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ÅKERMANITE: PHASE TRANSITIONS IN HEAT CAPACITY AND THERMAL EXPANSION, AND REVISED THERMODYNAMIC DATA*

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ABSTRACT

Small anomalies have been found in the thermal behavior of synthetic åkermanite: (1) a sharp anomaly in the heat capacity at 357.9 K, and (2) a discontinuity in the thermal expansion at 693 K as determined by X-ray diffraction. The enthalpy and entropy assigned to the heat-capacity anomaly, for the purpose of tabulation, are 679 J/mol and 1.9 J/(mol•K), respectively. These values were determined from the difference between the measured values of the heat capacity in the temperature interval 320 to 365 K and that given by equation

$$C_p^\circ = 78.146 + 0.165734\,T - 3.34372 \times 10^{-5}\,T^2 + 2864.64\,T^{-0.5} - 6.7905 \times 10^6\,T^{-2} \text{ in J/(mol•K)},$$

which was made to fit to the heat-capacity and heat-content data for åkermanite in the inverval 290 to 1731 K. Heat-capacity measurements are reported for the temperature range from 9 to 995 K. The entropy and enthalpy of formation of åkermanite at 298.15 K and 1 bar are 212.5 ± 0.4 J/(mol•K) and -3864.5 ± 4.0 kJ/mol, respectively. The thermal expansion coefficients for the equation $p = p_0 (1 - \alpha t - \beta t^2)$ (t in °C) are: in the interval 20 to 420°C, for a, $a_0 = 7.8321$ Å, $\alpha = 0.99 \times 10^{-5}$, $\beta = -0.15 \times 10^{-9}$, and for c, $c_0 = 5.0063$ Å, $\alpha = 0.53 \times 10^{-5}$, $\beta = 4.14 \times 10^{-9}$; in the interval 420 to 1100°C, for a, $a_0 = 7.8343$ Å, $\alpha = 0.82 \times 10^{-5}$, $\beta = 1.95 \times 10^{-9}$, and for c, $c_0 = 4.9871$ Å, $\alpha = 1.76 \times 10^{-5}$, $\beta = -3.37 \times 10^{-9}$. A set of weak satellite reflections has been observed on *hk*0 single-crystal X-ray patterns and electron-diffraction patterns of this material at room temperature. With *in situ* heating in the transmission electron-microscope, the satellite reflections decreased significantly in intensity above 358 K and completely disappeared at about 580 K. On cooling the satellite reflections reappear. A working hypothesis is that the anomalies are associated with local displacements of the calcium ions from the mirror plane (space group $P\bar{4}2_1m$) and accompanying distortion of the $MgSi_2O_7$ framework.

Keywords: åkermanite, disopside, thermodynamic data, thermal expansion, unit-cell dimensions, molar volume.

SOMMAIRE

L'åkermanite synthétique montre, dans son comportement thermique, certaines petites anomalies: (1) anomalie nette de la càpacité calorifique à 357.9 K, et (2) discontinuité de l'expansion thermique à 693 K, déterminée par diffraction X. L'enthalpie et l'entropie assignées, aux fins de tabulation, à l'anomalie de la capacité calorifique sont, respectivement, de 679 J/mol et 1.9 J/(mol•K). Ces valeurs ont été déterminées à partir de la différence entre les valeurs mesurées de la capacité calorifique dans l'intervalle de température de 320 à 365 K et celle que donne l'équation

$$C_p^\circ = 78.146 + 0.165734\,T - 3.34372 \times 10^{-5}\,T^2 + 2864.64\,T^{-0.5} - 6.7905 \times 10^6\,T^{-2} \text{ en J/(mol•K)},$$

Cette équation est compatible avec les données sur la capacité calorifique et la quantité de chaleur de l'åkermanite dans l'intervalle de température de 290 à 1731 K. La capacité calorifique a été mesurée entre 9 et 995 K. L'entropie et l'enthalpie de formation de l'åkermanite à 298.15 K et 1 bar sont, respectivement, 212.5 ± 0.4 J/(mol•K) et -3864.5 ± 4 kJ/mol. Les coefficients d'expansion thermique de l'équation $p = p_0 (1 - \alpha t - \beta t^2)$, t en °C, sont: entre 20 et 420°C, pour a, $a_0 = 7.8321$ Å, $\alpha = 0.99 \times 10^{-5}$, $\beta = -0.15 \times 10^{-9}$; et pour c, $c_0 = 5.0063$ Å, $\alpha = 0.53 \times 10^{-5}$, $\beta = 4.14 \times 10^{-9}$; entre 420 et 1100°C, pour a, $a_0 = 7.8343$ Å, $\alpha = 0.82 \times 10^{-5}$, $\beta = 1.95 \times 10^{-9}$, et pour c, $c_0 = 4.9871$ Å,

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$\alpha = 1.76 \times 10^{-5}$, $\beta = -3.37 \times 10^{-9}$. On observe de faibles réflexions satellitiques sur les clichés *hk*0 de diffraction (rayons X et électrons) obtenus sur cristal unique à température ordinaire. Le chauffage *in situ* dans le microscope électronique à transmission fait décroître, à partir de 358 K, l'intensité des réflexions satellitiques, qui disparaissent complètement vers 580 K. Au refroidissement, les satellites réapparaissent. Une hypothèse séduisante associerait les anomalies à des déplacements des ions calcium du plan miroir de $P\bar{4}2_1m$ et déformation concomitante de la charpente $MgSi_2O_7$.

(Traduit par la Rédaction)

Mots-clés: åkermanite, diopside, données thermodynamiques, expansion thermique, dimensions de maille, volume molaire.

