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A Study of the MgO–V_2O_5 System

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An investigation was made of solid–solid reactions in MgO/V_2O_5 mixtures of various stoichiometries. Three compounds were obtained, viz., $Mg_3V_2O_8$, $Mg_2V_2O_7$, and MgV_2O_6; no evidence was obtained to indicate formation of other MgO–V_2O_5 compounds reported in the literature. DTA data are listed for the three compounds and some observations are made on the mechanism of formation of the compounds. A new polymorph of $Mg_2V_2O_7$ was prepared, and its space group and cell parameters were deduced from the X-ray powder diffraction pattern. This polymorph undergoes a transition, reversible with difficulty, at 980–990°K.

Introduction

A number of phase studies have been made of the MgO–V_2O_5 system (*1–7*), but much of the data is contradictory. There is general agreement that the orthovanadate ($Mg_3V_2O_8$), the pyrovanadate ($Mg_2V_2O_7$), and the metavanadate (MgV_2O_6) are stable compounds and their crystal structures have recently been determined (*8–10*). However, King and Suber (*1*) and Speranskaya (*2*) find no evidence for metavanadate formation and suggest that this phase is $Mg_3V_4O_{13}$. On the other hand, Matveevicheva et al. (*3*), Wollast and Tazairt (*4*), and Pollert (*5*) find no evidence for $Mg_3V_4O_{13}$. The pyrovanadate has been reported to have one reversible transition at about 1185°K (*2, 4, 7*), but Wollast and Tazairt (*4*) suggest that another transition occurs at 1011°K. Other phases which have been reported include MgV_4O_{11} and $Mg_7V_6O_{22}$(*11*).

Of these investigations, only Speranskaya (*2*) and Wallast and Tazairt (*4*) have reported on the phases formed in MgO–V_2O_5 solid–solid reaction below liquidus temperatures and their results are not in agreement. The present investigation was therefore undertaken to resolve the phase contradictions and as a study of the nature of the solid–solid reactions between MgO and V_2O_5.

Experimental

V_2O_5 and MgO were laboratory-grade oxides preheated at 870 and 1070°K, respectively for 48 hr. The reaction mixtures were prepared by weighing out the oxides in the appropriate molar ratios, mixing being effected by shaking followed by thorough grinding in an agate mortar.

Reactions were carried out in air in a Nichrome-wound tube furnace and regulated to ± 2°K by means of a proportional controller, the samples being contained in platinum boats inside a 30-mm diameter silica tube. During heating, the samples were removed periodically and ground thoroughly to ensure complete reaction.

DTA curves were obtained using a Standata 5-50, fitted with Pt/13% Rh, Pt thermocouples and controlled by a Stanton–Redcroft linear temperature variable rate programmer. The reference material was Al_2O_3, previously ignited at 1270°K. Sample and reference (100 mg) were contained in platinum crucibles set in a ceramic block, and the heating rate (except where otherwise stated) was 10°K min^{-1}. All curves were obtained using a static air atmosphere, and all temperatures of thermal events were recorded as peak temperatures. The apparatus was calibrated with A.R. K_2SO_4; the extrapolated onset temperature of the $\alpha \rightarrow \beta$ transition in this salt was found to be 856 ± 2°K, in agreement with McAdie (*12*).

A Philips PW 1050/25 X-ray diffractometer set was used to record the X-ray powder patterns of the various reaction products. The radiation employed was Ni-filtered CuK_α and the scan speed was 0.125°/min.

The density of powdered $Mg_2V_2O_7$ quoted in the text was obtained by displacement of dry toluene from a specific gravity bottle.

Results and Discussion

Preparation and Properties of Magnesium Vanadates

The three compounds $Mg_3V_2O_8$, $Mg_2V_2O_7$, and MgV_2O_6 were prepared from $MgO-V_2O_5$ mixtures of appropriate stoichiometries by heating for up to 21 days at 1100, 1100, and 970°K, respectively. All three compounds gave X-ray powder diffraction patterns in good agreement with previously reported patterns (*3–5*, *7*, *13*) and with those calculated from published single-crystal data (*8–10*). DTA data for these compounds are given in Table I and agree well with previously published results (*2*, *4*, *7*, *14*). The small endotherm at 840°K in MgV_2O_6 has not been reported previously for this compound, though Speranskaya (*2*) attributed an endothermic event at 849°K to a polymorphic transition of $Mg_3V_4O_{13}$.

