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Thermodynamics and Structural Chemistry of Compounds in the System MgO–TiO_2

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Thermochemical and crystallographic properties of $MgTi_2O_5$, $MgTiO_3$, and Mg_2TiO_4 have been studied to characterize stability relations, structural variations, and order–disorder phenomena. Enthalpies of formation, decomposition, and order–disorder transitions were determined by high-temperature solution calorimetry and transposed-temperature-drop calorimetry on synthetic powders. X-Ray lattice parameter measurements and Rietveld refinements of neutron diffraction data were used to evaluate intracrystalline cation distributions and their variation with quenching temperature. $MgTiO_3$ is the most stable phase and apparently retains a fully ordered Mg–Ti distribution to at least 1673 K. Both $MgTi_2O_5$ and Mg_2TiO_4 are stable only at high temperature because of the configurational entropy arising from cation disorder. The disorder in $MgTi_2O_5$ appears to vary continuously throughout the range 773–1373 K and is accompanied by changes in lattice parameters. Mg_2TiO_4 undergoes a cubic–tetragonal transition at 933 ± 20 K involving the appearance of long-range order on octahedral sites. However, thermochemical evidence suggests that Mg–Ti octahedral short-range order changes gradually, perhaps over an interval of several hundred degrees. Models for describing the order–disorder and accompanying enthalpy changes are discussed.

Introduction

The system MgO–FeO–Fe_2O_3–TiO_2 is important both as a geochemical indicator of temperature and oxygen fugacity and as a constituent of refractory ceramics and magnetic materials. Four series of solid solutions are found in this system: the rock salt (MgO–$Fe_{1-x}O$), the pseudobrookite (Fe_2TiO_5–$FeTi_2O_5$–$MgTi_2O_5$), the ilmenite-corundum ($FeTiO_3$–$MgTiO_3$–Fe_2O_3), and the spinel (Fe_2TiO_4–Mg_2TiO_4–Fe_3O_4–$MgFe_2O_4$). In each of these series, cation distributions, defect equilibria, and order-disorder reactions may play a role in determining thermodynamic properties. As a step in understanding the complex phenomena in this system, we have studied the bounding binary, MgO–TiO_2, by a combination of high-temperature calorimetry for thermochemical characterization and X-ray and neutron diffraction to characterize structural state.

Sample Preparation and Characterization

All samples studied were powders synthesized by calcination of oxide mixes. Dried reagent-grade MgO and TiO_2 were weighed in stoichiometric proportions and ground manually under acetone in an agate mortar. Mixtures in Pt crucibles were heated in air at 1473 K for ~48 hr. Follow-

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ing an intermediate grinding, the powders were heated for ~24 hr at 1673 K. The furnace was then cooled to ~1073 K in 20–30 min after which the samples were removed and cooled to room temperature in a desiccator. The products were then ground to pass a 100-mesh sieve. X-Ray diffraction patterns and optical examination revealed only a single phase present in each synthesis.

Samples used for solution calorimetry were handled in the following manner. MgO was dried in a Pt crucible at 1673 K for ~17 hr in air. TiO_2 was dried at 1473 K for ~20 hr and had a light tan color. X-Ray diffraction confirmed these samples as periclase and rutile, respectively. $MgTiO_3$ was annealed at 1073 K for 7 days, but neither Mg_2TiO_4 nor $MgTi_2O_5$ were given any further heat treatment. All samples were ground and sieved. The −200, +325 mesh fraction was used in all solution calorimetry except for MgO, for which the −100, +200 mesh fraction was used.

Annealing experiments at 973 K and below were carried out in muffle furnaces. Quenching experiments were performed in a vertical tube furnace at temperatures between 1073 and 1773 K. Samples ~200 mg in size were enclosed in 0.0125-mm-Pt-foil capsules and suspended in air in the furnace by a Pt wire. Temperature was monitored by a thermocouple adjacent to the sample. Quenching was accomplished by melting the Pt wire with an electrical current, causing the sample to be dropped into a receptacle containing water.

Lattice parameters (Table I) were determined from Guinier camera X-ray films using $CuK\alpha_1$ radiation. Positions of the diffraction lines were calculated by reference to a Si standard mixed with each specimen, and the lattice parameters were refined by a least-squares procedure. For tetragonal

TABLE I

CRYSTALLOGRAPHIC DATA FOR MAGNESIUM TITANATES

Sample	Quench temp. (K)	Anneal time (hr)	Space group	Lattice parameters[a]		
				a_0 (Å)	b_0 (Å)	c_0 (Å)
MgO	1673	17	*Fm*3*m*	4.2122(2)		
TiO_2	1473	20	$P4_2/mnm$	4.5930(3)		2.9589(2)
Mg_2TiO_4	1673	7	*Fd*3*m*	8.4409(3)		
Mg_2TiO_4	973	20	*Fd*3*m*	8.4404(3)		
Mg_2TiO_4	773	1031	$P4_122$	5.9749(3)[b]		8.4139(4)[b]
$MgTiO_3$	1673	9	$R\bar{3}$	5.0560(3)		13.897(2)
$MgTiO_3$	1073	165	$R\bar{3}$	5.0547(2)		13.897(1)
$MgTi_2O_5$	1773	3	*Bbmm*	9.749(1)	9.984(1)	3.7463(5)
$MgTi_2O_5$	1673	1	*Bbmm*	9.750(1)	9.981(1)	3.7466(4)
$MgTi_2O_5$	1573	1	*Bbmm*	9.749(2)	9.984(1)	3.7458(6)
$MgTi_2O_5$	1473	1	*Bbmm*	9.751(1)	9.984(1)	3.7464(4)
$MgTi_2O_5$	1373	1	*Bbmm*	9.748(1)	9.984(1)	3.7462(5)
$MgTi_2O_5$	1273	1	*Bbmm*	9.747(2)	9.987(2)	3.7456(7)
$MgTi_2O_5$	1173	1	*Bbmm*	9.741(1)	9.990(1)	3.7452(5)
$MgTi_2O_5$	1098	39	*Bbmm*	9.734(1)	9.994(1)	3.7435(4)
$MgTi_2O_5$	973	1	*Bbmm*	9.724(1)	10.003(1)	3.7412(4)
$MgTi_2O_5$	773	500	*Bbmm*	9.724(1)	10.007(1)	3.7392(4)

[a] Measured from Guinier X-ray films, except where indicated. Number in parentheses is estimated standard deviation of least-significant units.

[b] Determined from Rietveld refinement of neutron diffraction data.

Mg_2TiO_4, the reported values are those determined in the neutron diffraction structure refinement because of problems of peak overlap in the X-ray studies. Agreement between lattice parameters measured by both X-ray and neutron methods for other samples was better than 5 parts in 10^4.

Neutron diffraction data were collected on the time-of-flight (TOF) powder diffractometer at the WNR pulsed neutron facility of Los Alamos National Laboratory. Details of structure refinements using the Rietveld method will be reported elsewhere, and only the final results are presented here (Table II).

