The heat capacity of $MgCr_2O_4$, $FeCr_2O_4$, and Cr_2O_3 at low temperatures and derived thermodynamic properties

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ABSTRACT

The heat capacity of synthetic eskolaite, Cr_2O_3, and of the synthetic spinels magnesiochromite, $MgCr_2O_4$, and chromite, $FeCr_2O_4$ were measured from 1.5 K to 340 K. For $MgCr_2O_4$, 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 $MgCr_2O_4 + SiO_2 = Cr_2O_3 + MgSiO_3$. The new calorimetric results for Cr_2O_3 indicate a standard entropy at 298.15 K of 82.8 ± 0.8 J/(mol·K). The measurements for $FeCr_2O_4$ 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 $FeCr_2O_4$, 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 $MgCr_2O_4$ and Cr_2O_3 from phase equilibrium data. For $FeCr_2O_4$, 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 lherzolite to garnet lherzolite, 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 ($MgCr_2O_4$) 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 Hemingway 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 θ/20 to θ/50 where θ is 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 $MgCr_2O_4$ (Klemme and O'Neill 1997). These results disagreed considerably with previous estimates from heat capacity measurements

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which extended down only to 54 K (Shomate 1944), since these missed a substantial magnetic contribution to the entropy which is known from the literature to occur at ~15 K (see below). Klemme and O'Neill (1997) proposed that the missing entropy amounted to about 16 J/(mol·K). The present study tests the results of Klemme and O'Neill (1997) by performing low-temperature heat-capacity measurements between 1.5 and 300 K.

$MgCr_2O_4$ synthesized at temperatures below 1300 °C has the cation distribution of a completely normal spinel at room temperature (O'Neill and Dollase 1994). The cation distribution of $FeCr_2O_4$ has not been determined directly, but from the general similarity of the site preference of Fe^{2+} to that of Mg in spinels (e.g., O'Neill and Navrotsky 1984), it too is expected to have a completely normal cation distribution at room temperature. Thus, unlike for other spinel group minerals such as $MgAl_2O_4$, the effect of variable cation distributions is not expected to be an issue here.

Calorimetric measurements were also performed on Cr_2O_3 and $FeCr_2O_4$. The existing data for Cr_2O_3 from different studies are in relatively poor agreement with each other, which makes the interpretation of phase equilibrium data for this key substance less secure than desirable (Holzheid and O'Neill 1995). For $FeCr_2O_4$, which contains two transition metal cations (Fe^{2+} and Cr^{3+}) in two different crystallographic sites, the heat capacity measurements also only extend down to 50 K; hence, some of the magnetic entropy of this phase may have been missed, too.

PREVIOUS WORK

Magnesiochromite

The heat capacities of $MgCr_2O_4$ were measured from 54 K to 296 K by Shomate (1944). The heat contents from 298–1773 K were measured by Naylor (1944). The entropy at 298.15 K (J/(mol·K)) was obtained by extrapolation to 0 K without considering magnetic or electronic contributions to the entropy (Shomate 1944). However, some evidence exists for magnetic contributions at lower temperatures with the long-range ordering temperature at 15 K from neutron diffraction at low temperatures (Plumier 1968; Shaked et al. 1970). These studies reported two distinct antiferromagnetically ordered states at 16 K and 13.5 K whereas Blasse and Fast (1963) reported a paramagnetic to antiferromagnetic transition at 15 K. From Mössbauer spectroscopy and X-ray techniques, Hartmann-Boutron et al. (1969) concluded that the transition was of first-order with a change in crystallographic (cubic-tetragonal) symmetry. Thus, a substantial contribution to the entropy of $MgCr_2O_4$ associated with this transition was missed in the calorimetric measurements of Shomate (1944).

Klemme and O'Neill (1997) investigated the thermodynamic properties of magnesiochromite by locating the position in pressure-temperature space of the univariant reaction: $MgCr_2O_4$ + SiO_2 = Cr_2O_3 + $MgSiO_3$. Interpretation of these results rests on the assumption that the thermodynamic data for SiO_2 (quartz), $MgSiO_3$ (enstatite), and Cr_2O_3 (eskolaite) are well known. This is probably the case for SiO_2 and $MgSiO_3$, but some doubts about the accuracy of the calorimetric data for Cr_2O_3 were recently raised by Holzheid and O'Neill (1995) (see below). Holzheid and O'Neill (1995) recommended 85.7 J/(mol·K) for

the entropy of Cr_2O_3 at 298.15 K, leading to $S^0_{298.15}$ = 122 ± 1 J/K·mol for magnesiochromite (Klemme and O'Neill 1997), which is 16 J/(mol·K) higher than the value of Shomate (1944).