$Mg_3V_2O_8$ and MgV_2O_6 could be prepared by heating appropriate mixtures of the component oxides for extended times at any temperature above 870 and 770°K, respectively (see Table III). However, $Mg_2V_2O_7$ prepared below 970°K showed a set of X-ray diffraction lines entirely different from those of preparations made at 1100°K, and the DTA curve of this low-temperature preparation showed an endothermic event at 1040°K in addition to the polymorphic transition at 1184°K (Table I).

TABLE I

DTA DATA FOR MAGNESIUM VANADATES TO 1250°K

Compound	Event	Intensity	Peak Temperature (°K)	Assignment	Comparison literature values (°K)	References
$Mg_3V_2O_8$	None					
$Mg_2V_2O_7$	Endotherm	M	1184	$\beta \rightarrow \gamma$ polymorphic transition	1183–1190	*2, 4, 7, 14*
MgV_2O_6	Endotherm	W	840	$\alpha \rightarrow \beta$ polymorphic transition	849[a]	*2*
	Endotherm	VS	1036	Peritectic melting to V_2O_5 and $Mg_2V_2O_7$	1029–1038	*4, 7, 14*

[a] Attributed to an $\alpha \rightarrow \beta$ polymorphic transition of $Mg_3V_4O_{13}$.

TABLE II

X-Ray Powder Diffraction Data for α-$Mg_2V_2O_7$[a]

d_{Obs} (pm)	*h k l*	$(I/I_0)_{Obs}$ (%)	d_{Calc} (pm)	$(I/I_0)_{Calc}$ (%)
480.6	1 1 $\bar{1}$	50	480.8	49
466.2	0 0 2	10	466.2	9
424.3	1 1 1	14	424.7	10
416.9	1 0 $\bar{2}$	13	416.9	14
407.8	0 1 2	16	407.8	16
384.0	0 2 1	12	383.5	11
373.6	1 1 $\bar{2}$	53	373.6	49
353.4	1 2 0	65	353.1	65
324.6	2 0 0	53	324.6	51
322.9	1 1 2	28	322.6	19
312.2	0 2 2	100	312.3	100
303.9	2 1 $\bar{1}$	45	303.8	43
303.1	2 1 0	60	302.9	63
296.2	1 2 $\bar{2}$	19	296.1	14
292.9	2 0 $\bar{2}$	17	292.9	11
291.7	0 1 3	85	291.6	89
276.8	2 1 $\bar{2}$	37	276.7	32
268.8	1 2 2	39	268.8	37
	0 3 1		268.6	
257.5	2 2 $\bar{1}$	62	257.6	60
	1 3 0		257.5	
	2 2 0		257.0	
250.1	1 1 3	11	250.2	8
	0 2 3		250.0	
245.8	2 0 2	31	245.9	33
	1 2 $\bar{3}$		245.9	
243.7	1 3 1	23	243.7	22
238.5	2 1 1	40	238.9	48
	2 1 $\bar{3}$		238.4	
236.2	2 1 2	14	236.1	14
232.9	1 0 $\bar{4}$	16	233.5	18
	0 0 4		233.1	
	1 3 $\bar{2}$		232.7	
224.6	1 1 $\bar{4}$	34	225.0	35
	0 1 4		224.6	
212.9	3 1 $\bar{1}$	10	212.8	9
212.4	2 3 $\bar{1}$	10	212.6	9
	2 2 2		212.3	
	2 3 0		212.2	
210.4	0 4 0	8	210.4	7
207.6	1 0 4	7	207.5	6
204.1	1 2 $\bar{4}$	10	204.2	10
	0 2 4		203.9	
195.0	3 2 $\bar{1}$	9	194.9	8
192.5	3 2 0	15	192.4	16
187.9	1 4 $\bar{2}$	18	187.8	21
186.8	2 2 $\bar{4}$	18	186.8	17
185.0	2 2 3	7	185.2	5
	2 3 2		184.9	
179.51	3 1 2	10	179.52	8
	1 3 $\bar{4}$		179.47	
	0 3 4		179.27	
171.07	2 1 4	8	171.02	7
164.34	3 3 1	6	164.29	5
162.08	4 1 $\bar{1}$	21	162.03	19
	3 2 $\bar{4}$		162.03	
159.91	4 1 $\bar{2}$	8	159.92	8
	2 4 2		159.86	
159.33	4 1 0	14	159.35	14
	1 5 1		159.23	
158.48	1 2 5	5	158.45	5
156.18	1 4 $\bar{4}$	11	156.30	12
	0 4 4		156.17	
	1 5 $\bar{2}$		15.606	
155.39	0 0 6	10	155.40	10
	0 3 5		155.29	
153.82	4 2 $\bar{1}$	17	153.71	16
	3 3 2		153.70	
151.49	1 5 2	33	151.62	34
	2 0 $\bar{6}$		151.48	
	4 2 0		151.42	
149.34	2 5 0	56	149.41	54
	2 3 $\bar{5}$		149.31	
	3 4 $\bar{2}$		149.25	
147.80	0 5 3	52	147.99	60
	2 1 5		147.82	
	1 2 $\bar{6}$		147.81	
	1 1 4		147.74	
145.15	1 0 6	20	145.18	23
	4 0 2		145.17	

