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ORIGINAL PAPER

Low-temperature heat capacities of $MgAl_2O_4$ and spinels of the $MgCr_2O_4$–$MgAl_2O_4$ solid solution

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Abstract We present results from low-temperature heat capacity measurements of spinels along the solid solution between $MgAl_2O_4$ and $MgCr_2O_4$. The data also include new low-temperature heat capacity measurements for $MgAl_2O_4$ spinel. Heat capacities were measured between 1.5 and 300 K, and thermochemical functions were derived from the results. No heat capacity anomaly was observed for $MgAl_2O_4$ spinel; however, we observe a low-temperature heat capacity anomaly for Cr-bearing spinels at temperatures below 15 K. From our data we calculate standard entropies (298.15 K) for $Mg(Cr,Al)_2O_4$ spinels. We suggest a standard entropy for $MgAl_2O_4$ of 80.9 ± 0.6 J mol^{-1} K^{-1}. For the solid solution between $MgAl_2O_4$ and $MgCr_2O_4$, we observe a linear increase of the standard entropies from 80.9 J mol^{-1} K^{-1} for $MgAl_2O_4$ to 118.3 J mol^{-1} K^{-1} for $MgCr_2O_4$.

Keywords Calorimetry · Heat capacity · Spinel · Chromite · $MgAl_2O_4$ · $MgCr_2O_4$ · Phase transition

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Introduction

Spinels are common minerals in the Earth's crust and mantle. Whilst most spinels in the crust contain low amounts of Cr, spinels in the Earth's mantle are usually rich in magnesium, iron and chromium with the most important endmembers being spinel "senso stricto" ($MgAl_2O_4$), hercynite ($FeAl_2O_4$), chromite ($FeCr_2O_4$), and magnesiochromite ($MgCr_2O_4$).

To further our general understanding of phase relations in the upper mantle and in the crust, a comprehensive set of thermodynamic data for all involved mineral phases is needed. However, thermodynamic data for many mantle minerals are still scarce.

Recent measurements have complemented the existing data base and new calorimetric data were presented for $MgCr_2O_4$, $MgFe_2O_4$, $FeCr_2O_4$, and $MgCr_2O_4$ (Klemme et al. 2000, 2005; Klemme and Van Miltenburg 2003). However, previous low-temperature measurements for $MgAl_2O_4$ extend only to 53 K (King 1955) and no measurements exist at lower temperatures. Moreover, no direct measurements of the entropies of intermediate spinels, i.e. solid solutions, exist. Interpretation of experimentally determined phase equilibria involving Cr-bearing spinels (e.g., Chatterjee and Terhart 1985; Klemme and Van Miltenburg 2004; Oka et al. 1984), however, critically depends on accurate knowledge of standard entropies both for endmembers and solid solutions. The present study aims to partially fill this gap.

As there are no previous low-temperature heat capacity data for $MgAl_2O_4$, we firstly set out to investigate the heat capacity for this phase between 1.5 and 300 K. Furthermore, we also investigated the heat capacities along the join $MgAl_2O_4$–$MgCr_2O_4$. Recent studies indicated that $MgCr_2O_4$ undergoes a phase transition at 12.5 K (Ehrenberg et al. 2002; Klemme et al. 2000) reflected by a large anomaly in the heat capacity curve at this temperature. However, there is no evidence for a structural transition in end-member $MgAl_2O_4$.

To investigate this further, we were interested how the phase transition and the associated heat capacity anomaly reacted to changes in composition.

Sample preparation and characterisation

Heat capacity measurements were performed on synthetic polycrystalline samples. The following spinels were prepared: $MgCr_{1.6}Al_{0.4}O_4$, $MgCr_{1.2}Al_{0.8}O_4$, $MgCr_{0.8}Al_{1.2}O_4$, $MgCr_{0.4}Al_{1.6}O_4$, $MgCr_{0.2}Al_{1.8}O_4$, and $MgAl_2O_4$. The samples used in our study were synthesised from mixtures of MgO (99.999% purity), Al_2O_3 (99.99% purity), and Cr_2O_3 (99.999% purity) and about 10 g of each spinel were prepared. Both MgO and Al_2O_3 starting materials were previously fired at 1,273 K for 12 h to release any absorbed water or hydroxide, and subsequently stored in a furnace at 383 K. The oxides were mixed stoichiometrically under acetone in an agate mortar and subsequently pressed into several pellets of 1.27 cm diameter. We placed the pellets in a vertical drop furnace in a small hand crafted basket made of platinum wire. The samples were fired in a continuous flow of pure CO_2 at 1,773 K for 24 h, then slowly cooled to 1,373 K for 24 h, slowly cooled to 973 K and held for another 24 h. This procedure was chosen to avoid uncontrolled degree of structural disorder in the samples (see discussion below). The samples were then rapidly drop-quenched in distilled water and dried at 383 K for 1 h. This entire procedure was repeated if necessary. Small chips of the samples were used for adiabatic calorimetry (see below). Results from X-ray diffraction indicated pure spinels and no impurities or other unreacted oxides from the starting materials were detected. $MgAl_2O_4$ had a cell parameter of $a_0 = 8.0848 \pm 0.009$ Å which compares well with previous results for close-to stoichiometric $MgAl_2O_4$ (Chamberlin et al. 1995; Navrotsky 1986). The other $Mg(Cr,Al)_2O_4$ spinels have cell parameters along the line of Vegard's rule (Vegard 1921), ranging linearly from $a_0 = 8.0848 \pm 0.009$ Å for endmember $MgAl_2O_4$ to $a_0 = 8.3301 \pm 0.011$ Å for $MgCr_2O_4$.

Low-temperature calorimetry

The heat capacities were measured in custom-built low-temperature vacuum calorimeters at the Max-Planck Institut für Festkörperforschung in Stuttgart, Germany. The calorimeters were immersed in a bath cryostat containing either liquid helium or liquid nitrogen, depending on the desired temperature range. The calorimeters were equipped with exchangeable miniature sample holders. Each holder consisted of a copper frame and a platform made of a thin sapphire disc suspended by three cotton threads from the frame. The platform carried the sample on top and a thin film heater (evaporated stainless steel, ca. 2 kΩ) on its lower side. In the calorimeter designed for temperatures ranging from about 1.5 K up to about 100 K, a calibrated Cernox temperature sensor was also placed on the lower side of the sapphire disc in order to measure sample temperatures (CX-1050, Lake Shore). Temperatures below 4.2 K were achieved by pumping the bath of liquid helium. To step up the temperature range from 77 K up to room temperature, a sample holder provided with a calibrated platinum miniature sensor (Pt-100, Rosemount) was used. Liquid nitrogen was the coolant in the latter case. The samples were in the shape of small, thin disks. They were mounted on top of the sapphire sample platform using a small amount (<10 mg) of Apiezon N high vacuum grease. The addenda contributions of the empty sample holder ensemble and of the Apiezon N grease were determined in separate runs and subtracted from the raw data of each run with a sample. A peak-shaped transition of the grease at about 298 K was taken into account (Schnelle et al. 1999). For measurements, the quasi-adiabatic (isoperibol) step-heating method (Nernst's method) was employed, using an isothermal shield control (Gmelin 1987; Schnelle and Gmelin 2002). To obtain the specific heat at a fixed temperature, the shield temperature was kept constant to within 0.2 mK. The typical residual drift rates of the base line were less than $\pm 10^{-5}$ K/s. Subsequently, a known small heat quantity was applied to the sample while recording the resulting temperature rise. The temperature increment during each heat pulse increased gradually from about 50 mK at lowest temperatures to about 1.5 K at 300 K. In general, each heat pulse was accompanied by heat loss of the sample ensemble due to thermal conduction along the suspension of the sapphire plate and also due to radiation. The latter phenomenon was most prominent when approaching room temperature and can give rise to increased scattering of the data. Heat loss is more pronounced for samples of small mass. This effect was taken into account by additionally recording the post-heating period (ca. 2 min) and applying a particular fitting procedure (Schnelle and Gmelin 2002). Thus a corrected temperature increment was obtained. The relaxation time constants for heat loss were increased

Table 1 Experimentally determined heat capacities of $MgAl_2O_4$ and $Mg(Cr,Al)_2O_4$ spinels

