Thermodynamic properties of hercynite (FeAl₂O₄) based on adiabatic calorimetry at low temperatures

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ABSTRACT

The low-temperature heat capacity of hercynite (FeAl₂O₄) was measured between 3 and 400 K, and thermochemical functions were derived from the results. The measured heat-capacity curve shows a small lambda-shaped anomaly peaking around 13 K. From our data, we suggest a standard entropy for hercynite at 298.15 K of 113.9 ± 0.2 J/(mol·K), which is some 7.6 J/(mol·K) higher than reported previously by a calorimetric study that missed the entropy contributions of the low-temperature anomaly.

INTRODUCTION

Spinels are ubiquitous minerals in the Earth’s mantle and crust. Because of the additional importance of spinels as furnace smelting products, phase relations and thermodynamic properties of spinels have been investigated by numerous authors (among many others: Turnock and Eugster 1962; Buddington and Lindsley 1964; Muan et al. 1972; Bohlen et al. 1986; Nell et al. 1989; Nell and Wood 1989; Woodland and Wood 1990; Nell and Wood 1991; Sack and Ghiorso 1991). Many of these studies have focussed on thermodynamic mixing properties of spinels, aiming to understand better the behavior of complex solid solutions, which is a prerequisite for thermodynamic calculation of phase relations in complex, natural compositions.

It is surprising, however, that fundamental thermodynamic properties for many spinels of end-member composition (e.g., MgCr₂O₄, FeCr₂O₄, FeAl₂O₄, ZnCr₂O₄, ZnAl₂O₄), which should be well known before attempting to understand complex solid solutions, are only poorly understood. For example, Klemme and O’Neill (1997) and Klemme et al. (2000) investigated the standard entropy of some selected Cr- and Fe-bearing spinels. Their results, employing high-pressure high-temperature experiments and adiabatic calorimetry at low temperatures, indicated large contributions to the standard entropy probably due to magnetic ordering or phase transitions at very low temperatures (e.g., at 12.5 K in the case of MgCr₂O₄). Previous heat-capacity measurements for these phases (Shomate 1944) missed the entropy contribution from these transitions because calorimetric measurements for these phases were performed only down to temperatures of around 50 K. This is the case for many other phases of interest to geologists, as most fundamental calorimetric studies were done in the 1940s and 1950s when low-temperature equipment did not allow studies at temperatures much lower than 50 K.

There are several other phases of geological interest that undergo magnetic ordering or exhibit phase transitions at temperatures lower than 50 K. One of these phases is hercynite (FeAl₂O₄). Previous heat-capacity measurements for FeAl₂O₄ extended only down to 51 K (King 1956), and the standard entropy of FeAl₂O₄ at 298.15 K (S²⁹⁸) was calculated using a smooth extrapolation to 0 K without consideration of possible magnetic contributions to the entropy [S²⁹⁸ = 106.3 J/(mol·K); King 1956]. Although magnetic ordering phenomena were subsequently reported to occur at around 8 K (Lotgering 1962; Roth 1964), many recent thermodynamic databases (e.g., Kubaschewski and Alcock 1983; Kubaschewski et al. 1993; Barin 1999; Robie and Hemingway 1995; Binnewies and Milke 1999) accept King’s (1956) value for the standard entropy for FeAl₂O₄. However, internally consistent sets of thermodynamic data (calibrated using mainly high-pressure, high-temperature experiments) indicate much higher values for the standard entropy but estimates of S²⁹⁸ for hercynite (FeAl₂O₄) vary substantially (Table 1).

Thermodynamic properties of FeAl₂O₄ are especially important to metamorphic geologists, as geothermobarometry of high-grade metamorphic rocks is based on several exchange equilibria involving hercynite, such as 3 FeAl₂O₄ + 3 Al₂SiO₅ = Fe₃Al₂Si₃O₁₂ + 5 Al₂O₃ or 3 FeAl₂O₄ + 5 SiO₂ = Fe₃Al₂Si₃O₁₂ + 2 Al₂SiO₅. These exchange equilibria have been investigated experimentally at high pressures and high temperatures by Hensen and Green (1971), Bohlen et al. (1986), and Shulters and Bohlen (1989). Extrapolation to more complex compositions (as to approximate natural compositions) or other temperatures and pressures than the experimental conditions requires a sound understanding of the thermodynamic properties of all involved end-member components as well as the appropriate mixing properties. For the aforementioned equilibria, thermodynamic properties of the end-members Al₂SiO₅, Al₂O₃, SiO₂, and Fe₃Al₂Si₃O₁₂ are sufficiently well understood (Robie and Hemingway 1995; see Anovitz et al. 1993 for discussion). However, those of FeAl₂O₄ are somewhat uncertain due to possible entropy contributions from magnetic ordering at low temperatures (Lotgering 1962; Roth 1964; Sack and Ghiorso 1991).

Moreover, thermodynamic phase-equilibria calculations in compositions approximating the Earth’s upper mantle (e.g.,