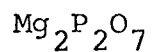


α - β PHASE TRANSITION IN $\text{Mg}_2\text{P}_2\text{O}_7$

A STUDY OF PHASE TRANSITION IN



BY MEASUREMENT OF SPECIFIC HEAT

by

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Content:

The specific heat of $(\text{Mg}_{1-x}\text{Mn}_x)_2\text{P}_2\text{O}_7$ was measured in the vicinity of the alpha-beta phase transition for $0 < x < 0.04$. The temperature and character of the phase transition were found to depend on the composition of the sample and the method of preparation. The results are discussed with relation to the crystal structures of $\text{Mg}_2\text{P}_2\text{O}_7$ and $\text{Mn}_2\text{P}_2\text{O}_7$.

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CHAPTER I
INTRODUCTION

1. An Outline of Some Problems of Current Interest in the Study of Solids.

An important problem in the study of the solid state of matter is the design of simple criteria by which the different type of solids that occur in nature can be classified. An informative way to characterize solids is with respect to the nature of the interaction that provides the dominant contribution to the binding energy between some simple and convenient units into which the solid can be divided. As an example, sodium chloride appears as a regular array of monovalent ions of opposite electric charge and is called an ionic crystal because the simple Coulomb interaction between the ions is the largest term in the Hamiltonian describing the solid state binding. Similarly, solids that are basically neutral molecules held together by van der Waals forces are called molecular crystals.

Not all solids are amenable to such simple description. In some - an example would be the various metal phosphates in the solid state - the binding energy is a sum of several terms of about equal magnitude. One such term would be the attraction between

a metal cation and anions of the form PO_4^{-n} . This interaction may be in varying degree ionic or covalent in character. Equally large is the energy residing in the various covalent bonds that bind the PO_4^{-n} radicals together in an interconnected pattern of three dimensions.

A principal task of the experimental study of solids is to find out where the various atoms are located in the unit cell. Since the number of atoms that form the unit cell is often very large for the family of phosphates presently discussed, an x-ray study of their crystal structure became feasible only fairly recently with the advent of large computers. Now the structure of many of them is known, with a large part of these determinations conducted by C. Calvo and his students at McMaster University. It became apparent that these phosphates could be classified (Robertson, 1967) according to the type of anion. Specifically, attention has been paid to a series of pyrophosphates, a group in which two PO_4 groups share one of their oxygen atoms to form a $\text{P}_2\text{O}_7^{-4}$ anion. Since these pyrophosphates exhibit interesting polymorphic behaviour that depends to a great extent on the size of the metallic ion, the pyrophosphates of Mn, Zn, Cu, Co and Mg were investigated, because these cations have comparable size with radii less than 1 \AA . A common feature of all these compounds is that they occur at some temperature with the structure C2/m ,

denoted hereafter as the β phase and, with the exception of $\text{Mn}_2\text{P}_2\text{O}_7$, make transitions to distinct, though related α phases at some lower temperature characteristic of each substance. The details of these structures, as well as the crystallographic aspects of the phase transitions, are described by Robertson (1967), Calvo, (1967) and their references.

The determination of the crystal structures is but a first step in the study of these solids. Further work may be needed to clear up certain minor structural ambiguities not readily resolved by conventional x-ray methods, for example by the technique of electron spin resonance (ESR) (Chambers et al., 1964). Once the positions of the atoms are known, the details of their interactions become of interest, for example the nature of ligand fields at the cation sites or the presence of exchange among the transition metal ions. ESR studies have already been reported on $\text{Zn}_2\text{P}_2\text{O}_7$ (Chambers et al., 1964) and on $\text{Mg}_2\text{P}_2\text{O}_7$ (Leung, 1964). Investigations, exploring mainly the magnetic properties of several transition metal pyrophosphates by the techniques of nuclear magnetic resonance, ESR, and measurement of magnetic susceptibility have either been completed, or are presently under way.¹ The work reported in this thesis was inspired by some problems that arose in investigations of this sort.

¹ C. V. Stager, private communication.

2. Past Investigations of Mg₂P₂O₇.

A phase transition of Mg₂P₂O₇ was first reported by Roy et al. (1948), whose differential thermal analysis and powder x-ray diffraction studies showed a transformation centered at $68 \pm 2^{\circ}\text{C}$, with the two phases coexisting over a temperature range of approximately 20°C . Their findings were corroborated by the more precise work of Oetting and McDonald (1963), whose measurement of the specific heat of Mg₂P₂O₇ assigned the temperature $69 \pm 1^{\circ}\text{C}$ to the transition, which again occurred over a 20°C temperature range.

The crystal structure of Mg₂P₂O₇ was reported in two papers by Calvo, (1965, 1966) in which it was shown to be monoclinic in both the α and β phases. The high temperature β phase was found to belong to the space group C2/m, and is therefore isostructural to the high temperature form of all other members of the series already described. Below the phase transition, the crystal appears in the α phase which has B2₁/c symmetry, and the a and c axes of the unit cell both double their values in the β phase.

The most prominent feature of the change in crystal structure is that the P-O-P group of the pyrophosphate ion changes from an apparently linear configuration in the β phase, to a form enclosing an angle of 144° in the α phase. Coupled with this is a change of one of the two crystallo-

graphically inequivalent magnesium ions from six to fivefold coordination with surrounding oxygen atoms.

3. A Statement of the Problem Presently Investigated.

The need for the present work mainly arose in trying to explain some questions brought to light by the ESR studies of Leung et al. (1964) on $\text{Mg}_2\text{P}_2\text{O}_7$. In this work the position of the magnetic axes and some of the Spin Hamiltonian Parameters were measured, both above and below, as well as during the phase transition, and it was found that the above described transformation occurred at 61°C , about 8°C lower than previously reported. Also, the two phases appeared to coexist only over a 4°C temperature interval. They studied small, $1\text{mm} \times 1\text{mm} \times 0.5\text{mm}$ crystals, doped with nominally 0.3% Mn^{2+} to serve as the paramagnetic probe, and observed similar results when the crystals were doped with Cu^{2+} . In the latter case, the transition appeared to take place between 63 and 66°C in a continuous manner.

Since their sample, aside from its impurity content, also differed from the specimens of earlier investigators in its method of preparation, being grown from the melt, it was thought that one of these differences could have caused the observed discrepancies. Measurement of the specific heat, as will be seen, is a sensitive method of monitoring phase

transitions, and the following is a report on such measurements carried out on $\text{Mg}_2\text{P}_2\text{O}_7$ samples with varying Mn^{2+} concentration, as well as having different thermal treatment and method of preparation. It was also hoped that by observing the enthalpy change that takes place during the transitions, a quantitative measure of the energy differences between the two related structures could be obtained.

CHAPTER II

THERMODYNAMIC THEORY OF PHASE TRANSITIONS

1. Macroscopic Description of Matter and the Concept of Phase

The question "which observables describe a system completely?" can be simply answered: they are the fewest number of parameters that allow reproducibility of experimental results. For example, when studying the magnetization of some solid as a function of external magnetic field, one soon learns that it is important to keep track of the temperature. It is the role of theory to devise functions that depend only on the experimentally independent parameters, and hopefully, no others. It is a common aim of theorists to do this in the simplest possible fashion.

It is not necessary to monitor the values of all independent parameters in all experiments, but only those that are allowed to change. In the above cited example, the pressure could be kept constant, and this way the experiment would reveal a relationship only among a limited number of variables, and such a relationship is often called an equation of state. The question arises whether a "Master Function" can be found that completely describes the system,

that depends only on parameters that are necessary to describe all performed experiments, and that contains some principle that prescribes how some new parameters that might arise in the course of some future experiment could be incorporated into the theory. Such a function ought to reduce somehow to an equation of state when the relationship among only a few of the parameters is considered.

A well known example of such a theory is the Lagrangian formulation of classical mechanics: it includes only the position and velocity coordinates of all particles as independent parameters, and the Lagrangian function, dependent only on these variables, completely describes the system. The simplicity of the theory can be summarized by stating that the behaviour of a system is governed by a single variational principle that seeks the extremal values of the Lagrangian.

A similar theory was formulated by L. Tisza (Callen, 1960) to describe thermodynamics. Here the "Master Function" is the energy (U), and it is a function of such parameters as the entropy (S), volume (V), and the partial molar concentrations of the component pure substances (N_i). Parameters of future experiments can be included through a recipe that augments the total differential of U by a term representing the work increment that is contributed to the system by allowing the new parameter to change. As this

work increment is clearly defined experimentally, the theory is easily extended to embrace future problems.