INTRODUCTION

Measurements of heat capacity by differential scanning calorimetry (DSC) are made to improve the constraints on smoothed analytical expressions derived from the simultaneous fitting of precision measurements of low-temperature adiabatic heat-capacity and literature values for heat contents obtained by the drop method. During the course of such measurements, a previously undetected anomaly was discovered in the heat capacity of åkermanite. Measurements of the heat capacity for synthetic åkermanite were made over the range 9 to 995 K. The anomaly was found at 357.9 K. A further study of the thermal expansion of åkermanite over the range 293 to 1373 K was made to determine the nature of the anomaly.

SAMPLES AND APPARATUS

An åkermanite sample (AKl) was prepared from a stoichiometric mix of Mallinckrodt 4071 Primary Standard $CaCO_3$, Baker Analyzed Reagent 2476 MgO, and Corning silica glass (the use of trade names is for descriptive purposes only and does not imply endorsement by the U.S. Geological Survey). The 108.2 g mix was heated slowly to 1000°C for 4 hours to allow decarbonation to occur. The mix was ground to -100 mesh and then heated in a platinum crucible at 1500 ± 20°C for 2 hours. The melt was quickly removed from the furnace and quenched on ice to a glass. The glass was ground to -50 mesh and heated for an additional 2 hours at 1500°C. The furnace temperature was slowly lowered to 1440°C and held for 2 hours, then lowered to 800°C and held for 12 hours. Crystals up to 2 cm in length were produced by this procedure.

Examination of the synthetic material by transmission electron-microscopy shows the presence of traces of another unidentified silicate phase, but in amounts so small as not to affect the thermal and X-ray studies described here. The average composition calculated from 24 microprobe analyses of five sample chips is $Ca_{1.97}Mg_{1.00}Si_{2.01}O_7$. Synthetic $CaSiO_3$ and $CaMgSi_2O_6$ were used as standards. Corrections to the heat capacities for deviations from the composition of stoichiometric åkermanite are smaller than the uncertainty in the DSC data. Therefore, the formula weight 272.633 g (based on the 1975 values given by the Commission on Atomic Weights, 1976) for stoichiometric åkermanite was used in the calculation of heat capacities.

A 27.3 g sample (AK2) of the stoichiometric composition for åkermanite was prepared using the procedure described above, with the exception that the melt was rapidly cooled from 1500 to 1440°C. This second sample was prepared to ensure that the anomalous behavior observed in the first sample was not related to the small deviation from stoichiometry. Sample AK2 showed growth twinning, possibly the result of more rapid crystal-growth than for sample AK1. However, the sample composition, $Ca_{1.97}Mg_{0.99}Si_{2.02}O_7$, as determined by microprobe analysis, is identical to that for sample AK1, within experimental error.

Heat-capacity measurements were made on a third sample of synthetic åkermanite (75014) prepared by Woodhead (1977). It was produced by growth-annealing at 1415 ± 10°C a glass of åkermanite composition prepared from Spectrosil fused silica, and Research Organic/Inorganic Chemical Corp. CA-12 CaO and ultrapure MgO. Again, microprobe analyses showed the sample composition ($Ca_{1.96}Mg_{1.00}Si_{2.02}O_7$) to be equivalent to that for sample AK1. Woodhead (1977) described his sample as having a dendritic growth-habit resulting from rapid nucleation and growth; this caused relative rotation of individual dendrites and misalignment of areas of the crystals. Inspection of a portion of the sample showed abundant subgrains (0.1 × 0.5 mm or smaller) separated by thin regions of glass. Twinning was not readily apparent optically; however, X-ray-diffraction results clearly show the presence of a (130) twin plane and (001) composition plane, as observed by Woodhead (1977) in his study of gehlenite.

High-temperature heat capacities of all three samples were measured by DSC following the procedures outlined by Hemingway *et al.* (1981). The samples were enclosed in unsealed gold pans. The sample weights were 42.482, 54.028, and 49.985 mg, respectively, for samples AK1, AK2 and 75014.

The cryostat used for the low-temperature heat-capacity measurements has been described by Robie & Hemingway (1972) and Hemingway *et al.* (1984). The calorimeter was sealed with 36.0879 g of sample AK1 and 0.0003 g of He gas.

For the study of thermal expansion, the Guinier-Lenné method was used (Lenné 1961). In this procedure the powdered sample is raised in temperature over the desired range continuously during a 24-hour period while a film holder is moved past a slit aperture where the diffraction pattern is registered. Thus the powder pattern developed on the film is two-dimensional, with 2*θ* dispersed on one axis, and time (temperature) on the other. The temperature axis is calibrated with a strip-chart recording of a Pt–$Pt_{90}Rh_{10}$ thermocouple response, and the 2*θ* axis is calibrated with a room-temperature Guinier–Hägg pattern made with the same sample.

LOW-TEMPERATURE HEAT CAPACITIES AND THERMODYNAMIC FUNCTIONS

The heat capacities of åkermanite sample AK1 have been measured from 9 to 374 K using the method of intermittent heating under quasi-adiabatic conditions. The measured values of heat capacity (corrected for curvature, *e.g.*, Robie & Hemingway 1972) are listed in chronological order (Series) in Table 1.

Smoothed values for the thermodynamic properties of åkermanite sample AK1 are listed in Table 2. The entropy calculated at 298.15 K is 212.5 J/(mol•K), significantly larger than the value of 209.2 J/(mol•K) reported by Weller & Kelley (1963). The heat capacities reported by Weller & Kelley (1963) are 1 J/(mol•K) lower than the values given in Table 2 near 50 K, and the difference increases to 2 J/(mol•K) near 298 K. Although Weller & Kelley (1963) saw no evidence of other phases, the procedure they followed to synthesize åkermanite (dry sintering at a maximum temperature of 1523 K) should have produced some wollastonite and diopside (*e.g.*, Schairer *et al.* 1966). One half the sum of the heat capacities of two wollastonite, plus periclase, lime, and diopside is 19.4 % lower than that of åkermanite at 100 K and about 2.6 % less at 298.15 K (*e.g.*, Krupka *et al.* 1985b).