$MgAl_2O_4$		$MgAl_{1.8}Cr_{0.2}O_4$		$MgAl_{1.6}Cr_{0.4}O_4$		$MgAl_{1.2}Cr_{0.8}O_4$		$MgAl_{0.8}Cr_{1.2}O_4$		$MgAl_{0.4}Cr_{1.6}O_4$	
T (K)	C_p (J mol^{-1} K^{-1})	*T* (K)	C_p (J mol^{-1} K^{-1})	*T* (K)	C_p (J mol^{-1} K^{-1})	*T* (K)	C_p (J mol^{-1} K^{-1})	*T* (K)	C_p (J mol^{-1} K^{-1})	*T* (K)	C_p (J mol^{-1} K^{-1})
4.33	0.0057	1.93	0.400	1.64	0.5634	1.64	0.5943	1.56	0.5130	1.56	0.4408
4.39	0.0056	2.01	0.398	1.67	0.5601	1.75	0.5948	1.63	0.5373	1.63	0.4746
4.46	0.0056	2.08	0.389	1.69	0.5582	1.81	0.5961	1.66	0.5471	1.66	0.4930
4.54	0.0063	2.01	0.398	1.73	0.5528	1.88	0.5984	1.70	0.5626	1.72	0.5296
4.62	0.0073	2.11	0.389	1.74	0.5497	1.95	0.5994	1.76	0.5843	1.74	0.5598
4.68	0.0062	2.22	0.374	1.74	0.5507	2.03	0.6010	1.85	0.6164	1.77	0.5619
4.75	0.0062	2.48	0.338	1.77	0.5498	2.14	0.6033	2.20	0.7137	1.92	0.6590
4.84	0.0061	2.54	0.330	1.77	0.5503	2.26	0.6144	2.35	0.7677	2.07	0.7659
4.91	0.0067	2.68	0.314	1.91	0.5332	2.55	0.6265	2.39	0.7765	2.17	0.8468
5.01	0.0051	2.75	0.306	2.09	0.5101	2.86	0.6069	2.43	0.7879	2.24	0.8785
5.11	0.0059	2.85	0.294	2.30	0.4834	2.98	0.6085	2.48	0.7979	2.26	0.9201
5.19	0.0063	2.95	0.284	2.49	0.4602	3.00	0.6088	2.52	0.8087	2.29	0.9120
5.29	0.0061	2.97	0.282	2.66	0.4405	3.01	0.6070	2.57	0.8188	2.52	1.0836
5.39	0.0066	3.06	0.274	2.84	0.4207	3.04	0.6074	2.88	0.8813	2.75	1.2337
5.48	0.0068	3.13	0.267	2.87	0.4178	3.08	0.6085	3.06	0.9122	2.81	1.2652
5.58	0.0070	3.15	0.264	2.94	0.4109	3.15	0.6100	3.15	0.9262	2.94	1.3625
5.68	0.0070	3.29	0.251	2.98	0.4073	3.17	0.6111	3.25	0.9455	2.94	1.3570
5.78	0.0070	3.34	0.248	3.04	0.4014	3.25	0.6128	3.26	0.9458	3.00	1.4110
5.87	0.0070	3.41	0.241	3.06	0.3998	3.37	0.6164	3.40	0.9680	3.13	1.4787
5.98	0.0073	3.54	0.231	3.12	0.3938	3.38	0.6174	3.55	0.9937	3.16	1.5036
6.08	0.0077	3.57	0.229	3.24	0.3843	3.42	0.6167	3.71	1.0154	3.25	1.5670
6.18	0.0086	3.65	0.223	3.24	0.3837	3.62	0.6259	3.76	1.0279	3.31	1.5941
6.30	0.0091	3.83	0.210	3.38	0.3736	3.85	0.6349	3.79	1.0302	3.36	1.6157
6.41	0.0086	3.85	0.209	3.47	0.3670	4.08	0.6437	3.88	1.0450	3.42	1.6550
6.51	0.0099	4.05	0.197	3.59	0.3585	4.32	0.6541	3.97	1.0639	3.51	1.7157
6.69	0.0093	4.07	0.195	3.70	0.3517	4.37	0.6502	3.99	1.0622	3.60	1.7598
6.81	0.0094	4.28	0.184	3.83	0.3445	4.42	0.6525	4.15	1.0871	3.62	1.7640
6.92	0.0100	4.29	0.186	3.94	0.3389	4.50	0.6563	4.29	1.1091	3.78	1.8622
7.04	0.0104	4.33	0.182	4.07	0.3326	4.57	0.6599	4.43	1.1304	3.87	1.9059
7.16	0.0106	4.38	0.179	4.12	0.3304	4.65	0.6641	4.48	1.1396	3.95	1.9560
7.28	0.0107	4.45	0.176	4.24	0.3258	4.74	0.6682	4.51	1.1416	4.12	2.0399
7.41	0.0117	4.53	0.173	4.29	0.3258	4.83	0.6734	4.58	1.1533	4.16	2.0714
7.53	0.0113	4.61	0.169	4.33	0.3225	4.92	0.6780	4.66	1.1655	4.37	2.1846
7.65	0.0126	4.70	0.166	4.38	0.3208	5.02	0.6836	4.69	1.1706	4.58	2.2832
7.78	0.0129	4.79	0.162	4.46	0.3185	5.12	0.6902	4.75	1.1779	4.59	2.2986
7.91	0.0131	4.88	0.159	4.53	0.3164	5.23	0.6950	4.84	1.1923	4.79	2.3889
8.03	0.0140	4.97	0.156	4.61	0.3139	5.34	0.7011	4.93	1.2049	5.02	2.5035
8.15	0.0148	5.07	0.153	4.70	0.3114	5.44	0.7078	5.03	1.2210	5.13	2.5506
8.29	0.0153	5.17	0.150	4.79	0.3092	5.56	0.7141	5.13	1.2359	5.26	2.6049
8.41	0.0157	5.26	0.148	4.88	0.3074	5.67	0.7207	5.23	1.2510	5.35	2.6461
8.54	0.0165	5.36	0.145	4.98	0.3061	5.78	0.7282	5.34	1.2663	5.45	2.6872
8.68	0.0173	5.46	0.143	5.07	0.3038	5.90	0.7356	5.45	1.2826	5.55	2.7295
8.81	0.0178	5.56	0.140	5.17	0.3028	6.02	0.7427	5.56	1.2983	5.66	2.7735
8.94	0.0192	5.66	0.138	5.26	0.3015	6.14	0.7502	5.67	1.3139	5.77	2.8139
9.07	0.0197	5.77	0.136	5.36	0.3007	6.26	0.7638	5.79	1.3300	5.88	2.8583
9.22	0.0205	5.87	0.134	5.46	0.2998	6.39	0.7657	5.90	1.3467	6.00	2.9006
9.35	0.0214	5.98	0.132	5.56	0.2992	6.52	0.7731	6.02	1.3641	6.12	2.9403
9.47	0.0222	6.08	0.131	5.67	0.2984	6.64	0.7808	6.14	1.3814	6.24	3.0049
9.57	0.0218	6.20	0.129	5.77	0.2982	6.78	0.7892	6.27	1.4090	6.37	3.0190
9.72	0.0243	6.30	0.130	5.88	0.2978	6.91	0.7983	6.39	1.4163	6.50	3.0549
9.93	0.0260	6.42	0.126	5.99	0.2978	7.05	0.8068	6.52	1.4336	6.63	3.0887
10.1	0.0270	6.53	0.126	6.10	0.2979	7.19	0.8164	6.65	1.4491	6.76	3.1238
10.3	0.0284	6.65	0.124	6.20	0.3000	7.33	0.8250	6.79	1.4663	6.90	3.1569
10.4	0.0299	6.76	0.124	6.32	0.2990	7.47	0.8352	6.92	1.4850	7.03	3.1916
10.6	0.0311	6.89	0.122	6.43	0.2998	7.62	0.8448	7.06	1.5054	7.18	3.2215
10.8	0.0325	6.99	0.123	6.55	0.3001	7.77	0.8559	7.20	1.5241	7.32	3.2485
11.0	0.0345	7.13	0.122	6.66	0.3014	7.92	0.8665	7.35	1.5405	7.47	3.2769
11.1	0.0356	7.24	0.122	6.80	0.3021	8.08	0.8775	7.49	1.5593	7.62	3.3037
11.3	0.0374	7.37	0.121	6.91	0.3043	8.24	0.8885	7.64	1.5800	7.77	3.3314

Table 1 continued

$MgAl_2O_4$		$MgAl_{1.8}Cr_{0.2}O_4$		$MgAl_{1.6}Cr_{0.4}O_4$		$MgAl_{1.2}Cr_{0.8}O_4$		$MgAl_{0.8}Cr_{1.2}O_4$		$MgAl_{0.4}Cr_{1.6}O_4$	
T (K)	C_p (J mol^{-1} K^{-1})	*T* (K)	C_p (J mol^{-1} K^{-1})	*T* (K)	C_p (J mol^{-1} K^{-1})	*T* (K)	C_p (J mol^{-1} K^{-1})	*T* (K)	C_p (J mol^{-1} K^{-1})	*T* (K)	C_p (J mol^{-1} K^{-1})
11.5	0.0392	7.48	0.122	7.04	0.3052	8.40	0.9002	7.80	1.5990	7.93	3.3561
11.7	0.0412	7.63	0.121	7.15	0.3076	8.56	0.9120	7.95	1.6191	8.09	3.3786
11.9	0.0428	7.74	0.123	7.30	0.3088	8.73	0.9245	8.11	1.6398	8.25	3.4022
12.1	0.0445	7.90	0.122	7.42	0.3116	8.90	0.9369	8.27	1.6591	8.42	3.4235
12.2	0.0462	8.01	0.124	7.58	0.3139	9.07	0.9495	8.43	1.6810	8.59	3.4434
12.4	0.0482	8.19	0.124	7.70	0.3170	9.24	0.9624	8.60	1.7002	8.76	3.4647
12.6	0.0501	8.30	0.126	7.83	0.3196	9.42	0.9756	8.77	1.7231	8.94	3.4843
12.8	0.0524	8.47	0.126	7.97	0.3225	9.60	0.9903	8.94	1.7435	9.12	3.5015
13.0	0.0542	8.57	0.129	8.10	0.3257	9.79	1.0027	9.12	1.7644	9.30	3.5180
13.1	0.0564	8.78	0.129	8.24	0.3289	9.97	1.0171	9.30	1.7879	9.48	3.5341
13.3	0.0586	8.89	0.132	8.37	0.3330	10.16	1.0314	9.48	1.8085	9.67	3.5496
13.5	0.0607	9.10	0.133	8.53	0.3368	10.36	1.0456	9.67	1.8306	9.87	3.5650
13.7	0.0631	9.22	0.137	8.67	0.3411	10.55	1.0599	9.85	1.8532	10.06	3.5783
13.8	0.0656	9.43	0.137	8.85	0.3453	10.75	1.0762	10.05	1.8754	10.26	3.5913
14.0	0.0680	9.54	0.142	8.98	0.3500	10.96	1.0915	10.24	1.8979	10.47	3.6027
14.2	0.0697	9.77	0.143	9.15	0.3545	11.16	1.1081	10.44	1.9207	10.68	3.6150
14.3	0.0718	9.90	0.148	9.29	0.3604	11.37	1.1235	10.64	1.9432	10.89	3.6294
14.5	0.0740	10.12	0.149	9.47	0.3651	11.59	1.1401	10.85	1.9656	11.10	3.6405
14.6	0.0769	10.25	0.154	9.60	0.3703	11.81	1.1574	11.06	1.9894	11.32	3.6524
14.8	0.0785	10.48	0.156	9.82	0.3765	12.03	1.1737	11.27	2.0129	11.55	3.6629
14.9	0.0834	10.61	0.162	9.95	0.3829	12.25	1.1920	11.49	2.0376	11.77	3.6765
15.0	0.0875	10.86	0.164	10.17	0.3896	12.48	1.2084	11.71	2.0599	12.01	3.6857
15.2	0.0857	11.00	0.171	10.32	0.3970	12.72	1.2270	11.94	2.0862	12.25	3.6983
15.3	0.0930	11.26	0.174	10.52	0.4026	12.95	1.2457	12.17	2.1101	12.49	3.7135
15.5	0.0905	11.39	0.181	10.67	0.4099	13.18	1.2641	12.40	2.1356	12.73	3.7246
15.6	0.0979	11.68	0.184	10.86	0.4163	13.41	1.2820	12.63	2.1607	12.97	3.7331
15.8	0.0960	11.82	0.192	11.01	0.4239	13.64	1.3001	12.87	2.1859	13.22	3.7465
15.9	0.103	12.13	0.196	11.24	0.4315	13.87	1.3182	13.11	2.2124	13.46	3.7570
16.0	0.105	12.27	0.204	11.40	0.4402	14.10	1.3367	13.34	2.2359	13.70	3.7702
16.1	0.109	12.60	0.209	11.64	0.4481	14.32	1.3555	13.58	2.2602	13.94	3.7848
16.4	0.107	12.75	0.218	11.80	0.4572	14.55	1.3741	13.81	2.2871	14.19	3.7986
16.5	0.110	13.08	0.223	12.04	0.4657	14.78	1.3921	14.04	2.3108	14.43	3.8118
16.8	0.118	13.21	0.232	12.21	0.4753	15.01	1.4126	14.28	2.3390	14.67	3.8260
17.2	0.125	13.53	0.236	12.48	0.4859	15.23	1.4287	14.51	2.3635	14.91	3.8412
17.5	0.132	13.65	0.245	12.64	0.4954	15.46	1.4497	14.74	2.3873	15.15	3.8569
17.9	0.140	13.97	0.245	12.92	0.5053	15.69	1.4678	14.98	2.4131	15.39	3.8686
18.2	0.149	13.76	0.249	13.08	0.5170	15.92	1.4888	15.21	2.4390	15.63	3.8875
18.6	0.158	14.11	0.255	13.37	0.5270	16.14	1.5061	15.44	2.4638	15.87	3.9057
19.0	0.168	14.22	0.265	13.53	0.5383	16.37	1.5286	15.67	2.4895	16.11	3.9199
19.3	0.178	14.59	0.272	13.82	0.5490	16.59	1.5445	15.91	2.5134	16.35	3.9351
19.7	0.190	14.69	0.281	13.97	0.5598	17.00	1.5751	16.14	2.5413	16.59	3.9559
20.1	0.201	15.05	0.287	14.29	0.5717	17.09	1.5886	16.37	2.5650	16.83	3.9736
20.5	0.214	15.15	0.298	14.45	0.5848	17.55	1.6228	16.60	2.5919	17.07	3.9899
21.0	0.227	15.54	0.305	14.76	0.5961	17.64	1.6382	16.83	2.6167	17.31	4.0153
21.4	0.241	15.64	0.315	14.91	0.6078	18.11	1.6750	17.06	2.6444	17.55	4.0305
21.8	0.257	16.01	0.319	15.23	0.6201	18.15	1.6861	17.29	2.6718	17.79	4.0520
22.2	0.272	16.00	0.333	15.35	0.6299	18.65	1.7249	17.52	2.6977	18.03	4.0739
22.7	0.290	16.70	0.351	15.67	0.6435	18.71	1.7338	17.75	2.7241	18.27	4.0909
23.2	0.307	16.79	0.362	15.82	0.6570	19.22	1.7785	17.98	2.7501	18.51	4.1168
23.6	0.325	17.32	0.345	16.13	0.6684	19.25	1.7882	18.21	2.7773	18.74	4.1410
24.1	0.346	17.39	0.389	16.27	0.6816	19.80	1.8303	18.44	2.8037	18.98	4.1631
24.6	0.368	17.78	0.394	16.59	0.6937	19.82	1.8413	18.67	2.8304	19.22	4.1863
25.1	0.392	17.87	0.408	16.73	0.7071	20.40	1.8929	18.90	2.8571	19.46	4.2104
25.6	0.415	18.22	0.417	17.04	0.7190	20.45	1.9043	19.12	2.8858	19.69	4.2309
26.1	0.441	18.33	0.418	17.16	0.7306	20.90	1.9364	19.35	2.9131	19.93	4.2545
26.6	0.467	18.54	0.433	17.54	0.7479	20.34	1.8929	19.58	2.9444	20.17	4.2810
27.1	0.494	18.90	0.450	17.66	0.7605	20.59	2.0517	19.81	2.9725	20.40	4.3103
27.6	0.523	19.26	0.467	18.03	0.7769	20.99	1.9242	20.04	3.0004	20.64	4.3329
28.1	0.553	19.65	0.483	18.15	0.7901	21.12	1.9835	20.27	3.0319	20.88	4.3601