Eskolaite

The thermochemical data for Cr_2O_3 (eskolaite) are debated. From calorimetric measurements, Bruce and Cannell (1977), Anderson (1937), and Volger (1952) report an antiferromagnetic transition at around 300 K, resulting in a substantial contribution to the entropy at 298.15 K. Unfortunately, the temperature of this transition is close to the customary join between low temperature adiabatic heat capacity measurements and high temperature heat content measurements, making it difficult to link the data sets. Chase et al. (1985), based mainly on heat capacity measurements of Anderson (1937), adopt values for the entropy and enthalpy of formation at 298.15 K for Cr_2O_3 of 81.1 ± 1.3 J/(mol·K) and –1134.7 ± 8.4 kJ/mol, respectively. Mah (1954) reports $\Delta_f H^0_{298.15}$ for Cr_2O_3 of –1141.7 ± 1.7 kJ/mol using oxygen bomb calorimetry, but electrochemical studies (Holzheid and O'Neill 1995 and references therein) disagree with this calorimetric value. Holzheid and O'Neill (1995) recommended $S^0_{298.15}$ (Cr_2O_3) of 85.74 ± 0.2 J/(mol·K) and $\Delta_f H^0_{298.15}$ (Cr_2O_3) of –1124.6 ± 2.5 kJ/mol. Holzheid and O'Neill's (1995) data are in agreement with the earlier and less precise calorimetric result of Roth and Wolf (1940), however.

Chromite

Naylor (1944) investigated the high-temperature heat contents of $FeCr_2O_4$ (386–1787 K). The low-temperature (53–296 K) heat capacities of $FeCr_2O_4$ were measured by Shomate (1944); the thermodynamic functions were derived by extrapolation to 0 K, neglecting possible magnetic or electronic contributions to the entropy at temperatures below 53 K.

Shomate (1944) reported a lambda-like C_P-anomaly between 90 and 140 K, resulting in a contribution to the entropy of ~2.4 J/(mol·K). The anomaly is associated with a cubic to tetragonal phase transition (Shirane et al. 1964). A second C_P anomaly near 75 K (Shomate 1944) coincides with the Néel temperature at 80 K (Shirane et al. 1964). The contribution of this anomaly to the entropy of $FeCr_2O_4$ is small (~0.75 J/(mol·K)). Sack and Ghiorso (1991) speculated that the majority of the magnetic entropy is either not developed at lower temperatures or is associated with the transformation from collinear to helicoidal spin found by Shirane et al. (1964) at 35 K. However, Sack and Ghiorso (1991) estimated the standard entropy as 142.7 J/(mol·K) for $FeCr_2O_4$, which is slightly less than the value 146.1±1.7 J/(mol·K) from Shomate (1944).

EXPERIMENTAL METHODS

Sample preparation and characterization

$MgCr_2O_4$ and $FeCr_2O_4$ were prepared from commercially sourced ultra-pure oxides (Cr_2O_3, MgO, and Fe_2O_3 = 99.99%) at 1 atmosphere in high-temperature, controlled atmosphere furnaces at the Research School of Earth Sciences. Oxides were dried at 1100 °C for several hours immediately before weighing. The oxides were mixed manually in appropriate proportions in an agate mortar for at least three hours, and then pressed

into pellets using tungsten carbide dies with a diameter of 0.5 inch.

$MgCr_2O_4$ was synthesized by heating the pellet in a flowing atmosphere of pure CO_2 at 1300 °C for 24 hours. The mixture was rapidly quenched, re-ground and run in a 30 mm large-capacity piston-cylinder apparatus at 1.0 GPa, 1300 °C for 12 hours to minimise the pore space of the specimen. Pellets of Cr_2O_3 were run in the piston-cylinder apparatus at 1300 °C and 1.0 GPa for 12 hours. The high-pressure techniques are similar to those described in Klemme and O'Neill (1997) and Klemme (1998).

$FeCr_2O_4$ was synthesized from the oxide mixture under a $CO:CO_2$ gas mixture of 9:1 at 1300 °C for 72 hours, then slowly cooled to 950 °C. The temperature was kept at 950 °C for a further 20 hours (all this under the same gas mixture), and the sample was then quenched rapidly by dropping into a vacuum chamber at the bottom of the furnace. Unlike many Fe-bearing spinels, essentially stoichiometric $FeCr_2O_4$ can be synthesized over a finite range of oxygen fugacities, because the electron exchange reaction $Fe^{2+} + Cr^{3+} = Fe^{3+} + Cr^{2+}$ ensures that at high temperature there is a finite activity of Fe_3O_4 even at atomic $Fe/Cr = 0.5$ exactly. However, we could not guarantee that some oxidation of the $FeCr_2O_4$ would not occur in the large-capacity piston-cylinder apparatus, hence the sample used for calorimetry was not densified by this treatment.