Structural Studies

The phase diagram for the system $MgO-TiO_2$ is shown in Fig. 1. Liquidus relations are taken from the recent revisions of Shindo (*1*) and subsolidus equilibria are calculated from the data obtained in the present study. Three compounds are formed: $MgTi_2O_5$, $MgTiO_3$, and Mg_2TiO_4.

TABLE II

CATION DISTRIBUTIONS FROM STRUCTURE REFINEMENTS

Mg_2TiO_4	973 K, cubic spinel	
	$Mg_A = 1.001(3)$[a]	$Ti_A = 0.001(3)$
	$Mg_B = 0.999(3)$	$Ti_B = 1.001(3)$
Mg_2TiO_4	773 K, tetragonal spinel	
	$Mg_A = 1.0$	$Ti_A = 0.0$
	$Mg_{B1} = 0.920(5) = 1 - x$[b]	$Ti_{B1} = 0.080(5) = x$
	$Mg_{B2} = 0.080(5) = x$	$Ti_{B2} = 0.920(5) = 1 - x$
$MgTiO_3$	1073 K, geikielite	
	$Mg_A = 0.995(2)$	$Ti_A = 0.005(2)$
	$Mg_B = 0.005(2)$	$Ti_B = 0.995(2)$
$MgTi_2O_5$	1773 K, "karrooite"	
	$Mg_{M1} = 0.605(4) = 1 - x$[c]	$Ti_{M1} = 0.395(4) = x$
	$Mg_{M2} = 0.395(4) = x$	$Ti_{M2} = 1.605(4) = 2 - x$
$MgTi_2O_5$	973 K, "karrooite"	
	$Mg_{M1} = 0.783(4) = 1 - x$	$Ti_{M1} = 0.217(4) = x$
	$Mg_{M2} = 0.217(4) = x$	$Ti_{M2} = 1.783(4) = 2 - x$

[a] Number in parentheses is standard deviation in last place. Considering all sources of error, uncertainty in x is probably ±0.01.

[b] Disorder parameter, x, defined analogously for cubic spinel as for tetragonal. For random distribution, $x = 0.500$.

[c] For random distribution, $x = 0.667$.

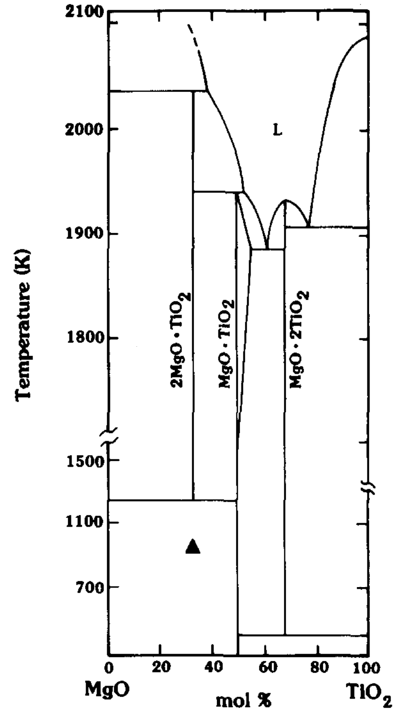

FIG. 1. Phase relations in air at atmospheric pressure in the system $MgO-TiO_2$. Liquidus relations are from Ref. (*1*). Equilibrium subsolidus decomposition temperatures for $MgTi_2O_5$ and for Mg_2TiO_4 spinel are calculated from the present work. The actual decompositions are kinetically hindered, and the cubic-to-tetragonal transition in Mg_2TiO_4 occurs at 933 ± 20 K (shown as a triangle) although both tetragonal and cubic spinels appear to be metastable with respect to decomposition to $MgTiO_3$ plus MgO at that temperature.

$MgTi_2O_5$

$MgTi_2O_5$ ("karrooite") has the pseudobrookite structure (*2*). The space group is *Bbmm*, and the structure consists of bands of edge-sharing octahedra extending in the *b* direction. Cations are accommodated in two distinct octahedral sites. The M1 site is larger and more distorted than M2.

The question of cation distribution is of interest because of the possibility of complete variation between normal and inverse arrangements. Lind and Housley (*3*) refined the structure of a synthetic single crystal of $MgTi_2O_5$ annealed at 1773 K and reported 31.6 ± 1.2% inverse character (i.e., Ti in M1). They also studied a synthetic crystal of armalcolite ($\sim Fe_{0.5}Mg_{0.5}Ti_2O_5$), which has the pseudobrookite structure, and concluded that the cation distribution was probably completely ordered, with all Mg and Fe in M1 and all Ti in M2. Smyth (*4*) and Wechsler *et al.* (*5*) found by X-ray structure refinements that natural lunar armalcolites had essentially completely ordered cation distributions. However, Wechsler (*6*) reported evidence for substantial cation disorder in synthetic armalcolite quenched from 1473 K as well as in a sample studied at 1373 K. Nearly complete ordering was observed to take place in initially disordered samples upon annealing at 673 K for 24 hr. Virgo and Huggins (*7*) likewise favored the presence of considerable disorder in quenched armalcolites, based upon Mössbauer spectra.

As was pointed out by Waldbaum (*8*), the cation distribution, and hence the configurational entropy, of materials such as $MgTi_2O_5$ is expected to be strongly temperature dependent. Navrotsky (*9*) argued further on the basis of thermochemical data that many pseudobrookites are entropy-stabilized.

In our work the lattice parameters (a, b, c) and volume (V) of $MgTi_2O_5$ were found to depend strongly on quench temperature. This dependence, shown in Fig. 2, is markedly sigmoid, with little change at low temperature (<973 K) or at high temperature (>1373 K). The difference in volume between the highest and lowest temperature samples is only 0.2%. Neutron diffraction studies yield values of the disorder parameter shown in Table II. The existence of a strong temperature dependence in the degree of inversion, and concomitant changes in lattice parameters, is confirmed and also supported by calorimetric data (see below).

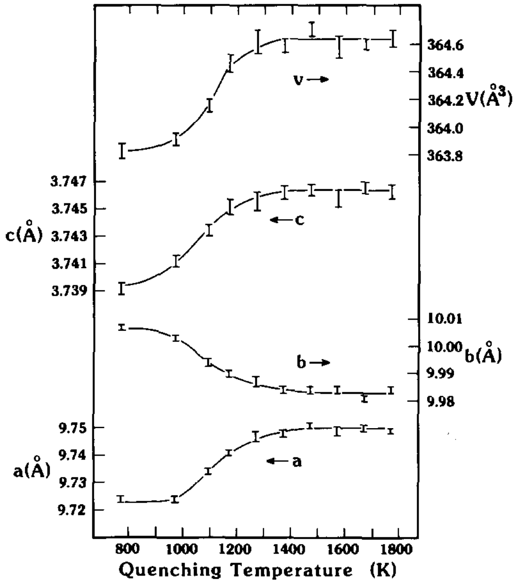

FIG. 2. Lattice parameters and unit cell volume at room temperature of $MgTi_2O_5$ as a function of annealing temperature for rapidly quenched samples. Curves are visual fits to the data.

