MINERALOGY AND THERMAL BEHAVIOR OF PHOSPHATES; I. MAGNESIUM PYROPHOSPHATE

RUSTUM ROY,* E. T. MIDDLESWARTH, AND F. A. HUMMEL,
The Pennsylvania State College, State College, Pennsylvania.

ABSTRACT

A solid phase inversion of $Mg_2P_2O_7$ apparently takes place near 68° C. The inversion was detected initially by the thermal expansion behavior and later confirmed by differential thermal analyses and high temperature *x*-ray patterns. A simplified furnace was used for obtaining *x*-ray patterns at elevated temperatures. The polymorphic change is of considerable theoretical interest since the inversion takes place with a marked change in volume. Incidental data on the thermal decomposition of $MgNH_4PO_4 \cdot 6H_2O$ have been obtained.

I. INTRODUCTION

The compound $Mg_2P_2O_7$ has long been used for the quantitative determination of magnesium in the field of analytical chemistry (1). The magnesium is precipitated in highly alkaline solution as the hydrated crystal, $MgNH_4PO_4 \cdot 6H_2O$, calcined at 1100° C., and weighed as $Mg_2P_2O_7$.

Various mechanisms have been proposed for the course of decomposition of the magnesium-ammonium salt (2). Kiehl and Hardt (3) showed that $MgNH_4PO_4 \cdot 6H_2O$ lost 5 mols of water but no ammonia below 50° C. They postulate the simultaneous decomposition of the monohydrate and of the ammonium salt itself above 60° C. They give the temperatures at which the dissociation pressure is 1 atmosphere as 105° for the hexahydrate, and 250° for the monohydrate. They find the dissociation pressure of the hexahydrate to be about 5 atmospheres at 159°; the monohydrate will decompose rapidly at this temperature if it is in an open vessel. Rapid heating will destroy this sequence of the decomposition due to the formation of primary ammonium salts, which volatilize slowly at these temperatures and also lose some P_2O_5. Others (4) have suggested the possibility of hydrates with fractional amounts of mols of water, and the true nature of the process is far from clear.

During the course of a thermal expansion run it was noted that the ignited compound $Mg_2P_2O_7$ first showed a contraction slightly above room temperature before the normal positive movement due to reversible thermal expansion took place. This unusual behavior demanded a more complete examination and location of the inversion temperature by means of thermal expansion and thermal analysis curves and by the change in *x*-ray patterns of the material as it was heated through the transformation point.

---

* Government of India scholar at the Pennsylvania State College.

II. Preparation of the Material

The material which was used for measurements of expansion, thermal analyses and *x*-ray analyses was prepared according to the standard procedure for the determination of magnesium as outlined in Hillebrand and Lundell (1). Small batches of material were made for individual measurements in order to maintain a higher degree of purity in each sample. C.P. magnesium nitrate was disssolved in distilled water, diammonium hydrogen phosphate was added in excess, and then ammonium hydroxide until the precipitation was complete. The precipitate was allowed to stand for twelve hours, then it was filtered and washed thoroughly with dilute ammonium hydroxide. Double precipitations were made in some cases to insure maximum purity and ideal composition of the precipitate. After drying at 110° C., the material was either used as such to investigate the thermal behavior of the hydrate or calcined to form the pyrophosphate.

III. Thermal Decomposition of $MgNH_4PO_4 \cdot XH_2O$

A. Thermal analyses

The samples used had been precipitated as described above and dried at 110° C. The drying process leads to a product which can now be referred to as $MgNH_4PO_4 \cdot XH_2O$. The white powder was passed through a 150 mesh screen before placing in the nickel block for thermal analysis. The apparatus used was of the automatically recording type, the rate of heating (400° C. per hour) was controlled by a Leeds and Northrup

