg\text{-}Fe}$ given above, but for a pressure of 50 kbar using $W^{Ol}_{V,Mg\text{-}Fe} = 0.014 \pm 0.009$ J/bar (one-cation basis) obtained by fitting the volume-composition data of Schwab and Küstner (1977).

method at the 2σ level. However, it could be argued that there may be a tendency for slightly negative ΔS^{xs} behavior based on results for most of the intermediate compositions. Negative entropies of mixing are seldom observed in solid solutions and in the case of silicates appear not to have been observed to date (Geiger 2001). They would tend to indicate that Fe-Mg olivine would become less stable with increasing temperature, something that contradicts typical solid-solution behavior in silicates. The compositions $Fa_{60}Fo_{40}$ and $Fa_{70}Fo_{30}$ seem to be partly at odds with the trend marked by the other data. If they would be excluded from the data set, slightly asymmetric and negative mixing behavior would seem to describe the entropy of mixing behavior. It remains to be determined by further experimental work if these two intermediate compositions represent experimental scatter or if their behavior, which deviates from the general ΔS^{xs} trend, has some underlying physical cause. We can only state, at this point, that the lattice dynamic properties of Fe-Mg olivine are not fully understood.

Thermodynamic mixing behavior and subsolidus phase relations

Our calorimetric results give $W_S \approx 0$ J/(mol·K) and this is consistent with the thermodynamic analysis of von Seckendorff and O'Neill (1993) and Kojitani and Akaogi (1994), for example, who proposed small excess entropies of mixing for the fayalite-forsterite binary [i.e., <2 J/(mol·K)]. However, for the sake of exercise, using a value of $W^{Ol}_{S,Mg\text{-}Fe} = -1.6$ J/(mol·K), one calculates $W^{Ol}_{G,Mg\text{-}Fe} = 6.9$ kJ/mol at 1000 K using the most recent solution calorimetric results (Kojitani and Akaogi 1994) on Fe-Mg olivine with $W^{Ol}_{H,Mg\text{-}Fe} = 5.3$ kJ/mol. This calorimetrically constrained W_G value, which should be considered a maximum upper limit for thermodynamic nonideality, is within the 2 to 8 kJ/mol range proposed by von Seckendorff and O'Neill (1993) using phase equilibrium data, but it is inconsistent with the value of $W^{Ol}_{G,Mg\text{-}Fe} = 10.17 \pm 0.25$ kJ/mol given by Sack and Ghiorso (1989).

We calculated the solvus for the Fe-Mg olivine binary for the first time, solely from calorimetric data, using $W^{Ol}_{H,Mg\text{-}Fe} = 5.3 \pm 1.7$ kJ/mol (Kojitani and Akaogi 1994) and $W^{Ol}_{S,Mg\text{-}Fe} = -1.6$ J/(mol·K) (Fig. 4). Its critical temperature is 70 °C that decreases to ~40 °C if $W^{Ol}_{S,Mg\text{-}Fe} = 0$ J/(mol·K) is used. Based on the volume data of Schwab and Küstner (1977) for Fe-Mg olivines, we derive $W^{Ol}_{V,Mg\text{-}Fe} = 0.014 \pm 0.009$ J/bar for the join (one-cation mixing). With this term, the pressure effect on the solvus can be calculated. Increasing pressure from 1 bar to 50 kbar causes an increase of the critical temperature by ~35 °C (Fig. 4). The calculation of all solvi includes a small S_{conf} contribution caused by slight Fe-Mg ordering and, thus, a slight deviation from random mixing of Fe and Mg on the M1 and M2 sites (Morozov et al. 2005). The solvus labeled "SG89," with a critical temperature of ~340 °C, is computed using $W^{Ol}_{G,Mg\text{-}Fe} = 10.2 \pm 0.3$ kJ/mol from Sack and Ghiorso (1989).

This study on Fe-Mg olivines demonstrates (see also Dachs and Geiger 2006) the important need for further calorimetric C_P investigations on silicate and oxide solid solutions at low temperatures. This is especially true for Fe-containing silicate systems that show low-temperature magnetic and electronic effects (i.e., Schottky anomaly). There is no simple way to obtain them or model them via calculations and there is a dearth of calorimetirc results on such systems. Heat-capacity behavior can only be determined experimentally and quantified through measurements at low temperatures.

Acknowledgments

This work was financed by the Austrian Science Fund under project number P15880-N11, which is gratefully acknowledged.

References cited

Berman, R.G. and Brown, T.H. (1985) Heat capacity of minerals in the system Na_2O-K_2O-CaO-MgO-FeO-Fe_2O_3-Al_2O_3-SiO_2-TiO_2-H_2O-CO_2: representation, estimation and high temperature extrapolation. Contributions to Mineralogy and Petrology, 89, 168–183.