The formulation in the above form contains variables that are hard to control experimentally, for example the volume. The experimentally convenient parameters, such as the pressure, appear in the above formulation as the derivatives of the "Master Function" with respect to one of the independent variables. It is possible though to obtain "Master Functions" which have these derivatives as the independent variables: they are constructed by a Legendre Transformation that defines new "Master Functions", usually called thermodynamic potentials or free energies, which again completely describe the system, and in which the old parameters assume the role of the derivatives. For example, the Gibbs free energy, as a function of temperature and pressure, would describe volume as the derivative with respect to pressure. This latter relationship, arrived at by simple differentiation, is an equation of state, which would completely account for a limited experiment. That this equation of state does not possess all the possible information about the system is seen by noting that through differentiation one always introduces some indeterminacy.

The aims of thermodynamics are well summarized by some of the salient characteristics of a "Master Function", for example the energy as the function of a suitable number

of parameters.

To begin with, it gives no information on how a system changes, but rather, on the equilibrium conditions of the system when isolated or in contact with a reservoir of known properties. The function determines the locus of points of possible final states of the system in the configuration space of the chosen parameters. The final state of the system is selected from the range of the function by the criterion that, if one parameter is allowed to vary and all others are kept constant, then the system settles down to that value of the variable parameter that makes the thermodynamic potential representing the system a minimum. The different thermodynamic potentials are selected according to the characteristics of the reservoir with which the system makes contact: it would be the energy for an isolated system, and the Gibbs free energy for a reservoir at constant temperature and pressure.

One can now define the concept of phase: it is a homogeneous distribution of matter in space that can be characterized by a single thermodynamic potential. It is possible of course that different regions of space are filled by matter of the same chemical composition, but described by thermodynamic potentials defined over an identical domain of independent parameters and having different functional characteristics (e.g., having different ranges).

When such regions are in direct contact, one speaks of coexistence of phases.

2. Principles Governing Coexistence of Phases

Since the equilibrium state of a system selects the minimum value of a free energy over that domain of independent variables that is allowed to vary, if there are two functional dependences available describing two coexisting phases, at the equilibrium point of independent variables these functions must assign to the free energy equal values. Assuming a mixture of two substances coexisting in two phases, one could select the Gibbs free energy which is a function of independent variables T , P and X_1^I , X_1^{II} , to describe the system. Here X_1^I denotes the amount of the first substance in phase I. One need not specify similar concentration for the second substance, since the sum $X_1 + X_2$ remains constant. The condition for coexistence will be

$$\mu_1^I(T, P, X_1^I) = \mu_1^{II}(T, P, X_1^{II})$$

$$\mu_2^I(T, P, X_1^I) = \mu_2^{II}(T, P, X_1^{II})$$

where μ_2^I denotes the chemical potential of substance 2 in phase I. Since one has four independent variables and only two conditions, for any values of X_1^I and X_1^{II} specified, one

can still assign arbitrary values of T or P. However, if one had a pure substance existing in two phases, there would be the condition

$$\mu^{\text{I}}(T,P) = \mu^{\text{II}}(T,P)$$

on the two variables T and P, which would allow one to be assigned arbitrarily. The above considerations were a simplified statement of Gibb's phase rule, and show that a pure system can break up into two phases only at a single value of temperature when the pressure is kept constant.

3. Classification of Phase Transitions and Connection With Microscopic Description of Matter.

The mathematical condition that the appropriate free energy be a minimum is that its total differential (dU) vanish, and that its second differential (d^2U) be positive. The first condition will lead to some restrictions on the first derivatives of a "Master Function" such as T and P, while the second condition, the one ensuring stability, will mean conditions on certain second derivatives of the "Master Function", for example on the compressibility or specific heat.

Phase transitions are tied in with the stability of a system: they occur when small departures from equilibrium, brought about by fluctuations to neighbouring microstates

that are allowed by the specified independent variables of the system, lead to stable macrostates with new physical properties and from which the system does not return. The condition of positive definiteness of the second differential of free energy leads to certain restrictions on the first and higher derivatives of the free energy. Since the two competing free energies in a transformation have, as was indicated above, equal values at the transition point, the required difference in the functional characteristics of the two free energies will have to manifest itself in differences of the derivatives of some order. A classification, due to Ehrenfest (Callen, 1960) differentiates between transitions of different order depending on the lowest order of derivatives where discontinuities occur. Since only first order derivatives (essentially equations of state) and second order derivatives (the likes of specific heat and compressibility) are readily observed experimentally, only discontinuities in these have been observed thus far. A detection of discontinuity in, say, a derivative of specific heat, would require considerable improvement in the precision of measurement of specific heat itself and must be viewed, experimentally, as a problem an order of magnitude more difficult. For this reason, most theoretical efforts have been directed toward examining which are the characteristics of a system that contribute to the discontinuity of first

and second order derivatives. The problem has been almost always attacked, with some success, by two methods. One, attempting an explicit calculation of the partition function for a mathematically tractable model, will be briefly described in the next section. The other, developed by Landau, (Landau and Lifshitz, 1958) using arguments regarding symmetry so familiar in physics, will be examined now.

It has been known for a long time that a transition between two phases of the same symmetry, such as the liquid and gaseous state of some substance, can occur in either discontinuous or continuous fashion. (Figure 1).

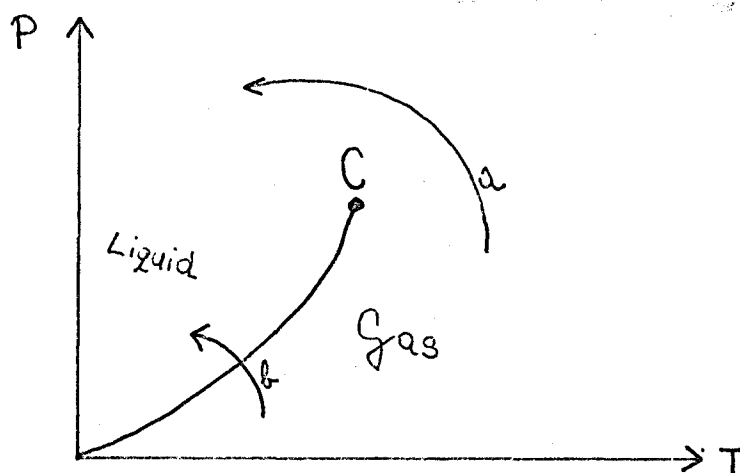


Figure 1. a) continuous path b) discontinuous path
Point C is the critical point.

One can ask the question as to what type of transitions can take place when there is a change of symmetry in the state of the system. Given two phases, each characterized by a different symmetry, the transition cannot go in both

continuous and discontinuous ways as in Figure 1: path a) cannot exist, for at each point on it, the specific symmetry, and therefore, the specific phase, either does or does not exist. In fact, it becomes evident that if a symmetry change takes place in an abrupt manner, such as sudden change in coordination number or strength of interaction, then already such quantities as specific volume and entropy will be affected and it will be a first order change. On the other hand, if the symmetry change takes place in a way that can be described by continuously varying a single parameter expressing deviation from a given symmetry, then the equations of state are continuous at the transition point, and this point fulfills the symmetry requirements of either phase. One sees that this is possible only in the event that the symmetry group of one phase is a subgroup of the other. Such could be the case when the symmetry changes by continuous elongation of a single lattice parameter, as in changing cubic symmetry to tetragonal.

Landau's theory, explaining the continuous type of transformation provides a direct bridge between the functional properties of the free energy and the symmetry of distribution of matter in a solid. This distribution is expanded in terms of the basis functions, $\phi_i^{(n)}$, of the group of the high symmetry phase in the following form:

$$\rho = \rho_0 + \delta\rho$$

$$\delta\rho = \sum_n \sum_i \eta c_i^{(n)} \phi_i^{(n)}$$

Here ρ is the density distribution in the low symmetry phase and ρ_0 that in the high symmetry phase. η is a continuously varying parameter, which ensures that $\delta\rho$ vanishes at the transition point in a continuous manner. The above expansion leads to a corresponding expansion of the free energy in terms of the coefficients c_i of the functions ϕ_i above, the latter assumed to be constant near the transition point. One obtains

$$\phi = \phi_0 + \sum_p \sum_n \sum_\alpha A_{\alpha n}^{(p)}(P,T) f_{\alpha n}^{(p)} \eta^p$$

where $f_{\alpha n}^{(P)}$ is one of the α invariants of the p^{th} order that can be constructed from the c_i 's appearing in the n^{th} irreducible representation. The fact that, by algebraic considerations, no linear invariants exist, means that no linear terms in η appear in the above expansion. There is only one second order invariant for each representation, and since it is positive definite, one has to impose the condition that $A_{1n}^{(2)}(T,P)$ vanish at the transition point. This is a condition on P and T . In order to preserve at least one degree of freedom in configuration space, only one such condition can be imposed. Therefore, the conclusion is arrived at that the expansion of density in the high and low symmetries can differ by only one irreducible representation. By stability criteria, third order terms in η must vanish identically, which restricts transitions between high and

low symmetry groups that have no third order invariants at all. These and similar restrictions on the $c_i^{(n)}$'s completely determine the related symmetry groups among the ones appearing in solids that can be transformed into one another by a second order transition.