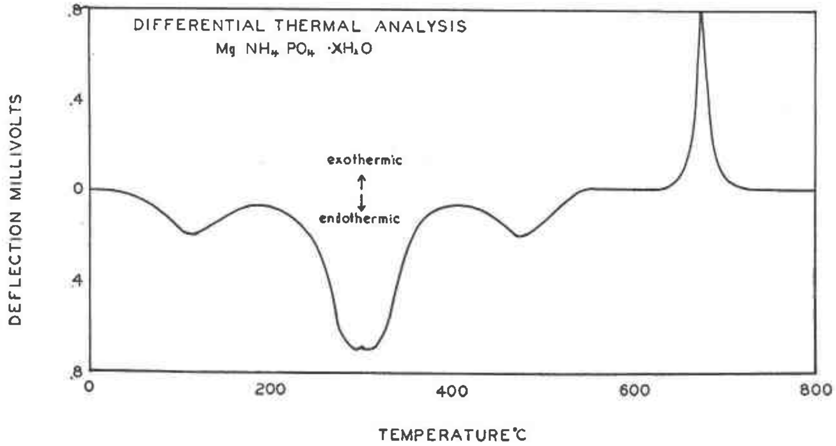

Fig. 1

recording instrument, and the differential peaks were registered by a General Electric photoelectric potentiometer.

During the heating of $MgNH_4PO_4 \cdot XH_2O$, four principal peaks were observed on the differential thermal curve. The first three peaks were endothermic, the last exothermic. The endothermic peaks occurred in the region 50–150° C., 200–400° C., and 450–500° C., while the exothermic peaks occurred between 650–700° C. The reaction from 200–400° C. was by far the largest of the endothermic peaks, giving a deflection corresponding to 0.7 millivolt at 300° C., its maximum. The heat effects at 50–150° C. and 450–500° C. were nearly equal in magnitude, having maxima at 110° C. and 475° C., respectively, with deflection corresponding to 0.2 millivolt at these temperatures. The exothermic peak was very sharp and gave a deflection corresponding to approximately 0.8 millivolt at 675° C. Figure 1 shows an average curve of the differential heat effects.

The endothermic reactions probably signify losses of H_2O and NH_3 while the exothermic peak is apparently due to the heat of formation of the new magnesium pyrophosphate lattice. Samples heated to 600° C. for three hours gave no diffraction pattern indicating that the rearrangement had

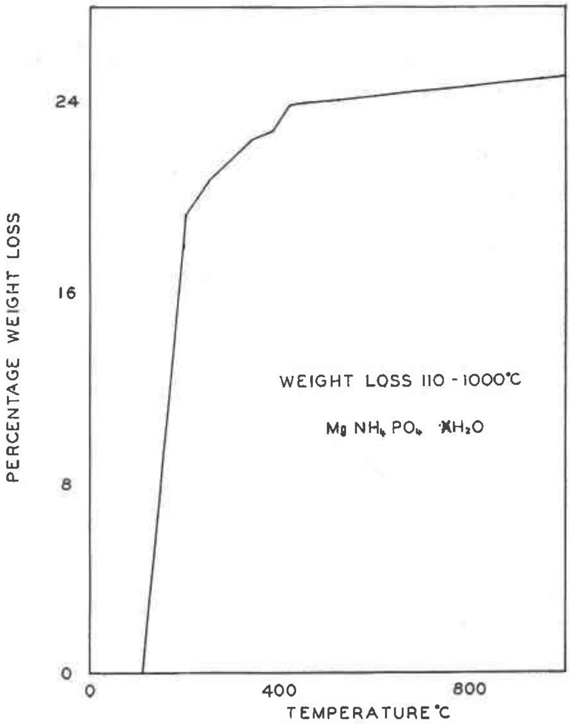

FIG. 2

not yet taken place while other samples heated to 800° C. for eight hours gave the complete pattern of $Mg_2P_2O_7$. These *x*-ray data then give further evidence for the formation of the pyrophosphate lattice around 675° C.

B. Weight loss measurements

According to the equation, $2MgNH_4PO_4 \cdot 6H_2O \rightarrow 2NH_3 \uparrow + 13H_2O \uparrow + Mg_2P_2O_7$ a 54.7% weight loss is encountered after complete calcination at 1100° C. Since the thermal decomposition of the hydrate was of only secondary interest, no attempt was made to determine weight losses which occurred below 110° C. Other weight loss measurements were made between 110° C. and 1000° C.