Without the determination of the disorder parameter, x, for samples quenched from several other temperatures, a detailed evaluation of the variation of lattice parameters with changing cation distribution cannot be made. The variation of lattice parameters can be used, however, to infer a qualitative picture of the kinetics of cation redistribution. A series of experiments was performed in which material that was originally furnace-cooled to near 1073 K, and with lattice parameters corresponding to about 1113 K (from Fig. 2), was annealed at temperatures between 673 and 1773 K for various lengths of time before quenching. One hour at 973 K produced material having lattice parameters very similar to those of a sample annealed for 20 hr at the same temperature; 1 hr at 873 K produced no change in lattice parameters, 21 days at 773 K produced a slight change (giving values similar to those of the 973 K sample), and 32 days at 673 K produced no change. Thus it appears that the cation distribution may equilibrate on a time scale of weeks at 773

K, days at 873 K, an hour or less at 973 K, and presumably much faster at higher temperatures. The fact that samples quenched from 1373 to 1773 K all showed essentially identical lattice parameters may imply that cation equilibration above 1373 K is too rapid to be quenched. On the other hand, one cannot completely preclude a markedly nonlinear relation between lattice parameters and disorder parameter, leading to virtually constant lattice parameters despite changing x for $x > 0.4$.

These results suggest that our 1773 K samples may actually have a cation distribution characteristic of a somewhat lower temperature, perhaps near 1373 K. The 1773 K sample studied by neutron diffraction may have equilibrated to a temperature slightly lower than that of the sample used for drop calorimetry because it was annealed in a large batch (~15 g) and quenched in water. Its lattice parameters are similar to those of a small batch (~200 mg) quenched in water from 1273 K.

Lind and Housley's $MgTi_2O_5$ was probably cooled by shutting off furnace power, with no attempt made at quenching (M. D. Lind, personal communication, 1983). The X-ray structure refinement does show a somewhat more ordered cation distribution ($x = 0.316 \pm 0.012$), suggestive of slower cooling. Unfortunately, the lattice parameters reported by Lind and Housley are not precise enough to allow us to infer an equilibration temperature from the data in Fig. 2.

$MgTiO_3$

$MgTiO_3$ (geikielite) has the ilmenite structure (*10, 11*), with space group $R\bar{3}$. The structure is derived from that of corundum by ordering the cations into two nonequivalent octahedral sites. Mg and Ti are ordered into layers that alternate along the hexagonal c direction.

$MgTiO_3$ is confirmed by our neutron diffraction studies to be a fully ordered ilmenite. Its lattice parameters agree with those reported in the literature (*12*). Although a slightly larger value of a_0 was measured for a sample quenched from 1673 K, the difference is not statistically significant. The absence of any measurable effects in transposed-temperature-drop calorimetry (see below) also suggests that $MgTiO_3$ is fully ordered between 973 and 1673 K at atmospheric pressure; however, we cannot completely rule out the possibility of some nonquenchable disorder at 1673 K. The material quenched from 1673 K had a light pink color, which faded upon annealing at 973 K. This suggests the presence of defects (Ti^{3+} and/or vacancies) at the higher temperature, but these are almost certainly present in concentrations too small to affect bulk thermodynamic or structural properties. Coloration in high-temperature quenched specimens, which disappeared on annealing at 973 K, was also seen in $MgTi_2O_5$ (gray) and Mg_2TiO_4 (pink).

Mg_2TiO_4

Mg_2TiO_4 has the inverse spinel structure although one cannot rule out absolutely the possibility of a small deviation from completely inverse character (*13–16*). The observation of $Fd3m$ symmetry implies that, on average, the distribution of Mg and Ti over the octahedral sites is random.

Delamoye and Michel (*17*) reported that Mg_2TiO_4 annealed for a month at 753 K transformed to a structure with tetragonal symmetry, space group $P4_122$ (or its enantiomorphic equivalent, $P4_322$). Some $MgTiO_3$ was also observed after the annealing, indicating a small amount of decomposition. Similar transformations in Mn_2TiO_4 and Zn_2TiO_4 have been studied (*18, 19*).

$Zn_{2-x}(Co,Ni)_xGeO_4$ spinels also show an analogous transition (*20*). In the $P4_122$ structure, there are two distinct octahedral sites (on which Mg and Ti are ordered) as well as two different oxygen positions. Thus, the transition appears to be associated with ordering of the two octahedral cations (Mg,Ti) into nonequivalent sites. Billiet *et al.* (*21*) enumerated the possible superstructures resulting from 1 : 1 ordering on the spinel octahedral sites. Haas (*22*) analyzed possible phase transitions resulting from cation ordering in terms of Landau's theory and concluded that the transition from $Fd3m$ to $P4_122$ must be first order.

A random distribution of Mg and Ti on the octahedral site of the cubic spinel results in a configurational contribution to the entropy of 11.5 J mole^{-1} K^{-1} relative to both the normal cation arrangement, $[Ti]_A[Mg_2]_BO_4$, and the completely ordered tetragonal structure. This entropy may have a significant impact upon the thermochemical stability of the spinel phase.

Our own experiments showed that after annealing at 773 K for 2 weeks, superstructure reflections indicative of the tetragonal phase were present in X-ray diffraction patterns. These were more intense following an additional 2 weeks at 773 K, but no further change was observed in a second month of annealing. Cubic Mg_2TiO_4 annealed at 673 K for 5 months remained cubic. We did not find any $MgTiO_3$ in experiments at 673 and 773 K, although very small X-ray peaks attributable to $MgTiO_3$ and MgO were observed in Mg_2TiO_4 annealed at 1073 K (1 month) and 1173 K (1 week). Accordingly, the tetragonal sample for neutron diffraction was prepared by annealing at 773 K for 43 days.

Lattice parameter measurements indicate a slight contraction along c and expansion along a in going from the cubic to the tetragonal structure. The overall molar volume change is about -0.1%. It was assumed previously that the low-temperature phase has complete ordering of Mg and Ti on the octahedral sublattice and the high-temperature cubic phase has octahedral sites occupied by Mg and Ti distributed essentially at random. The structure refinements (see Table II) confirm this picture only partially; both phases have no tetrahedral titanium, but the tetragonal phase has a slightly disordered Mg–Ti distribution, with disorder parameter, x (mole fraction of "wrong" ions on B1 or B2 sites), equal to 0.08 ± 0.01.