4. The Partition Function Method and the Tobolsky Model for Diffuse Phase Transitions

Corresponding to the "Master Equation" in thermodynamics, one has distribution functions of microstates of a system that are functions of the same macroscopic variables that determine the "Master Equation", with the true energy of interaction among the components replaced by that prescribed by some mathematically feasible model. Such a distribution is the partition function for an ensemble determined by the type of free energy one wants to account for microscopically.

A mathematically tractable model is the Ising Model (Huang, 1963) which enables one to evaluate the partition function for a system of components positioned along a chain, with only nearest neighbours interacting. Once the partition function is determined for a system, everything else, such as the entropy and specific heat, is easily determined by differentiation.

It was mentioned earlier that as a consequence of the Gibbs Phase Rule, in a single component system a first order phase transition must occur isothermally if the pressure is kept constant. It is evident from the literature that some phase transitions, which have to be classified as being of first order on account of the discontinuity of the entropy, occur in a continuous manner over some finite temperature range. Transitions of this type were already noted by Meyer and Streeter in 1939, and were called diffuse phase transitions by them. In the intervening years, a considerable amount of data has accumulated about transitions of this type: the transition of $\text{Mg}_2\text{P}_2\text{O}_7$ was classified as being an example by Oetting and McDonald (1963). Data documenting the coexistence of the α and β phases over a range of temperature, as revealed by the simultaneous appearance of x-ray reflections characteristic of the two symmetries is contained in the paper of Calvo (1967).

No basic theory exists that can account for the simultaneous appearance of the two phases at different temperatures. However, it is possible to account for the details of the transition, such as the general shape of the C_p vs T curve, by constructing a partition function whose principal feature is the ad hoc introduction of the two principal phases and a third boundary phase separating them, each with its characteristic energy. Such a partition

function from which all other thermodynamic quantities can be derived, was already sketched by Meyer and Streeter. An explicit formulation, using the one dimensional Ising Model to construct the partition function, and designed mainly to account for the specific heat anomalies that have now been observed for so many solid-solid transitions, was advanced by Tobolsky et al. (1965).

They construct a partition function by the Ising Matrix Method from the quantities $y = f_{\beta}/f_{\alpha}$, the ratio of the partition functions of individual molecules in phases β and α respectively, and $\epsilon = (f_K/f_{\alpha})^2$, where f_K is the partition function of a molecule in the postulated boundary phase. Since

$$y = \exp -[(\Delta G_t)/RT],$$

and

$$\Delta G_t = \Delta H_t - T\Delta S_t,$$

with

$$\Delta H_t = \int \Delta C_p(T) dT \quad \text{and} \quad \Delta S_t = \int \frac{C_p(T)}{T} dT$$

y can be directly observed by measuring the specific heat over the transition region. Once y is found, all their theoretical expressions, for the molar fractions of the phases α and β , and K , as well as for the excess specific heat, ΔC_p , all functions of temperature, contain only one parameter, ϵ , that connects the theory to a particular substance. This one parameter is computed by comparing the experimentally measured excess specific heat to the value

given by the theoretical expression at the "transition point" which is taken to be the maximum of the C_p vs T curve. The excess specific heat, for either phase, is found by subtracting from the actually measured specific heat the value found by extrapolation from the "normal region" base line on either side of the above defined transition temperature. In their analysis, the particular molar ratios of each phase at a specific temperature at which they exist in equilibrium depend on the manner in which y and ϵ depend on the temperature: it turns out that most of the dependence comes from y , and ϵ is taken to be approximately constant over the transition region. This procedure results in a symmetric curve; the inclusion of the temperature dependence of ϵ can be used to account for curves that are observed to be asymmetric. Since the only connection between this formulation and experiment is the value of the excess specific heat, a very great precision in the establishment of base lines is required for any meaningful analysis of experimental results.

5. The Connection of Some Concepts Used in the Description of the Experiment with the Theory Described.

When energy is transferred to a single component system (e.g., the system is heated) in such a way that the pressure is held constant, the appropriate free energy is

the enthalpy (H), which is a function of S and P. Its total derivative is

$$dH = \left. \frac{\partial H}{\partial S} \right|_P dS + \left. \frac{\partial H}{\partial P} \right|_S dP = TdS + VdP$$

At constant pressure one has

$$dH|_P = TdS|_P = dQ$$

$$\left. \frac{dH}{dT} \right|_P = \left. \frac{dQ}{dT} \right|_P = C_p$$

So it is seen that the experimental definition of specific heat, which is the increment of energy needed to cause unit temperature rise, can be expressed as a derivative of the "Master Function".

The total enthalpy change that occurs when some substance is heated from temperature T_1 to T_2 is

$$\Delta H(T) = \int_{T_1}^{T_2} C_p dT \quad (1)$$

The integral $H(T) = \int_0^T C_p dT$ may not vary continuously with T. If there is a discontinuity, then this corresponds to a discontinuity of the first derivative of the Gibbs free energy. This is seen as follows:

$$dG = -SdT + VdP$$

$$-\left. \frac{dG}{dT} \right|_P = S$$

But since $dH = TdS$ at constant pressure,

$$S(T) = \int_0^T \frac{dH}{T} dT = \int_0^T \frac{C_P}{T} dT \quad (2)$$

If there is a discontinuity in integral (1), there will be one in integral (2). But this latter is the first derivative of the Gibbs free energy, and therefore the transition will be of first order by the Ehrenfest criterion.

CHAPTER III

DESCRIPTION OF THE METHOD OF MEASUREMENT AND THE APPARATUS

1. Methods of Measurement of the Specific Heat. The Continuous Heating Method.

The specific heat at constant pressure has already been defined as $C_p = \left. \frac{dQ}{dt} \right|_p$, where Q is the energy (in form of heat) imparted to one mole of substance.

This definition renders C_p as a directly measurable quantity: one is to compare the ratios of very small increments of heat (ΔQ) and temperature rise (ΔT), much the same way as these concepts occur in the definition of the derivative in the calculus. This last reminder, of the calculus, is meant to bring to mind some of the experimental difficulties. To determine the specific heat at some temperature, one would have to observe the temperature rise corresponding to an infinitesimal heat input. There are two experimental limitations common to all methods of measuring the specific heat that prevent this. One is that the amount of temperature change that can be observed is limited by the properties of the thermometer used. If one

were to use, say, thermocouples to monitor the temperature, it would be difficult to find potentiometers that could resolve voltage changes that correspond to temperature changes less than a millidegree. But this is not all the trouble one encounters. One would have to make sure that the measured ΔQ that one imparted to the sample is the only one responsible for the rise in the temperature. Since no sample can be in practice ideally isolated, the minimum heat increment input, and therefore the minimum temperature interval over which the averaging process is taken, has to be considerably larger than the amount of heat lost to or from the sample. So one can easily see that both ΔQ and ΔT are experimentally limited from becoming mathematically ideal infinitesimals. Before mentioning two different approaches toward the measurement of the specific heat, yet another problem has to be mentioned, one that goes to the very foundations of thermodynamics. It is the question of equilibrium. It was already indicated that the usual thermodynamic functions describe matter only in an equilibrium state. So when a mass of some extent is heated by a definite heat input, one has to make sure that the sample has come to equilibrium before drawing conclusions about the changes observed. This is difficult even in the best of cases - the longer one waits, the more likely it becomes that other influences will reach the isolated sample - but it is a

particularly hard problem in the region where phase changes take place. As was already mentioned, in the vicinity of the transition point the system has more than one stable macrostate to choose from, as well as some metastable states that form a bridge between the two possible equilibrium states. In such cases, final equilibrium is sometimes reached only after very long times. The length of the time involved may be anywhere from years downward, and provides perhaps the most fundamental obstacle in studying phase transitions.