Table 1 continued

$MgAl_2O_4$		$MgAl_{1.8}Cr_{0.2}O_4$		$MgAl_{1.6}Cr_{0.4}O_4$		$MgAl_{1.2}Cr_{0.8}O_4$		$MgAl_{0.8}Cr_{1.2}O_4$		$MgAl_{0.4}Cr_{1.6}O_4$	
T (K)	C_p (J mol^{-1} K^{-1})	T (K)	C_p (J mol^{-1} K^{-1})	T (K)	C_p (J mol^{-1} K^{-1})	T (K)	C_p (J mol^{-1} K^{-1})	T (K)	C_p (J mol^{-1} K^{-1})	T (K)	C_p (J mol^{-1} K^{-1})
28.6	0.582	20.06	0.502	18.53	0.8055	21.77	2.0296	20.49	3.0575	21.12	4.3857
29.1	0.614	20.45	0.522	18.63	0.8181	21.69	2.0337	20.72	3.0861	21.36	4.4100
29.6	0.646	20.87	0.540	19.02	0.8359	21.90	2.0701	20.95	3.1149	21.59	4.4357
30.1	0.681	21.30	0.563	19.35	0.8412	22.16	2.0652	21.18	3.1456	21.83	4.4722
30.6	0.718	21.72	0.585	19.43	0.8681	22.34	2.1180	21.41	3.1746	22.07	4.4990
31.1	0.753	22.16	0.608	19.81	0.8861	22.59	2.1312	21.64	3.2057	22.30	4.5282
31.6	0.792	22.61	0.631	19.92	0.9005	22.81	2.1523	21.86	3.2372	22.54	4.5519
32.1	0.835	23.07	0.657	20.31	0.9180	23.02	2.1850	22.09	3.2649	22.78	4.5869
32.6	0.876	23.54	0.683	20.41	0.9319	23.27	2.2007	22.32	3.2949	23.30	4.6407
33.1	0.916	24.00	0.710	20.83	0.9526	23.48	2.2287	22.54	3.3276	23.62	4.6761
33.6	0.966	24.48	0.739	20.93	0.9666	23.70	2.2623	22.77	3.3592	24.06	4.7403
34.1	1.005	24.97	0.768	21.38	0.9900	23.94	2.2777	23.00	3.3876	24.54	4.7990
34.6	1.052	25.48	0.800	21.49	1.0069	24.15	2.3098	23.22	3.4258	25.02	4.8655
35.1	1.103	25.98	0.833	21.94	1.0260	24.38	2.3317	23.45	3.4478	25.53	4.9401
35.6	1.150	26.48	0.865	22.02	1.0406	24.61	2.3549	23.68	3.4846	26.02	5.0144
36.1	1.196	26.96	0.897	22.46	1.0652	24.83	2.3882	23.91	3.5174	26.52	5.0816
36.6	1.261	27.46	0.926	22.58	1.0759	25.05	2.4118	24.14	3.5518	27.03	5.1666
37.1	1.320	27.97	0.966	23.02	1.1088	25.21	2.4176	24.36	3.5842	27.53	5.2230
37.6	1.371	28.46	1.002	23.48	1.1429	25.59	2.4623	24.59	3.6150	28.03	5.3162
38.1	1.431	28.96	1.040	23.96	1.1783	26.07	2.5200	24.82	3.6462	28.52	5.3948
38.6	1.493	29.47	1.079	24.44	1.2165	26.57	2.5843	25.04	3.6861	29.02	5.4796
39.1	1.553	29.96	1.121	24.93	1.2550	27.07	2.6448	25.27	3.6995	29.51	5.5622
39.6	1.618	30.45	1.161	25.43	1.2960	27.56	2.6986	25.60	3.7451	30.02	5.6499
40.1	1.687	30.94	1.203	25.93	1.3366	28.07	2.7735	26.06	3.8147	30.51	5.7361
40.6	1.750	31.44	1.248	26.43	1.3802	28.56	2.8369	26.54	3.8892	31.01	5.8264
41.1	1.812	31.94	1.294	26.93	1.4231	29.05	2.9058	27.05	3.9668	31.52	5.9218
41.6	1.894	32.44	1.341	27.43	1.4635	29.56	2.9773	27.55	4.0359	32.02	6.0211
42.1	1.955	32.94	1.387	27.94	1.5103	30.07	3.0463	28.05	4.1225	32.51	6.1195
42.6	2.039	33.44	1.439	28.44	1.5584	30.57	3.1235	28.56	4.2017	33.01	6.2139
43.1	2.111	33.94	1.492	28.94	1.6089	31.06	3.1946	29.05	4.2913	33.50	6.3182
43.6	2.185	34.44	1.542	29.44	1.6563	31.55	3.2709	29.55	4.3701	34.01	6.4203
44.1	2.267	34.93	1.595	29.94	1.7080	32.04	3.3472	30.04	4.4520	34.51	6.5161
44.6	2.361	35.43	1.649	30.43	1.7619	32.55	3.4286	30.55	4.5406	35.01	6.6236
45.1	2.433	35.93	1.707	30.93	1.8133	33.06	3.5122	31.04	4.6249	35.52	6.7315
45.6	2.525	36.42	1.764	31.44	1.8688	33.56	3.5944	31.53	4.7222	36.02	6.8435
46.1	2.594	36.92	1.831	31.94	1.9283	34.05	3.6773	32.04	4.8174	36.51	6.9498
46.6	2.693	37.42	1.888	32.44	1.9839	34.54	3.7617	32.54	4.9060	37.00	7.0594
47.1	2.792	37.91	1.956	32.94	2.0444	35.05	3.8496	33.03	5.0007	37.44	7.1719
47.6	2.871	38.41	2.017	33.45	2.1046	35.56	3.9382	33.53	5.0985	37.85	7.2596
48.1	2.971	38.91	2.082	33.95	2.1685	36.05	4.0280	34.04	5.1964	38.31	7.3594
48.6	3.070	39.40	2.149	34.45	2.2355	36.55	4.1208	34.53	5.2986	38.79	7.4880
49.1	3.171	39.90	2.215	34.95	2.2982	37.03	4.2117	35.03	5.4001	39.28	7.6002
49.6	3.267	40.40	2.286	35.45	2.3659	37.54	4.2984	35.53	5.5056	39.77	7.7182
50.1	3.377	40.89	2.359	35.95	2.4317	38.03	4.3999	36.03	5.6105	40.26	7.8383
50.6	3.475	41.38	2.431	36.45	2.5039	38.52	4.4959	36.52	5.7176	40.77	7.9557
51.1	3.584	41.88	2.512	36.95	2.5762	39.02	4.5974	37.01	5.8207	41.26	8.0787
51.6	3.706	42.38	2.593	37.46	2.6517	39.52	4.6940	37.52	5.9310	41.76	8.2261
52.1	3.819	42.87	2.668	37.96	2.7269	40.01	4.7908	38.01	6.0372	42.27	8.3549
52.6	3.902	43.38	2.768	38.46	2.8050	40.51	4.9081	38.51	6.1560	42.76	8.4798
53.1	4.045	43.87	2.837	38.96	2.8768	41.02	5.0090	39.01	6.2702	43.26	8.6305
53.6	4.141	44.36	2.922	39.46	2.9637	41.52	5.1164	39.51	6.3805	43.75	8.7560
54.1	4.466	44.86	3.004	39.97	3.0412	42.01	5.2225	40.00	6.5048	44.25	8.8910
54.6	4.393	45.35	3.090	40.47	3.1278	42.50	5.3305	40.49	6.6105	44.75	9.0295
55.4	4.577	45.84	3.189	40.98	3.2117	43.00	5.4495	41.00	6.7386	45.25	9.1734
56.3	4.828	46.34	3.280	41.48	3.2995	43.51	5.5535	41.51	6.8592	45.75	9.3070
57.3	5.095	46.83	3.372	41.98	3.3777	44.00	5.6806	42.00	6.9836	46.25	9.4503
58.3	5.362	47.33	3.475	42.48	3.4788	44.48	5.7928	42.50	7.1101	46.74	9.5836
59.3	5.641	47.83	3.561	42.99	3.5664	44.97	5.9081	42.99	7.2372	47.23	9.7257
60.3	5.947	48.32	3.670	43.49	3.6635	45.48	6.0396	43.47	7.3629	47.73	9.9006