Subsequent to the neutron diffraction work, we reevaluated the temperature and kinetics of the cubic–tetragonal transition in Mg_2TiO_4. These experiments bracket the transition temperature of our material between 903 and 973 K. The rate of transformation in either direction appears to be very sluggish at 923–943 K, suggesting that this is close to the equilibrium temperature, while at 973 K the transition from tetragonal to cubic occurs in less than 1 hr. Therefore we conclude that the transition temperature is 933 ± 20 K. We also found that the tetragonal phase with fully developed superstructure reflections can be prepared in just a few days (or less) at 903 K. Calorimetric results on tetragonal materials prepared at 773 and at 873 K (see below) are indistinguishable from one another, indicating that energetically there is no significant difference between these two preparations.

Calorimetric Studies

Experimental

Solution calorimetry was carried out in a twin Calvet-type microcalorimeter (*23*) maintained at 973–975 K. Samples weighing 10–50 mg were dissolved in ~15 g of molten sodium molybdate, $3Na_2O \cdot 4MoO_3$. After loading, samples were generally held in the calorimeter for 16–20 hr before the reactions were begun. The solvent was held in Pt crucibles and was used for one to three dissolutions.

In preliminary solution experiments, samples were held in Pt holders with perforated foil bottoms. However, TiO_2-bearing specimens did not fully dissolve even with vigorous stirring. A greenish residue, consisting at least partly of rutile, was always found in the sample cups. A new sample holder was designed consisting of a hinged, hemispherical solid Pt cup attached by Pt wire to a silica glass rod that could be manipulated from outside the calorimeter. This arrangement permitted us to upend the sample cup, thereby dumping the entire sample into the solvent at the start of the reaction. Relatively little stirring was required to ensure complete dissolution of the sample, and examination of the sample holders, solvent, and crucibles following the experiments never revealed any trace of residue. Note, however, that this flux crystallizes upon cooling and therefore proof of complete dissolution by visual inspection alone is somewhat inadequate. Given the good reproducibility of our measurements and the agreement between our measured ΔH_{sol} for TiO_2 (rutile) with that of Mitsuhashi and Kleppa (*24*), we are confident that complete dissolution was obtained using this technique.

Small stirring corrections, corresponding typically to heat effects on the order of 0.2 J, and almost always less than 0.4 J, were applied to some data. These were determined in separate experiments in which stirring was carried out as in a solution run, but with no sample present. "Total heat effects measured in solution experiments were on the order of (in J) −0.4 ($MgTiO_3$), +2.0 ($MgTi_2O_5$), −6.0 (Mg_2TiO_4), +8.0 (TiO_2), and −23.0 (MgO)."

Samples for transposed-temperature-drop calorimetry were enclosed in Pt capsules made of 0.0125-mm foil. Capsule and sample weights were both typically on the order of 45–50 mg, and in general the heat effect due to the sample was about 85% of the total heat effect. Each sample drop was preceded by the drop of a Pt calibration piece of known heat content. After the first drop, each sample was recovered and dropped a second time, following the same procedures.

Transposed-Temperature-Drop Calorimetry of Phases Quenched from Various Temperatures

Annealing experiments on $MgTi_2O_5$ and Mg_2TiO_4 demonstrated that significant structural changes, which are almost certainly associated with redistribution of Mg and Ti, occur rapidly at 973 K (i.e., within 1 hr). Because such changes take place on the time scale of a calorimetric experiment, an appropriate technique for studying the order–disorder reaction is transposed-temperature-drop calorimetry. In this method, a sample is dropped from room temperature into the calorimeter at high temperature with no solvent present, and allowed to equilibrate its structural state during the calorimetric experiment. This is in contrast to high-temperature solution calorimetry, in which structural reequilibration would take place during the several hours of thermal preequilibration prior to dissolution. The drop calorimetry approach, therefore, allows one to determine the enthalpy difference (at 298 K) between the structural state characteristic of some quenching temperature and that characteristic of the calorimeter temperature, 973 K. Results of these experiments are summarized in Table III.

For $MgTiO_3$, the first and second drops of samples quenched from 1673 K gave essentially identical results. This indicates that no significant structural changes took place and is consistent with $MgTiO_3$ being fully ordered at both 973 and 1673 K. The value of the heat content, $H(973\text{ K}) - H(298\text{ K})$, obtained in this study, 76.3 kJ $mole^{-1}$, is in reasonable agreement with the data of Naylor and Cook (*25*), 79.4 kJ $mole^{-1}$.

In $MgTi_2O_5$, the sample quenched from 1773 K released 4.2 (±2.4) kJ $mole^{-1}$ on the first anneal at 973 K. The sample quenched from 773 K gave essentially identical heat

TABLE III

RESULTS OF TRANSPOSED TEMPERATURE DROP CALORIMETRY ON MAGNESIUM TITANATES

Sample	Quench temp. (K)	Anneal time (hr)	Heat content, H(973 K) − H(298 K), kJ mole^{-1}	
			First drop	Second drop
Mg_2TiO_4	(Tetragonal)			
	773	933	110.9 ± 1.0[6][a]	109.5 ± 0.8[5]
	873	162	110.5 ± 0.9[4]	109.8 ± 1.5[4]
Mg_2TiO_4	(Cubic)			
	1673	7	106.2 ± 0.6[6]	108.5 ± 1.2[6]
$MgTiO_3$	1673	9	76.2 ± 1.0[4]	76.3 ± 1.2[4]
$MgTi_2O_5$	1773	3	117.0 ± 1.8[5]	121.2 ± 1.5[5]
$MgTi_2O_5$	773	837	123.7 ± 1.9[2]	124.0 ± 1.7[2]

[a] Uncertainty is two standard deviations of the mean, number in brackets is number of experiments performed.

contents on first and second drops. The average value of heat content on second drops, 122.0 kJ mole^{-1}, is in reasonable agreement with a reported value of 124.6 kJ mole^{-1} (*26*).

For Mg_2TiO_4, the enthalpy increment associated with converting the tetragonal material formed at 773 K to the cubic material equilibrated at 973 K is 1.4 ± 1.3 kJ mole^{-1} while for the tetragonal material formed at 873 K, it is 0.7 ± 1.7 kJ mole^{-1}. An enthalpy increment of −2.3 ± 1.3 kJ mole^{-1} is observed when material quenched from 1673 K is dropped into the calorimeter at 973 K. The average heat content of Mg_2TiO_4 measured on second drops, 109.2 kJ mole^{-1}, compares well with the data of Orr and Coughlin (*26*), 110.5 kJ mole^{-1}.

One might question whether the cubic Mg_2TiO_4 produced by heating the tetragonal form for 1 hr at 973 K is energetically identical to the cubic material synthesized at higher temperature, never transformed to the tetragonal form, and annealed for days or weeks at 973 K. We performed solution calorimetry on the cubic material obtained from the tetragonal (see Table IV). Its heat of solution is identical within experimental error to that of cubic spinel which had never been annealed below 973 K, although the data show more scatter.