While there are many ways to measure the specific heat, all direct methods can be put roughly in one of two categories. In one kind, the changes due to a pulse-like heat input are observed. Very good isolation is required, for it is usually difficult to keep the environment at the same temperature during the brief heating spell. In the other method, both the sample and the environment are heated continuously, usually at constant power input. There are several advantages to the latter method when studying substances in regions of phase change. First of all, since the onset of phase changes immediately shows up in the specific heat, one would want to have data at as many points as possible. In the continuous method, the averaging weighs equally all temperature values. Another point in favour of the continuous heating method is that with steady power input, usually smaller energy per unit time is

imparted to the sample, and therefore one is closer to equilibrium. In the pulse heating method, the sample usually starts out somewhat below the temperature of the environment, and ends up above it, to approximately balance heat exchange. This serves to introduce greater temperature inhomogeneity, and therefore makes equilibrium even harder to attain. In contrast, in the continuous heating method the environment must be very close at all times to the temperature of the sample, to reduce heat exchange over the long period of heating. For this reason, it is sensitive to accumulated error, and perhaps more limited in precision so far as the absolute value of the specific heat at a certain temperature is involved. On the other hand, it is generally believed that it gives a more faithful picture of the anomalous specific heats that characterize critical phenomena.

The general design principles that determine the apparatus used in the experiments presented here will be evident from the description in the next section. It is sufficient to say that since the transition point falls about midway between the freezing and boiling points of water, the principal insulation problem was that of preventing heat exchange by conduction through the electrical leads. The minor extent of radiation at these temperatures allowed some compromise to be made in the design of the adiabatic shield.

2. The Adiabatic Calorimeter.

The design of our equipment for the measurement of heat capacity by the Continuous Heating Method follows in principle those outlined in the literature, e.g. by Dauphinee, et al. (1954). No specific effort was made to develop an apparatus that compared in precision with the best that has been reported in the literature for the measurement of heat capacity, since our main purpose was to measure the temperature of the phase transition and the width of the specific heat anomaly.

The apparatus, (Figure 2), essentially consists of a copper calorimeter, surrounded by a copper adiabatic shield, suspended in an evacuated glass jacket. The calorimeter consists of a copper cylinder of typically 3.8 cm height and 2.7 cm diameter, with a concentric cylindrical well of 1.4 cm diameter and 2.8 cm depth extending from its top. The copper shell of the calorimeter was typically of 0.07 cm thickness, except at its bottom, where a rim of about 0.2 cm height and 0.12 cm thickness was machined to support a removable copper lid. All these dimensions varied about 10% from one run to another, for a calorimeter served for only two or three measurements. The calorimeter weighed about 20 g, and contained a powdered sample of about the same weight. The calorimeter was charged

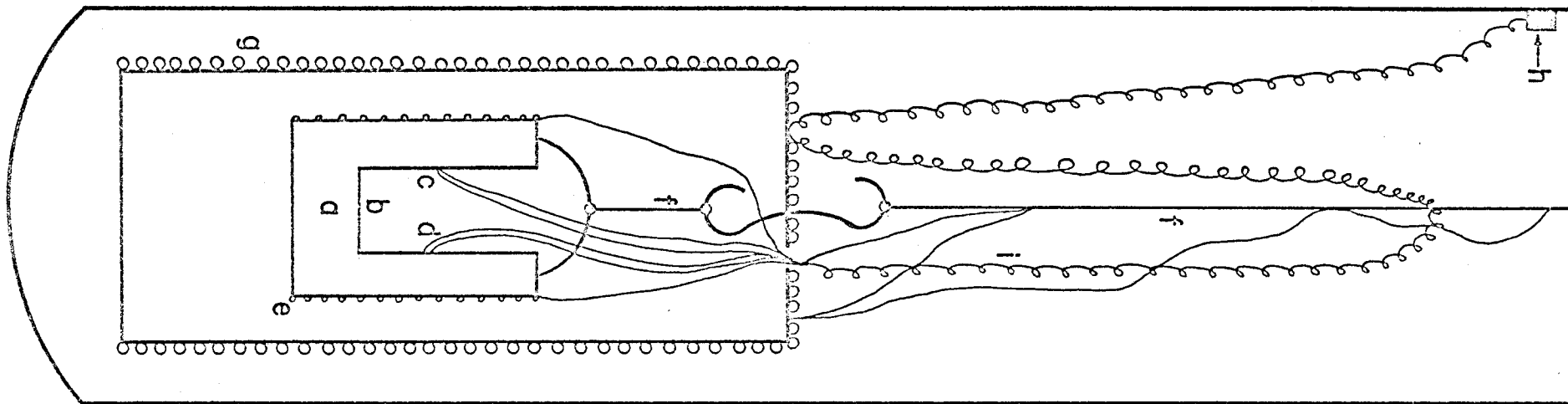


Fig.2. The Calorimeter Assembly: (a) calorimeter containing the sample, (b) well ensuring thermal homogeneity, (c) difference thermocouple between calorimeter and shield, (d) "absolute" thermocouple, (e) calorimeter heating coil, (f) cotton thread, (g) shield heating coil, (h) small magnet, (i) thermocouple and heating wires looped together.

through its bottom, after which it was closed by soldering a copper lid to the supporting rim. A small hole was punctured into the lid to allow the expanded air to escape during the soldering process; this hole was closed by a drop of solder when the calorimeter cooled to room temperature. When closed, the calorimeter contained air at atmospheric pressure to assure uniform temperature distribution inside the calorimeter. The cylindrical well served the dual purpose of facilitating uniform thermal distribution within the sample and providing an entry and good thermal contact for a pair of copper-constantan thermocouples. These thermocouples were made of 0.0042 in. diameter copper and constantan wires welded together, glued to and electrically insulated from the calorimeter by a common type G.C. Electronics No. 30-2 Service Cement. One thermocouple served to measure the absolute temperature of the calorimeter, the other was connected to monitor the difference in temperature between the calorimeter and the middle of the outer wall of the adiabatic shield. An enamel insulated wire, of 142 ohms per foot resistance, wound around the calorimeter at about 12 turns per cm and glued to it by the same type of cement, was used as the heating element of the calorimeter. The calorimeter was suspended, without touching the sides of the shield, from the center of the top of the shield cover by a cotton thread making a connection to the center of the

lid and the calorimeter respectively. The six wires entered the shield through a small hole bored through the shield cover. The adiabatic shield consisted of a copper cylinder 10.3 cm long and 4.1 cm in diameter, with grooves cut into its outside surface at about 4 turns per cm. The thickness of its wall was of the order of 0.2 cm, with a copper disc of about 0.15 cm thickness soldered on to close one end. A flat copper disc of 0.15 cm thickness secured tightly by six small screws to a rim 0.9 cm wide, machined around the top of the shield, served as a lid to close the shield. A small hook soldered to the outside center of the lid served to suspend the shield from the top of the evacuated glass jacket. A silk-insulated German Silver heater wire laid in the grooves around the shield, and along the outside surface of its top and bottom, with a total resistance of around 200 ohms, provided the heat input to the shield. The length of the glass jacket was about 70 cm, so that the shield was hung by a cotton thread approximately 60 cm long, with care taken to avoid contact with the wall of the glass jacket. In order to attain minimum heat conductance between the copper block closing the top of the glass jacket and the shield, the 8 wires were made at least twice the length of the glass jacket. B.&S. Gauge 42 enamel insulated copper wires were used in making connections to the calorimeter heater coil,

the shield heater coil, to the copper terminal of the absolute thermocouple, and to the copper terminals of the difference thermocouple: one at the calorimeter, the other on the outer side of the shield. A constantan wire of the above described type served as the eighth lead, with a similar constantan lead of about 50 cm of length connecting the two junctions of the difference thermocouple. The six leads emerging from the shield were glued together at points separated by about 10 cm, and were hung from several joints with the supporting cotton thread in a loose fashion, before being looped back to make thermal contact with the side of the shield. From this point on, the five leads originating on the calorimeter, and the three coming from the shield, were glued together at several points, and were led, at about the half point of their remaining length, to a small magnet where a good thermal contact was made. This magnet, introduced to affect motion through the vacuum, was pressed to the inner wall of the glass jacket at about the middle of the latter's length by a similar magnet on the outside: this is the only point where the lead wires came into contact with the glass jacket. Finally, the light leads were fed through the copper block that, with an interposed rubber O-ring sealed the vacuum. In all, there was always at least some 60 cm in length of looped leads separating the calorimeter from the shield, an equal length between the shield

anchor point and the thermal contact on the small magnet, and finally a similar length leading from this point up to the electrical feed-throughs in the copper block at the top.