TABLE 1. EXPERIMENTAL LOW-TEMPERATURE HEAT CAPACITIES FOR ÅKERMANITE, $Ca_2MgSi_2O_7$

Temp.	Heat capacity	Temp.	Heat capacity	Temp.	Heat capacity
K	J/(mol·K)	K	J/(mol·K)	K	J/(mol·K)
Series 1		Series 3		Series 5	
302.10	216.1	358.79	256.7	144.50	125.4
306.75	217.8	359.39	241.1	148.79	128.9
311.56	220.5	359.87	228.6	153.06	132.1
316.39	222.3	360.23	232.8	157.33	135.3
321.18	224.1	360.64	237.1	161.60	138.5
325.96	226.7	361.06	233.3	165.86	141.5
330.73	228.7	361.49	235.0	170.13	144.5
335.49	230.4			174.40	147.6
340.24	233.2	Series 4		178.67	150.7
				182.96	153.4
Series 2		9.09	0.1357		
		10.29	0.2702	Series 6	
343.33	234.9	11.21	0.4464		
344.59	235.7	12.35	0.6287	187.27	156.1
345.79	236.3	13.80	0.9622	191.89	159.2
347.11	238.4	15.33	1.404	196.88	162.4
348.55	237.6	17.06	1.990	201.96	165.6
350.11	239.8	19.00	2.814	206.69	168.5
351.67	241.8	21.14	3.892	211.44	171.0
353.22	243.9	23.54	5.281	216.23	173.9
354.77	249.8	26.25	7.093	221.09	176.6
356.30	265.0	29.29	9.412	226.05	179.2
357.56	542.3	32.71	12.39	231.14	181.9
359.05	273.9	36.58	15.67	236.30	184.6
360.96	235.1	40.85	20.49	241.54	187.5
362.38	235.1	45.52	25.44	246.83	190.1
363.61	233.4	50.67	31.08	252.19	192.9
365.11	232.8	56.20	37.38	257.59	195.3
366.66	233.0	61.71	43.68	262.99	198.0
368.22	234.9			268.41	200.6
369.78	234.5	Series 5		273.84	203.1
371.33	234.0			279.26	205.6
372.89	235.3	67.13	49.98	284.64	208.2
374.44	235.5	72.15	55.67	290.00	210.7
		76.62	60.65	295.34	213.5
Series 3		81.24	65.69	300.68	214.7
		85.95	70.80	305.99	217.5
355.17	253.4	90.67	75.89	311.28	219.2
355.63	257.8	95.46	80.86	316.55	221.7
356.05	260.5	100.17	85.66		
356.48	261.2	104.81	90.33	Series 7	
356.89	276.1	109.39	94.70		
357.29	320.1	113.91	99.04	357.69	309.6
357.63	514.8	118.37	103.2		
357.91	894.4	122.81	107.1	Series 8	
358.26	406.1	127.20	111.1		
		131.56	114.8	359.23	241.7
		135.89	118.4	360.21	233.8
		140.20	122.0	361.15	233.5
				362.08	233.5

TABLE 2. SMOOTHED LOW-TEMPERATURE THERMODYNAMIC PROPERTIES FOR ÅKERMANITE, $Ca_2MgSi_2O_7$

Temp.	Heat capacity	Entropy	Enthalpy function	Gibbs energy function
T	C°_P	$S^\circ_T-S^\circ_0$	$(H^\circ_T-H^\circ_0)/T$	$-(G^\circ_T-H^\circ_0)/T$
Kelvin	J/(mol·K)			
5	0.021	0.008	0.005	0.002
10	0.248	0.065	0.050	0.015
15	1.306	0.329	0.262	0.068
20	3.330	0.957	0.754	0.203
25	6.353	2.010	1.557	0.452
30	10.00	3.467	2.639	0.828
35	14.35	5.330	3.996	1.333
40	19.41	7.566	5.598	1.969
45	24.86	10.17	7.435	2.732
50	30.38	13.07	9.452	3.619
60	41.74	19.61	13.88	5.727
70	53.21	26.91	18.68	8.224
80	64.36	34.74	23.70	11.04
90	75.15	42.95	28.82	14.13
100	85.49	51.41	33.97	17.43
110	95.33	60.02	39.11	20.91
120	104.7	68.72	44.19	24.53
130	113.5	77.45	49.18	28.27
140	121.8	86.17	54.07	32.09
150	129.8	94.85	58.86	35.99
160	137.3	103.5	63.53	39.94
170	144.5	112.0	68.08	43.92
180	151.4	120.5	72.52	47.94
190	158.0	128.8	76.85	51.98
200	164.3	137.1	81.06	56.03
210	170.3	145.3	85.17	60.08
220	175.9	153.3	89.17	64.14
230	181.4	161.3	93.06	68.19
240	186.6	169.1	96.85	72.23
250	191.7	176.8	100.5	76.26
260	196.6	184.4	104.1	80.27
270	201.3	191.9	107.7	84.27
280	206.0	199.3	111.1	88.25
290	210.6	206.6	114.4	92.20
300	214.9	213.9	117.7	96.14
310	219.2	221.0	120.9	100.1
320	223.6	228.0	124.1	103.9
330	228.3	235.0	127.1	107.8
340	233.4	241.8	130.2	111.6
350	238.9	248.7	133.2	115.5
273.15	202.8	194.3	108.7	85.52
298.15	214.1	212.5	117.1	95.41

TABLE 3. ENTHALPY OF FORMATION OF DIOPSIDE, $CaMgSi_2O_6$, AT 298.15 K

Enthalpy of formation kJ/mol	Reference
-3205.5	Neuvonen (1952)
-3217.0	Kracek (1953)
-3198.6	Navrotsky & Coons (1976)
-3203.3	Helgeson et al. (1978)
-3201.0	Charlu et al. (1981)
-3204.4	Wood & Holloway (1984)
-3199.9	Calculated from equilibrium data in Metz (1983) and Slaughter et al. (1975)

The enthalpy of formation of åkermanite (-3876.4 kJ/mol) was determined by Neuvonen (1952) using aqueous solution calorimetry. Charlu *et al.* (1981) obtained -3866.4 kJ/mol and Brouse *et al.* (1984) found -3865.0 kJ/mol using solution in molten $Pb_2B_2O_5$ and in eutectic $(Li,Na)BO_2$, respectively. Robie *et al.* (1979) and Helgeson *et al.* (1978) both adopted Neuvonen's value, inasmuch as it was the only information available at that time.