TABLE IV

ENTHALPIES OF SOLUTION IN $3Na_2O \cdot 4MoO_3$ AT 973 K FOR MAGNESIUM TITANATES

Sample	ΔH_{sol} (kJ mole^{-1})
MgO	−37.6 ± 0.6[12][a]
TiO_2	+15.7 ± 0.5[9]
$MgTiO_3$	−0.8 ± 1.1[10]
$MgTi_2O_5$	+7.8 ± 1.2[8]
Mg_2TiO_4[b]	−55.4 ± 1.8[10]
Mg_2TiO_4[c]	−55.9 ± 5.5[4]

[a] Uncertainty is two standard deviations of the mean, number in brackets is number of experiments performed. As discussed in the text, the structural state (cation distribution) of Mg_2TiO_4 and $MgTi_2O_5$ is probably that representing equilibrium at 973 K.

[b] Cubic spinel.

[c] Material which had been transformed to tetragonal at 773 K and then back to cubic by a short treatment at 973 K.

Solution Calorimetry at 973 K

The measured enthalpies of solution are shown in Table IV. From the discussion above, it is reasonable to conclude that these values represent enthalpies of solution of samples with structural state equilibrated at 973 K. The value of the heat of solution of MgO, -37.6 ± 0.6 kJ $mole^{-1}$, is in good agreement with earlier values of -37.1 ± 0.3 kJ $mole^{-1}$ (*27*) and -35.8 ± 1.0 kJ $mole^{-1}$ (*28*). Our value for TiO_2 rutile (15.7 ± 0.5 kJ $mole^{-1}$) is in agreement with that reported by Mitsuhashi and Kleppa (*24*), 14.8 ± 0.8 kJ $mole^{-1}$, but higher than that initially reported by Navrotsky and Kleppa (*27*), 10.0 ± 0.3 kJ $mole^{-1}$. Our results confirm the observation of Mitsuhashi and Kleppa that, without careful and vigorous stirring, not all of the sample dissolves. Our new value for Mg_2TiO_4, -55.4 ± 1.8 kJ $mole^{-1}$, is considerably larger in magnitude than the -39.0 ± 0.4 kJ $mole^{-1}$ given by Navrotsky and Kleppa (*27*). As in the case of TiO_2, we suspect that in the early experiments, using solid-bottomed sample cups, the samples did not dissolve completely.

TABLE V

ENTHALPIES OF FORMATION, DECOMPOSITION, AND CHANGES IN STRUCTURAL STATE OF MAGNESIUM TITANATES

Reaction	ΔH (kJ $mole^{-1}$)
$MgO + TiO_2 = MgTiO_3$	-21.1 ± 1.3[a,b]
$MgO + 2TiO_2 = MgTi_2O_5$	-14.0 ± 1.7[b]
$2MgO + TiO_2 = Mg_2TiO_4$	-4.2 ± 2.2[b]
$MgTi_2O_5 = MgTiO_3 + TiO_2$	-7.1 ± 1.7[b]
$Mg_2TiO_4 = MgTiO_3 + MgO$	-16.9 ± 2.2[b]
$MgTi_2O_5$ (x of 1773 K) = $MgTi_2O_5$ (x of 973 K)	-4.2 ± 2.4[c]
$MgTi_2O_5$ (x of 773 K) = $MgTi_2O_5$ (x of 973 K)	-0.3 ± 2.5[c]
Mg_2TiO_4 (tetragonal, x of 773 K) = Mg_2TiO_4 (cubic, x of 973 K)	$+1.4 \pm 1.3$[c]
Mg_2TiO_4 (tetragonal, x of 873 K) = Mg_2TiO_4 (cubic, x of 973 K)	$+0.7 \pm 1.7$[c]
Mg_2TiO_4 (cubic, x of 1673 K) = Mg_2TiO_4 (cubic, x of 973 K)	-2.3 ± 1.3[c]

[a] Uncertainties are two standard deviations, calculated by propagation of errors from the heat of solution or drop calorimetry data.

[b] ΔH at 973 K, from solution experiments.

[c] ΔH at 298 K, from drop experiments, x = disorder parameter as defined in Table II.

Thermodynamics of Formation, Models of Order–Disorder, and Phase Stability

Formation and Decomposition Relations

Table V summarizes the enthalpies associated with formation of the intermediate compounds from MgO and TiO_2, with decomposition of Mg_2TiO_4 and $MgTi_2O_5$ to $MgTiO_3$-bearing assemblages, and with changes in structural state.

We found the enthalpies of formation from the oxides at 973 K of Mg_2TiO_4, $MgTiO_3$, and $MgTi_2O_5$, to be -4.2 ± 2.2, -21.1 ± 1.3, and -14.0 ± 1.7 kJ $mole^{-1}$. Kelley *et al.* (*29*) measured the enthalpies of solution of magnesium titanates in aqueous HF–HCl mixtures at 347 K. Using these data and appropriate heat content corrections, they obtained enthalpies of formation from the oxides at 973 K of -15.1, -23.9, and -16.0 kJ $mole^{-1}$, respectively. Their values are 10.9, 2.8, and 2.0 kJ more exothermic than ours for Mg_2TiO_4, $MgTiO_3$, and $MgTi_2O_5$, respectively. The difference between the two sets of data is roughly a factor of four greater for Mg_2TiO_4 than for $MgTiO_3$ and $MgTi_2O_5$, suggesting that there may be a problem with the heat of solution of MgO or of MgO-rich samples in one of the sets of data. In our study, crystalline MgO dissolved readily and completely with a heat of solution reproducible among three different sets of measurements (this work and (*27*, *28*)). It is possible that in the acid calorimetry, MgF_2 precipitation for Mg-rich compositions may not have been avoided completely.

$MgTi_2O_5$ Order–Disorder

The two octahedral sites (M1 and M2) in the pseudobrookite structure remain crystallographically distinct even if occupied by a random distribution of cations, which makes the disordering process nonconvergent and analogous to octahedral–tetrahedral disorder in spinels. The simplest thermodynamic approach is the "simple equilibrium model" of Navrotsky and Kleppa (*30*), which assumes that the enthalpy of interchange is independent of the degree of disorder, and the entropy of interchange is the change in configurational entropy only, with the assumption that the distribution on each sublattice is random. Then for degree of disorder x (i.e., Ti in M1), the interchange reaction and enthalpy are given by

$$\mathrm{Mg_{M1} + Ti_{M2} = Mg_{M2} + Ti_{M1}} \qquad (1)$$

$$x^2(1-x)^{-1}(2-x)^{-1} = \exp(-\Delta H_{\mathrm{int}}/RT). \qquad (2)$$

From the measurement by neutron diffraction of $x = 0.217$ for a sample quenched from 973 K, we calculate $\Delta H_{\mathrm{int}} = 27.4$ kJ. For our 1773 K sample, $x = 0.395$, and $\Delta H_{\mathrm{int}} = 26.9$ kJ. The error in ΔH_{int} arising from the 0.01 uncertainty in x is about ± 1.5 kJ. Thus these values of ΔH_{int} agree with each other and with the value of ΔH_{int} determined directly from the transposed-temperature-drop calorimetry results as follows. The sample quenched from 1773 K has $x = 0.395$ while that quenched from 973 K has $x = 0.217$. This corresponds to an enthalpy of 4.2 (± 2.4) kJ for an increase of x of 0.178 or $\Delta H_{\mathrm{int}} = 23.6$ (± 13.5) kJ mole^{-1}. Using an average value of $\Delta H_{\mathrm{int}} = 27.2$ (± 2) kJ, one can calculate the enthalpy change upon changing the cation distribution from that at 973 K to that at temperature, T, as