3. The Method of Measurement.

The heat capacity was measured by the continuous heating method. After the specimen was enclosed in the above described assembly, and a vacuum of 10^{-5} mm of Hg or better attained, a steady D.C. power was applied to the calorimeter heater coil from a car battery capable of delivering between 8-10V. The voltage applied to and the current flowing through the heater coil were measured as the potential drops across two standard resistors by the potentiometer, to the nearest microvolt. The voltages measured, and thereby the power input to the calorimeter were recorded every 6 to 8 minutes: the maximum fluctuation during this interval was not more than 1 part in 10,000 for the voltage and 2 parts in 10,000 for the current. The temperature rise was recorded at steady intervals corresponding to $30\mu\text{V}$ change in the thermocouple reading, but much smaller increments were taken in regions where the specific heat of the sample underwent change. The heat capacity of the sample was calculated as the average heat

input divided by the rise in temperature over a $90\mu\text{V}$ interval, except, as noted before, in regions of the phase transitions, where points as close to each other as 0.1°C were recorded. A general guide to the averaging is that each point corresponds to at least 8 minutes of heating at constant power input.

The thermal isolation of the calorimeter was provided by the adiabatic shield, whose temperature was manually controlled to be as close as possible to that of the calorimeter. The power source for the shield heating coil was a Variac providing continuously adjustable currents of 0-60 ma. The temperature difference between the well in the calorimeter and the middle of the outer side of the shield was monitored by the direct connection of the output of the difference thermocouple to a galvanometer with a sensitivity of $0.0014\ \mu\text{a/mm}$; this way temperature differences of 0.003°C could be detected. By continuously varying the current in the heating coil, it was possible to keep the shield within $\pm 0.005^{\circ}\text{C}$ of the temperature of the calorimeter, with, for long stretches at a time, no noticeable differences in temperature. Tests were made to find that there was no appreciable temperature inhomogeneity across the side of the shield and bottom which was soldered on to it. The more massive screwed-on top was harder to keep at the same temperature as the rest of the shield and showed increasing deviations, up to $\pm 0.015^{\circ}\text{C}$,

mostly in the 60-80°C temperature range, in an oscillatory fashion. This is considered the major source of error. In every run, tests were made, at least at two temperatures, one close to that of the transition, in which the temperature of the surrounding bath was adjusted so, that with no power applied to the calorimeter, a steady shield current of the regular operational maximum of 50-60 ma was required to maintain the shield at the same temperature as that of the calorimeter. This way, the shield current was manually controlled in the way already described: no temperature change was noted in the sample to the nearest μV after 30 minutes. Normally, a temperature rise of about 250 μV would have occurred during this period. In addition, the bath surrounding the evacuated jacket was much closer in temperature to the shield, and therefore would have caused much less inhomogeneity.

The temperature of the calorimeter was measured by a copper-constantan thermocouple and a potentiometer capable of measuring voltages to an accuracy of 0.2 μV . This represents a possible error of 0.005°C in each temperature measurement. The absolute value of the temperature is believed to be accurate within 0.05°C.

4. Preparation of Samples.

The samples studied were prepared in two steps: first magnesium and manganese in the desired ratio were co-precipitated as $\text{Mg}_{1-x}\text{Mn}_x\text{NH}_4\text{PO}_4$, and this precipitate was ignited to form $(\text{Mg}_2)_{1-x}(\text{Mn}_2)_x\text{P}_2\text{O}_7$. The co-precipitation of magnesium (manganese) ammonium phosphate followed the procedure described by Rieman, Neuss and Naiman (1942). The Mg^{2+} ion was provided by drying reagent grade $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ at 105°C to constant weight, and then dissolving accurately weighed amounts of MgHPO_4 in 6 N hydrochloric acid. The Mn^{2+} ion was introduced, in the required ratio, from an aqueous solution of reagent grade $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, which was measured out with precision from a burette. Methyl orange indicator was added to the solution mixture, and then 6 N ammonia added until a colour change occurred in the indicator. The solution was made acidic again by the addition of 1 N hydrochloric acid, diluted, and heated to 90°C . The ammonium phosphates were precipitated by the addition of 2 M solution of diammonium hydrogen phosphate. The precipitates were allowed to digest on a hot plate in excess of 30 minutes, and were let stand. The precipitates were collected by filtering and washing with 0.1 M diammonium phosphate, and were dried. Following this, the precipitates were ignited at 900°C to form the phosphates. Five samples

were obtained this way of $(\text{Mg}_2)_{1-x}(\text{Mn}_2)_x\text{P}_2\text{O}_7$ with x taking the values of 0, 0.005, 0.01, 0.02, and 0.04 in samples 1, 2, 3, 4, and 5 respectively, assuming that both the Mg^{2+} and Mn^{2+} ions precipitated in the ratios originally added. A neutron activation analysis showed that the relative amount of Mn^{2+} impurities were in the above quoted ratios within 5% maximum deviation; the absolute values of doping were not checked. X-ray powder photographs were taken of all samples, which indicated the presence of $\text{Mg}_2\text{P}_2\text{O}_7$, with some additional lines and broadening of the $\text{Mg}_2\text{P}_2\text{O}_7$ lines appearing with increased Mn concentration.

After x-ray and specific heat measurements on samples 1 and 5, which involved several heating cycles between 0 and 100°C , all five samples were placed in covered vitreosil crucibles and their temperature raised by 6 hours of uniform heating to 1470°C and then they were brought back to room temperature in about 12 hours. The melting point of $\text{Mg}_2\text{P}_2\text{O}_7$ is 1395°C ; there was visual evidence that all our samples were melted.

Another sample of undoped magnesium pyrophosphate, hereafter referred to as sample 1b, was prepared by heating MgHPO_4 to 900°C for form the pyrophosphate and then sintering it at a temperature slightly below the melting point.

The purity of the samples was checked by the use of

powder x-ray diffraction techniques. There was some evidence of a slight contamination of $\text{Mg}(\text{PO}_3)_2$ in samples 1 to 5, before melting. After melting, the $\text{Mg}(\text{PO}_3)_2$ concentration had decreased to a level undetectable by x-ray techniques. No evidence of a similar contamination was found in sample 1b.

CHAPTER IV

RESULTS AND DISCUSSION

1. Results.

As was noted earlier, ESR studies indicated that the phase transition in Mn-doped $\text{Mg}_2\text{P}_2\text{O}_7$ occurred some 8°C lower than was reported by Roy et al. (1948) and Oetting and McDonald (1963). The ESR sample was melted to form large single crystals, whereas the sample of Oetting and McDonald was only sintered. It could be surmised that this deviation was due to either the presence of the Mn impurity in the ESR specimen, or to some changes induced by the heating of the sample during preparation, as for example, by the loss of some P_2O_5 , as suggested by Hoffman and Lundell (1930).

Two series of experiments were performed to examine these possibilities. The first sequence was begun by the measurement of the specific heat of pure $\text{Mg}_2\text{P}_2\text{O}_7$ sintered at 1300°C (sample 1b): the results are shown as curve (b) of Fig. 3, indicating a phase transition about 3°C lower than that observed by Oetting and McDonald, having approximately the same full width at half maximum (FWHM), but a peak height almost double that reported by these authors.