In the hope of resolving this discrepancy between the different values for the enthalpy of formation of åkermanite, we have used our new heat-capacity data for åkermanite, those for calcite and CO_2 from Robie *et al.* (1979) and those for diopside ($CaMgSi_2O_6$) from Krupka *et al.* (1985a) in combination with the equilibrium $P(CO_2)$ data for the reaction $CaCO_3 + CaMgSi_2O_6 = Ca_2MgSi_2O_7 + CO_2$ from Walter (1963) to extract an independent value of the enthalpy of formation for åkermanite. From a third-law analysis of the equilibrium data of Walter (1963), we obtain 151.5 kJ for the enthalpy of the reaction. Before we can compare this value with the values derived calorimetrically, we must first adopt a value for the enthalpy of formation of diopside, because the value given in Robie *et al.* (1979) appears to be seriously in error.

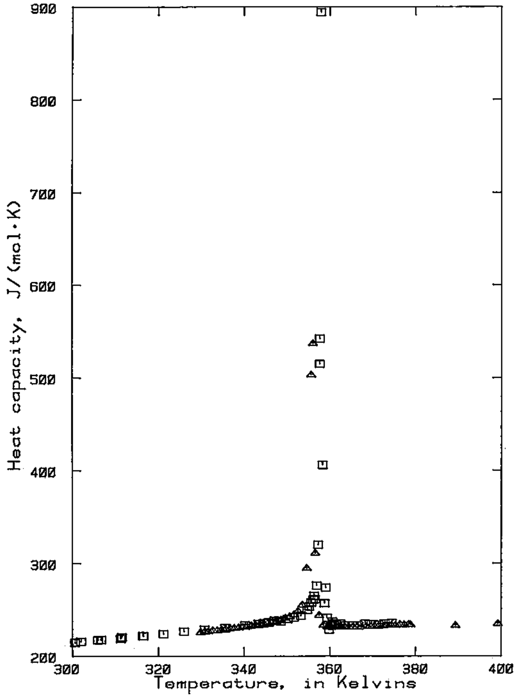

FIG. 1. Thermal anomaly in the heat-capacity data from DSC (triangles) and low-temperature adiabatic calorimeter (squares) for åkermanite sample AK1. The DSC peak is offset, as discussed in the text.

In Table 3 we summarize the existing values for the enthalpy of formation of diopside. Four of these values were obtained by calorimetry, two each by aqueous HF and by molten salt, and four were obtained by phase-equilibrium calculations. If we exclude the value by Kracek (1953), the average value is -3202.1 (± 3.5 e.s.d.) kJ/mol, which we shall adopt.

Combining the enthalpy of reaction calculated above from Walter's (1963) equilibrium data with values for the enthalpy of formation of calcite and CO_2 from Robie *et al.* (1979) and the value for diopside calculated above, we get -3864.5 kJ/mol for the enthalpy of formation for åkermanite. This result agrees favorably with the value measured by Brouse *et al.* (1984).

A thermal anomaly in the heat capacity of åkermanite was first observed in DSC measurements of sample AK1. The anomalous heat-capacity region lies within the range of the low-temperature calorimeter, providing a good opportunity to evaluate both the temperature scale and accuracy of enthalpy measurements of the DSC near room temperature.

The experimental values of heat capacity measured with each system in the region of the thermal anomaly are shown in Figure 1. Integration of the heat capacities from 330 to 365 K yields enthalpies that agree to 0.2%. However, the temperatures of the maximum heat-capacity for each data-set differ by 2.3 K. The difference in peak shape and maximum temperature reflects the difference in heating (scan) rates for the two systems (2.5 K/min for the DSC and 0.1 K/min for the low-temperature adiabatic calorimeter).

The temperature scale of the DSC is defined from 427 to 944 K as a practical scale based upon fixed points (extrapolated onset temperatures) established by the National Bureau of Standards and released as Standard Reference Materials 758 and 759 (see McAdie *et al.* 1972). Because the temperature sensors for the DSC are located in the base of the measurement cell, thermal resistance causes the sample temperature to lag behind the temperature indicated during the dynamic conditions under which heat capacities are measured. The amount of lag is proportional to the scan rate (*e.g.*, Richardson & Savill 1975). Errors resulting from thermal resistance can be minimized if the instrument is calibrated at the scan rate to be used for heat-capacity measurements. Figure 2 provides information on thermal lag measured for two commonly quoted transition fixed points, extrapolated onset temperature and peak temperature (*e.g.*, McAdie *et al.* 1972), for åkermanite sample AK1. Because we have calibrated these fixed points against our low-temperature scale, åkermanite sample AK1 has been added to our practical temperature-scale.

From the data provided in Figure 2 we can calculate the expected offset in the peak temperature for a scan made at 2.5 K/min on an instrument calibrated for 10 K/min. That difference of 2.3 K was left in the DSC data to help provide graphical clarity in Figure 1. The temperatures reported in Table 4 have been corrected for the difference in thermal lag.