Bowen, N.L. and Schairer, J.F. (1935) The system MgO-FeO-SiO_2. American Journal of Science, 229, 151–217.

Dachs, E. and Bertoldi, Ch. (2005) Precision and accuracy of the heat-pulse calorimetric technique: low-temperature heat capacities of milligram-sized synthetic mineral samples. European Journal of Mineralogy, 17, 251–261.

Dachs, E. and Geiger, C.A. (2006) Heat capacities and entropies of mixing of pyrope-grossular ($Mg_3Al_2Si_3O_{12}$-$Ca_3Al_2Si_3O_{12}$) garnet solid solutions: A low temperature calorimetric and a thermodynamic investigation. American Mineralogist, 91, 894–906.

Dachs, E., Geiger, C.A., von Seckendorff, V., and Grodzicki, M. (2007) 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. Journal of Chemical Thermodynamics, in press.

Geiger, C.A. (2001) Thermodynamic mixing properties of binary oxide and silicate solid solutions determined by direct measurements: The role of strain. In C.A. Geiger, Ed., Solid solutions in silicate and oxide systems, 3, p. 71–100. EMU Notes in Mineralogy, Eötvös University Press, Budapest.

Gopal, E.S.R. (1966) Specific heats at low temperatures. Plenum Press, New York.

Kojitani, H. and Akaogi, M. (1994) Calorimetric study of olivine solid solutions in the system Mg_2SiO_4–Fe_2SiO_4. Physics and Chemistry of Minerals, 20, 536–540.

Morozov, M., Brinkmann, C., Lottermoser, W., Tippelt, G., Amthauer, G., and Kroll, H. (2005) Octahedral cation partitioning in Mg, Fe^{2+}-olivine. Mössbauer spectroscopic study of synthetic $(Mg_{0.5}Fe^{2+}_{0.5})_2SiO_4$ (Fa_{50}). European Journal of Mineralogy, 17, 495–500.

O'Neill, H.St.C., Pownceby, M.I., and McCammon, C.A. (2003) The magnesiowüstite: iron equilibrium and its implications for the activity-compositional relations of $(Mg,Fe)_2SiO_4$ olivine solid solutions. Contributions to Mineralogy and Petrology, 146, 308–325.

Robie, R.A., Finch, C.B., and Hemingway, B.S. (1982a) Heat capacity and entropy of fayalite (Fe_2SiO_4) between 5.1 and 383 K: comparison of calorimetric and equilibrium values for the QFM buffer reaction. American Mineralogist, 67, 463–469.

Robie, R.A., Hemingway, B.S., and Takei, H. (1982b) Heat capacities and entropies of Mg_2SiO_4, Mn_2SiO_4, and Co_2SiO_4 between 5 and 380 K. American Mineralogist, 67, 470–482.

Sack, R.O. and Ghiorso, M.S. (1989) Importance of considerations of mixing properties in establishing an internally consistent thermodynamic database: thermochemistry of minerals in the system Mg_2SiO_4-Fe_2SiO_4-SiO_2. Contributions to Mineralogy and Petrology, 102, 41–68.

Schwab, R.G. and Küstner, D. (1977) Präzisionsgitterkonstantenbestimmung zur Festlegung röntgenographischer Bestimmungskurven für synthetische Olivine der Mischkristallreihe Forsterit-Fayalit. Neues Jahrbuch Mineralogie Monatshefte, 1977(5), 205–215.

Thierry, P., Chatillon-Colinet, C., Mathieu, J.C., Regnard, J.R., and Amosse, J. (1981) Thermodynamic Properties of the Forsterite–Fayalite (Mg_2SiO_4–Fe_2SiO_4) solid solution. Determination of heat of formation. Physics and Chemistry of Minerals, 7, 43–46.

von Seckendorff, V. and O'Neill, H.St.C. (1993) An experimental study of Fe-Mg partitioning between olivine and orthopyroxene at 1173, 1273 and 1423 K and 1.6 GPa. Contributions to Mineralogy and Petrology, 113, 196–207.

Wiser, N.M. and Wood, B.J. (1991) Experimental determination of activities in Fe-Mg olivine at 1400 K. Contributions to Mineralogy and Petrology, 108, 146–153.

Wood, B.J. and Kleppa, O.J. (1981) Thermochemistry of forsterite-fayalite olivine solutions. Geochimica et Cosmochimica Acta, 45, 529–534.

Manuscript received September 28, 2006
Manuscript accepted November 1, 2006
Manuscript handled by Bryan Chakoumakos