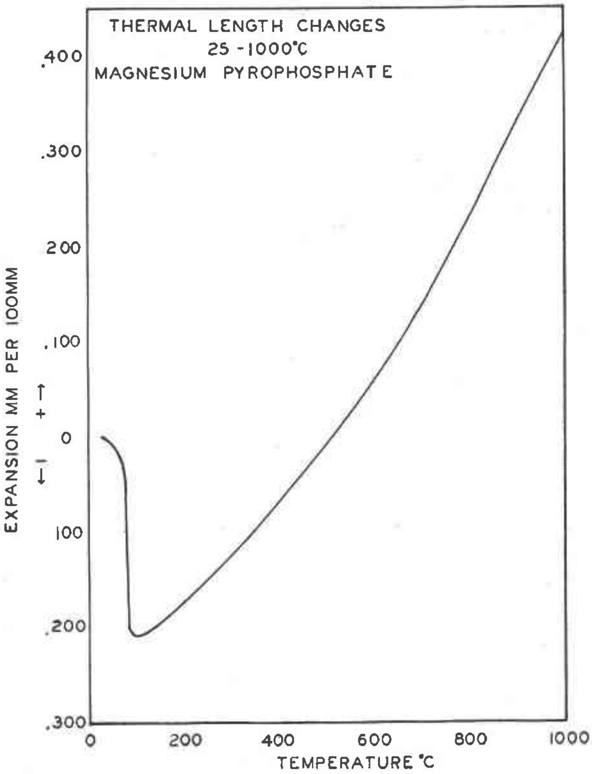

FIG. 3

Figure 2 illustrates average percentage weight losses, over the interval 110°–1000° C. Calculations at each temperature are based on the original weight of the sample dried at 110° C. The greatest loss in weight occurred below 200° C. In the interval 110°–200° C., it was approximately 19%. Above 200° C. losses in weight were relatively small and amounted to less than 6% in the range 200–1000° C.

IV. SOLID PHASE INVERSION OF $Mg_2P_2O_7$

A. Results of thermal expansion measurements

The samples used for expansion runs were made from magnesium pyrophosphate which had been calcined one hour at 1150° C., passed through a 120 mesh screen, temporarily bonded with a water solution of Carbowax and Methocel, pressed into bar samples approximately $4'' \times \frac{1}{2}'' \times \frac{1}{2}''$ in size, and finally fired for $\frac{1}{2}$ hour at 1320° C. An expansion apparatus utilizing a fused silica sample holder, fused silica transmission rod and dial gauge reading to one ten-thousandth of an inch was used to measure length changes.

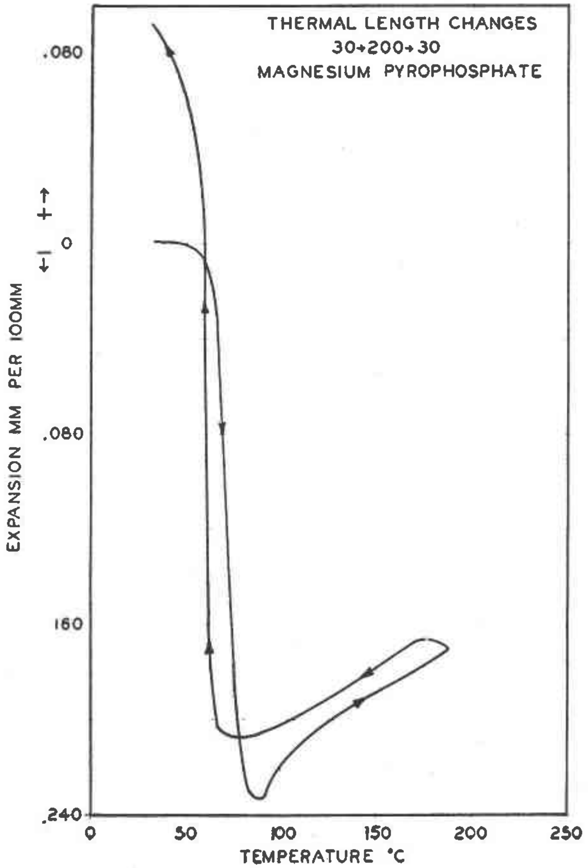

FIG. 4

It was found that in a regular expansion run, while heating at a rate of 100° C. per hour from room temperature to 1000° C., the sample contracted very rapidly from about 50°–90° C. and reached a minimum at about 95° C. At this point, expansion began, and proceeded at a regular rate until the run was completed, at 1000° C. This period of contraction coincides nicely with the temperature region near 68° C., where the inversion from low to high magnesium pyrophosphate takes place, as determined by thermal analyses and *x*-ray patterns.