Table 1 continued

$MgAl_2O_4$		$MgAl_{1.8}Cr_{0.2}O_4$		$MgAl_{1.6}Cr_{0.4}O_4$		$MgAl_{1.2}Cr_{0.8}O_4$		$MgAl_{0.8}Cr_{1.2}O_4$		$MgAl_{0.4}Cr_{1.6}O_4$	
T (K)	C_p (J mol^{-1} K^{-1})	T (K)	C_p (J mol^{-1} K^{-1})	T (K)	C_p (J mol^{-1} K^{-1})	T (K)	C_p (J mol^{-1} K^{-1})	T (K)	C_p (J mol^{-1} K^{-1})	T (K)	C_p (J mol^{-1} K^{-1})
61.3	6.249	48.82	3.775	43.99	3.7554	45.97	6.1591	43.98	7.4961	48.23	10.045
62.3	6.540	49.32	3.880	44.48	3.8262	46.46	6.2679	44.47	7.6248	48.73	10.176
63.3	6.858	49.81	3.984	44.98	3.9507	46.96	6.3961	44.96	7.7526	49.23	10.358
64.3	7.173	50.31	4.094	45.48	4.0560	47.46	6.5248	45.47	7.8960	49.73	10.521
65.3	7.517	50.81	4.205	45.98	4.1617	47.96	6.6653	45.96	8.0316	50.23	10.645
66.3	7.860	51.31	4.296	46.49	4.2825	48.46	6.7859	46.45	8.1637	50.72	10.812
67.3	8.184	51.81	4.433	46.98	4.3776	48.96	6.9333	46.94	8.2855	51.22	10.964
68.3	8.528	52.30	4.535	47.49	4.4920	49.46	7.0773	47.45	8.4402	51.72	11.178
69.3	8.922	52.79	4.666	47.99	4.6019	49.95	7.1926	47.94	8.5655	52.22	11.323
70.3	9.270	53.29	4.791	48.49	4.7147	50.46	7.3210	48.43	8.7283	52.72	11.497
71.3	9.657	53.78	4.909	49.00	4.8390	50.96	7.4747	48.94	8.8794	53.22	11.626
72.3	10.0	54.27	5.031	49.50	4.9464	51.45	7.6004	49.44	9.0131	53.71	11.787
73.3	10.4	54.77	5.157	50.01	5.0779	51.96	7.7511	49.94	9.1857	54.20	11.978
74.3	10.8	55.26	5.272	50.51	5.2082	52.45	7.9143	50.45	9.3325	54.71	12.163
75.3	11.2	55.75	5.423	51.01	5.3213	52.95	8.0528	50.95	9.4928	55.20	12.308
76.3	11.6	56.25	5.538	51.52	5.4496	53.45	8.1907	51.44	9.6198	55.70	12.524
77.3	12.0	56.75	5.676	52.02	5.5813	53.94	8.3330	51.95	9.7868	56.20	12.677
78.3	12.5	57.25	5.811	52.52	5.7037	54.43	8.5163	52.44	9.9365	56.69	12.860
79.3	12.9	57.74	5.952	53.03	5.8325	54.92	8.6469	52.94	10.106	57.18	13.062
80.3	13.3	58.23	6.096	53.53	5.9788	55.42	8.8183	53.44	10.277	57.68	13.193
81.3	13.8	58.73	6.235	54.03	6.1058	55.92	8.9672	53.93	10.437	58.18	13.389
82.3	14.2	59.22	6.394	54.53	6.2399	56.42	9.1250	54.44	10.594	58.68	13.595
83.3	14.7	59.72	6.528	55.03	6.3832	56.91	9.2787	54.93	10.767	59.17	13.766
84.3	15.1	60.21	6.676	55.54	6.5388	57.40	9.4479	55.43	10.964	59.68	13.985
85.3	15.6	60.71	6.834	56.04	6.6497	57.90	9.6107	55.92	11.099	60.17	14.155
86.3	16.0	61.21	7.006	56.54	6.8233	58.41	9.7832	56.42	11.277	60.67	14.352
87.3	16.5	61.70	7.158	57.05	6.9769	58.90	9.9311	56.92	11.427	61.16	14.515
88.3	17.0	62.20	7.286	57.55	7.1153	59.39	10.122	57.41	11.612	61.67	14.732
89.3	17.5	62.69	7.454	58.09	7.2740	59.89	10.292	57.91	11.813	62.17	14.936
90.3	17.9	63.18	7.611	58.55	7.4087	60.39	10.444	58.40	11.996	62.68	15.131
91.3	18.4	63.67	7.766	59.02	7.5728	60.89	10.628	58.90	12.145	63.18	15.296
92.3	18.5	64.16	7.930	59.60	7.7614	61.38	10.825	59.40	12.305	63.67	15.508
93.3	19.2	64.64	8.070	60.06	7.9069	61.88	10.977	59.89	12.497	64.16	15.721
94.3	19.8	65.13	8.264	60.56	8.0830	62.37	11.175	60.39	12.704	64.66	15.934
95.2	20.4	65.63	8.320	61.32	8.3122	62.87	11.325	60.89	12.879	65.15	16.115
96.2	20.8	66.12	8.616	62.30	8.6476	63.37	11.511	61.38	13.062	65.64	16.293
97.3	21.4	66.61	8.789	63.31	8.9520	63.86	11.681	61.88	13.249	66.14	16.524
98.2	21.9	67.28	9.029	64.31	9.3456	64.35	11.882	62.37	13.426	66.63	16.714
99.3	22.4	67.67	9.129	65.30	9.6975	64.85	12.094	62.87	13.598	67.12	16.925
100.3	22.8	68.14	9.291	66.28	10.060	65.35	12.229	63.37	13.842	67.60	17.122
101.6	23.2	68.63	9.506	67.28	10.439	65.83	12.465	63.87	14.024	68.10	17.391
102.6	23.7	69.13	9.689	68.27	10.803	66.32	12.683	64.36	14.198	68.59	17.569
103.6	24.3	69.62	9.925	69.26	11.225	66.82	12.832	64.85	14.431	69.08	17.783
104.6	24.8	70.13	10.05	70.25	11.604	67.31	12.998	65.34	14.630	69.58	17.989
105.6	25.3	70.61	10.25	71.25	11.999	67.80	13.246	65.84	14.768	70.05	18.371
106.6	25.9	71.11	10.42	72.25	12.411	68.30	13.406	66.34	15.000	70.56	18.446
107.6	26.4	71.61	10.65	73.26	12.821	68.80	13.628	66.83	15.189	71.04	18.660
108.5	27.0	72.11	10.80	74.27	13.263	69.29	13.785	67.32	15.425	71.54	18.843
109.5	27.5	72.61	10.96	75.27	13.658	69.79	14.009	67.80	15.586	72.06	19.085
110.5	28.1	73.11	11.27	76.27	14.078	70.29	14.237	68.30	15.816	72.57	19.333
111.5	28.7	73.61	11.40	77.27	14.574	70.79	14.436	68.81	16.028	73.09	19.513
112.5	29.2	74.13	11.63	78.27	14.990	71.28	14.613	69.32	16.228	73.61	19.793
113.5	29.7	74.62	11.80	79.27	15.416	71.78	14.803	69.82	16.464	74.29	20.095
114.5	30.3	75.12	12.02	80.26	15.909	72.28	15.067	70.31	16.692	74.69	20.226
115.5	30.9	75.62	12.28	81.26	16.344	72.79	15.308	70.80	16.834	75.15	20.499
116.5	31.5	76.11	12.44	82.26	16.798	73.29	15.482	71.30	17.048	75.64	20.645
117.5	32.0	76.61	12.59	84.21	17.219	73.78	15.699	71.80	17.310	76.13	20.992
118.5	32.6	77.10	12.83	85.04	17.614	74.29	15.940	72.31	17.516	76.63	21.202
119.5	33.2	77.60	13.06	85.89	18.023	74.79	16.161	72.81	17.706	77.13	21.436