$$\Delta H(T) - \Delta H(973\ \mathrm{K}) = 27.2[x(T) - x(973\ \mathrm{K})], \qquad (3)$$

with $x(T)$ given by Eq. (2). This enthalpy increment is shown as a function of temperature by the curve in Fig. 3A, as are the two calorimetric data points. The cation distribution is shown as a function of temperature in Fig. 3B, with our experimental points as circles and that of Lind and Housley (*3*) as a triangle. We noted above that it may not be possible to obtain a complete quench of the cation distribution from tem-

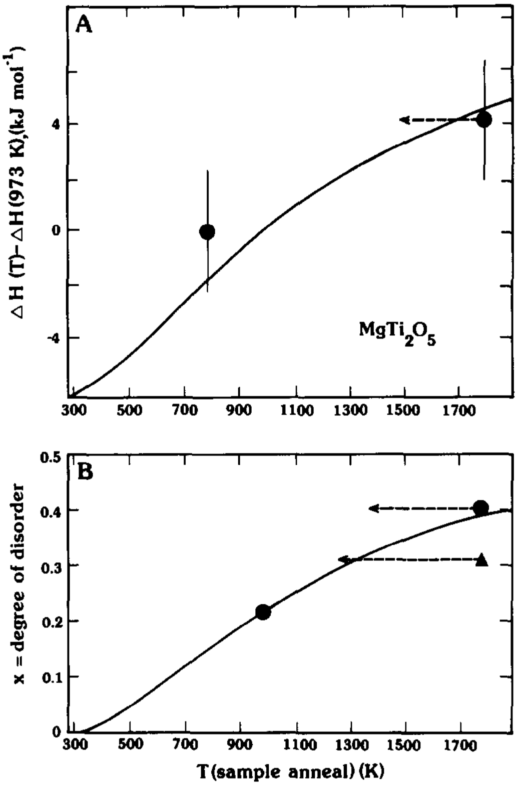

FIG. 3. Enthalpy difference between structural state at T and structural state at 973 K (A) and degree of disorder, x (B) for $MgTi_2O_5$ equilibrated at different temperatures. Solid curves are for simple equilibrium model, with $\exp(-\Delta H_{\mathrm{int}}/RT) = x^2(1-x)^{-1}(2-x)^{-1}$, and $\Delta H_{\mathrm{int}} = 27.2$ kJ. Circles in (A) are enthalpies determined by transposed-temperature-drop calorimetry. Circles in (B) are cation distribution parameters (x) determined from structure refinements. Triangle is value of x determined by Lind and Housley (*3*). The dashed arrows on the 1773 K points indicate that the quench may not have completely preserved the high-temperature distribution, as discussed in the text.

peratures above about 1373 K. If our 1773 K sample represents a faster quench than Lind and Housley's, the discrepancies between the two values of x may be explained. The possible errors arising from this problem are shown as dashed arrows in the figure. If one assumes that our sample quenched from 1773 K has a cation distribution characteristic of 1373 K, then $\Delta H_{\mathrm{int}} = 20.9$ kJ. This probably places a lower limit on ΔH_{int}. These uncertainties notwithstanding, it appears that the simple equilibrium model, with $\Delta H_{\mathrm{int}} = {\sim}27$ kJ, explains both the calorimetric results and the variation of disorder parameter with temperature.

In the simple equilibrium model, the energetic cost of interchanging the cations does not decrease as the extent of ordering diminishes; no cooperativity is invoked in the disordering process. Recently both O'Neill and Navrotsky (*31*) and Urusov (*32*) suggested that this simple model can be improved by realizing that the disordering enthalpy may depend on the degree of disorder. We have not included such considerations here because the data are not sufficient to warrant fitting more than one parameter.

In the simple equilibrium model, complete disorder is not achieved until the temperature approaches infinity. The cation distribution varies with T, as does the contribution of disorder to the enthalpy, entropy, and free energy of the phase involved. This variation must be taken into account when calculating phase equilibria. Simply adding a constant configurational entropy term to a mineral's thermodynamic properties to account for disorder (*33, 34*), though a useful first approximation, may not be a sufficiently accurate description.

Mg_2TiO_4 Order–Disorder

The following evidence suggests that the octahedral site ordering process in Mg_2TiO_4 does not occur solely at the tetragonal-to-cubic transition. First, the tetragonal phase annealed for 43 days at 773 K is not fully ordered but has about 8% disorder, as shown by the neutron study. Assuming that this phase has reached equilibrium, one concludes that a small amount of disorder can exist below the tetragonal-to-cubic transition. Second, the enthalpy change associated with transforming the tetragonal spinel to the cubic form is on the order of 1.0 kJ mole^{-1} (see Table V). If the transformation occurs as a first-order transition at 933 K, its entropy change is 1.1 J mole^{-1} K^{-1}. The configurational entropy change associated with totally disordering a completely ordered octahedral Mg,Ti distribution is $2R\ln 2 = 11.5$ J mole^{-1} K^{-1}, an order of magnitude larger than that observed. Since the tetragonal form is largely ordered, this observation suggests that the cubic form at 933 to 973 K exhibits a very large degree of short-range order. Third, an enthalpy increment is associated with drop experiments on Mg_2TiO_4 annealed at 1673 K (Table V) suggesting that an enthalpy of ~2.3 kJ mole^{-1} is needed to change the structural state characteristic of 973 K to one characteristic of 1673 K. This argues for the 1673 K sample being more disordered. Although the errors associated with individual differences of enthalpies in transposed-temperature-drop experiments are large, the overall consistency of the effects at different quench temperatures and the correspondence between calorimetric and structural data suggest that the measured effects are indeed real.

One can apply two limiting types of models to this apparently gradual disordering. The first is the "simple-equilibrium" model, analogous to that used for $MgTi_2O_5$. Since there are two octahedral sites involved, one can write the interchange reaction as

$$\mathrm{Mg_{B1}} + \mathrm{Ti_{B2}} = \mathrm{Mg_{B2}} + \mathrm{Ti_{B1}} \qquad (4)$$

with

$$x^2(1 - x)^{-2} = \exp(-\Delta H_{\text{int}}/RT). \quad (5)$$

If $x = 0.08$ at 773 K, then $\Delta H_{\text{int}} = 31.4$ kJ. Figure 4 shows values of the enthalpy increment, $\Delta H(T) - \Delta H(973\text{ K})$ and of the degree of disorder, x, as functions of temperature. The thermochemical data fit this model reasonably well.