All synthesis products were checked for homogeneity and unreacted oxides using X-ray powder diffraction techniques. Electron microprobe analyses suggest that the spinels are homogenous and stoichiometric. No impurities or unreacted oxides could be detected by either electron microprobe analyses or X-ray diffraction. The pellets are grey-green and highly dense for $MgCr_2O_4$, dark green and highly dense for Cr_2O_3, and black and not as dense for $FeCr_2O_4$. The flat disks weigh 1.2224 g (Cr_2O_3; M = 151.9902 g/mol), 1.1389 g ($MgCr_2O_4$; M = 192.2946 g/mol), and 0.4846 g ($FeCr_2O_4$; M = 223.8366 g/mol), respectively.

Calorimetry

The heat capacities were measured in two vacuum calorimeters designated Cal I and Cal III) at the Max-Planck Institut für Festkörperforschung in Stuttgart. The calorimeters are essentially identical except that Cal III is specially designed for measurements in high magnetic fields. Cal I is inserted into a bath cryostat and cooled by filling with liquid helium. After vaporization of the He bath the calorimeter is cooled by the cold helium gas and liquid nitrogen in the annular chamber around the He tank. Cal III (1.5–100 K) is inserted into the 52 mm diameter bore of a 16 T superconducting solenoid and is always kept submerged in liquid helium.

Both calorimeters are equipped with exchangeable miniature sample holders. The holders consist of a frame and a platform made of a thin sapphire disc suspended by three threads from the frame. The platform carries the sample which can be heated by a thin film heater on the lower side of the platform. In Cal I (for temperatures $T > 20$ K) a calibrated platinum miniature sensor (Pt-100 118MF; Rosemount) was used for thermometry. For measurements from 1.5 K (2.35 K for $FeCr_2O_4$) up to approximately 30 K a calibrated Cernox temperature sen-

sor was used (CX-1050; Lake Shore). In high magnetic fields, magnetoresistance corrections were applied that were obtained by an in-situ calibration of the sensor, using a capacitance sensor (Oxford) as a transfer thermometer.

Samples are mounted on top of the sapphire sample platform with a small amount (maximal 10 mg) of Apiezon N high vacuum grease. The addenda contributions of the sample holder ensemble and of the Apiezon N grease (Schnelle et al. 1999) were determined in separate runs and subtracted from the raw data of each run.

The quasi-adiabatic, isoperibol heat pulse method (Nernst's Method) was used with an isothermal shield control. The shield temperature was kept constant to within 0.5 mK (Cal I) or better than 0.2 mK (Cal III). The typical residual drift rates of the base line before the heat pulse were $\pm 2 \cdot 10^{-6}$ K/s. Typical heat pulse heights for $T > 5$ K are 2% or less of the absolute temperature or maximal 1.0 K. Due to the relatively small sample masses, the heat leak of the sample ensemble to the isothermal shield resulted in external relaxation time constants (τ^{ext}) of 220–4100 s, depending on the temperature range and sample ensemble heat capacity. Because of the excellent heat diffusivity of the Cr_2O_3 and the $MgCr_2O_4$ samples, respectively, these short τ^{ext} caused no problems, except for the highest temperatures measured. The $FeCr_2O_4$ sample has about half the mass of the others, and a much smaller thermal diffusivity, resulting in longer internal equilibration times τ^{int} and comparatively short external relaxation times τ^{ext}.

The estimated uncertainties are 0.6% for C_P (200 K $< T <$ 300 K), 0.4% for C_P (20 K $< T <$ 200.0 K), and 0.7% for C_P (T <20.0 K) for the Cr_2O_3 and $MgCr_2O_4$ samples. The error margins for $FeCr_2O_4$ are roughly twice as large, especially at elevated temperatures.

To investigate the sharp phase transition in $MgCr_2O_4$ at approximately 12.5 K, heat pulses spanning temperature intervals as small as 15 mK were used. The magnetic field dependence of the transition temperature was tested in an applied field of 14 T. To check for hysteresis, cooling curves of the sample holder ensemble were recorded: The sample ensemble and the shield were heated to 30 K and then allowed to cool to the bath temperature of 4.2 K. The resulting cooling data $T(t)$ were converted numerically to $[1/(dT/dt)]$ (T). The resulting curve was then plotted for temperatures near the phase transition and normalized to the C_P(T) data in warming.

RESULTS

Magnesiochromite

At about 12.55 ± 0.05 K an extremely sharp peak in heat capacity is observed (Fig. 1, Appendix table[1]). This is interpreted as the antiferromagnetic transition, previously observed by Shaked et al. (1970), Blasse and Fast (1963), and Hartmann-

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[1]For a copy of Appendix table, document item AM-00-059, contact the Business Office of the Mineralogical Society of America (see inside front cover of recent issue) for price information. Deposit items may also be available on the American Mineralogist web site (http://www.minsocam.org or current web address).