Figure 3 shows the expansion in mm./100 mm. plotted against temperature, and illustrates the contraction of the sample during the period 50°–90° C., with normal expansion from 95°–1000° C. The coefficient of expansion of the high temperature form of $Mg_2P_2O_7$ over the range 100° C. to 1000° C. was approximately 70×10^{-7} cm./cm.° C.

Thermal length changes were also measured on a sample which was heated from room temperature to 200° C. and then cooled from 200° C. to room temperature. The rate of heating in these runs was considerably slower (about 60° C. per hour), and magnified curves of thermal expansion and contraction near the inversion temperature were obtained. These curves, as expected, showed rapid contraction between 50–90° C. on heating and a gradual expansion from 95–200° C. On cooling from 200° C., there was a gradual contraction of the sample until 70° C. was reached. Here a very rapid expansion took place, tapering off gradually below 50° C. and leaving the sample with a permanent length change of approximately 0.1%. The solid phase inversion, it would appear, is reversible. The following curve (Fig. 4) shows graphically the results of the expansion-contraction run between room temperature and 200° C.

The fact that the inversion took place within a narrower temperature range on cooling may be due simply to the existence of a more uniform temperature distribution in the sample on cooling as compared with the distribution during the heating cycle. After repeated heating through the inversion range, bar samples showed many cracks over their entire length, giving further physical evidence of the disruptive force of the reversible volume change.

B. Results of thermal analyses

The samples used were magnesium pyrophosphate powder which had been calcined one hour at 1150° C., cooled, then passed through a 150 mesh sieve. The apparatus used was the same as that described in Part A of Section II above.

There was but one peak on the differential heating curve. This peak was endothermic, with a deflection corresponding to about 0.4 millivolt and had its maximum at 68–70° C. The endothermic peak, Fig. 5, represents a change in lattice structure from the low temperature monoclinic

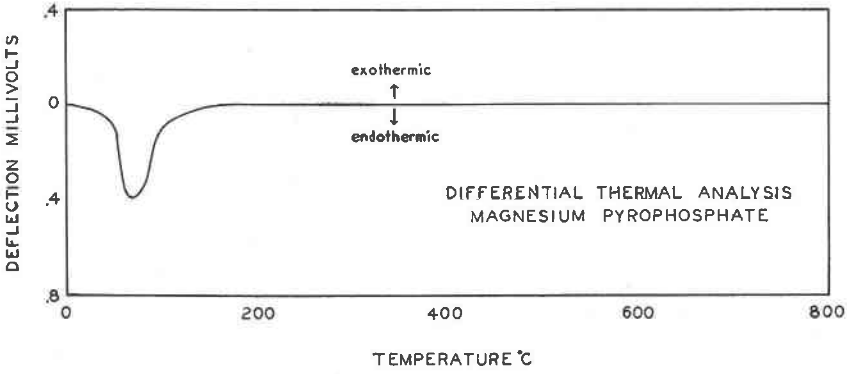

Fig. 5

form usually reported (5) to some high temperature form, the crystal structure of which has not yet been determined.

Further evidence of the reversibility of the inversion was obtained by recording the heat effects shown by the above samples on both heating and cooling. Figure 6 is a plot of these effects.

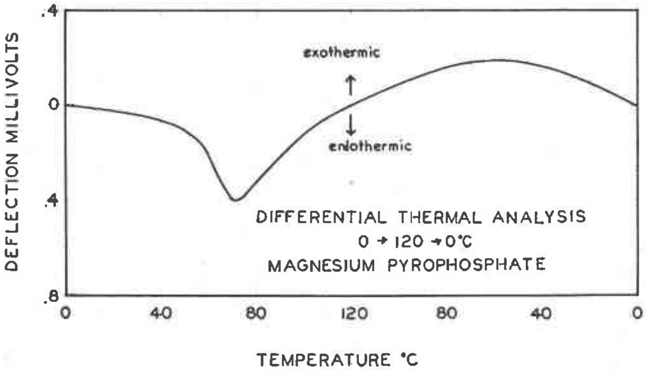

Fig. 6

The height of the endothermic peak was greater than that of the exothermic peak, but the areas under both curves were approximately equal.

C. Results of x-ray analyses

The *x*-ray data were obtained by the use of two different machines, the first being a General Electric, Model XRD, Type 1, giving iron radiation ($\lambda = 1.93$ Å) passed through a beryllium window. Conventional Debye-Scherrer powder photographs were made with a camera of 7.16 cm. radius. The tube was operated at 5 milliamperes and exposures were made for six hours.