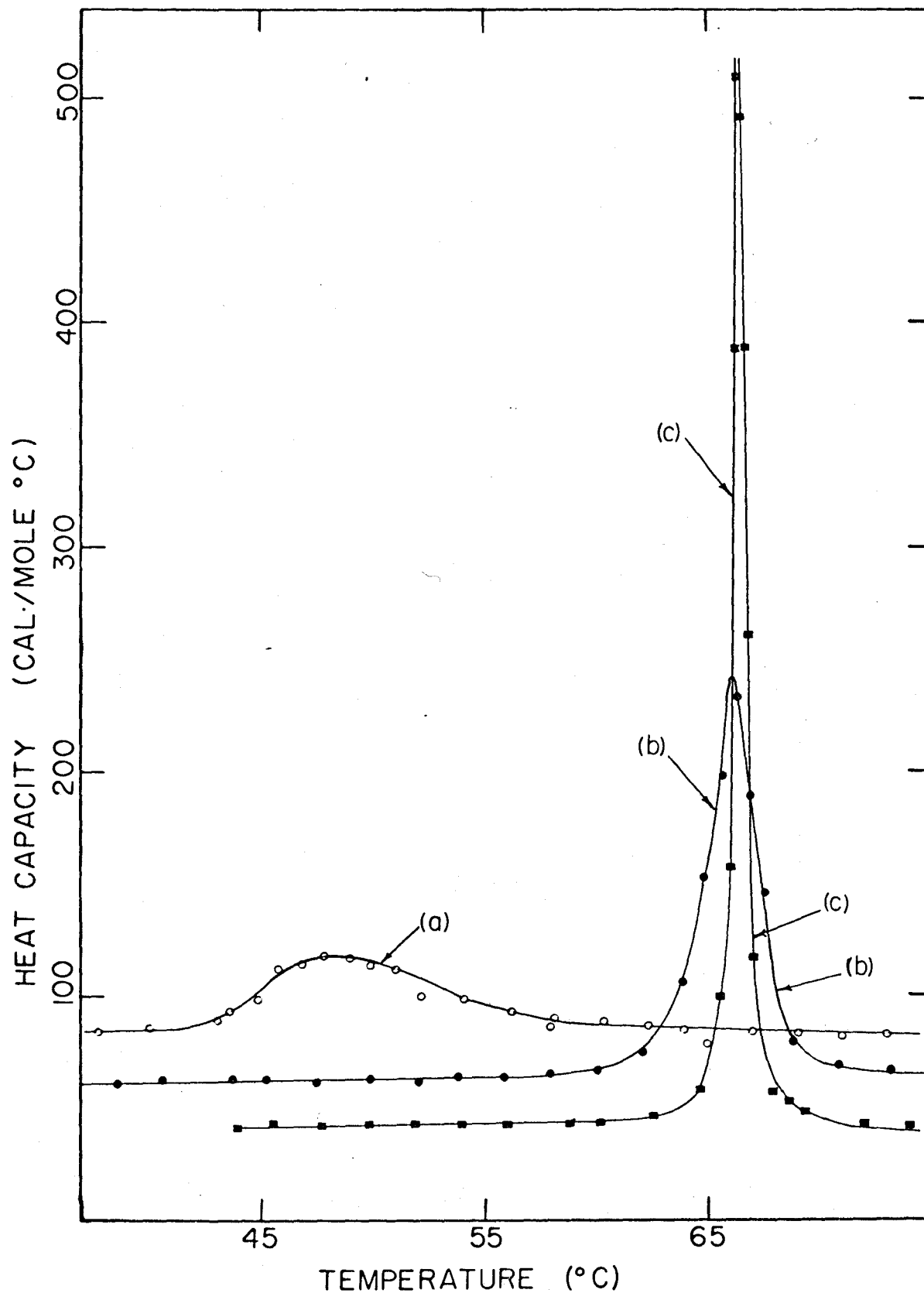


Fig.3. Heat capacity of $Mg_2P_2O_7$: (a) sample No. 1, after preparation at $900^\circ C$ but before melting, (b) sample 1b, (c) sample No. 1 after melting. Curves (b) and (a) have been displaced upwards, by 20 and 40 cal/mol $^\circ C$ respectively, for clarity.

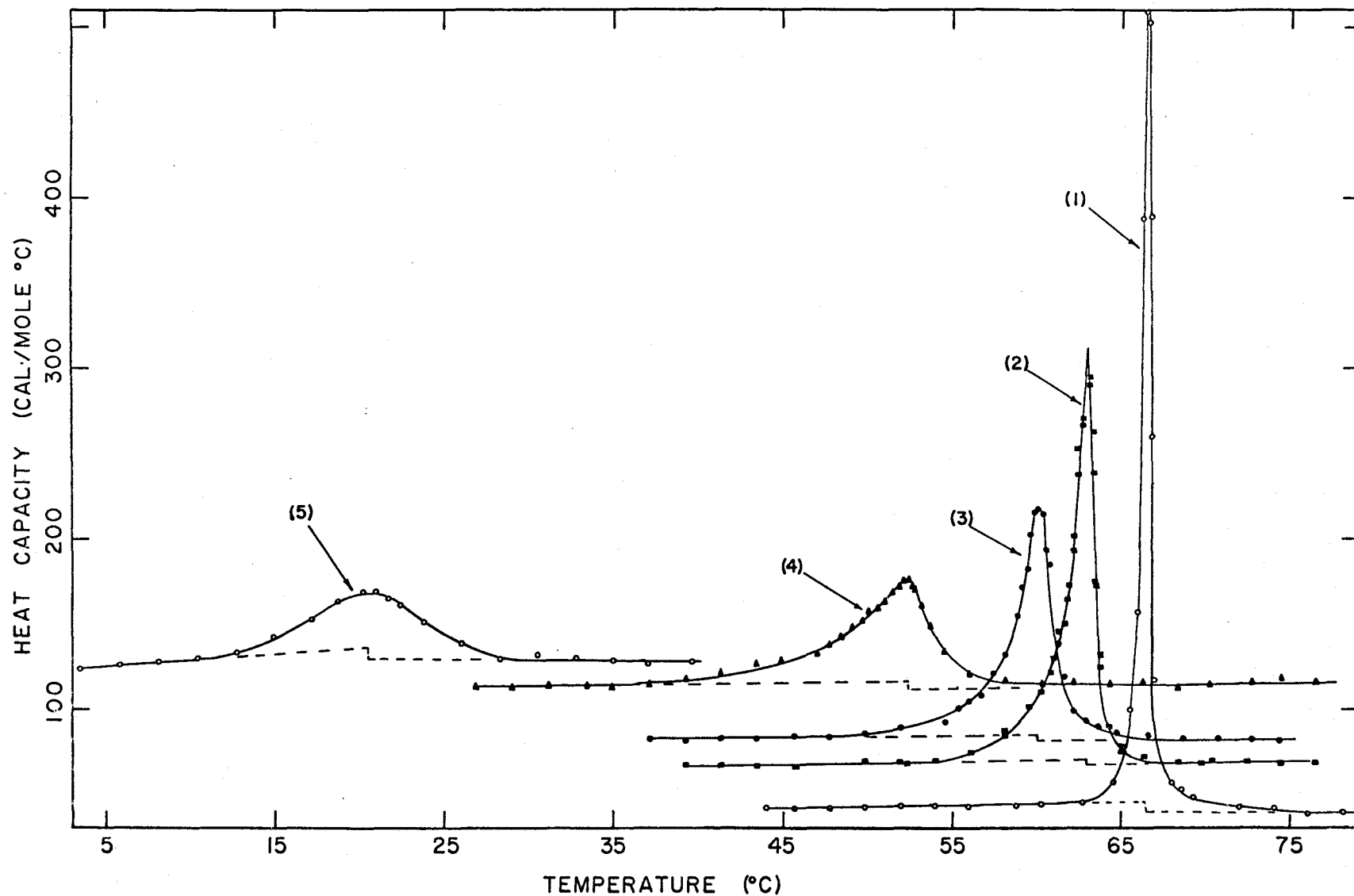


Fig.4. Heat capacity of $(Mg_{1-x}Mn_x)_2P_2O_7$: (1) $x = 0.00$, (2) $x = 0.005$, (3) $x = 0.01$, (4) $x = 0.02$, and (5) $x = 0.04$. Curves 2,3,4, and 5 have been displaced upwards, by 20, 40, 60, and 80 cal/mole°C respectively, for clarity.

This was followed by the measurement of the specific heat of sample 1, prepared as already described, up to and including the conversion of MgNH_4PO_4 into $\text{Mg}_2\text{P}_2\text{O}_7$ at 900°C . The result obtained is the extremely diffuse transition shown as curve (a) of Fig. 3, centered at approximately 48°C , or about 20°C lower than that found by Oetting and McDonald. Following this, sample 1 was melted and the specific heat was again measured, giving curve (c) of Fig. 3. The phase transition was now extremely sharp (FWHM about 0.5°C) and centered at 66.5°C .

In addition to the specific heat measurements described, x-ray diffraction studies were made of sample 1b and the unmelted sample 1. These measurements, conducted to reveal the co-existence of the two phases of $\text{Mg}_2\text{P}_2\text{O}_7$, confirmed the findings of Roy et al., with the characteristic lines of the α and β phases appearing over about 15°C for sample 1b, and some 35°C for the unmelted sample 1.