Boutron et al. (1969). Detailed susceptibility measurements (W. Schnelle, personal communication) confirm the antiferromagnetic character of the phase transition.

In contrast to Shaked et al. (1970) who found two distinct transitions to magnetically ordered states at ~16 K and at ~13.5 K, only one sharp peak was observed. However, close inspection of the heat capacity anomaly (Fig. 2) reveals a "foot" on the high-temperature side which indicate a second, almost degenerate magnetic transition ~0.2 K above the main transition. Surprisingly, the entropy involved in the phase transition is only R ln 2 for one formula unit. Magnetic short range correlations are clearly visible in $C_P(T)$ up to 100 K. A crude estimate of the total magnetic contribution to the specific heat capacity up to 200 K using a constant Debye temperature of 760 K yields a total magnetic entropy of which is close to 2 R ln 4, i.e., 2 R ln (2S+1) implying S=3/2 for Cr^{3+}.

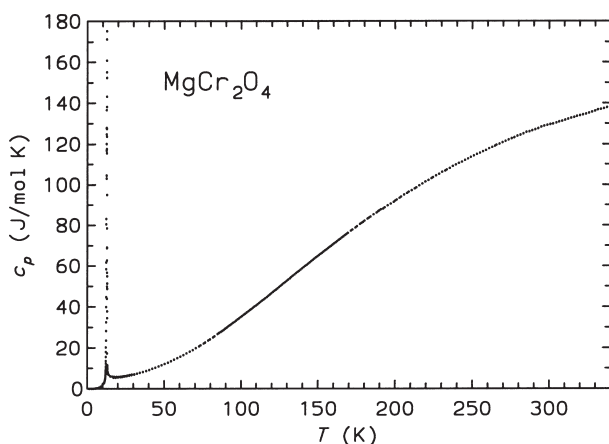Some preliminary measurements were performed to inves-

FIGURE 1. The heat capacity $C_P(T)$ of polycrystalline $MgCr_2O_4$ measured between 1.5 K and 340 K. A very sharp heat capacity anomaly is observed, peaking at the Néel temperature T_N = 12.55 ± 0.05 K.
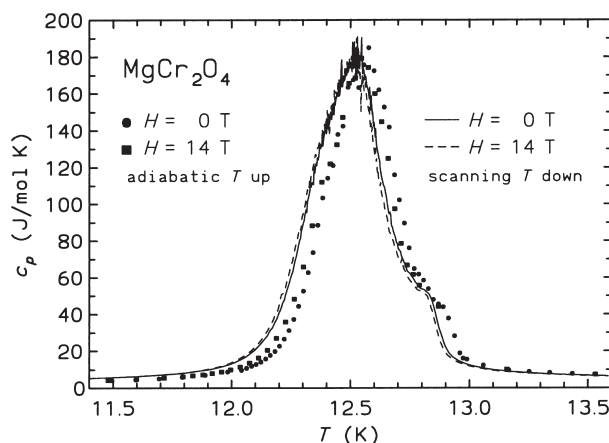

FIGURE 2. Heat capacity $C_P(T)$ of $MgCr_2O_4$ in magnetic fields of 14 Tesla (squares) as well in the zero-field (circles). The solid and dashed curves are the negative inverse cooling rate (see text) of the sample in arbitrary units for zero and 14 Tesla magnetic fields, respectively. These curves are proportional to the heat capacity of the sample near the transition in cooling.

tigate the influence of a strong magnetic field on the transition. A field of 14 Tesla resulted in only a small downshift (10–20 mK) of the transition temperature (Fig. 2). From the cooling measurements in scanning mode with and without a 14 Tesla magnetic field, curves were obtained representing the heat capacity in cooling. A small temperature hysteresis of about 80 mK was observed between cooling and warming measurements, consistent with a first order phase transition (Hartmann-Boutron et al. 1969).

Fitting the experimental C_P data from 250–338 K (92 data points) in conjunction with 13 heat content data (Naylor 1944) using a weighted least squares algorithm, yielded the form

$$C_P \text{ (MgCr}_2\text{O}_4) \text{ in (J/K·mol)} = 221.24 - 0.00102030 \cdot T - 1757210 \cdot T^{-2} - 1247.9 \cdot T^{-0.5} \quad (1)$$

The uncertainties for this study were assumed to be 0.6% (200 < T < 300 K), 0.4% (20 < T <2 00 K), 0.7% (T < 20 K) while the uncertainty of the heat content data is estimated at 0.2%. Although this equation is based on experimental data to 1800 K, it appears well-behaved at higher temperatures, permitting modest extrapolation. The standard entropy at 298.15 K was calculated from the C_P data (using a T^3 extrapolation to 0 K) and resulted in $S^0_{298.15}$ 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 $MgCr_2O_4$ is in good agreement with the re-evaluated experimental results of Klemme and O'Neill (1997): ($S^0_{298.15}$ = 119.6 ± 0.9 J/(mol·K) and $\Delta_f H^0_{298.15}$ = −1762 ± 1.4 kJ/mol), using the calorimetric data for Cr_2O_3, as discussed below.