TABLE 4. EXPERIMENTAL DSC HEAT CAPACITIES FOR ÅKERMANITE, $Ca_2MgSi_2O_7$, SAMPLE AK1

Temp. K	Heat capacity J/(mol•K)	Temp. K	Heat capacity J/(mol•K)	Temp. K	Heat capacity J/(mol•K)
Series 1		Series 3		Series 6	
369.4	228.9	697.8	271.9	966.8	288.2
379.4	231.0	707.7	274.0	976.8	289.6
389.3	233.1	717.7	274.0	986.7	292.6
399.2	235.0	727.7	275.9	995.6	292.8
409.1	236.4	737.6	276.4		
419.0	238.5	746.6	277.8	Series 7	
429.0	240.6				
439.0	242.3	Series 4		332.7	226.5
448.9	244.9			334.6	227.5
458.9	246.9	697.8	275.6	336.6	228.4
468.9	249.1	707.7	276.2	338.6	229.8
478.8	251.0	717.7	276.6	340.6	230.8
488.8	253.1	727.7	277.8	342.6	232.0
497.8	254.7	737.6	277.6	343.6	232.7
		747.6	278.0	344.6	233.9
Series 2		757.6	279.4	345.6	234.5
		767.5	279.9	346.5	235.2
468.6	248.3	777.5	281.3	347.5	236.2
478.6	249.5	787.5	281.8	348.5	237.0
488.5	251.2	797.4	283.7	349.5	237.7
498.5	252.0	807.4	282.9	350.5	238.9
508.5	253.8	817.3	283.3	351.5	240.5
518.4	255.5	826.3	284.1	352.5	242.2
528.4	256.8			353.5	244.6
538.3	258.0	Series 5		354.5	248.1
548.3	258.8			355.5	254.9
558.3	260.3	817.3	282.2	356.5	294.6
568.2	261.0	827.3	282.3	357.5	503.1
578.2	263.4	837.3	283.5	357.9	536.9
588.2	263.7	847.2	283.7	358.5	310.8
598.1	265.0	857.2	284.4	359.4	243.8
608.1	266.2	867.2	285.4	360.4	233.5
618.1	267.3	877.1	285.5	361.4	231.7
628.0	267.9	887.1	286.3	362.4	231.2
638.0	269.4	897.1	285.6	363.4	231.5
647.0	270.3	907.0	286.9	364.4	231.9
		917.0	288.8	365.4	231.8
Series 3		926.0	287.8	366.4	231.8
				367.4	231.6
618.1	267.8	Series 6		368.4	231.7
628.0	270.6			369.4	231.8
638.0	269.0	897.1	286.9	370.4	232.1
648.0	269.7	907.0	286.8	371.3	232.0
657.9	270.2	917.0	286.2	372.3	232.4
667.9	270.6	927.0	287.1	373.3	232.6
677.8	272.5	936.9	288.3	374.3	232.9
687.8	270.1	946.9	289.4	376.3	233.5
		956.8	287.9	378.3	234.1
				379.3	233.6

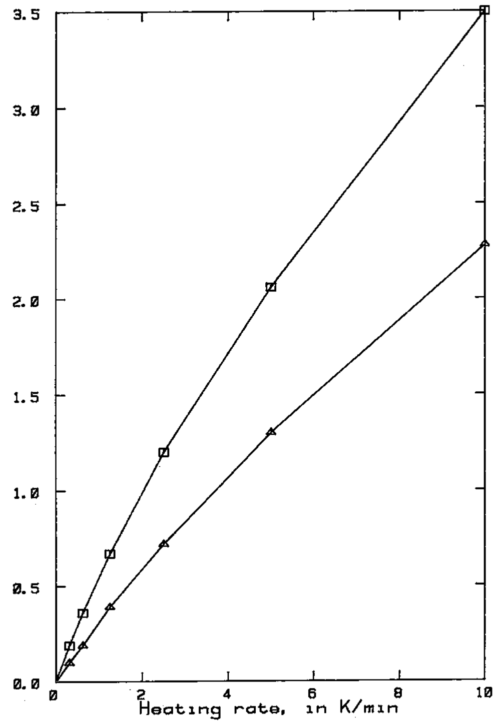

FIG. 2. Thermal lag measured for the extrapolated onset (triangles) and peak (squares) temperatures for åkermanite as a function of heating (scan) rate.

HIGH-TEMPERATURE HEAT CAPACITIES AND THERMODYNAMIC FUNCTIONS

The experimental values of heat capacity for åkermanite sample AK1 are listed in Table 4. The experimental results were combined with the low-temperature heat-capacity results discussed earlier in this paper and the high-temperature heat contents of Proks *et al.* (1977) and Pankratz & Kelley (1964). The data set was fit to an equation of the form suggested by Haas & Fisher (1976). The heat-capacity and heat-content data for åkermanite were combined and fit with equation (1):

$$C°_P = 78.146 + 0.165734\ T - 3.34372 \times 10^{-5}\ T^2 + 2864.64 T^{-0.5} - 6.7905 \times 10^6\ T^{-2} \text{ in J/(mol•K)} \quad (1)$$

with an average deviation of 0.6 % over the temperature range from 290 to 1731 K (excluding the region of the anomaly). Smoothed values of the heat capacity and derived thermodynamic functions are listed in Table 5.

The following special considerations were made in treating the data. Firstly, the enthalpy and entropy assigned to the thermal anomaly at 357.9 K were calculated from the difference between equation (1) and