[a] Cell parameters: $a = 660.5 \pm 0.3$ pm; $b = 841.5 \pm 0.5$ pm; $c = 948.7 \pm 0.9$ pm; $\beta = 1.756 \pm 0.002$ rad. Space group: $P2_1/c$.

Microscopic examination showed this preparation to be a single crystalline phase, and it was convertible by heating for a few minutes at 1070°K into a product identical with the pyrovanadate prepared by reaction at 1100°K. The DTA endotherm at 1040°K

TABLE III

PRODUCTS OBTAINED BY REACTION OF VARIOUS $MgO-V_2O_5$ MIXTURES FOR 14 DAYS AT VARIOUS TEMPERATURES[a]

	1010°K							870°K							770°K						
	7:2	3:1	5:2	2:1	3:2	1:1	2:3	7:2	3:1	5:2	2:1	3:2	1:1	2:3	7:2	3:1	5:2	2:1	3:2	1:1	2:3
$Mg_3V_2O_8$	1	1	1					1	1	1					3	3	3				
α-$Mg_2V_2O_7$								3	2	1	1	1			1	1	1	1	2		
β-$Mg_2V_2O_7$		3	1	1	1																
MgV_2O_6					1	1	1				3	1	1	1				3	1	1	1
MgO	2							2	2	3	3	3	3		1	2	2	3	3	3	
V_2O_5							2							2					3	3	2

[a] Key to symbols: 1, major constituents; 2, minor constituents (>10%); 3, trace constituents (<10%).

is therefore assignable to a transition between two polymorphic forms. The temperature of this endotherm, however, was found to vary significantly with the DTA heating rate, and the equilibrium transition temperature is considerably lower than 1040°K. This is discussed more fully below.

The existence of the low-temperature polymorph has been reported by Wollast and Tazairt (*4*), but the X-ray powder pattern published by these workers indicates that they did not prepare it in a pure form. Pedregosa et al. (*15*) have recently reported a polymorph of $Mg_2V_2O_7$ isostructural with α-$Mg_2P_2O_7$ (*16*). However, no X-ray data are given. In the present study, a product free from X-ray lines of residual oxides and of other vanadates was obtained by heating an oxide mixture of stoichiometry $2MgO:V_2O_5$ at 930°K for 15 days. The infrared absorption spectrum (to be published) and the X-ray powder pattern of the product closely resembled those of cobalt pyrovanadate, $Co_2V_2O_7$, which is monoclinic with space group $P2_1/c$ (*17*). The $Mg_2V_2O_7$ polymorph was therefore taken to be isostructural with $Co_2V_2O_7$, and the powder pattern was indexed accordingly (Table II). The calculated cell parameters were: $a = 660.5 \pm 0.3$ pm; $b = 841.5 \pm 0.5$ pm; $c = 948.7 \pm 0.9$ pm; $\beta = 1.756 \pm 0.002$ rad. The density of the powder calculated from these parameters, with $Z = 4$ as in cobalt pyrovanadate (*17*), is 3.365×10^3 kg m^{-3}. The experimentally measured density was 3.39×10^3 kg m^{-3}.