Eskolaite

The heat capacity of Cr_2O_3 (Fig. 3, Appendix table) shows a lambda-shaped heat capacity anomaly at the Néel temperature at 305.5 K, due to antiferromagnetic ordering. Good agreement exists with the results of Bruce and Cannell (1977) (Fig. 3), whereas the present curve lies considerably below the data points of Volger (1952) and somewhat higher than the curve of Anderson (1937). Integration of the low-temperature C_P data, with a T^3 extrapolation to 0 K, yields an entropy at 298.15 K for Cr_2O_3 = 82.8 ± 0.8 J/(mol·K).

Occurrence of the lambda anomaly close to the reference temperature of 298.15 K poses a logistical nuisance in applying the data. As the C_P equation will mostly be used for calculations well above room temperature, we adopt the following procedure: a heat capacity function is derived that ignores the C_P anomaly, and the entropy that is missed by doing this is added to the standard entropy, to produce a "virtual" value for the standard entropy. This simple ruse returns the correct thermodynamic values above 340 K, but not between 298.15 K and 340 K.

Accordingly, the heat content data of Moore and Kelley (1944) were adjusted to 340 K, using $H_{340}-H_{298.15}$ = 4899 J. A combination of five C_P data from this study at 335–340 K and 16 heat content data (Moore and Kelley 1944) were used to derive the following equation from least squares fitting:

$$C_P \text{ (Cr}_2\text{O}_3) \text{ in (J/K·mol)} = 227.25 - 0.02132 \cdot T + 3543029 \cdot T^{-2} - 2567.3 \cdot T^{-0.5} \quad (2)$$

This equation is based on data to 1774 K. However, it returns a maximum in the C_P vs. T curve at 1430 K at a value of 130.6 J/K·mol, with a slight decrease to 129.5 J/K·mol at 1800 K. Such a maximum in the heat capacity curve is unusual and suggests caution be exercised in extrapolation.

To compensate for the part of the entropy between 298 and 340 K that is omitted by our fitting procedure, 0.8 J/(mol·K) needs to be added to the true entropy at 298.15 K, to produce a "virtual" standard entropy at 298.15 K for Cr_2O_3 of 83.6 J/(mol·K), for use in conjunction with this C_P expression.

Re-evaluation of the EMF data on the free energy of formation of Cr_2O_3

The free energy of formation of Cr_2O_3 is defined by the reaction $2 Cr + 3/2 O_2 = Cr_2O_3$. The calorimetric data needed for third law analysis are in Table 1. All 74 EMF data of Holzheid and O'Neill (1995) were used, results are depicted in Figure 4. In contrast to Holzheid and O'Neill (1995) it was opted to use all their data, although the high temperature data ($T > 1350$ K) appear to show some systematic deviations from the trend established at temperatures between 900 and 1300 K. Regres-

sion of the calculated values of $\Delta_f H^0_{298.15}$ gives $\Delta_f H^0_{298.15} (\pm 256) =$ $-752206 (\pm 230) + 0.350 (\pm 0.195) \cdot T$ [J/mol], implying $\Delta(\Delta S^0_{298.15})$ = 0.35. Hence, per mole of Cr_2O_3, we recommend $\Delta_f H^0_{298.15}$ $(Cr_2O_3) = -1128.2 \pm 0.4$ kJ/mol and $S^0_{298.15} (Cr_2O_3) = 82.3 \pm 0.3$ J/(mol·K). The value of the "virtual" $S^0_{298.15} (Cr_2O_3)$ to be used with the heat capacity equation is 83.1 J/(mol·K).

As a next step, the experimental results on the reaction $MgCr_2O_4 + SiO_2 = Cr_2O_3 + MgSiO_3$ were re-evaluated, after Klemme and O'Neill (1997). Using the new calorimetric estimates of $S^0_{298.15} = 83.1$ J/(mol·K) and $\Delta_f H^0_{298.15} = -1128.2$ kJ/mol for Cr_2O_3 (this study), new standard thermochemical data for $MgCr_2O_4$ are derived ($S^0_{298.15} = 119.6 \pm 0.9$ J/(mol·K) and $\Delta_f H^0_{298.15}$ $= -1762 \pm 1.4$ kJ/mol). These new estimates for $S^0_{298.15}$ of $MgCr_2O_4$, based on the new calorimetric results for Cr_2O_3, are in even better agreement with the calorimetric measurements for $MgCr_2O_4$ of $S^0_{298.15} = 118.3 \pm 1.2$ J/(mol·K) (see above).