TABLE 5. SMOOTHED HIGH-TEMPERATURE THERMODYNAMIC PROPERTIES FOR ÅKERMANITE, $Ca_2MgSi_2O_7$

Temp.	Heat capacity	Entropy	Enthalpy function	Gibbs energy function
T	C_P°	$S_T^\circ - S_0^\circ$	$(H_T^\circ - H_{298}^\circ)/T$	$-(G_T^\circ - H_{298}^\circ)/T$
kelvin			J/(mol·K)	
298.15	214.1	212.5	0.000	212.5
300	214.8	213.8	1.322	212.5
357.9	231.6	253.3	37.329	216.0
357.9	231.6	255.2	39.226	216.0
400	239.9	281.4	59.928	221.5
500	253.6	336.5	97.388	239.2
600	263.6	383.7	124.29	259.4
700	272.2	425.0	144.82	280.2
800	280.0	461.9	161.23	300.6
900	287.3	495.3	174.84	320.4
1000	294.2	525.9	186.44	339.5
1100	300.8	554.2	196.54	357.7
1200	306.9	580.7	205.48	375.2
1300	312.5	605.5	213.50	392.0
1400	317.7	628.8	220.76	408.1
1500	322.5	650.9	227.39	423.5
1600	326.7	671.9	233.46	438.4
1700	330.4	691.8	239.06	452.7
1731	331.4	697.8	240.70	457.1
1731	382.0	769.7	312.57	457.1
1800	382.0	784.6	315.23	469.4

smoothed curves drawn through the experimental results in the temperature range from 320 to 365 K. Secondly, the temperatures reported by Pankratz & Kelley (1964) were adjusted to the IPTS–68 temperature scale (a correction of + 1.1 to 1.7 K between 1100 and 1700 K). Finally, the melting point was corrected to 1731 K on the IPTS–68 scale from 1727 K on the Geophysical Laboratory temperature scale (Osborn & Schairer 1941). The corrections between temperature scales have been discussed by Biggar (1972).

Excessively large deviations of some of the heat-content values between 357 and 590 K led Pankratz & Kelley (1964) to speculate that a small thermal anomaly might exist in åkermanite. A thermal peak, centred at about 357.9 K, was detected in our heat-capacity data for åkermanite (Fig. 1). The heat-capacity anomaly showed no signs of hysteresis and could not be quenched. The enthalpy and entropy assigned to the anomaly at 357.9 K, for the purpose of tabulation, are 679 J/mol and 1.9 J/(mol•K), respectively.

The enthalpy and entropy of fusion, calculated from the heat-content data of Proks *et al.* (1977) and

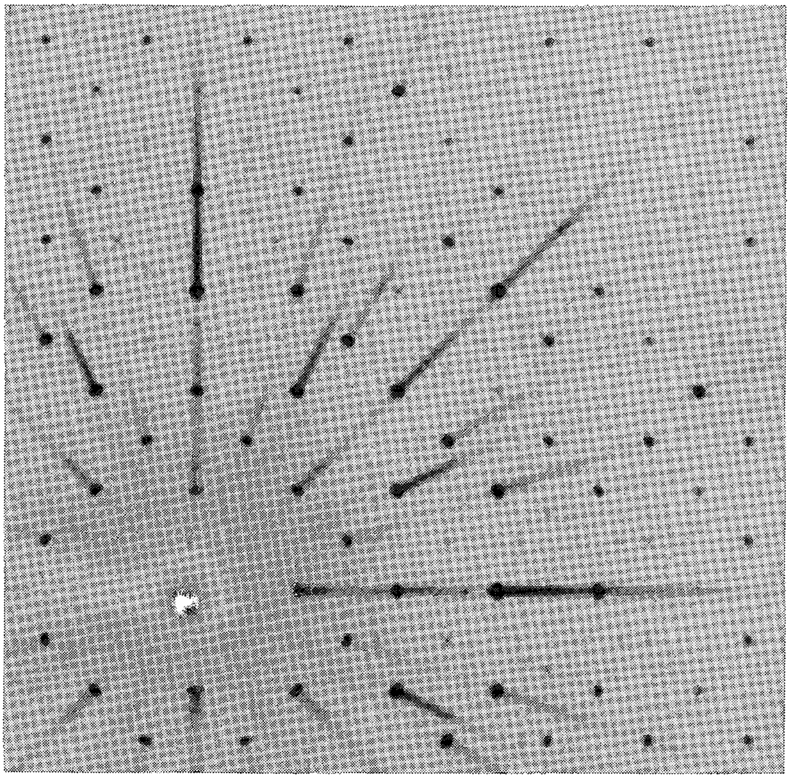

FIG. 3. Detail of a precession photograph (Mo$K\alpha$ radiation) of the $hk0$ net of synthetic åkermanite sample AKl, showing superstructure reflections. The a^* axes lie at 45°.

equation (1), are 123.6 ± 3.2 kJ/mol and 71.4 ± 1.8 J/(mol•K), respectively, at 1731 K, in good agreement with the analysis of Proks *et al.* (1977).

CRYSTALLOGRAPHY AND THERMAL EXPANSION OF ÅKERMANITE

The unit-cell parameters of åkermanite (tetragonal) were measured at 25°C (T,K = *t*,°C + 273.15) by the Guinier–Hägg method, from powder patterns made with monochromatized Cu$K\alpha_1$ radiation ($\lambda = 1.540562$ Å). Bragg angles for 41 lines were measured and scaled by a quadratic function determined by an internal standard (Si, NBS SRM 640, $a = 5.43075$ Å). The cell parameters were determined independently by diffractometer also using SRM 640 as an internal standard (least-squares fit to 32 lines). The following unit-cell edges (space group $P\bar{4}2_1m$) were found, and are compared with published values:

a,Å	*c*,Å	*V*,Å^3	Reference
7.8332(6)	5.0070(6)	307.26(5)	this work (Guinier–Hägg)
7.8345(7)	5.0073(4)	307.34(5)	this work (diffractometer)
7.8303(4)	5.0064(3)	306.96(3)	Woodhead (1977)
7.835(1)	5.010(1)	307.5(1)	Kimata & Ibaraki (1981)
7.8330(2)	5.0068(2)	307.22(1)	Morris *et al.* (1984)

These values yield a molar volume of 92.54(4) cm^3.