Table 1 continued

$MgAl_2O_4$		$MgAl_{1.8}Cr_{0.2}O_4$		$MgAl_{1.6}Cr_{0.4}O_4$		$MgAl_{1.2}Cr_{0.8}O_4$		$MgAl_{0.8}Cr_{1.2}O_4$		$MgAl_{0.4}Cr_{1.6}O_4$	
T (K)	C_p (J mol^{-1} K^{-1})	T (K)	C_p (J mol^{-1} K^{-1})	T (K)	C_p (J mol^{-1} K^{-1})	T (K)	C_p (J mol^{-1} K^{-1})	T (K)	C_p (J mol^{-1} K^{-1})	T (K)	C_p (J mol^{-1} K^{-1})
120.5	33.7	78.09	13.28	86.74	18.481	75.29	16.352	73.31	17.826	77.62	21.655
121.5	34.3	78.58	13.43	87.61	18.941	75.78	16.609	73.80	18.196	78.12	21.845
122.5	34.9	79.08	13.71	88.49	19.376	76.27	16.825	74.30	18.403	78.61	22.024
123.5	35.5	79.57	13.89	89.37	19.774	76.77	16.987	74.80	18.615	79.58	22.527
124.5	36.0	80.06	14.10	90.26	20.262	77.27	17.280	75.31	18.815	80.07	22.784
125.5	36.6	80.56	14.26	91.17	20.718	77.77	17.436	75.80	18.991	80.57	23.067
126.4	37.2	81.05	14.53	92.08	21.181	78.26	17.680	76.30	19.257	81.07	23.299
127.4	37.8	82.34	14.85	92.99	21.640	78.75	17.903	76.79	19.488	81.57	23.538
128.4	38.4	83.09	15.18	93.92	22.120	79.24	18.034	77.28	19.727	82.06	23.792
129.4	39.0	83.89	15.53	94.86	22.600	79.74	18.347	77.78	19.960	82.56	24.096
130.4	39.5	84.72	15.90	95.81	23.106	80.23	18.588	78.28	20.205	83.05	24.309
131.4	40.1	85.56	16.41	96.76	23.600	80.72	18.776	78.77	20.426	83.55	24.484
132.4	40.7	86.42	16.93	97.73	24.110	81.21	19.022	79.25	20.580	84.04	24.799
133.4	41.2	87.29	17.32	98.71	24.629	81.71	19.237	79.74	20.855	84.53	25.012
134.4	41.8	88.17	17.74	99.69	25.154	82.21	19.534	80.23	21.172	85.03	25.345
135.4	42.4	89.05	18.14	100.7	25.685	82.71	19.718	80.72	21.351	87.45	25.801
136.4	43.0	89.94	18.61	101.7	26.220	83.20	19.927	81.22	21.627	88.32	26.251
137.4	43.6	90.84	19.04	102.7	26.770	83.69	20.251	81.71	21.785	89.21	26.675
138.4	44.1	91.74	19.48	103.7	27.333	84.19	20.371	82.19	21.991	90.10	27.175
139.4	44.7	92.66	19.98	104.7	27.879	84.68	20.773	82.63	22.269	91.00	27.626
140.4	45.3	93.58	20.44	105.6	28.398	85.18	20.938	83.12	22.516	91.91	28.102
141.4	45.9	94.52	20.92	106.6	28.974	85.67	21.130	83.63	22.801	92.82	28.575
142.4	46.5	95.46	21.41	107.6	29.553	86.17	21.371	84.15	23.022	93.75	29.082
143.3	47.1	96.41	21.89	108.6	30.099	86.65	21.678	84.65	23.309	94.68	29.578
144.3	47.6	97.37	22.43	109.6	30.632	87.14	21.851	85.15	23.481	95.63	30.091
145.3	48.2	98.35	22.91	110.6	31.212	87.64	22.100	86.75	23.858	96.58	30.600
146.3	48.7	99.33	23.46	111.6	31.778	88.13	22.389	87.61	24.288	97.54	31.117
147.3	49.4	100.32	23.98	112.6	32.359	88.62	22.560	88.49	24.717	98.52	31.635
148.3	50.0	101.31	24.52	113.6	32.926	89.12	22.790	89.37	25.213	99.50	32.192
149.3	50.6	102.31	25.06	114.6	33.476	89.60	23.091	90.26	25.668	100.49	32.744
150.3	51.2	103.30	25.62	115.6	34.072	90.06	23.381	91.17	26.125	101.48	33.307
151.3	51.8	104.29	26.15	116.6	34.638	90.52	23.587	92.07	26.591	102.48	33.874
152.3	52.4	105.29	26.70	117.6	35.215	91.01	23.804	92.99	27.064	103.47	34.360
153.3	52.8	106.28	27.23	118.6	35.794	91.51	24.114	93.92	27.586	104.46	34.955
154.3	53.4	107.28	27.81	119.6	36.368	92.00	24.302	94.86	28.070	105.46	35.515
155.3	54.1	108.27	28.37	120.6	37.079	92.50	24.639	95.80	28.554	106.45	36.090
156.3	54.7	109.26	28.92	121.6	37.545	93.00	24.899	96.76	29.061	107.44	36.644
157.3	55.1	110.26	29.51	122.5	38.112	93.50	25.148	97.73	29.589	108.44	37.214
158.2	55.8	111.25	30.05	123.5	38.702	94.00	25.353	98.70	30.104	109.43	37.779
159.2	56.0	112.24	30.66	124.5	39.272	94.49	25.645	99.69	30.650	110.42	38.364
160.2	56.9	113.24	31.27	125.5	39.890	94.99	25.859	100.7	31.182	111.42	38.953
161.3	57.4	114.23	31.75	126.5	40.454	95.48	26.128	101.7	31.756	112.41	39.511
162.2	58.0	115.22	32.36	127.5	41.038	95.98	26.452	102.7	32.276	113.41	40.066
163.2	58.7	116.21	32.83	128.5	41.601	96.48	26.620	103.7	32.850	114.40	40.670
164.2	59.1	117.17	33.48	129.5	42.135	96.97	26.932	104.7	33.396	115.39	41.233
165.2	59.8	118.12	34.04	130.5	42.789	97.47	27.026	105.6	33.944	116.39	41.826
166.2	60.3	119.19	34.67	131.5	43.341	97.96	27.417	106.6	34.515	117.38	42.424
167.2	60.9	120.19	35.07	132.5	43.943	98.46	27.620	107.6	35.066	118.38	42.986
168.2	61.3	121.18	35.65	133.5	44.548	98.97	27.866	108.6	35.667	119.37	43.526
169.2	62.0	122.18	36.21	134.5	45.106	99.46	28.247	109.6	36.199	120.36	44.142
170.2	62.5	123.17	36.82	135.5	45.709	99.96	28.451	110.6	36.754	121.36	44.707
171.2	63.0	124.16	37.39	136.5	46.290	101.2	28.725	111.6	37.325	122.35	45.281
172.2	63.7	125.16	38.02	137.5	46.908	102.2	29.249	112.6	37.956	123.35	45.909
173.2	64.3	126.15	38.64	138.4	47.436	103.2	29.820	113.6	38.481	124.34	46.479
174.2	64.8	127.15	39.17	139.4	47.902	104.2	30.350	114.6	39.086	125.33	47.083
175.2	65.4	128.14	39.80	140.4	48.592	105.2	30.897	115.6	39.616	126.33	47.717
176.2	65.9	129.14	40.39	141.4	49.178	106.1	31.446	116.6	40.218	127.32	48.370
177.2	66.4	130.13	40.96	142.4	49.763	107.1	32.010	117.6	40.773	128.31	48.862
178.2	67.0	131.12	41.58	143.4	50.351	108.1	32.559	118.6	41.323	129.31	49.410

Table 1 continued

$MgAl_2O_4$		$MgAl_{1.8}Cr_{0.2}O_4$		$MgAl_{1.6}Cr_{0.4}O_4$		$MgAl_{1.2}Cr_{0.8}O_4$		$MgAl_{0.8}Cr_{1.2}O_4$		$MgAl_{0.4}Cr_{1.6}O_4$	
T (K)	C_p (J mol^{-1} K^{-1})	T (K)	C_p (J mol^{-1} K^{-1})	T (K)	C_p (J mol^{-1} K^{-1})	T (K)	C_p (J mol^{-1} K^{-1})	T (K)	C_p (J mol^{-1} K^{-1})	T (K)	C_p (J mol^{-1} K^{-1})
179.1	67.4	132.12	42.18	144.4	51.002	109.1	33.124	119.6	41.936	130.30	50.021
180.1	68.2	133.11	42.75	145.4	51.579	110.1	33.685	120.6	42.540	131.30	50.614
181.1	68.7	134.11	43.37	146.4	52.166	111.1	34.252	121.5	43.071	132.29	51.205
182.1	69.1	135.10	43.97	147.4	52.737	112.1	34.822	122.5	43.682	133.28	51.805
183.1	69.7	136.09	44.59	148.4	53.352	113.1	35.409	123.5	44.270	134.28	52.399
184.1	70.2	137.09	45.11	149.4	53.907	114.1	35.969	124.5	44.901	135.27	52.960
185.1	70.9	138.08	45.78	150.4	54.483	115.1	36.532	125.5	45.413	136.26	53.619
186.1	71.4	139.08	46.35	151.4	55.149	116.1	37.109	126.5	46.045	137.26	54.082
187.1	71.9	140.07	46.96	152.4	55.649	117.1	37.709	127.5	46.589	138.25	54.719
188.1	72.4	141.06	47.53	153.4	56.312	118.1	38.258	128.5	47.135	139.24	55.296
189.1	72.7	142.06	48.16	154.4	56.852	119.1	38.833	129.5	47.740	140.24	55.969
190.1	73.5	143.05	48.74	155.3	57.487	120.1	39.428	130.5	48.379	141.23	56.510
191.1	73.9	144.05	49.35	156.3	57.926	121.1	39.960	131.5	48.897	142.22	57.165
192.0	74.5	145.04	49.88	157.3	58.640	122.0	40.587	132.5	49.530	143.22	57.651
193.0	74.9	146.03	50.62	158.3	59.248	123.0	41.148	133.5	50.108	144.21	58.287
194.0	75.4	147.03	51.18	159.3	59.773	124.0	41.731	134.5	50.738	145.21	58.865
195.0	76.0	148.02	51.69	160.3	60.258	125.0	42.316	135.5	51.287	146.20	59.470
196.0	76.3	149.02	52.38	161.3	60.886	126.0	42.925	136.5	51.897	147.19	60.076
197.0	77.2	150.01	52.93	162.3	61.535	127.0	43.521	137.5	52.446	148.19	60.679
198.0	77.5	151.01	53.51	163.3	61.872	128.0	44.079	138.4	52.963	149.18	61.301
199.0	78.0	152.00	54.23	164.3	62.582	129.0	44.627	138.9	53.154	150.18	61.787
200.0	78.6	153.00	54.80	165.3	63.095	130.0	45.199	140.0	53.892	151.17	62.428
201.0	79.1	153.99	55.37	166.3	63.721	131.0	45.828	141.0	54.426	152.16	63.007
202.0	79.8	154.98	55.99	167.3	64.173	132.0	46.384	142.0	54.989	153.16	63.572
203.0	80.4	155.98	56.59	168.3	64.967	133.0	47.014	143.0	55.623	154.15	64.138
203.9	80.5	156.97	57.11	169.3	65.490	134.0	47.541	143.9	56.107	155.15	64.728
204.9	81.2	157.96	57.93	170.3	65.784	135.0	48.166	144.9	56.787	156.15	65.275
205.9	81.8	158.96	58.27	171.3	66.492	136.0	48.783	145.9	57.356	157.14	65.907
206.9	82.3	159.95	58.92	172.2	67.016	137.0	49.332	146.9	57.883	158.14	66.327
207.9	82.4	160.95	59.55	173.2	67.700	137.9	49.896	147.9	58.463	159.13	66.941
208.9	83.3	161.94	60.11	174.2	68.309	138.9	50.486	148.9	59.058	160.12	67.549
209.9	83.7	162.94	60.77	175.2	68.691	139.9	51.125	149.9	59.675	161.12	68.061
210.9	83.9	163.93	61.35	176.2	69.174	140.9	51.580	150.9	60.246	162.11	68.645
211.9	84.8	164.93	61.96	177.2	69.802	141.9	52.306	151.9	60.859	163.11	69.342
212.9	84.9	165.92	62.60	178.2	70.385	142.9	52.885	152.9	61.345	164.10	69.813
213.8	85.7	166.92	63.10	179.2	70.824	143.9	53.431	153.9	61.976	165.10	70.382
214.8	86.0	167.91	63.66	180.2	71.552	144.9	54.018	154.9	62.516	166.09	70.946
215.8	86.8	168.91	64.34	181.2	72.088	145.9	54.621	155.9	63.171	167.09	71.430
216.8	87.1	169.90	64.85	182.2	72.511	146.9	55.239	156.9	63.748	168.08	71.966
217.8	87.3	170.90	65.35	183.2	73.259	147.9	55.846	157.9	64.302	169.08	72.479
218.8	88.1	171.89	66.02	184.2	73.771	148.9	56.387	158.9	64.908	170.07	73.110
219.8	88.6	172.89	66.53	185.2	74.200	149.9	57.035	159.9	65.466	171.06	73.594
220.8	89.0	173.88	67.21	186.2	74.658	150.9	57.603	160.9	65.954	172.06	74.285
221.8	89.6	174.87	67.73	186.8	75.266	151.9	58.113	161.8	66.465	173.05	74.854
222.7	89.7	175.87	68.45	187.7	75.539	152.9	58.757	162.8	67.115	174.05	75.262
223.7	90.6	176.86	68.84	188.7	75.954	153.9	59.267	163.8	67.689	175.04	75.771
224.7	90.9	177.85	69.48	189.7	76.491	154.8	59.811	164.8	68.187	176.03	76.448
225.7	91.5	178.84	70.04	190.7	76.896	155.8	60.405	165.8	68.842	177.03	76.759
226.7	91.7	179.83	70.69	191.7	77.457	156.8	61.030	166.8	69.301	178.02	77.369
227.7	92.4	180.83	71.18	192.7	78.015	157.8	61.630	167.8	69.910	179.01	77.794
228.7	92.5	181.82	71.72	193.7	78.616	158.8	62.173	168.8	70.478	180.00	78.560
229.7	93.4	182.81	72.35	194.7	79.070	159.8	62.706	169.8	71.046	180.99	78.883
230.6	93.7	183.80	72.91	195.7	79.502	160.8	63.181	170.8	71.574	181.99	79.511
231.6	94.2	184.79	73.65	196.7	79.858	161.8	63.776	171.8	72.120	182.98	80.220
232.6	94.4	185.78	73.97	197.6	80.423	162.8	64.296	172.8	72.540	183.98	80.527
233.6	95.2	186.77	74.59	198.6	81.003	163.8	65.064	173.8	73.208	184.97	81.036
234.6	94.8	187.76	75.10	199.6	81.454	164.8	65.515	174.8	73.615	185.96	81.481
235.6	95.6	188.76	75.64	200.6	82.072	165.8	66.136	175.8	74.238	186.96	82.190
236.6	96.9	189.75	76.27	201.6	82.468	166.8	66.620	176.8	74.759	187.95	82.699