Since in the limit of complete disordering the two octahedral sites become indistinguishable, a model invoking much more cooperativity may be more reasonable. To limit this treatment to one parameter (since we know x at only one temperature), we employ the simple Bragg–Williams model (*35, 36*). An order parameter, s, is defined as

$$s = \frac{x(\text{observed}) - x(\text{completely disordered})}{x(\text{completely ordered}) - x(\text{completely disordered})} = 1 - 2x. \quad (6)$$

The value of s is related to an energy parameter, W (for equimolar amounts of Mg and Ti) by

$$s = \tanh(Ws/2RT). \quad (7)$$

For 2 mole of ions on B sites, the enthalpy change on disordering is

$$\Delta H = H(s = s) - H(s = 1) = 0.5W(1 - s^2). \quad (8)$$

If $x = 0.08$ at 773 K, $s = 0.84$, and $W = 18.7$ kJ from Eq. (7). Using Eqs. (7) and (8), the enthalpy increment, $\Delta H(T) - \Delta H(973\text{ K})$, and the disorder parameter, x, are calculated as functions of temperature. They fit the observed enthalpy data reasonably well (see Fig. 4).

Since one cannot measure short-range order in the cubic phase directly, one cannot determine by structural means whether the cation distribution is essentially random ($x = 0.5$) above about 1073 K as suggested by the Bragg–Williams model or if substantial order persists to the melting point ($x = 0.26$ at 1873 K) as suggested by the simple equilibrium model. The drop calorimetric data are not accurate enough to discriminate among these possibilities, either. This question, however, can be attacked using free-energy arguments from the observed phase equilibria (see below) which favor an essentially random cation distribution above 1273 K. Thus we conclude that the

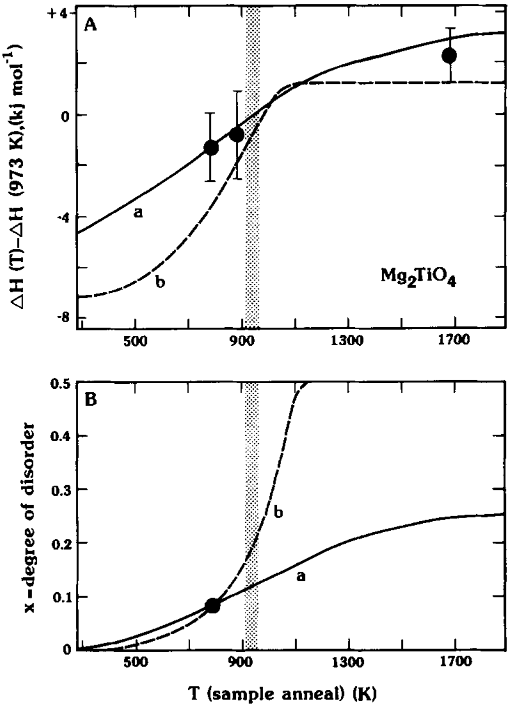

FIG. 4. Enthalpy difference between structural state at T and structural state at 973 K (A) and degree of disorder, x (B) for Mg_2TiO_4 equilibrated at different temperatures. Solid curves (a) are for simple equilibrium disordering model, $\exp(-\Delta H_{\text{int}}/RT) = x^2(1 - x)^{-2}$ with $\Delta H_{\text{int}} = 31.4$ kJ. Dashed curves (b) are for Bragg–Williams model, $\tanh(Ws/RT) = s$, where $s = 1 - 2x$, and $W = 18.7$ kJ. Circles in (A) are enthalpies determined by transposed-temperature-drop calorimetry. Circle in (B) is cation distribution from structure refinements. Shaded area indicates the region of the tetragonal-to-cubic transition temperature, 933 ± 20 K.

cation distribution among octahedral sites in Mg_2TiO_4 changes from almost complete order at 773 K ($x = 0.08$), to substantial local order at 973 K, to essentially complete disorder above 1273 K. The Bragg–Williams approach is almost certainly too simplistic to describe this process accurately in detail, but the simple equilibrium model appears to spread the order–disorder transition out over too wide a range of temperature.

The thermochemical and neutron diffraction data suggest that the order–disorder transition and the tetragonal-to-cubic transition are somewhat distinct phenomena. The former appears to occur relatively gradually, perhaps in the range 673–1273 K. The latter occurs quite sharply, probably as a first-order transition, at 933 ± 20 K, where the distribution parameter, x, is greater than the value of 0.08 observed at 773 K and probably less than about 0.3 (see Fig. 4). The total energy of disordering $\Delta H(x = 0) - \Delta H(x = 0.5)$ is 15.7 kJ in the simple equilibrium model and 9.4 kJ in the Bragg–Williams model. Either of these values is an order of magnitude greater than the enthalpy seen in the conversion of the tetragonal phase synthesized at 773 or 873 K to the cubic phase with structure characteristic of 973 K. Similarly, the entropy associated with the tetragonal-to-cubic transition is an order of magnitude less than that required for complete disordering.

A similar situation has been described by Carpenter *et al.* (*37*) for the process of Al,Si ordering in cordierite. Metastable hexagonal cordierite produced by the crystallization of glass does not exhibit orthorhombic symmetry until a rather late stage of ordering. Most of the energy and entropy changes associated with short-range order of Al and Si occur within the hexagonal phase and no discontinuity in curves of enthalpy vs annealing time is seen at the hexagonal-to-orthorhombic transition. We suggest that such behavior may occur frequently, and a change in symmetry is often a product of an ordering reaction in its final stages, rather than an indication of a sharp order–disorder transformation.

Free Energies and Subsolidus Phase Equilibria

The free energies of formation of the magnesium titanates have been estimated from phase equilibria in the systems MgO–CoO–TiO$_2$ at 1573 K (*38*) and NiO–MgO–TiO$_2$ at 1673 K (*39*). For the reaction $MgO + TiO_2 = MgTiO_3$, the values obtained were $\Delta G^0_{1573} = -20.1 \pm 4.2$ kJ, and $\Delta G^0_{1673} = -21.3 \pm 2.1$ kJ. Combining our value of $\Delta H^0_{973} = -21.1 \pm 1.3$ kJ with appropriate heat content corrections (*26*) and the above free energies suggests that ΔS^0 for this reaction is small. This result is in accord with third-law values of ΔS^0 obtained from heat capacity data, $\Delta S^0_{298} = -2.7$ J mole^{-1} K^{-1}, $\Delta S^0_{1000} = +2.1$ J mole^{-1} K^{-1} (*34*) and supports the conclusion that configurational disorder is not important in $MgTiO_3$.

