The heat capacity of MgCr$_2$O$_4$, FeCr$_2$O$_4$, and Cr$_2$O$_3$ at low temperatures and derived thermodynamic properties

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ABSTRACT

The heat capacity of synthetic eskolaite, Cr$_2$O$_3$, and of the synthetic spinels magnesiochromite, MgCr$_2$O$_4$, and chromite, FeCr$_2$O$_4$ were measured from 1.5 K to 340 K. For MgCr$_2$O$_4$, a substantial magnetic contribution to the entropy is revealed by a sharp peak in the heat capacity curve at 12.55 ± 0.05 K, which indicates the transition to antiferromagnetic long-range order. Integration of the heat capacity curve yields a value of 118.3 ± 1.2 J/(mol·K) for the standard entropy at 298.15 K, which is in excellent agreement with that calculated from phase equilibria studies on the reaction MgCr$_2$O$_4$ + SiO$_2$ = Cr$_2$O$_3$ + MgSiO$_3$. The new calorimetric results for Cr$_2$O$_3$ indicate a standard entropy at 298.15 K of 82.8 ± 0.8 J/(mol·K). The measurements for FeCr$_2$O$_4$ show three distinct heat capacity anomalies, one of which (peaking at 36.5 ± 0.2 K) was missed by previous low temperature heat capacity measurements, which only extend down to 53 K. Integration of the heat capacity curve yields a value for the standard entropy at 298.15 K of 152.2 ± 3.0 J/(mol·K) for FeCr$_2$O$_4$, some 6 J/(mol·K) greater than the previous calorimetric value.

These low-temperature heat capacity data were combined with high-temperature heat content measurements from the literature to derive heat capacity equations for all three phases to 1800 K. The resulting heat capacity equations were then used to extract revised recommended values of the standard enthalpies of formation and entropies of MgCr$_2$O$_4$ and Cr$_2$O$_3$ from phase equilibrium data. For FeCr$_2$O$_4$, the phase equilibrium data are of dubious accuracy, the enthalpy of formation is only approximate.

INTRODUCTION

Spinels are constituents of many igneous and metamorphic rocks due to their stability over a wide range of pressures and temperatures. In ultramafic rocks spinels are typically chromium-rich (e.g., Meyer 1987). Thermodynamic modeling of Cr-bearing mineral assemblages in the upper mantle (e.g., the transition from spinel hherzolite to garnet hherzolite, cf. Klemme and O’Neill 2000a) requires accurate knowledge of the thermochemical properties of chromium spinels, chromium pyroxenes and chromium-bearing garnets (Klemme and O’Neill 1998; Klemme and O’Neill 2000b). In particular, accurate and reliable thermodynamic data for Cr spinels are needed to anchor the data for other Cr species. However, the properties of even the simple end-member Cr spinels are not well known, as demonstrated for magnesiochromite (MgCr$_2$O$_4$) by Klemme and O’Neill (1997).

Entropies of many minerals can be determined directly from heat capacity measurements (e.g., Hemminger and Höhne 1979; Kleppa 1982; Robie et al. 1979; Robie and Hemmingway 1995). For temperatures below that of liquid nitrogen, high precision calorimeters are not commercially available, so heat capacity ($C_p$) measurements at temperatures below that of liquid nitrogen are comparatively rare (Gmelin 1985; Navrotsky 1994). Hence in many older studies, at least for geologically relevant substances, the heat capacity was usually measured only down to ~50 K, and then extrapolated to 0 K, under the assumption that only lattice vibrations contribute to $C_p$. This permits such extrapolations to be made in accord with Debye’s theory. The simple prediction that the heat capacity function of a mono-atomic solid at low temperatures is proportional to $T^3$ (Chatterjee 1991) is, however, usually only valid for temperatures smaller than the initial Debye temperature of the material. The situation is more complicated in compounds with atoms of strongly differing atomic masses. For minerals, the spectrum is modeled in a more complicated fashion (Kieffer 1979), such that fitting parameters (e.g., the lowest frequency) are adjusted to match the existing calorimetric data (Hofmeister and Ito 1992) and the entropy is then extracted. In addition to the errors inherent to these extrapolations, if there is a phase transition below the range of the calorimeter, it will go undetected, and the contribution of the phase transition to the standard entropy at 298.15 K will be missed. The same problem can occur with Schottky anomalies from the crystalline electric field splitting of ion magnetic ground states. The additional entropy contribution of such a Schottky term can be as large as $R \ln (2J+1)$, where $J$ is the total angular momentum quantum number of the magnetic groundstate. Magnetic ordering transitions and ion magnetic Schottky anomalies are likely to be of particular importance for minerals containing transition metals.

Recently, high-pressure, high-temperature experiments were used to extract thermodynamic properties for MgCr$_2$O$_4$ (Klemme and O’Neill 1997). These results disagreed considerably with previous estimates from heat capacity measurements...