Table 1 continued

$MgAl_2O_4$		$MgAl_{1.8}Cr_{0.2}O_4$		$MgAl_{1.6}Cr_{0.4}O_4$		$MgAl_{1.2}Cr_{0.8}O_4$		$MgAl_{0.8}Cr_{1.2}O_4$		$MgAl_{0.4}Cr_{1.6}O_4$	
T (K)	C_p (J mol^{-1} K^{-1})	T (K)	C_p (J mol^{-1} K^{-1})	T (K)	C_p (J mol^{-1} K^{-1})	T (K)	C_p (J mol^{-1} K^{-1})	T (K)	C_p (J mol^{-1} K^{-1})	T (K)	C_p (J mol^{-1} K^{-1})
237.6	96.4	190.74	76.76	202.6	82.910	167.8	67.302	177.8	75.123	188.94	83.156
238.5	96.7	191.73	77.45	203.6	83.619	168.8	67.817	178.8	75.960	189.94	83.691
239.5	97.4	192.72	78.03	204.6	84.027	169.8	68.333	179.7	76.424	190.93	84.104
240.5	97.8	193.71	78.66	205.6	84.510	170.8	68.887	180.7	76.926	191.92	84.868
241.5	97.7	194.71	79.10	206.6	85.150	171.8	69.475	181.7	77.381	192.92	85.301
242.5	98.8	195.70	79.70	207.6	85.312	172.7	69.911	182.7	78.115	193.91	85.778
243.5	99.2	196.69	80.29	208.6	86.003	173.7	70.408	183.7	78.552	194.90	86.211
244.5	99.4	197.68	80.78	209.5	86.623	174.7	71.051	184.7	79.219	195.90	86.801
245.4	99.7	198.67	81.14	210.5	87.100	175.7	71.694	185.7	79.570	196.89	87.065
246.4	100.8	199.57	81.99	211.5	87.112	176.7	72.157	186.7	79.989	197.88	87.802
247.4	100.6	200.65	82.17	212.5	87.923	177.7	72.826	187.7	80.702	198.87	88.237
248.4	100.9	201.65	82.95	213.5	88.495	178.7	73.173	188.7	81.136	199.86	88.732
249.4	100.4	202.64	83.57	214.5	88.841	179.7	73.832	189.7	81.552	200.85	89.184
250.4	101.6	203.63	84.10	215.5	89.610	180.7	74.370	190.7	82.270	201.85	89.714
251.3	102.2	204.62	84.78	216.5	89.798	181.7	74.876	191.7	82.653	202.84	90.046
252.3	102.8	205.61	85.29	217.5	90.612	182.7	75.457	192.7	83.181	203.83	90.664
253.3	101.6	206.60	85.56	218.5	91.069	183.7	75.851	193.7	83.752	204.82	91.263
254.3	103.3	207.59	86.15	219.4	91.073	184.7	76.469	194.7	83.987	205.81	91.470
255.3	103.8	208.58	87.01	220.4	91.887	185.7	77.062	195.6	84.642	206.80	91.934
256.3	104.1	209.57	87.38	221.4	92.008	186.7	77.598	196.6	85.251	207.78	92.667
257.2	104.3	210.56	87.76	222.4	92.754	187.7	78.072	197.6	85.505	208.77	92.904
258.2	105.5	211.55	88.32	223.4	92.961	188.6	78.645	198.6	86.192	209.76	93.440
259.2	106.0	212.53	88.94	224.4	93.721	189.6	79.106	199.6	86.403	210.75	93.977
260.2	107.1	213.52	89.56	225.4	94.098	190.6	79.549	200.6	87.176	211.74	94.371
261.2	107.5	214.51	90.10	226.4	94.506	191.6	80.139	201.6	87.500	212.72	94.917
262.2	106.1	215.50	90.40	227.4	94.567	192.6	80.682	202.6	88.265	213.71	95.168
263.1	106.9	216.49	91.03	228.3	95.687	193.6	80.982	203.6	88.697	214.70	95.722
264.1	107.1	217.48	91.97	229.3	95.772	194.6	81.565	204.6	89.208	215.69	96.078
265.1	107.8	218.46	92.14	230.3	96.407	195.6	82.066	205.6	89.458	216.68	96.880
266.1	107.7	219.45	92.39	231.3	97.067	196.6	82.439	206.6	90.207	217.66	97.291
267.1	107.7	220.44	92.87	232.3	97.105	197.6	83.061	207.5	90.600	218.65	97.486
268.0	108.6	221.43	93.34	233.3	97.815	198.6	83.597	208.5	90.985	219.64	97.964
269.0	109.1	222.41	93.95	234.3	97.984	199.6	83.980	209.5	91.420	220.63	98.389
270.0	109.6	223.40	94.58	235.3	98.623	200.6	84.596	210.5	92.088	221.61	99.049
271.0	109.4	224.39	94.96	236.2	99.398	201.6	84.866	211.5	92.456	222.60	99.192
272.0	109.3	225.38	95.39	237.2	99.159	202.5	85.389	212.5	92.996	223.59	99.933
272.9	110.1	226.36	95.99	238.2	99.589	203.5	85.996	213.5	93.408	224.57	100.30
273.9	110.2	227.35	96.90	239.2	100.20	204.5	86.403	214.5	93.980	225.56	100.75
274.9	110.2	228.34	97.10	240.2	100.66	205.5	86.942	215.5	94.477	226.54	101.16
275.9	111.2	229.32	97.48	241.2	100.87	206.5	87.655	216.5	94.804	227.53	101.74
276.9	111.5	230.31	98.00	242.2	101.13	207.5	87.909	217.5	95.210	228.52	101.87
277.8	112.2	231.29	98.35	243.2	101.89	208.5	88.480	218.5	95.504	229.51	102.23
278.8	112.5	232.28	98.79	244.1	102.14	209.5	88.850	219.4	96.269	230.50	102.91
279.8	112.5	233.26	98.98	245.1	102.34	210.5	89.232	220.4	96.314	231.48	103.32
280.8	113.7	234.25	99.82	246.1	103.45	211.5	89.816	221.4	97.107	232.47	103.85
281.8	112.8	235.23	100.23	247.1	103.81	212.5	90.274	222.4	97.594	233.46	104.11
282.7	113.4	236.22	100.38	248.1	104.43	213.4	90.750	223.4	98.086	234.45	104.76
283.7	114.2	237.20	100.96	249.1	104.39	214.4	91.177	224.4	98.302	235.44	104.99
284.7	114.5	238.19	101.54	250.1	104.25	215.4	91.508	225.4	98.758	236.43	105.08
285.7	114.0	239.17	102.12	251.0	104.33	216.4	92.184	226.4	99.251	237.41	105.95
286.7	115.3	240.16	102.34	251.7	105.00	217.4	92.460	227.4	99.657	238.39	106.32
287.6	116.2	241.14	102.77	252.5	105.30	218.4	93.060	228.3	100.22	239.38	106.59
288.6	116.4	242.12	103.13	253.3	104.64	219.4	93.434	229.3	100.23	240.36	106.88
289.6	116.2	243.11	103.63	254.1	105.70	220.4	93.846	230.3	100.99	241.35	107.42
290.6	117.4	244.09	103.80	254.8	106.82	221.4	94.397	231.3	101.47	242.33	107.79
291.5	117.1	245.07	104.49	255.6	106.11	222.3	94.968	232.3	101.92	243.31	107.94
292.5	118.0	246.05	104.95	256.4	106.46	223.3	95.243	233.3	102.46	244.30	108.49
293.5	118.3	247.03	105.57	257.1	106.65	224.3	95.886	234.3	102.55	245.28	108.45
294.5	118.2	248.02	105.62	257.9	107.62	225.3	96.119	235.2	103.09	246.26	109.12