Structure factors were calculated using atomic positional parameters identical with those of cobalt pyrovanadate (*17*) and using published atomic scattering factors for Mg^{2+}, V^{3+}, and O^- (see *9*, p. 2491). From 50 peaks, an R value of 0.048 was obtained.

In the following discussion, this monoclinic form of $Mg_2V_2O_7$ will be referred to as the α-form, and the triclinic polymorph into which it is converted at the first transition will be referred to as the β-form. The third polymorph, stable above the second polymorphic transition (at 1184°K) is called the γ-form. These correspond respectively to the β, α, and α′ polymorphs described by Wollast and Tazairt (*4*).

Solid-Solid Reactions in $MgO-V_2O_5$ Mixtures

Oxide mixtures were prepared with $MgO:V_2O_5$ molar ratios of 7:2, 3:1, 5:2, 2:1, 3:2, 1:1, and 2:3, and samples were heated at 1010, 870, and 770°K for 14 days. The phases present in the products of these reactions, as determined by X-ray powder diffractometry, are given in Table III. DTA curves of all products were also obtained.

(*i*) *1010°K*. The 3:1, 2:1, and 1:1 mixtures each formed a single compound, corresponding in stoichiometry to the composition of the mixture; thus, the 3:1 mixture produced $Mg_3V_2O_8$ and the 1:1 mixture formed MgV_2O_6. The 2:1 mixture produced β-$Mg_2V_2O_7$.

The intermediate mixtures (5:2, 3:2) each formed two compounds, the 5:2 mixture yielding $Mg_3V_2O_8$ and β-$Mg_2V_2O_7$ while the 3:2 mixture produced β-$Mg_2V_2O_7$ and MgV_2O_6. No evidence was found, either in the X-ray powder pattern or in the DTA curves of the products of 3:2 mixtures, to suggest the formation of the compound $Mg_3V_4O_{13}$ (*1*, *2*). These conclusions on the question of the existence of $Mg_3V_4O_{13}$ are in agreement with those of Matveevicheva *et al.* (*3*) and of Wollast and Tazairt (*4*).

The extreme compositions (7:2, 2:3) each produced the compound having stoichiometry nearest to that of the mixture, with one or other oxide in excess. No evidence was found for the formation of MgV_4O_{11} or $Mg_7V_6O_{22}$ (*11*).

(*ii*) *870°K*. The results obtained at this temperature were similar to those at 1010°K, except that the reactions were less complete, particularly in mixtures of high MgO content, and that α-$Mg_2V_2O_7$ was formed in place of the β-polymorph. The DTA curve of the α-form showed the two endotherms, at 1040 and 1184°K, corresponding respectively to the $\alpha \rightarrow \beta$ and $\beta \rightarrow \gamma$ transitions; the former transition is discussed in more detail below. A small amount of $Mg_2V_2O_7$ was detected in the products of the 3:1 reaction; however, the 3:1 reaction still yielded mainly $Mg_3V_2O_8$. The product of the 1:1 reaction showed a small endotherm at 960°K, corresponding to MgV_2O_6/V_2O_5 eutectic melting (*4*, *7*), indicating the presence of a little unchanged V_2O_5 in the product.

The 3:2 oxide mixture again formed MgV_2O_6 and $Mg_2V_2O_7$, rather than $Mg_3V_4O_{13}$. The DTA curve of the product showed a large endotherm at 1033°K, assignable to the combined processes of MgV_2O_6 peritectic melting and the $Mg_2V_2O_7$ $\alpha \rightarrow \beta$ transition. (These peaks are resolved under some conditions; see 770°K results).

(*iii*) *770°K*. In most cases, the products obtained at this temperature were the same as those produced at 870°K, though the reactions were in general much less complete. The 3:1 and 7:2 oxide mixtures, however, produced mainly α-$Mg_2V_2O_7$ with much unchanged MgO, the yield of $Mg_3V_2O_8$ being small. This behavior is discussed further below.

The 3:2 reaction again produced a mixture of α-$Mg_2V_2O_7$ and MgV_2O_6, though with some unchanged oxides. In the DTA curve of this mixture of products, the MgV_2O_6 peritectic melting endotherm and the $Mg_2V_2O_7$ $\alpha \rightarrow \beta$ transition endotherm were again coincident, though in the earlier stages of reaction (e.g., 3:2 oxide mixture heated at 770°K for 3–4 days) they were partially resolved into a doublet.