Additional *x*-ray patterns were obtained with a Norelco Geiger-counter *x*-ray Spectrometer, Type 42322, with CuKα radiation (λ= 1.537 Å), filtered through nickel. The peaks from this machine are automatically recorded on a Brown "Electronik" strip chart potentiometer. Ninety minutes were required to traverse the 90° goniometer arc and the tube was operated at 5.7 milliamperes.

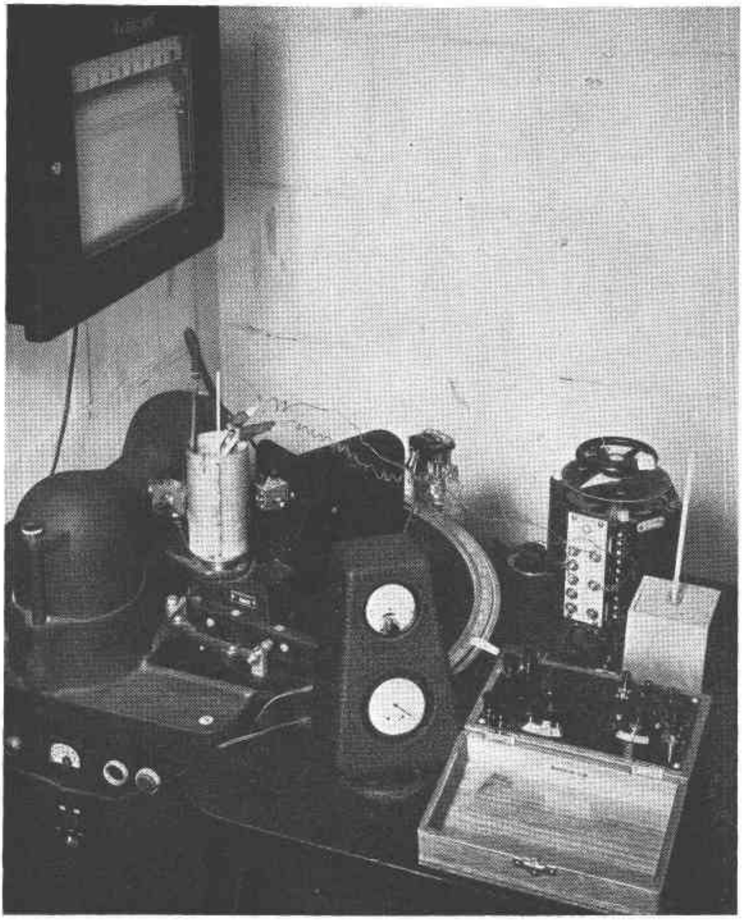

FIG. 7

The heating furnace which was used on this latter machine was of simple design and was constructed in the instrument shop of the School. It was similar in many of its essential features to the recently published (6) Bureau of Standards design as can be seen in Figs. 7 and 8.

To test the furnace element one may calibrate it by using known inversions as fixed points, or as shown by Jay (7), by actually measuring the expansion of a known substance.

The expansion of quartz was determined from room temperature to 700° C., and good agreement was obtained with the known values. The break in the curve at the inversion temperature (Jay, 7 cit.) was found to be at 575° C. ± 5. The constancy of temperature over the sample face, as also over the period of time concerned, was ± 5° C. Standardization in the range of the sample studied was obtained with ammonium nitrate as used by Buerger (8), et al. The inversion temperature obtained was 83° C. which is in excellent agreement with previous values. To deter-