A heavily exposed single-crystal precession *hk*0 pattern was made, on which was discovered a complex set of satellite reflections (Fig. 3). These satellites are associated with the normal lattice points, but their spacings are incommensurate with the basic *hk*0 net. Kimata & Ibaraki (1981) did not observe these satellites, but their Weissenberg patterns may not have been exposed long enough to reveal them. An identical array of satellite reflections was registered by crystals from preparations AK1, AK2 and 75014. The same satellites are more intensely developed on electron-diffraction patterns because of dynamic interactions. A preliminary electron-diffraction study

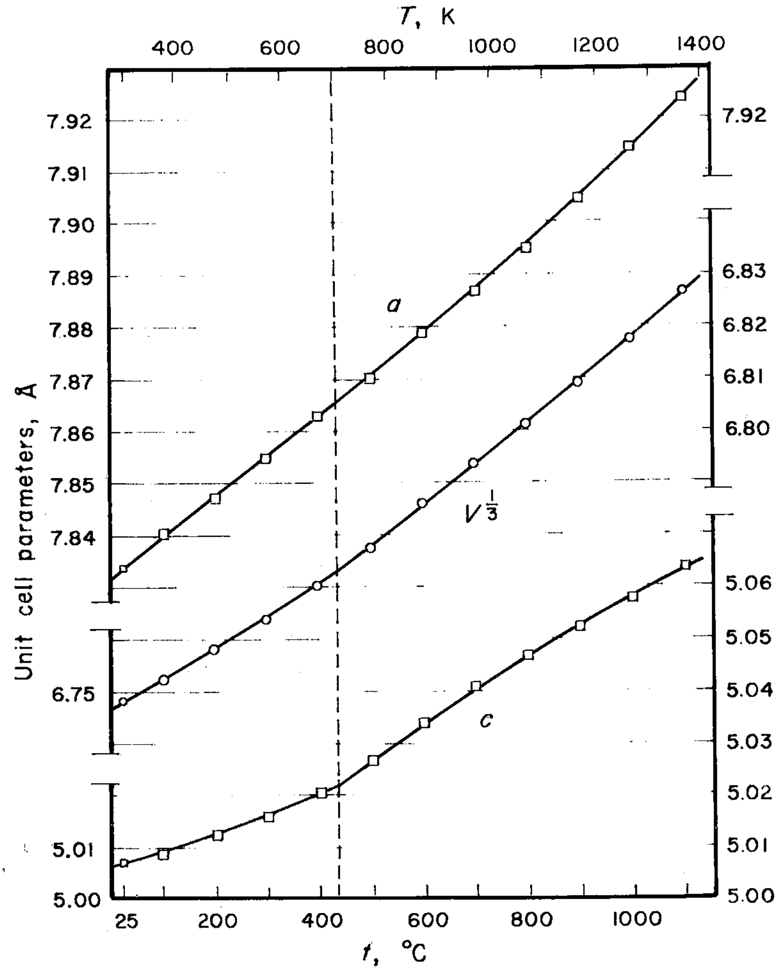

FIG. 4. Change of unit-cell parameters with temperature in åkermanite sample AKl.

by *in situ* heating has shown that the satellite reflections weaken abruptly at 358 K and reappear, as abruptly, as the sample is cooled. Above this point, very faint and diffuse satellites can still be discerned, which fade gradually and can no longer be detected above about 580 K. These phenomena are all reversible at least up to 800 K. This behavior may be explained by local displacements of the Ca ions from the mirror planes accompanied by distortion of the $MgSi_2O_7$ framework. This phenomenon, together with results of a detailed crystal-structure analysis, will be more fully described in another paper.

The change in the cell constants of åkermanite was measured by the Guinier–Lenné method over the temperature range 20–1100°C using monochromatized Cu*K*α radiation. The 2*θ* values of 41 indexed lines were measured at intervals of 100°C, and used to derive the corresponding unit-cell parameters (tetragonal) by least-squares analysis at each temperature. The results of this analysis are given in Table 6 and plotted in Figure 4.

Unfortunately, facilities were not available to extend the thermal X-ray study to temperatures below room temperature, which would have been desirable to look for any anomaly in expansion in the region of the heat-capacity anomaly described in the previous section. No perceptible change was seen in the X-ray pattern near 80°C, corresponding to the observed heat-capacity anomaly. The thermal expansion is nearly linear, but at about 430°C, a small but clearly discernable change in slope in the expansion curves is apparent (at the dashed line in Fig. 4), particularly in that of the *c* axis. Various fits of the coefficients α and β were attempted by least-squares analysis for the empirical equation $p = p_0(1 + \alpha t + \beta t^2)$, where p is the parameter in question (p_0 its value at 0°C) and t the temperature in °C. The standard deviations of the observations (in Å) indicate the quality of fit in each case, as follows:

	$\sigma(a)$	$\sigma(c)$	$\sigma(VT^{1/3})$
Single line ($\beta = 0$)	0.0015	0.0023	0.0018
Single quadratic	0.0006	0.0015	0.0005
Two lines:			
20–400°C	0.00059	0.00058	0.00036
500–1100°C	0.00082	0.00093	0.00054
Two quadratics:			
20–400°C	0.00060	0.00033	0.00027
500–1100°C	0.00042	0.00053	0.00044

The best fit is provided by the two quadratic curves, and the corresponding coefficients are given in Table 6. The two curves intersect at 420 ± 15°C.

TABLE 6. CELL CONSTANTS AND THERMAL EXPANSION PARAMETERS FOR ÅKERMANITE

Temperature, °C	a, Å	c, Å	V, Å^3	V, Å$^{1/3}$
		Cell constants		
±5	±0.0011	±0.0009	±0.09	±0.0006
20	7.8334	5.0070	307.24	6.7477
100	7.8405	5.0089	307.91	6.7526
200	7.8472	5.0127	308.67	6.7582
300	7.8551	5.0158	309.48	6.7641
400	7.8630	5.0202	310.38	6.7707
500	7.8700	5.0265	311.32	6.7775
600	7.8788	5.0337	312.47	6.7858
700	7.8867	5.0409	313.55	6.7936
800	7.8949	5.0466	314.55	6.8009
900	7.9045	5.0520	315.66	6.8088
1000	7.9141	5.0575	316.77	6.8168
1100	7.9232	5.0637	317.89	6.8258
		Parameters for quadratic equations of thermal expansion		
20-420°C				
p_0	7.8321	5.0063	307.09	6.7467
α ($\times 10^5$)	0.99	0.53	2.49	0.83
β ($\times 10^9$)	-0.15	4.14	4.35	1.53
420-1100°C				
p_0	7.8343	4.9871	306.04	6.7419
α ($\times 10^5$)	0.82	1.76	3.44	1.02
β ($\times 10^9$)	1.95	-3.37	0.70	1.01
$\sigma(p)$ overall	0.00050	0.00047	0.040	0.00039