The second series of specific-heat measurements employed Mn-doped $\text{Mg}_2\text{P}_2\text{O}_7$. The results for samples 1 to 5 are shown as the successive curves of Fig. 4; the temperatures of transition, the FWHM of the different samples and the integrated area under the curve, the enthalpy of transformation, are shown as a function of Mn concentration in Table VII. It is apparent that there is a depression of the temperature of the transition, as well as a broadening

of the temperature interval of specific-heat anomaly with increasing Mn content. The transition temperature and the FWHM appear to vary linearly with Mn concentration for the FWHM and approximately linearly in the case of the depression of the transition temperature. The enthalpy of transformation is found to decrease monotonically with added Mn^{++} .

While the maximum possible error in the absolute value of the specific heat is hard to estimate, the reliability of the shape and width of the transitions can be inferred from the scattering of the measured points. The entire curve for sample 1 was repeated, and the temperature of transition was found to agree within 0.4°C . The shape of the curve also reproduced very well, with the exception of some minor disagreement in the base line just above the transition. The only data available for comparison are those of Oetting and McDonald, and they are only for undoped $\text{Mg}_2\text{P}_2\text{O}_7$, which was produced by sintering. The value of the specific heat given by these authors at 16.9°C was compared with our data at the same temperature. This temperature is well below the transition temperature and region of anomalous specific heat for all our samples except No. 5. The percentage deviation in the case of samples 1, 2 and 3 is about 3% or less, while sample No. 5 cannot be compared for the reasons given above. The percentage deviation for

TABLE I

Specific Heat of Sample 1, Melted

Temperature (°C)	Cp (cal./mole °C)	Temperature (°C)	Cp (cal./mole °C)
43.9	42.3	66.7	389.4
45.6	42.7	66.8	259.6
47.7	42.1	67.0	116.5
49.8	42.7	67.9	56.7
51.9	42.8	68.6	52.6
54.0	42.7	69.3	47.7
56.0	42.8	72.0	42.7
58.8	43.0	74.0	42.3
60.2	44.3	76.0	39.4
62.6	46.1	78.0	39.8
64.6	57.6	80.0	39.0
65.5	100.4	81.9	39.4
66.0	156.7	83.9	38.3
66.3	387.6	85.9	38.5
66.4	510.1	87.9	37.8
66.5	492.1	89.8	35.6

TABLE Ib
Specific Heat of Sample lb

Temperature (°C)	Cp (cal./mole °C)	Temperature (°C)	Cp (cal./mole °C)
36.9	40.6	64.8	132.3
38.5	40.8	65.7	177.8
40.6	43.1	66.3	212.7
42.7	42.7	66.9	168.8
45.1	42.9	67.5	124.9
47.4	41.5	68.8	60.4
49.8	42.7	70.8	47.7
51.9	42.0	73.1	46.6
53.8	44.0	75.1	44.9
55.8	43.8	77.1	43.8
57.9	44.5	79.1	43.1
60.0	46.8	81.1	42.2
62.0	55.0	82.8	41.5
63.8	86.1	85.0	42.6

TABLE II

Specific Heat of Sample 2, Melted

Temperature (°C)	Cp (cal./mole °C)	Temperature (°C)	Cp (cal./mole °C)
31.2	45.5	69.7	48.0
32.7	46.2	52.2	48.2
34.9	45.9	54.0	49.4
37.0	46.2	56.0	54.0
39.2	46.6	58.1	64.4
41.3	46.9	59.5	80.8
43.4	47.3	60.2	95.5
45.6	47.3	60.8	101.7
49.8	48.5	61.3	125.9
51.9	48.5	61.8	144.7
54.0	49.2	62.2	181.6
56.0	54.2	62.4	218.3
58.1	67.4	62.7	249.9
59.5	80.5	63.0	274.8
60.2	90.0	63.3	243.6
61.0	110.1	63.5	154.4
61.6	130.1	63.8	104.5
61.9	153.0	64.3	68.8
62.2	173.0	65.0	58.4
62.4	233.3	66.3	51.3
62.7	247.1	68.3	48.5
63.0	271.3	70.4	49.6
63.3	219.4	72.4	49.4
63.5	153.0	74.4	48.9
63.8	112.2	76.4	49.4
64.3	70.4	78.4	48.0
65.0	56.1	80.4	48.9
66.3	42.6	82.4	49.4
68.3	48.9	84.4	49.9

TABLE III
Specific Heat of Sample 3, Melted

Temperature (°C)	Cp (cal./mole °C)	Temperature (°C)	Cp (cal./mole °C)
7.0	39.3	54.5	51.7
8.9	39.1	55.3	61.4
11.2	40.9	56.0	64.5
13.4	40.6	56.7	67.6
15.7	40.8	57.4	81.2
17.9	40.6	58.1	91.8
20.2	41.1	58.8	113.5
22.4	41.5	59.1	131.8
24.6	41.5	59.4	142.3
26.9	41.3	59.6	162.0
29.0	42.0	59.8	175.0
30.9	42.8	60.0	176.7
32.6	42.7	60.3	173.9
34.8	42.2	60.5	153.2
28.3	41.3	60.7	144.8
30.5	41.9	61.2	99.1
32.6	42.8	61.6	80.4
34.8	42.2	62.2	59.0
37.0	42.6	62.9	53.2
39.2	42.2	63.6	50.4
41.3	43.3	64.7	47.2
43.4	43.0	66.5	45.3
45.6	44.4	68.6	44.2
47.7	44.4	70.8	43.3
49.8	45.5	72.8	42.0
51.9	48.6	76.0	42.4

TABLE III (cont'd)
Specific Heat of Sample 3, Melted

Temperature (°C)	Cp (cal./mole °C)
78.0	43.0
80.0	42.0
81.9	42.2
84.2	42.4
85.9	40.8
87.8	40.4
89.8	41.1
91.8	39.3
93.1	39.3
64.5	46.6
66.5	44.6
68.6	42.8
70.6	43.3
72.6	42.8
74.3	42.4
76.0	42.2
78.0	41.3
80.0	42.6
84.3	41.1
85.9	41.3
87.8	40.8
90.2	41.5
91.8	40.0

TABLE IV
Specific Heat of Sample 4, Melted

Temperature (°C)	Cp (cal./mole °C)	Temperature (°C)	Cp (cal./mole °C)
17.9	52.4	66.3	55.1
20.2	53.1	68.3	55.5
22.4	54.2	72.4	56.1
24.6	53.7	74.4	57.9
26.9	53.8	77.0	58.1
29.0	54.2	78.4	59.4
31.2	55.1	80.4	59.8
33.4	55.3	82.4	60.9
35.6	56.8	84.0	60.2
39.2	58.3	88.0	59.9
41.3	62.0	34.9	53.9
43.5	65.7	37.0	55.1
45.7	70.7	39.2	57.6
47.7	76.8	41.3	62.4
49.3	87.4	43.4	66.5
50.4	96.3	44.8	68.5
51.2	99.6	47.0	73.1
51.9	102.4	47.7	77.8
52.5	99.1	48.4	83.0
52.9	93.2	49.1	87.6
53.5	84.7	49.7	92.4
54.2	71.2	50.1	97.2
55.6	57.9	50.6	98.9
58.1	51.3	51.0	102.6
60.5	48.7	51.5	109.2
62.5	46.6	51.8	112.2
64.3	54.4	52.1	115.7

TABLE IV (cont'd)
Specific Heat of Sample 4, Melted

Temperature (°C)	Cp (cal./mole °C)
52.3	115.7
52.6	112.2
52.8	110.7
53.1	101.1
53.7	88.4
54.5	73.8
56.0	61.0
58.1	56.6
60.2	56.2
62.2	56.6
64.3	55.0
66.3	56.1
68.3	54.4
70.4	54.6
72.7	56.1
74.4	58.5

TABLE V

Specific Heat of Sample 5, Melted

Temperature (°C)	Cp (cal./mole °C)	Temperature (°C)	Cp (cal./mole °C)
1.8	43.8	34.9	48.7
3.5	44.3	37.0	46.7
5.8	46.4	39.5	48.4
8.1	47.8	41.3	47.3
10.4	50.3	43.4	47.5
12.7	53.1	45.6	47.3
14.9	61.5	47.7	48.1
17.2	73.2	49.8	48.7
18.7	82.7	51.9	48.4
19.5	85.3	54.0	48.9
20.2	88.6	56.0	48.7
21.0	88.6	58.1	48.7
21.7	85.0	60.2	49.5
22.4	81.1	62.2	48.9
23.9	70.5	64.3	49.8
26.1	58.2	66.3	48.9
28.3	48.9	68.3	48.4
30.5	51.5	70.4	50.9
32.7	50.3	72.4	50.3