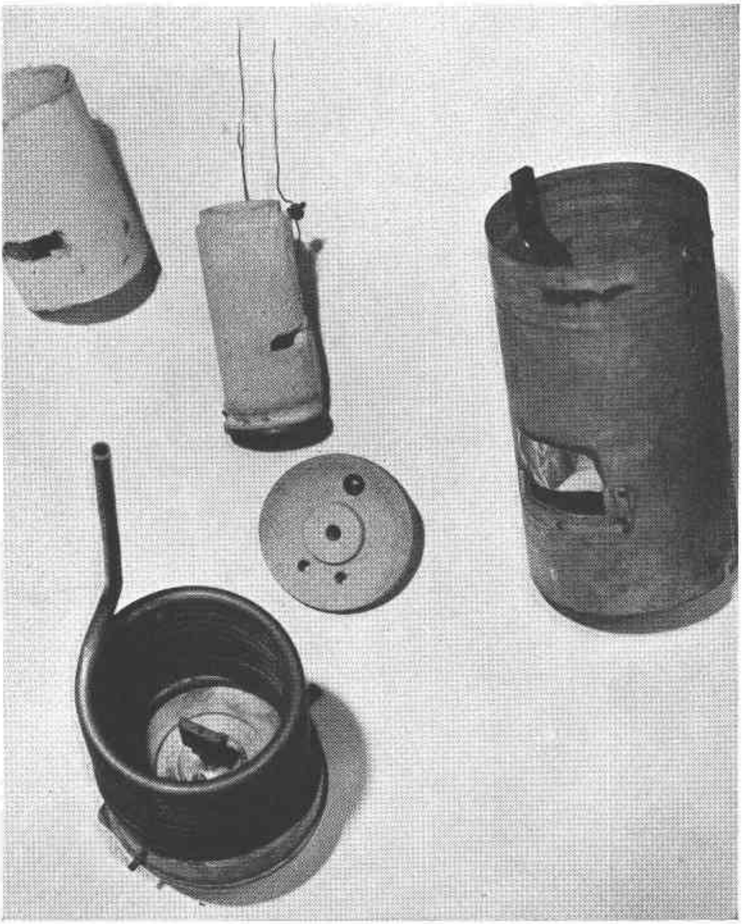

Fig. 8

mine the temperature of inversion, x-ray patterns were taken at temperatures above and below the expected temperature, in a regular series. This gave the limits within which the inversion had taken place. To avoid the more tedious process of taking a large number of complete patterns at each of a series of closely spaced temperatures, the following modification was devised: The Geiger-counter arm was fixed at an angle where the phase to be formed has an intense peak corresponding to a reflection. The temperature of the furnace was then raised or lowered very slowly across the range. Since there was not control to insure a uniform rate of rise of temperature, temperatures were read and recorded frequently. The shape of the curve obtained as a record of the intensity of the reflection gives an excellent indication of the temperature of inversion. The two changes in slope and two level areas will be seen to stand out well in Fig. 9, the actual record for NH_4NO_3.

TABLE 1. SPACINGS FOR LOW AND HIGH TEMPERATURE FORMS OF $Mg_2P_2O_7$

ASTM card catalogue low temperature form		Norelco machine				General Electric machine low temperature form	
		low temperature form, 25° C.		high temperature form, 250° C.			
"d"	Rel. Int.	"d"	Rel. Int.	"d"	Rel. Int.	"d"	Rel. Int.
4.14	.10	4.14	.19	4.175	.2		
3.85	.04	3.85	.07				
3.45	.05	3.465	.09				
		3.15	.09				
3.00	1.0	3.00	1.0	3.01	1.0	2.995	1.0
		2.97	.45	2.92	.35	2.965	.50
2.51	.08	2.52	.14	2.535	.09		
2.40	.05	2.41	.10				
		1.87	.04	1.865	.08		
1.85	.10	1.846	.05	1.828	.08		
2.30	.01						
2.15	.02						
2.09	.15	2.09	.11	2.10	.11		
		1.714	.02	1.72	.04		
1.69	.08	1.70	.06	1.68	.03		
1.57	.10	1.57	.08	1.585	.16	1.57	.30
1.465	.07	1.469	.02	1.48	.05		
1.38	.06	1.385	.02	1.385	.06	1.38	.16
1.322	.07					1.32	.1
1.250	.05						
						1.138	.2
						1.05	.3
						1.011	.1
						1.00	.8