For the reaction $MgO + 2TiO_2 = MgTi_2O_5$, the free-energy values are $\Delta G^0_{1573} = -28.5 \pm 4.2$ kJ and $\Delta G^0_{1673} = -30.5 \pm 4.2$ kJ. Using the equilibrium disordering model ($\Delta H_{\text{int}} = 27.2$ kJ) to correct ΔH^0 for the varying degree of disorder, we estimate $\Delta S^0_{1573} = 11.7 \pm 2.9$ J mole^{-1} K^{-1} and $\Delta S^0_{1673} = 13.0 \pm 2.9$ J mole^{-1} K^{-1}. The configurational entropy calculated using this model is 13.3 J mole^{-1} K^{-1} at 1573 K ($x = 0.36$) and 13.6 J mole^{-1} K^{-1} at 1673 K ($x = 0.38$), while for complete disorder ($x = 0.667$) the configurational entropy would be 15.9 J mole^{-1} K^{-1}. Since the change in vibrational entropy for the above reaction is expected to be small, the comparison between observed and configurational entropies lends further support to the hypothesis that at high temperature $MgTi_2O_5$ is significantly but probably not completely disordered, as implied by the simple equilibrium model.

For the reaction, $2MgO + TiO_2 =$

Mg_2TiO_4, $\Delta G^0_{1573} = -21.3 \pm 2.1$ kJ, and $\Delta G^0_{1673} = -24.3 \pm 3.8$ kJ. Applying the simple equilibrium model and our enthalpy of formation at 973 K to these free energies, one obtains $\Delta S^0_{1573} = 13.0 \pm 2.9$ J mole^{-1} K^{-1} and $\Delta S^0_{1673} = 13.8 \pm 2.9$ J mole^{-1} K^{-1}. By comparison, the configurational entropy calculated from this model is $S_{\text{conf}} = 9.5$ J mole^{-1} K^{-1} at 1573 K ($x = 0.26$) and $S_{\text{conf}} = 9.7$ J mole^{-1} K^{-1} at 1673 K ($x = 0.27$). Using the Bragg–Williams model, the spinels at 1573 and 1673 K are predicted to be completely disordered on octahedral sites, with $S_{\text{conf}} = 11.5$ J mole^{-1} K^{-1}. Using the above approach, with correction to ΔH calculated using the Bragg–Williams model (see also Fig. 4) we get $\Delta S^0_{1573} = 11.7 \pm 2.9$ and $\Delta S^0_{1673} = 13.0 \pm 2.9$ J mole^{-1} K^{-1}.

Brezny and Muan (*38*) and Evans and Muan (*39*) noted that their free energies disagree with those calculated based on the heats of formation obtained by acid solution calorimetry by Kelley (*29*). The consistency of Muan's free-energy data and the heats of formation obtained in this work supports the validity of both our calorimetric data and our interpretation of order–disorder phenomena.

The heat of solution data suggest that $MgTi_2O_5$ and Mg_2TiO_4 are unstable with respect to $MgTiO_3$ at low temperature since the enthalpies of decomposition reactions (see Table V) are negative. We may calculate the free energies of these decomposition reactions using our enthalpies of solution, the existing heat-content data, and the disordering models. For the reaction $MgTi_2O_5 = MgTiO_3 + TiO_2$, the decomposition temperature is calculated to be 403 K if one assumes the simple equilibrium model and that cation equilibrium is maintained. If a 773 K distribution is frozen-in, decomposition would occur at 503 K. In either case, it is clear that $MgTi_2O_5$, though not stable to absolute zero, is stable to temperatures low enough to make decomposition kinetically unfavorable. Lindsley *et al.* (*40*) studied the breakdown of $MgTi_2O_5$ at high pressure (1–2 GPa) as well as the stability at zero pressure of $MgTi_2O_5$–$FeTi_2O_5$ solid solutions. These experiments strongly suggest that at low pressure $MgTi_2O_5$ becomes unstable relative to $MgTiO_3 + TiO_2$ at some temperature below 973 K, consistent with the thermochemical data.

For the reaction $Mg_2TiO_4 = MgTiO_3 + MgO$, the situation is more complex. Fig. 5 shows three calculations of the free energy of this reaction. The solid curve, marked "a," assumes our thermochemical data and a temperature-dependent cation distribution given by the simple equilibrium model. The dashed curve, marked "b," uses the thermochemical data and a cation distribution given by the Bragg–Williams model. In the temperature range of the figure (1200–1900 K) this implies a completely disordered octahedral cation distribution, and a correction has been applied to the ΔH^0

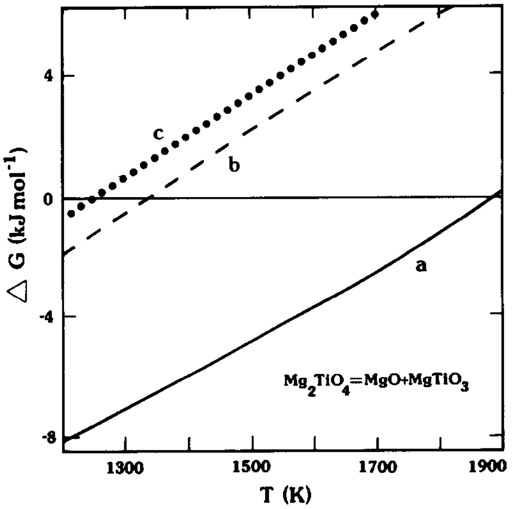

FIG. 5. Free energy of the decomposition reaction $Mg_2TiO_4 = MgTiO_3 + MgO$ as a function of temperature. Curve "a" (solid) is calculated using the thermochemical data and the simple equilibrium model, curve "b" (dashed) uses the Bragg–Williams model, and curve "c" (dotted) assumes that the octahedral cation distribution is completely random at all temperatures above the tetragonal-to-cubic transition.

measured at 973 K to account for the additional enthalpy of disordering. The dotted curve, marked "c," assumes that Mg_2TiO_4 has complete octahedral disorder at all temperatures at and above 973 K and that the enthalpy of decomposition need not be corrected for a changing cation distribution. Curve "a" predicts that the spinel is stable only above 1873 K, whereas it is readily synthesized at temperatures as low as 1573 K. Thus the simple equilibrium model clearly underestimates the entropy of the spinel at 1573–1873 K, as already noted above. The two other calculations give estimates of the decomposition temperature of 1273–1373 K. This is in accord with high-pressure decomposition experiments of Akimoto and Syono (*41*) which predict a breakdown temperature near 1273 K at zero pressure. The tetragonal spinel is stabilized by at most several hundred Joules (in free energy) relative to the cubic spinel, and therefore must also be metastable with respect to $MgTiO_3$ + MgO. These observations have been added to the phase diagram shown in Fig. 1.

We conclude that cation order–disorder in $MgTi_2O_5$ and Mg_2TiO_4 play a crucial role in determining the stability of phases in the MgO–TiO$_2$ system. The structural, calorimetric, and phase equilibrium data, taken together, provide a consistent picture and constrain the order–disorder relations more strongly than any one set of measurements considered individually.

Acknowledgments

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