DISCUSSION

Heat-capacity measurements were also made on synthetic samples AK2 and 75014 to ensure that the thermal anomaly observed in the heat-capacity data is not related to the small deviation of sample AK1 from the stoichiometric åkermanite composition or to impurities in the starting materials. Sample AK2, prepared as stoichiometric åkermanite from the same starting materials as AK1, and sample 75014, prepared with a different procedure and from different starting materials, both show small thermal anomalies in the same region of temperature as sample AK1; however, the magnitude and transition temperature vary significantly (Fig. 5); yet microprobe analyses yield exactly the same composition, within the limits of experimental error.

The thermal anomaly exhibited by samples AK2 and 75014 is smaller and at a lower temperature than for sample AK1. Between 330 and 365 K, the values of entropy associated with the thermal anomaly in samples AK2 and 75014 are about 75 and 25%, respectively, of that for sample AK1. The temperature assigned to the anomaly is 352.6 and 347.6 K, respectively, for AK2 and 75014. The anomaly shape and temperature are somewhat dependent upon the scan rate of the DSC, as shown in Figure 5, where the anomaly in sample AK1 is shown for scan rates of 2.5 and 5 K/min. The values of entropy were calculated from DSC scans at 5 K/min and were referred to the same empty and corundum (standard) scans (*e.g.*, Hemingway *et al.* 1981).

In Figure 5, it can be seen that accompanying the decrease in size and temperature, there is also a broadening of the interval of anomalous heat-capacity. Although these features could be caused by dilution of a chemical component responsible for the thermal anomaly, this is considered highly unlikely here. Such behavior is typical of increased strain in the crystals, creating local distortions of the crystal field at the site where a transition takes place. Small size of crystals (high surface/volume ratio) and the presence of a high density of dislocations, either free or at subgrain boundaries and twin boundaries, as well as misfit distortions at twin boundaries are factors that can contribute to strain in crystals.

Samples AK2 and 75014 show a moderate density of growth twins and a decrease in average grain-size. The increase in number of growth twins and decrease in grain size directly correlate with the decrease in the observed thermal anomalies and, therefore, growth twinning and grain size likely alter the local crystal-fields responsible for the transition in åkermanite.

Woodhead (1977) examined twinning in synthethic gehlenite, $Ca_2Al(Al,Si)O_7$, and concluded that growth twinning most likely had (001) as the composition plane with a twin law of (130), a mirror operation, and bonding through the Ca ions. Woodhead (1977) further concluded that of each 20 Ca ions on the composition plane of the twins, the oxygen co-ordination polyhedra of 8 Ca ions would be slightly strained, and 4 of the polyhedra would be highly strained.

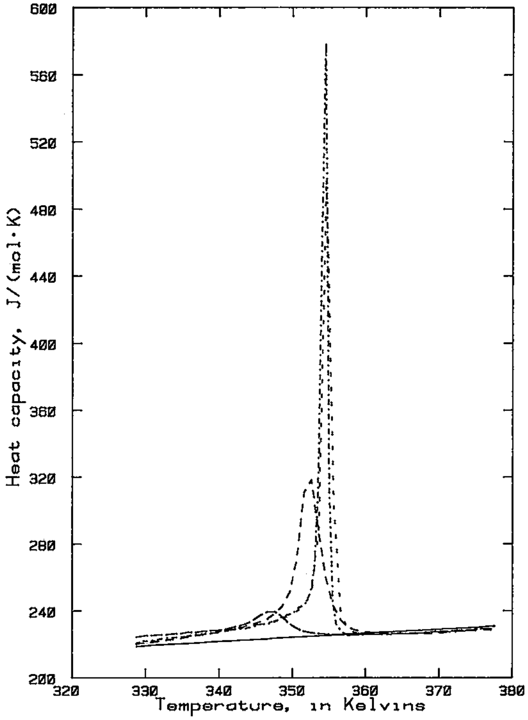

FIG. 5. Heat capacities of several samples of synthetic åkermanite between 328 and 378 K. The effect of DSC scan rate may be seen from a comparison of the heat capacities of sample AK1 determined at 5 K/min (small dash – large space pattern) and at 2.5 K/min (dash-dot pattern). Samples AK2 and 75014 are shown as medium- and long-dash patterns, respectively (DSC rate was 5 K/min). The smooth curve is from equation (1).

Åkermanite is isostructural with gehlenite and should develop twinning following the same twin law. The decrease in the thermal anomaly in åkermanite possibly is correlated with increased distortion of the oxygen polyhedra surrounding the Ca ions. This interpretation is consistent with the interpretation of the incommensurate satellite-reflections discussed in the preceding section.

CONCLUSION

The thermal behavior of synthetic åkermanite is generally normal, except for two unexpected, small anomalies: (1) a small heat-effect at about 357.9 K observed in the calorimetric but not in the expansion measurements, and (2) a small, but distinct, abrupt change in thermal-expansion behavior at 693 K observed in the X-ray unit-cell measurements but not in the calorimetric measurements. The source of these anomalies is unknown. There is probably some connection between them and the single-crystal satellite X-ray reflections referred to earlier, since the latter weaken markedly and reappear reversibly at the same temperature as the heat-capacity anomaly at 358 K. Our working hypothesis is that they are probably involved with local displacements of the calcium ions from the mirror planes, accompanied by distortions in the $MgSi_2O_7$ framework.

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