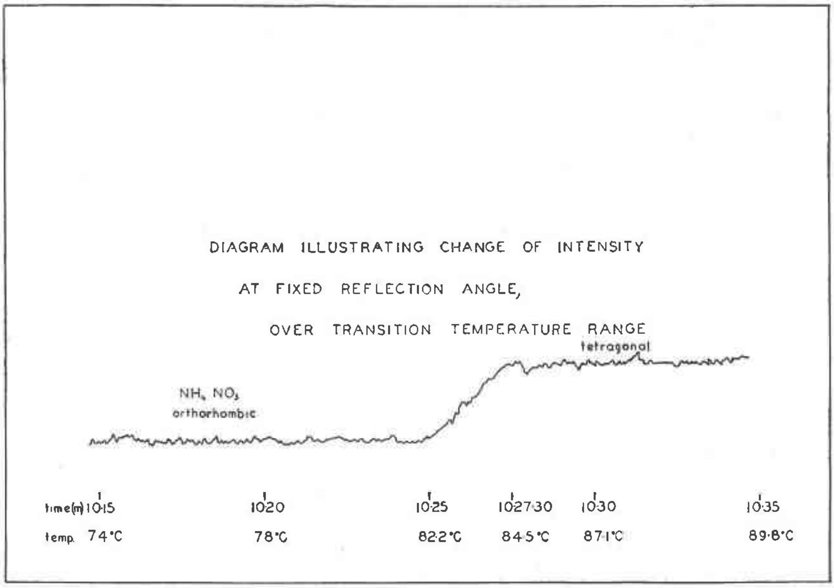

FIG. 9

Table 1 gives the three sets of "*d*" values for the monoclinic low form of $Mg_2P_2O_7$ obtained, (a) with the sample in the furnace on the Norelco machine, (b) by the General Electric machine, (c) from the ASTM manual, each at 25° C. Comparison of the experimental values with the ASTM data shows some definite omissions in the latter, due probably to lack of resolution of some doublets. Complete recordings over the arc 2–90° were run at temperatures as low as 7° C. and also at 20, 40, 60, 80, 100, 250, 450 and 850° C.

A distinct change was noticed between the temperature of 60° C. and 80° C. The main differences may be noticed in the disappearance of the peak at 30° 27′ and the appearance of a new peak at 30° 55′. These same peaks were examined at temperatures of 62, 64, 66, 67, 68, 70 and 73° and the appearance of the change is illustrated by Fig. 10, and the temperature of the inversion could therefore be put at $68 \pm 2°$ C. The simultaneous existence of the two peaks, in the light of the immediate low to high reversible type of change admits of two explanations. Firstly, that some of the material at all these temperatures is at a different temperature from the rest, due to air currents and surface cooling; secondly, that the change actually takes place over a very small range of temperature. The former is the more probable explanation although the latter would be very interesting if true.

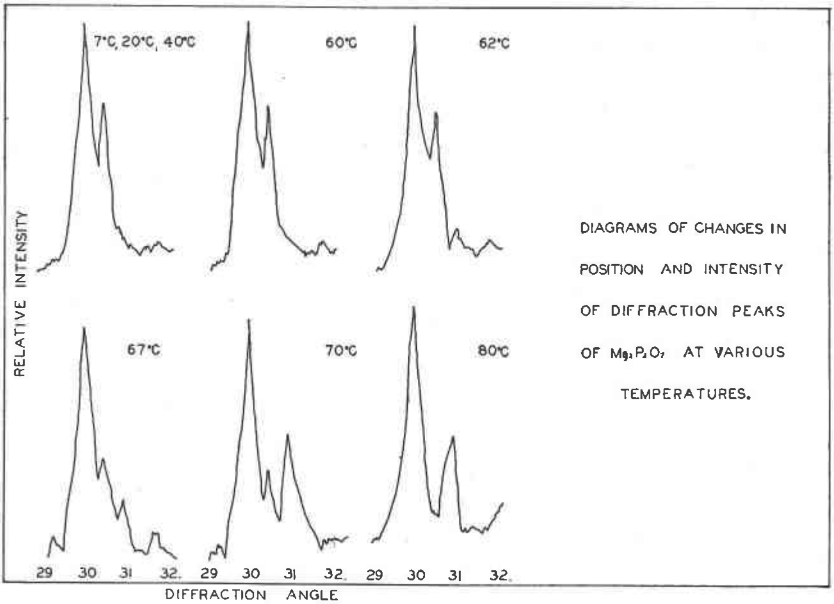

FIG. 10

This rapid and simple method of determining inversions should find wide application. The extension of the upper temperature limit to 1500° C. with an alumina holder and a platinum-wound furnace is a simple step, and the study of high temperature forms, especially in the rapidly reversible type systems, should be much simplified. The chief difficulty lies in the falling of the sample from the holder due to decomposition, or due to inversions accompanied by large volume changes. The remedy for this would appear to be the construction of the Geiger-counter type of instrument with the entire Geiger tube arm and the arc lying in a vertical instead of a horizontal plane, which would then allow the sample to be placed and subsequently heated on a horizontal surface.

