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Cr-Spinels in the Earth's Mantle: Thermodynamics and Phase Relations at High Pressures and High Temperatures

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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, moreover, chromium spinels are often used as indicator minerals in diamond exploration.

Thermodynamic modeling of Cr-bearing mineral assemblages in the upper mantle (e.g. the transition from spinel lherzolite to garnet lherzolite) requires accurate knowledge of the thermochemical properties of chromium spinels, chromium pyroxenes and chromium-bearing garnets. In particular, accurate and reliable thermodynamic data for Cr spinels are needed to anchor the data for other Cr species.

However, the thermodynamic properties of even the simplest end-member Cr-spinels are not well known, as recently demonstrated for magnesio-chromite (MgCr2O4) by Klemme and O'Neill (1997). Klemme and O'Neill (1997) performed reversal experiments on the univariant reaction MgCr2O4 + SiO2 = Cr2O3 + MgSiO3 at high pressures and high temperatures. They proposed a standard entropy for MgCr2O4 which is much higher than previous estimates derived from previous calorimetric measurements (Shomate 1944 - S298.15 = 106 J/(mol K)), predicting a large heat capacity anomaly at very low temperatures (i.e. below 52 K).

The present study intends to test the results of Klemme and O'Neill (1997) by performing low-temperature heat-capacity measurements for MgCr2O4 between 1.5 and 300 K. We have also performed measurements for FeCr2O4 and Cr2O3.

Results for magnesio-chromite show that at about 12.5 K an extremely sharp peak is observed which is interpreted to coincide with the antiferromagnetic transition, previously observed by a number of workers (e.g. Hartmann-Boutron et al. 1969). The standard entropy at 298.15 K was calculated from the Cp data (using a T3 extrapolation to 0 K) and resulted in S298.15 of 118.3 ±1.2 J/(mol K) indicating a magnetic contribution to the entropy in the order of 12 J/(mol K). The resulting S298.15 for MgCr2O4 is in excellent agreement with the re-evaluated experimental results of Klemme and O'Neill (1997), using the new calorimetric data for Cr2O3.

The specific heat capacity function of FeCr2O4 was measured from 2.4 K to 337 K. Three heat capacity anomalies are observed peaking at 37 K, 69 K and 124 K. The two higher temperature Cp-anomalies were observed previously by Shomate (1944) in his calorimetric measurements, but the anomaly at 37 K was of course missed, since his measurements extended only down to 53 K. Consequently, Shomate's value for the standard entropy of FeCr2O4 at 298.15 K lacks the contribution to the entropy from this transition, and is too low. Integration of the present low-temperature Cp-data results in a value for the entropy of FeCr2O4 at 298.15 K of about 152 J/(mol K), which includes a T3 extrapolation from 2.4 K down to 0 K. This is some 6 J/(mol K) higher than Shomate's (1944) value of ca. 146 J/(mol K).

These differences in the standard entropy of MgCr2O4 and FeCr2O4 may appear small at first sight, however, they are sufficiently large to substantially effect position and slope of calculated phase equilibria at high pressures and high temperatures (Klemme and O'Neill 1997). Calculated phase equilibria in chromium bearing systems will be presented and the effect of Cr on the transition from garnet lherzolite to spinel lherzolite in depleted bulk compositions will be discussed.

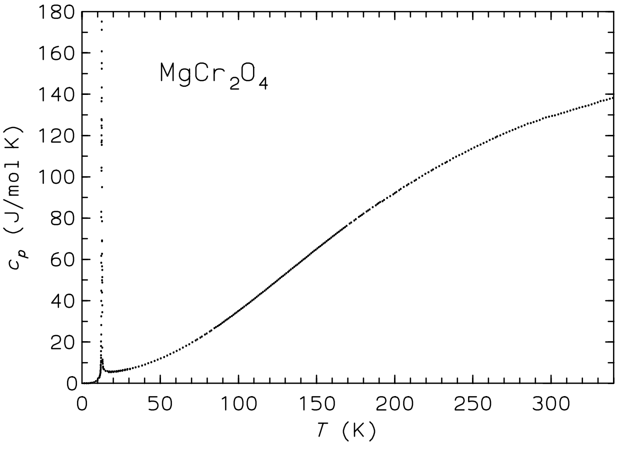

Figure 1: The heat capacity [Cp(T)] of polycrystalline magnesio-chromite (MgCr2O4) measured between 1.5 K and 340 K.

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