Table 1 continued

$MgAl_2O_4$		$MgAl_{1.8}Cr_{0.2}O_4$		$MgAl_{1.6}Cr_{0.4}O_4$		$MgAl_{1.2}Cr_{0.8}O_4$		$MgAl_{0.8}Cr_{1.2}O_4$		$MgAl_{0.4}Cr_{1.6}O_4$	
T (K)	C_p (J mol^{-1} K^{-1})	T (K)	C_p (J mol^{-1} K^{-1})	T (K)	C_p (J mol^{-1} K^{-1})	T (K)	C_p (J mol^{-1} K^{-1})	T (K)	C_p (J mol^{-1} K^{-1})	T (K)	C_p (J mol^{-1} K^{-1})
295.4	118.7	249.00	106.30	258.7	107.34	226.3	96.750	236.2	103.78	247.25	109.41
296.4	119.8	249.98	106.52	259.6	108.50	227.3	97.225	237.2	104.13	248.23	109.77
297.4	120.0	250.96	106.85	260.3	108.49	228.3	97.767	238.2	104.20	249.21	110.19
298.4	120.3	251.94	107.31	261.1	108.15	229.3	97.884	239.2	104.95	250.19	111.10
299.3	120.3	252.92	107.95	262.0	108.95	230.1	98.164	240.2	105.13	251.18	111.11
300.3	120.8	253.90	108.32	262.8	109.74	231.2	98.673	241.2	105.55	252.16	111.37
301.3	121.8	254.89	108.20	263.6	109.47	232.2	99.290	242.1	106.22	253.14	111.78
302.3	121.8	255.87	108.82	264.4	111.54	233.2	99.746	243.1	106.38	254.13	112.66
303.2	121.5	256.85	109.32	265.3	109.78	234.2	100.05	244.1	106.91	255.11	112.37
304.2	121.9	257.83	109.78	266.1	110.29	235.2	100.50	245.1	106.97	256.09	112.91
305.2	123.9	258.81	110.11	266.9	110.58	236.2	101.02	246.1	107.38	257.06	113.05
		259.80	110.34	267.8	111.79	237.1	101.39	247.1	108.09	258.05	114.10
		260.78	111.06	268.6	111.55	238.1	101.48	248.1	108.55	259.04	114.38
		261.76	111.02	269.4	111.37	239.1	101.96	249.1	108.35	260.02	114.36
		262.74	111.35	270.3	111.81	240.1	102.52	250.0	109.13	261.00	115.09
		263.72	111.90	271.2	111.69	241.1	103.14	251.0	109.68	261.98	115.64
		264.70	112.24	272.0	111.89	242.1	103.35	252.0	109.97	262.97	115.37
		265.68	112.74	272.9	114.17	243.1	103.76	253.0	110.40	263.95	115.77
		266.66	113.05	273.7	112.43	244.0	104.27	254.0	110.98	264.93	116.24
		267.64	113.09	274.6	114.49	245.0	104.32	255.0	110.52	265.91	116.55
		268.62	113.35	275.5	113.84	246.0	105.05	255.9	111.21	266.89	117.35
		269.60	114.42	276.4	114.80	247.0	105.55	256.9	111.57	267.87	117.29
		270.58	113.16	277.2	116.23	248.0	105.78	257.9	111.83	268.85	117.53
		271.56	114.08	278.1	115.54	249.0	106.31	258.9	112.55	269.83	117.89
		272.54	116.33	279.0	115.41	250.0	106.33	259.9	113.01	270.81	117.86
		273.52	115.74	279.9	116.36	250.9	106.82	260.9	113.22	271.79	118.27
		274.49	115.73	280.8	116.24	251.9	107.23	261.8	113.31	272.77	119.30
		275.48	116.76	281.6	115.61	252.9	107.80	262.8	113.64	273.75	119.40
		276.45	116.90	282.5	116.07	253.9	108.10	263.8	114.63	274.77	119.15
		277.43	117.40	283.4	116.87	254.9	108.28	264.8	114.37	275.71	119.18
		278.41	116.35	284.3	117.97	255.9	108.89	265.8	115.04	276.70	121.05
		279.39	117.66	285.2	117.63	256.8	109.23	266.7	115.27	277.67	120.85
		280.37	118.24	286.1	116.96	257.8	109.22	267.7	115.82	278.66	121.48
		281.35	118.11	286.9	117.78	258.8	109.80	268.7	116.17	279.64	121.48
		282.32	118.05	287.8	118.76	259.8	110.28	269.7	116.43	280.60	122.22
		283.31	119.11	288.7	118.61	260.8	111.03	270.7	116.86	281.59	122.39
		284.27	119.07	289.6	119.42	261.8	110.96	271.6	116.81	282.56	122.65
		285.27	119.60	290.5	119.64	262.7	111.48	272.6	117.49	283.55	123.14
		286.22	119.39	291.4	119.04	263.7	111.57	273.6	117.79	284.50	122.97
		287.20	118.96	292.3	119.82	264.7	111.96	274.6	117.80	285.49	123.22
		288.17	120.37	293.2	120.93	265.7	112.43	275.6	117.97	286.46	123.43
		289.15	120.44	294.1	121.60	266.7	112.94	276.6	119.03	287.45	123.83
		290.12	120.81	295.0	120.52	267.6	112.82	277.6	119.54	288.42	124.25
		291.09	121.11	295.8	122.55	268.6	113.30	278.5	119.22	289.42	124.08
		292.07	122.04	296.7	121.78	269.6	113.63	279.5	119.33	290.37	124.98
		293.05	122.87	297.6	123.27	270.6	113.97	280.5	120.75	291.34	124.85
		294.02	122.70	298.5	122.74	271.6	114.64	281.5	121.07	292.32	126.58
		294.99	124.22	299.4	123.02	272.5	114.78	282.5	120.62	293.29	126.63
		295.96	123.47	300.3	123.30	273.5	114.92	283.4	120.89	294.26	125.69
		296.94	123.49	301.2	123.02	274.5	115.63	284.4	121.49	295.24	126.15
		297.90	123.04	302.2	124.80	275.5	115.77	285.4	121.53	296.23	126.19
		298.88	123.52	303.1	123.74	276.5	115.88	286.4	121.77	297.21	126.73
		299.85	123.89	304.0	125.02	277.5	115.83	287.4	121.71	298.18	126.26
		300.82	124.45	304.9	125.08	278.4	116.85	288.3	122.20	299.14	126.67
		301.80	124.42			279.4	117.20	289.3	123.33	300.12	127.52
		302.78	126.09			280.4	117.28	290.3	123.05	301.11	127.39
		303.74	126.35			281.4	117.87	291.2	123.63	302.06	127.34
		304.72	127.73			282.4	118.22	292.2	124.00	303.03	128.02
		305.69	128.19			283.3	118.31	293.2	124.91	304.01	129.25

Table 1 continued

$MgAl_2O_4$		$MgAl_{1.8}Cr_{0.2}O_4$		$MgAl_{1.6}Cr_{0.4}O_4$		$MgAl_{1.2}Cr_{0.8}O_4$		$MgAl_{0.8}Cr_{1.2}O_4$		$MgAl_{0.4}Cr_{1.6}O_4$	
T (K)	C_p ($J\ mol^{-1}\ K^{-1}$)	*T* (K)	C_p ($J\ mol^{-1}\ K^{-1}$)	*T* (K)	C_p ($J\ mol^{-1}\ K^{-1}$)	*T* (K)	C_p ($J\ mol^{-1}\ K^{-1}$)	*T* (K)	C_p ($J\ mol^{-1}\ K^{-1}$)	*T* (K)	C_p ($J\ mol^{-1}\ K^{-1}$)
		306.66	127.33			284.3	119.23	294.2	125.32	304.99	128.67
		307.63	127.44			285.3	118.75	295.1	126.32	305.96	129.14
		308.59	128.60			286.3	119.35	296.1	126.12		
		309.57	128.25			287.2	119.66	297.1	126.81		
						288.2	119.80	298.1	126.57		
						289.2	120.08	299.0	126.87		
						290.2	120.84	300.0	127.36		
						291.2	121.33	301.0	126.95		
						292.1	121.62	302.0	127.56		
						293.1	122.57	302.9	127.55		
						294.1	122.85	303.9	128.23		
						295.0	123.46	304.9	128.02		
						296.0	123.30	305.9	128.59		
						297.0	123.49	306.8	129.12		
						298.0	123.56	307.8	129.28		
						298.9	124.22	308.8	130.04		
						299.9	124.86	309.8	130.64		
						300.9	124.59				
						301.9	125.17				
						302.8	125.62				
						303.8	126.02				
						304.8	126.17				
						305.8	126.44				
						306.7	127.37				
						307.7	127.25				
						308.7	128.27				
						309.7	128.96				

from about 10 s at 1.5 K to ca. 2,000 s at 100 K eventually dropping to a few 100 s at 300 K (increased loss by radiation). The estimated uncertainties for the heat capacities were 0.5%.

Results and discussion

The experimental values for the low-temperature heat capacities of $MgAl_2O_4$ and $Mg(Al,Cr)_2\ O_4$ spinels are compiled in Table 1. The values have been corrected for the contribution of the empty calorimeter. The uncertainties for the heat capacities were assumed to be within 0.5 %. The standard entropy at 298.15 K ($S°_{298}$) was calculated from the C_p data (using a T^3 extrapolation to 0 K). It should be noted that the extrapolation to 0 K accounts for less than 0.01% of the standard entropy at 298.15 K.