Another possible method for high temperature work which would not involve radical changes in the design of the present *x*-ray machine would be the use of a thin sheet of beryllium metal foil for holding the sample in a "pocket" between the foil and the glass slide.

V. SIGNIFICANCE WITH REGARD TO ISOMORPHISM AND POLYMORPHISM

The investigation of the thermal behavior of $Mn_2P_2O_7$ is planned since this compound has been reported to be isomorphous with $Mg_2P_2O_7$ (9). A study of the behavior of other divalent pyrophosphates of zinc, nickel, cobalt and iron might reveal similar inversions due to the close proximity of the ionic radii of each of these elements to that of magnesium. Similar inversions for zinc pyrophosphate and copper pyrophosphate have already been detected here, although the ionic radius of copper is considerably larger than that of magnesium.

The fact that these inversion temperatures can be determined quite accurately, that the pyrophosphate group is common to all the compounds, and that the ionic or atomic radii of these divalent cations are well known from independent data may serve to shed some light on the nature of polymorphic changes.

When the structures of the high temperature forms of the pyrophosphates are determined, it may be possible to state whether the change is due to rotating molecular groups, such as has been suggested for ammonium nitrate (10), or whether increased thermal motion causes a partial dislocation of certain atoms similar to the well-known cristobalite transition.

VI. SUMMARY AND CONCLUSIONS

A thermal study of the decomposition of $MgNH_4PO_4 \cdot XH_2O$ reveals no new data relative to the mechanism and temperature of loss of H_2O and NH_3.

By means of thermal analyses, thermal expansions, and *x*-ray data, a solid phase inversion of $Mg_2P_2O_7$ has been placed at approximately 68° C. *X*-ray data indicate an accuracy of ±2° C. for the rapid low to high inversion.

A large volume contraction and an endothermic heat effect attend the change from the low temperature monoclinic form to a high temperature form whose crystal system has not yet been determined.

The density and refractive indices previously reported (11) for $Mg_2P_2O_7$ are apparently for the low temperature monoclinic form, while the melting point data (11) are for the high temperature form.

ACKNOWLEDGMENT

Appreciation is expressed to Dr. T. F. Bates of the Department of Earth Sciences for suggestions concerning the construction of the high temperature *x*-ray furnace and to Dr. E. C. Henry and Dr. H. M. Davis of the Department of Mineral Technology for encouragement during the course of the work.

REFERENCES

1. Applied Inorganic Analysis, Chapter XI, Hillebrand and Lundell, John Wiley and Sons, New York.
2. Treatise on Inorganic Chemistry, Mellor, J. W., Macmillan, London.
3. Dissociation of $MgNH_4PO_4 \cdot 6H_2O$ and some related substances, Kiehl, S. J., and Hardt, H. G.: *Jour. Am. Chem. Soc.*, **55**, 605 (1933).

4. Phosphates, IV, pyrophosphates of some divalent metals and their double salts, and solid solution with sodium pyrophosphate, Bassett, Henry, Bedwell, Wm. L., Hutchinson, J. B.: *Jour. Chem. Soc.*, 1412–1429 (1936).
5. Microscopic Characters of Artificial Minerals, Winchell, A. N., John Wiley and Sons, New York.
6. High temperature *x*-ray diffraction apparatus, Van Valkenburg, A., and McMurdie, H. F.: *Bull. Amer. Ceramic Society*, **26** (5) 139 (1947).
7. The thermal expansion of quartz by *x*-ray measurements, Jay, A. H.: *Proc. Royal Society*, A **142,** 237–247 (1933).
8. Apparatus for making *x*-ray powder photographs at controlled elevated temperatures, Buerger, M. J., Buerger, N. W., and Chelsey, F. G.: *Am. Mineral.*, **28** (5), 285 (1943).
9. The crystallographic and optic properties of magnesium and manganese pyrophosphates, Andersen, O.: *Jour. Wash. Acad. Sci.*, IV, 318–325 (1914).
10. Group rotation in solid ammonium and calcium nitrates, Kracek, F. C., Hendricks, S. B., and Posnjak, E.: *Nature*, **128.** 410–411 (1931).
11. Data on chemicals for ceramic use: *Bull. of the National Research Council*, **107** (June 1943).