The early stages of reaction in 2:1 and 3:1 mixtures at 870°K were studied using X-ray powder diffractometry to estimate the composition of samples withdrawn at intervals

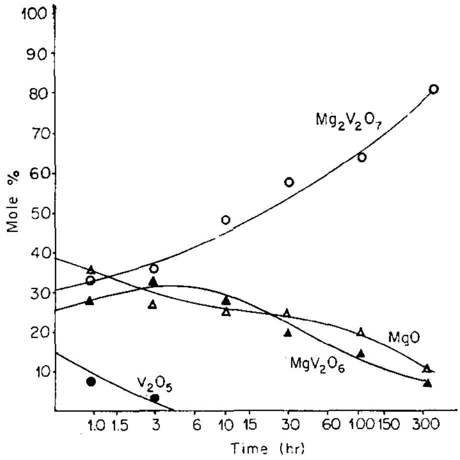

FIG. 1. Composition of products obtained from a $2MgO:V_2O_5$ mixture heated at 870°K.

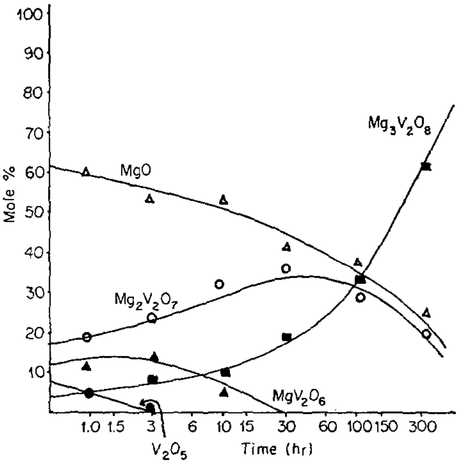

FIG. 2. Composition of products obtained from a $3MgO:V_2O_5$ mixture heated at 870°K.

from the reacting mixtures. The variation of composition with time for the two systems is shown in Figs. 1 and 2. Both systems produced significant amounts of MgV_2O_6 in the early stages of reaction, and preliminary experiments in which single MgO crystals were embedded in powdered V_2O_5 and heated also confirmed this tendency, X-ray diffractometry and electron microprobe analysis both detecting only MgV_2O_6 in the product of the single-crystal reaction after 4 days at 820°K.

This evidence, together with the observation that $Mg_2V_2O_7$ is a major product of incomplete reaction of 3:1 and 7:2 mixtures at 770°K, indicates that MgV_2O_6 is the first detectable product of solid–solid reaction between MgO and V_2O_5, and that $Mg_2V_2O_7$ and $Mg_3V_2O_8$ are formed sequentially by further reaction with MgO in the presence of sufficient amounts of this oxide, at sufficiently elevated temperatures.

The $Mg_2V_2O_7$ $\alpha \rightarrow \beta$ Polymorphic Transition

In pure $Mg_2V_2O_7$, the $\alpha \rightarrow \beta$ transition temperature measured by DTA was found to vary markedly with heating rate. At a heating rate of 10°K min^{-1}, the observed transition temperature was 1040°K, whereas at 2°K min^{-1} it was 1032°K and at 0.5°K min^{-1}, 1025°K. The true equilibrium transition temperature is therefore below 1025°K. Further evidence to support this contention is the observation that when a $2MgO:V_2O_5$ mixture was heated at 980°K, α-$Mg_2V_2O_7$ was formed, while reaction at 1000°K produced the β-polymorph. At 990°K, a mixture of both forms was obtained. The equilibrium transition temperature is therefore in the range 980–1000°K, though the rate of conversion of α-$Mg_2V_2O_7$ to the β-form is low at temperatures below 1025°K.

Variation of the observed transition temperature was also seen in impure α-$Mg_2V_2O_7$ samples containing MgO. The effect was particularly marked in the products of the 5:2, 3:1 and 7:2 reactions at 770°K, all of which contained α-$Mg_2V_2O_7$ and unchanged MgO and showed an upward displacement of the $\alpha \rightarrow \beta$ transition temperature (Fig. 3), together with a slight depression of the $\beta \rightarrow \gamma$ transition temperature. It therefore seems probable that MgO stabilizes the α and γ forms relative to the β-polymorph; similar behavior has been noted by Angenault (*18*) in $Cd_4V_2O_9$/CdO mixtures.