Chromite

Three heat capacity anomalies are observed (Fig. 5, Appendix table) peaking at 36.5 ± 0.2 K, 68.7 ± 0.2 K and 124.1 ± 0.2 K. The interpretation of these anomalies is not straightforward
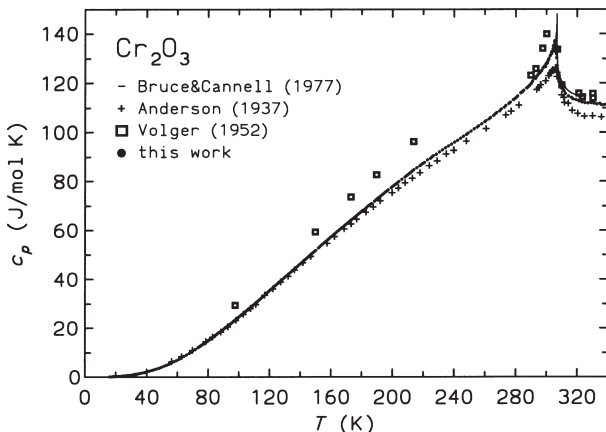

FIGURE 3. The heat capacity of polycrystalline Cr_2O_3 as investigated between 1.5 K and 340 K. The lambda-shaped heat capacity anomaly peaks at the Néel temperature $T_N = 305.5 \pm 0.2$ K. Compared to this work are studies from Bruce and Cannell (1977), Volger (1952), and Anderson (1937).
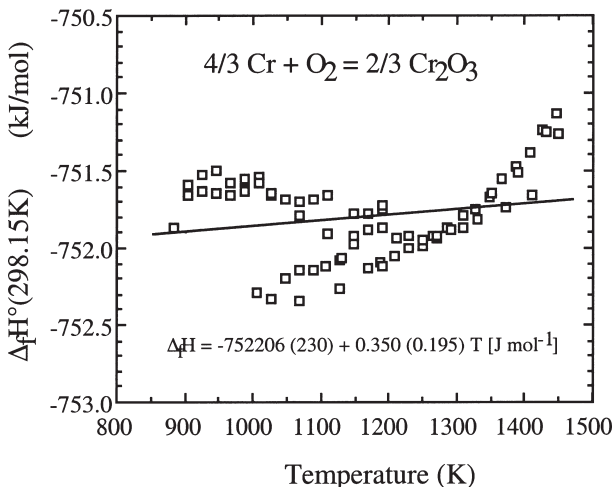

FIGURE 4. Values of $\Delta_f H^0_{298.15}$ for Cr_2O_3 calculated from the third-law analysis of the EMF data (Holzheid and O'Neill 1995), using the calorimetric data listed in Table 1. Perfect agreement between electrochemical and calorimetric data would result in calculated values of $\Delta_f H^0_{298.15}$ independent of temperature. The slightly positive slope of 0.35 J/(mol·K) indicates a discrepancy between the calorimetric and electrochemical data of this magnitude.

TABLE 1. Thermodynamic data

	Calorimetric $S^0_{298.15}$ (J/mol·K)	Recommended $S^0_{298.15}$ (J/mol·K)	Recommended $\Delta_f H^0_{298.15}$ (kJ/mol)	C_P a	b	c	d	e	Source
O_2	205.15			47.255	−4.542E-4	0	−393.5	440223	Chase et al. (1985)
Cr	25.24			−101.42	0.058012	−5.49845	2724.1	−5353833	Chase et al. (1985)
Cr_2O_3	83.6* ± 0.8	83.1* ± 0.3	−1128.2 ± 0.4†	227.25	−0.02132	0	−2567.3	3543029	this study
$MgCr_2O_4$	118.3 ± 1.2	119.6 ± 0.9	−1762 ± 1.4	221.24	−0.0010203	0	−1247.9	−1757210	this study
$FeCr_2O_4$	152.2 ± 3.0	152.2 ± 3.0	≈ −1433‡	139.75	0.029408	0	474.8	−3359576	this study

* "Virtual entropies" for Cr_2O_3, for use with the heat capacity equations. The real values of $S^0_{298.15}$ are 82.8 ± 0.8 J/mol·K (calorimetric) or 82.3 ± 0.3 J/mol·K (recommended) (see text).
† "Virtual" value for use with "virtual" entropy and C_p equations. The real value of $\Delta_r H^0_{298.15}$ would be −1128.0 kJ/mol.
‡ Based on $\Delta_r H^0_{298.15} = \approx -610$ kJ/mol for 2 Fe + 2 Cr_2O_3 + O_2 = 2 $FeCr_2O_4$ (see Fig. 6). $C_p = a + bT + cT^2 + dT^{-0.5} + eT^{-2}$ (J/mol·K).