$MgAl_2O_4$: spinel ''senso stricto''

Figure 1 depicts the heat capacity of $MgAl_2O_4$ as a function of temperature. The data fit a relatively smooth and continuous curve at temperatures between 4 and 300 K. Integration of the C_p/T function resulted in $S°_{298} = 80.9 \pm 0.6\ J\ mol^{-1}\ K^{-1}$ which is in excellent agreement with the value reported by King

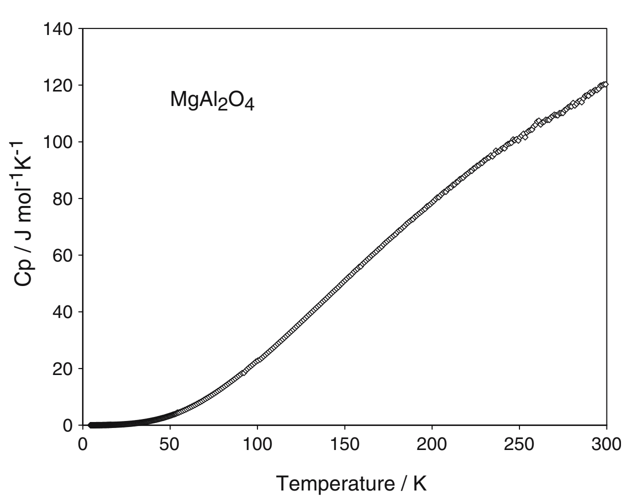

Fig. 1 Heat capacity measurements for $MgAl_2O_4$

Table 2 Selected previous results for $MgAl_2O_4$

$S°_{298}$ (J mol^{-1} K^{-1})	Reference	Type
80.6 ± 0.4	King (1955)[a]	Adiabatic calorimetry
84.535	Berman (1988)	ICSTD
81.5	Holland and Powell (1998)	ICSTD
80.63	Helgeson (1978)	ICSTD
80.4 ± 0.4	Chatterjee et al. (1998)	ICSTD
81.87 ± 0.08	Gottschalk (1997)	ICSTD
80.9 ± 0.6	This study	Adiabatic calorimetry

ICSTD internally consistent set of thermodynamic data

[a] King (1955) measured C_p between 53 and 298 K and calculated $S°_{298}$ using an extrapolation to 0 K assuming no low-temperature structural phase transitions

Table 3 $S°_{298}$ for $Mg(Al,Cr)_2O_4$

	$S°_{298}$ (J mol^{-1} K^{-1})
$MgAl_2O_4$	80.9 ± 0.6
$MgAl_{1.8}Cr_{0.2}O_4$	85.8 ± 0.4
$MgAl_{1.6}Cr_{0.4}O_4$	88.2 ± 0.4
$MgAl_{1.2}Cr_{0.8}O_4$	95.2 ± 0.5
$MgAl_{0.8}Cr_{1.2}O_4$	102.5 ± 0.5
$MgAl_{0.4}Cr_{1.6}O_4$	109.3 ± 0.5
$MgCr_2O_4$	118.3 ± 1.2

$S°_{298}$ calculated from C_p measurements (cf., Table 1). The data for $MgCr_2O_4$ was taken from Klemme et al. (2000)

(1955) who found $S°_{298}$ = 80.6 ± 0.4 J mol^{-1} K^{-1} (Table 2). However, King's (1955) results have previously been criticised (e.g., Chamberlin et al. 1995) as the $MgAl_2O_4$ sample was prepared at 1,773 K and then rapidly quenched. It is important in this context that cation disorder in spinels changes as a function of temperature from a ‘‘normal'' distribution of cations on sites at lower temperatures (i.e., Al^{3+} solely on octahedral sites) to a more ‘‘inverse‘‘ cation distribution with increasing amount of Al^{3+} on tetrahedral sites with increasing temperature. Previous work (Millard et al. 1992; Wood et al. 1986; Redfern et al. 1999; Warren et al. 2000) showed that samples quenched from $T > 1{,}000$°C cannot retain the high-temperature state of disorder but rather freeze the state of disorder of about 900 or 1,000°C, respectively. Moreover, as the freezing of the disordered state is somewhat not reproducible, it remains unknown which state of structural disorder the samples by King (1955) exactly represent. However, based on in situ measurements of the disorder at 1,273 K (Peterson et al. 1991), we can estimate the degree of disorder for King's samples at $x = 0.35$, where x is the fraction of tetrahedral sites occupied by Al^{3+}. Nevertheless, Chamberlin et al. (1995) found King's calorimetric value for the standard entropy of $MgAl_2O_4$ in excellent agreement with their results using the Pd equilibration technique (see Table 2) despite the fact that most of Chamberlin et al.'s experiments were conducted at much higher temperatures. This made Chamberlin et al. (1995) conclude that C_p, and thus $S°_{298}$, is not significantly affected by different states of disorder which further substantiates previously published results (Richet and Fiquet 1991). Our calorimetric data also support this notion as our $MgAl_2O_4$ spinel should represent the cation disorder state of 973 K, but the calculated S° is, within the uncertainties, identical to results by King (1955).

There is considerable disagreement between internally consistent estimates for the standard entropy of $MgAl_2O_4$ (cf., Table 2). Our new data are close to estimates by Chatterjee et al. (1998), Helgeson et al. (1978), and Holland and Powell (1998), but considerably disagree with results by Gottschalk (1997), and especially with results by Berman (1988).

Solid solution between $MgAl_2O_4$ and $MgCr_2O_4$

We prepared several synthetic spinels along the join between $MgAl_2O_4$ and $MgCr_2O_4$. These samples were prepared in an identical manner as the $MgAl_2O_4$ samples. The results of our C_p measurements are given in Table 1. Thermodynamic properties of spinels on the $MgAl_2O_4$–$MgCr_2O_4$ join are given in Table 3. $S°_{298}$ varies linearly from $MgAl_2O_4$ to $MgCr_2O_4$ (Fig. 3). However, the shape of the actual heat capacity curves varies substantially with composition. $MgCr_2O_4$ exhibits a first-order phase transition at 12.5 K (Ehrenberg et al. 2002), with a pronounced peak in C_p (Fig. 2) coinciding with the phase transition from cubic to tetragonal symmetry (Ehrenberg et al. 2002). However, this sharp peak disappears in Al-bearing spinels along the join $MgAl_2O_4$–$MgCr_2O_4$. For spinels of $MgAl_{0.4}Cr_{1.6}O_4$ composition, only a small hump occurs in the C_p curve between 5 and 10 K. Whereas there seems to be no evidence for peaks in the C_p curve for $MgAl_{0.8}Cr_{1.2}O_4$ and $MgAl_{1.2}Cr_{0.8}O_4$, our measurements for both $MgAl_{1.6}Cr_{0.4}O_4$ and $MgAl_{1.8}Cr_{0.2}O_4$ indicate small peaks or humps at very low temperatures below 2 K. Unfortunately, we could not investigate these anomalies further in more detail as the available techniques in our laboratories allowed us only to cool to a minimum temperature of about 1.5 K.

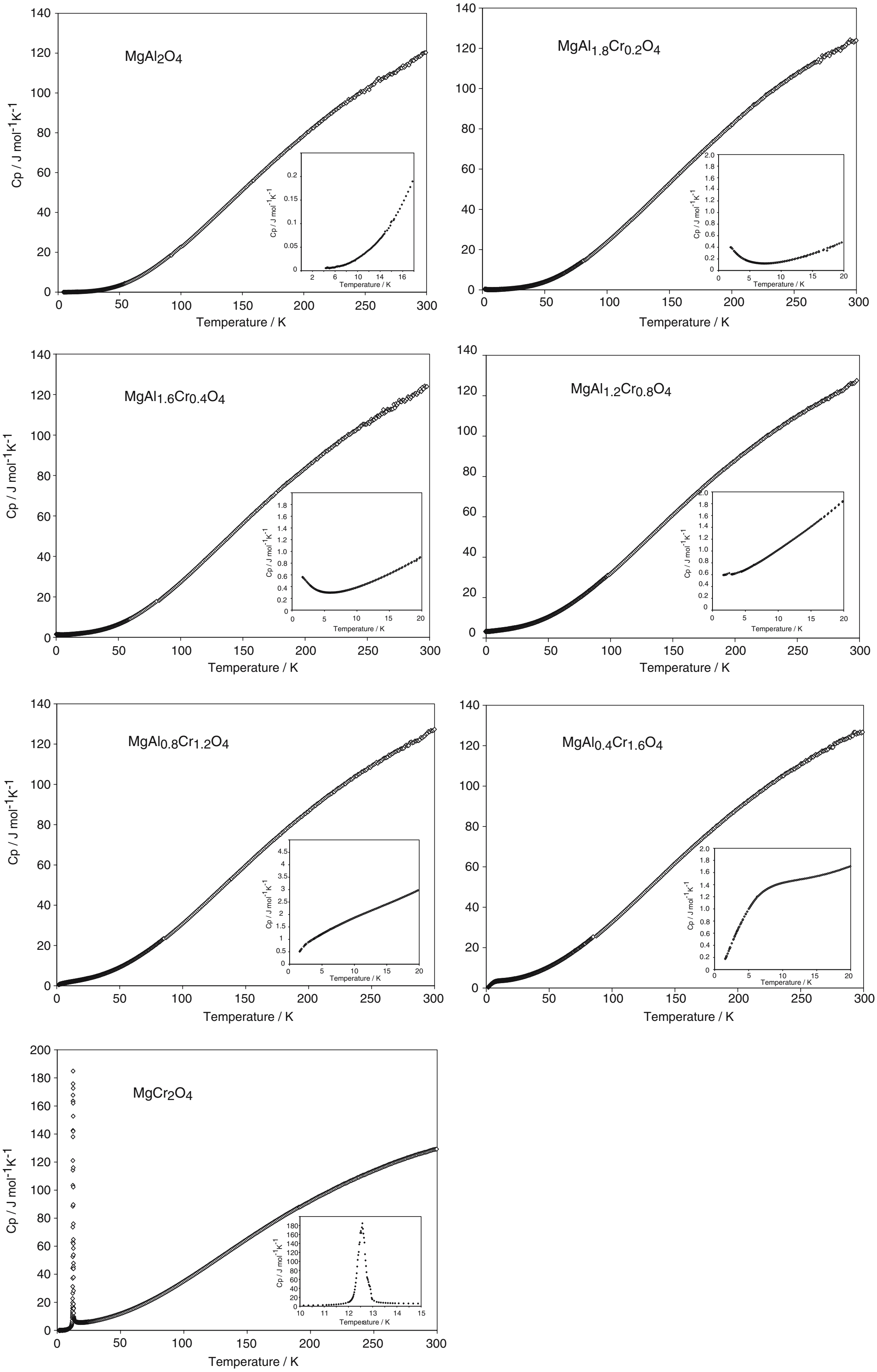

Fig. 2 Heat capacities for spinels along the join $MgAl_2O_4$–$MgCr_2O_4$

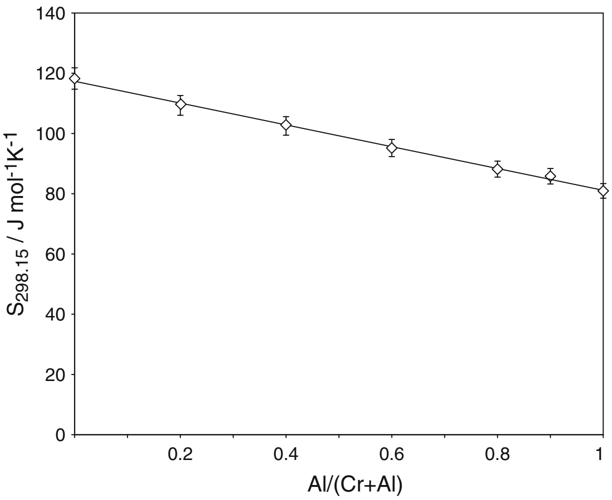

Fig. 3 $S°_{298}$ for $Mg(Al,Cr)_2O_4$ spinels calculated from heat capacity measurements

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