The $\alpha \rightarrow \beta$ transition is a particularly energetic one; the DTA endotherm due to this transition has approximately twice the area of the $\beta \rightarrow \gamma$ transition endotherm, and a quantitative DTA determination of the $\alpha \rightarrow \beta$ transition enthalpy (ΔH_T) at a heating rate of 10°K min^{-1}, using the K_2CrO_4 $\alpha \rightarrow \beta$ transition at 938°K as calibrant, led to a value of 26.0 ± 1.5 kJ mol^{-1}.

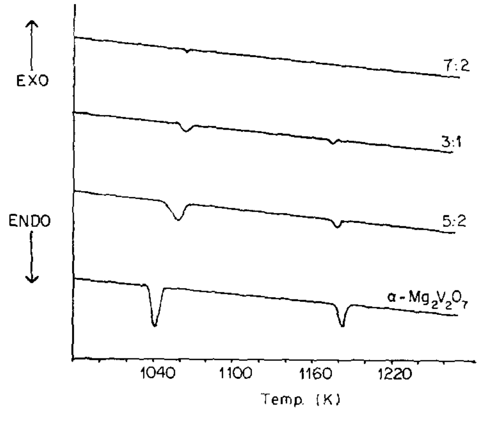

FIG. 3. DTA curves of products obtained by reaction of various MgO–V_2O_5 mixtures for 14 days at various temperatures.

This high value of ΔH_T may be due to the large difference in the distances between adjacent $V_2O_7^{4-}$ ions in the α and β forms. In the β-form, the eight V–O bond lengths of the $V_2O_7^{4-}$ ion range from 163 to 182 pm, and there are two additional weak bonds of 244 and 287 pm between adjacent $V_2O_7^{4-}$ ions (*9*). Since the atomic positional parameters of $Co_2V_2O_7$ (*17*) satisfactorily account for the observed X-ray line intensities of α-$Mg_2V_2O_7$, the V–O bond lengths in the latter must be very similar to those of the former. These range from 164 to 185 pm for the eight bonds of the $V_2O_7^{4-}$ ion, and the next nearest neighbors of the vanadium atoms are oxygen atoms of adjacent $V_2O_7^{4-}$ ions at 330 pm. The effective coordination number of vanadium in the two polymorphs is therefore significantly different and may account for the high value of ΔH_T.

Unlike the $\beta \rightarrow \gamma$ transition, the $\alpha \rightarrow \beta$ transition is not easily reversed on cooling. Reconversion of the β-form to the α-form was found to occur only when the β-form was heated for extended periods at temperatures below 980–990°K, indicating that the equilibrium transition temperature lies in the range 980–990°K. The reconversion is virtually complete in 2–3 hr at 920°K or in 200 hr at 780°K. Since the reconversion process involves breakage of two V–O bonds of 244 and 287 pm per $V_2O_7^{4-}$ ion, it would be expected that the activation energy of the $\beta \rightarrow \alpha$ transition would be larger than that of the $\alpha \rightarrow \beta$ transition. Hence, the $\beta \rightarrow \alpha$ transition is the slower process. The process of transition may be complex, since it was observed that if β-$Mg_2V_2O_7$ was partly converted to the α-form by heating at 850°K for 1 hr, the DTA curve of the product showed a doublet endotherm at the transition temperature, whereas in the pure α-form the endotherm is a singlet. The X-ray powder pattern of the partly converted $Mg_2V_2O_7$ showed only the lines of the two polymorphic forms.

The gradual nature of the $\alpha \rightarrow \beta$ transition and the apparent ability of the two forms to coexist at about 990°K are paralleled in the behavior of α- and β-magnesium pyrophosphates ($Mg_2P_2O_7$). The α-polymorph of $Mg_2P_2O_7$ is isostructural with α-$Mg_2V_2O_7$ (*16*) and undergoes a transition at approximately 341°K to produce β-$Mg_2P_2O_7$ (*19*). X-ray diffraction and DTA studies of this transition (*20*) indicate that a gradual phase transition takes place, with the two polymorphs apparently coexisting over the temperature range 333–353°K. Specific heat measurements support this view (*21*).

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