because the magnetic structure of $FeCr_2O_4$ is complicated (Francombe 1957; Bachella and Pinot 1964; Shirane et al. 1964; Kose and Iida 1984). From neutron diffraction work, Shirane et al. (1964) describe satellite reflections, which they claim are characteristic of a cone-spiral magnetic structure, that disappear near 35 K, corresponding to the first anomaly in the heat capacity data. Shirane et al. (1964) claim that the magnetic spins are then collinear from 35 K to the Néel temperature, which they put at 80 K (vs. our observed peak at 69 K). The anomaly at 124 K (135 K in the study of Shirane et al. 1964) is associated with a tetragonal-to-cubic phase transition, in which the regular tetrahedral coordination environment of Fe^{2+} in the high-temperature cubic phase undergoes a Jahn-Teller distortion. The temperature of this latter anomaly is given as 137 K by Kose and Iida (1984) from XRD, magnetization and specific heat measurements, in agreement with Shirane et al. (1964); but Bacchella and Pinot (1964) report 123 K from an XRD study, in agreement with our observations. The cause of this discrepancy is unknown. Kose and Iida (1984) determined the temperature of the transition as a function of composition along the join $FeCr_2O_4$-Fe_3O_4 and showed that the effect of adding the Fe_3O_4 component is to decrease the temperature only very slightly. Perhaps the discrepancy reflects differences in the coupled Fe^{3+}-vacancy concentrations that presumably occur on oxidation of $FeCr_2O_4$ if the atomic Fe/Cr ratio is maintained at the stoichiometric value of 0.5.

The two higher temperature C_P-anomalies were observed previously by Shomate (1944) in his calorimetric measurements, his measurements were at higher T than the anomaly at 36.5 K. Consequently, Shomate's value for the standard entropy of $FeCr_2O_4$ at 298.15 K is too low, lacking the contribution from this transition. Integration of the present low-temperature C_P-data results in a value for the entropy of $FeCr_2O_4$ at 298.15 K of 152.2 ± 3.0 J/(mol·K), which includes a T^3 extrapolation from 2.4 K down to 0 K. This is ~6 J/(mol·K) higher than Shomate's (1944) value of 146.1 ± 1.7 J/(mol·K).

The heat capacity data for $FeCr_2O_4$ are of lesser quality than those for the other two samples studied, mainly because the

$FeCr_2O_4$ pellet was less dense with lower thermal diffusivity than $MgCr_2O_4$ or Cr_2O_3. The uncertainties for the present C_P data are estimated to be 1.2% (200 < T < 300 K), 0.8% (20 < T < 200 K) and 1.4% (T<20 K). The heat content data (Naylor 1944) are also found to scatter substantially. The estimated uncertainties in the heat content data are 0.2% at T > 600 K and 2% at T < 600 K. Fitting sixty-nine heat capacity data (this study, 250–310 K) in conjunction with thirteen heat content data (Naylor 1944) provide

C_P ($FeCr_2O_4$) in (J/K·mol) = 139.75 + 0.029408 · T – 3359576 · T^{-2} + 474.8 · $T^{-0.5}$ (3)

Although this equation is based on experimental data to 1800 K, it appears well-behaved at higher temperatures, permitting modest extrapolation. The C_P data at temperatures higher than 310 K were excluded from the fit, because the data at these temperature are compromised by the strongly decreasing viscosity of the Apiezon N high vacuum grease that is used for mounting of the sample on the sapphire sample holder. During the fitting procedure, one heat content datum at 386.2 K (Naylor 1944) could not be fitted well, indicating too low values for the heat capacity.

Free energy of formation of $FeCr_2O_4$

There have been several attempts (Katsura and Muan 1964; Rezukhina et al. 1965; Tretjakow and Schmalzried 1965; Novokhatskii and Lenev 1966; Jacob and Alcock 1975) to measure the free energy of formation of $FeCr_2O_4$ from the reduction reaction: 2 $FeCr_2O_4$ = 2 Fe + 2 Cr_2O_3 +O_2.

One problem is that this reduction reaction occurs at oxygen fugacities below that at which stabilized-zirconia oxygen-specific electrolytes work reliably (Jacob and Alcock 1975). Thus the study of Tretjakow and Schmalzried (1965) will not be considered further. Both Rezukhina et al. (1965) and Jacob and Alcock (1975) used thoria-based electrolytes, which should work satisfactorily. Novokhatskii and Lenev (1966) used a gas equilibration method with H_2-H_2O gases, whereas Katsura and Muan (1964) used CO-CO_2 gas. Another problem, apparently unrecognized by any of these above-mentioned studies, is that the Fe-Cr spinel in equilibrium with Fe-rich metal and Cr_2O_3 is not stoichiometric $FeCr_2O_4$, but a solid solution between $FeCr_2O_4$ and Cr_3O_4, with an extensive amount of the latter component at high temperatures. Toker et al. (1991) determined that the spinel solid solution in equilibrium with Fe (liquid metal) and Cr_2O_3 at 1600 °C has atomic Fe/(Cr + Fe) = 0.22 (cf. 0.33 for stoichiometric $FeCr_2O_4$), indicating that the mole fraction of the $FeCr_2O_4$ component is only 0.66.

Lacking further information, we ignored this complication in assessing the literature studies by a third-law analysis. Figure 6 shows the reanalysis, using the new data reported in this paper. Considerable disagreement exists among these studies; moreover, none of the studies which report measurements over a range of temperature are in agreement with the temperature-dependence calculated from our new calorimetric data. The work of Jacob and Alcock (1975) agreed well with the old value of $S^0_{298.15}$ for $FeCr_2O_4$; also, their results using Mo-MoO_2 as the reference electrode agree well with their results using Fe-"FeO"
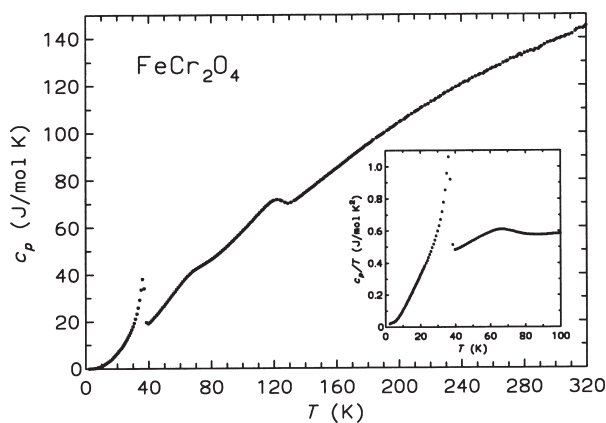

FIGURE 5. The heat capacity of polycrystalline $FeCr_2O_4$ measured from 2.4 to 337 K. The insert shows the sharp heat capacity anomaly peaking at $T = 36.5 \pm 0.2$ K in more detail.
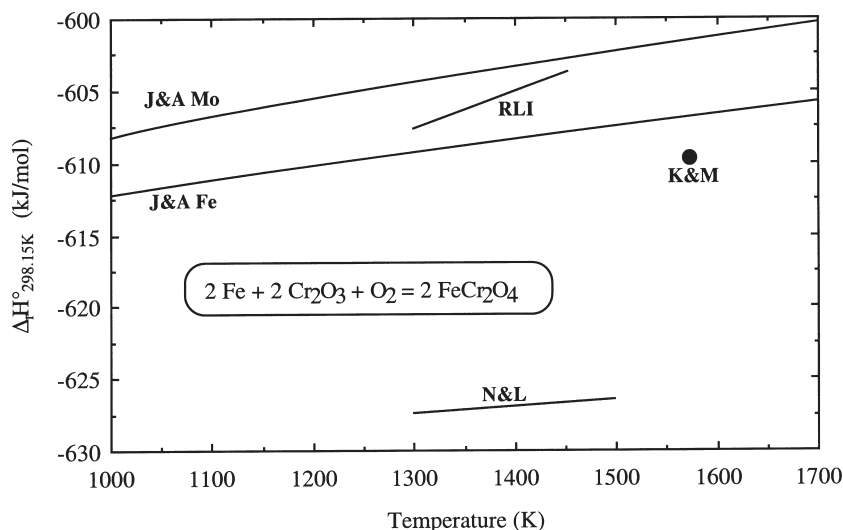
FIGURE 6. Third-law analysis of the reaction using the calorimetric data (Table 1). K&M = Katsura and Muan (1964); RLI = Rezukhina et al. (1965); N&L = Novokhatskii and Lenev (1966); J&A = Jacob and Alcock (1975), data recalculated from their EMF vs. T equations using the values of O'Neill (1986) for the Mo-MoO$_2$ reference electrode (Mo) and O'Neill and Pownceby (1993) for the Fe-"FeO" reference electrode (Fe). The data for metallic Fe are taken from Holmes et al. (1986).

as the reference electrode if their own values for Mo-MoO$_2$ are used, rather than the values of O'Neill (1986) which are adopted here. The study of Novokhatskii and Lenev (1966) shows the greatest discrepancy with the other studies, being ≈15 kJ/mol more reducing than the consensus. The data of Novokhatskii and Lenev (1966) for the Cr-Cr$_2$O$_3$ equilibrium are also more reducing than the values recommended here, the difference ranging from 5.5 kJ per mole of O$_2$ at 1220 K to 3.6 kJ/mol at 1620 K. The datum of Katsura and Muan (1964) corresponds to a CO:CO$_2$ ratio of about 99:1. Such extreme ratios are difficult to measure and control precisely, hence the accuracy of this datum may be questionable. In view of the scatter of the data and the possible experimental uncertainties discussed above, it is premature to recommend a value for the free energy of formation of FeCr$_2$O$_4$.

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