TABLE VI

Specific Heat of Sample 1 after Heating at 900°C,
but Before Melting

Temperature (°C)	Cp (cal./mole°C)	Temperature (°C)	Cp (cal./mole°C)
5.8	39.6	49.9	76.0
8.1	40.6	51.0	72.0
10.4	40.2	52.2	59.9
12.7	39.6	54.0	58.6
14.9	40.2	56.1	53.6
17.2	42.2	58.1	50.4
19.5	41.5	60.2	49.5
21.7	42.2	62.3	46.4
23.9	43.5	57.9	45.6
26.4	43.8	60.3	49.0
28.3	45.8	62.1	47.4
30.5	45.2	63.9	45.4
32.6	48.4	65.0	39.4
35.6	45.9	66.9	44.1
37.0	42.5	68.9	42.8
33.6	43.8	75.1	42.5
35.6	43.7	79.1	40.6
37.7	43.8	36.8	45.4
39.9	46.3	38.9	45.4
42.0	47.6	43.5	53.6
43.6	52.6	44.8	64.3
44.7	57.5	45.6	69.5
45.7	71.5	46.9	73.4
46.8	73.9	47.8	74.7
47.8	78.6	48.5	69.2
48.9	77.3		

sample 4 was 25%. However, on removing this sample from the calorimeter after the completion of the run, it was found that the sample had become contaminated. The most plausible explanation is that water seeped into the calorimeter during the sealing procedure. Sufficient additional sample was not available to repeat this measurement and it did not appear worthwhile to repeat the entire set. Therefore the results for this sample should be taken with caution.

The value of the specific heat at constant pressure, C_p , for the various samples is compiled in Tables I to VI.

2. Discussion.

The observed phase transition has already been classified as one of first order according to the Ehrenfest criterion by Oetting and McDonald (1963). As was shown in the section on theory, in such a transition one observes a discontinuous change in an observable corresponding to a first derivative of the Gibbs free energy with respect to temperature or pressure. A discontinuous change of volume has been directly observed by Roy et al. in 1948, and has been inferred in the course of the present investigations from an apparent change in the index of refraction of $Mg_2P_2O_7$ by observing it during the transition with a hot-stage

microscope. A discontinuity of entropy has been suggested by Oetting and McDonald, and is confirmed in this work as being equivalent to the enthalpy change indicated by the extrapolation lines in Figure 4.

A first order phase transition should occur isothermally at constant pressure according to the Gibbs Phase Rule. Since the observed transition occurs over a temperature range of varying width, it seems appropriate to describe it by the term "Diffuse First Order Transition" first introduced by Meyer and Streeter (1939). While the basic thermodynamic nature of such a transition has not been explained by these authors, it is clear that it can be accounted for only - excluding the possibility of the sample not being in equilibrium - by introducing the presence of some new degree of thermodynamic freedom.

There seems to be compelling evidence that shows that the samples were in equilibrium. X-ray diffractometer traces were taken of Sample 1, unmelted, in the middle of the transition region 12 hours apart, and no change in the spectrum was detected. The narrowness of the transition region, and the necessary stringent temperature control required prevented a similar study of the melted sample. However, additional investigations using the diffractometer showed that the degree of α - β transformation was limited by the thermal inertia of the oven and not by the kinetics

of the transition, for the height of the x-ray diffraction peaks indicating the coexistence of the two phases seemed to be a well-defined function of temperature. The observations by Leung (1964) of the ESR lines characteristic of the environment of the Mn^{2+} ion in the two phases appear to corroborate these results.

The presence of non-equilibrium thus ruled out, one has to turn to some new thermodynamic degree of freedom to explain the coexistence of two phases over a temperature interval. Two possibilities come to mind. If some impurity, Mn^{2+} , or some decomposition product in the "pure" samples, had different solubilities in the two phases, one would have a binary mixture, and an additional degree of freedom. Such an occurrence has to be ruled out in light of the rapid kinetics of this transformation, for it would require atomic diffusion which one would expect to take place very slowly at 60°C , some 1300°C below the melting point of $\text{Mg}_2\text{P}_2\text{O}_7$.

Another alternative would be the presence of an additional variable in the form of some strain, or inhomogeneity, that could be associated with the boundary between the two phases. The work of Roy et al. cited above suggests the possible presence of hysteresis, which could be an added sign of some domain structure. It must be emphasized that the x-ray and ESR data, as far as they go, show a reversible transition. While a "boundary phase", such as the

one postulated by Tobolsky et al. mentioned above would be too small in bulk to be detectable by x-ray techniques, it would, by limiting the size of the domains in the α and β phases, cause broadening of the lines characteristic of these phases. While Tobolsky's model shows a definite correlation between the domain size and the specific heat anomaly, the precision of the present experiment does not allow meaningful analysis. In any event, no broadening of x-ray lines has been reported.

There remains to discuss the dependence of the specific heat anomalies on the method of preparation and impurity concentration. Since both these causes show their influence on a microscopic level and the measurement of specific heat is a bulk property, there is tangible evidence for little more than speculation.

By far the more difficult to explain is the influence of the method of preparation. The disturbing question exists whether the different thermal treatments that preceded the measurements of specific heat could have caused the decomposition of parts of the sample, for example, by the loss of P_2O_5 above $1200^\circ C$ as was reported by Hoffman and Lundell (1930). Figure 3 shows that successively higher temperatures of preparation give rise to sharper transitions. The $Mg_3(PO_4)_2$ or MgO resulting from the decomposition would have to be dissolved in the $Mg_2P_2O_7$ to have an effect on

the transition. Small concentrations of dissolved impurities would be unobservable by x-ray techniques; however, deviations from stoichiometry are an unlikely explanation as they would be more likely to broaden the transition. The broadening could have been caused by the presence of $\text{Mg}(\text{PO}_3)_2$ detected in the unmelted samples. This metaphosphate could decompose, dissolve in $\text{Mg}_2\text{P}_2\text{O}_7$ or form a glass. The resulting product of decomposition would be MgO , which might react with the remaining metaphosphate to form $\text{Mg}_2\text{P}_2\text{O}_7$. However, MgO lines could not be detected in the Debye-Sherrer patterns, and dissolving in $\text{Mg}_2\text{P}_2\text{O}_7$ would lead to nonstoichiometry which, as has already been pointed out, is unlikely to cause a narrowing of the transition. It is also well to note that sample lb shown in Figure 3 exhibited no signs of presence of $\text{Mg}(\text{PO}_3)_2$.

The dependence of the width of the transitions on the method of preparation is most likely a result of the particle size of the samples involved. If the Tobolsky model is realistic, the free energy could strongly depend on the ratio of matter in the boundary phase to that in the two bulk phases; this ratio is likely to depend on particle size. The average particle size would tend to increase with the temperature that the material was subjected to, and it is also possible that the thermal motion that is enhanced by heating to higher temperatures would promote

TABLE VII

α - β phase transition in $(\text{Mg}_{1-x}\text{Mn}_x)_2\text{P}_2\text{O}_7$
 (The numbers in parentheses are the estimated
 limits of error)

Sample no.	% of manganese	Transition temperature ($^{\circ}\text{C}$)	FWHM ($^{\circ}\text{C}$)	Heat of transformation (cal./mole)
1b	0	66.2(2)	2.7(3)	562(30)
1	0	66.8(2)	0.5(1)	†
2	0.5	62.9(5)	1.2(2)	514(25)
3	1.0	60.0(5)	2.3(3)	456(25)
4	2.0	52.1(10)	4.8*	382*
5	4.0	20.6(20)	7.3(5)	419(50)

* As explained in the text, results for sample No. 4 are suspect.

† The shape of the curve makes a meaningful integration impossible.

the development of the bulk phases at the expense of the intermediate phase. This way, greater nonuniformity in particle size as well as metastable states associated with a comparatively large volume of boundary phase could cause a broader transition in the sample that was exposed to only lower temperatures.

Figure 4 and Table VII show the effect of the addition of small amounts of $\text{Mn}_2\text{P}_2\text{O}_7$ on the specific heat, transition temperature, and the FWHM of the transition. The linearity of the shift in transition temperature, at low concentrations of added Mn^{++} , can easily be predicted from thermodynamics. The slope can be shown to depend upon the ratio of the difference of partial molal enthalpies in the two phases to the difference in activity coefficients of Mn^{++} in the two phases. Since separate data on these quantities are not available, one cannot pursue this further. From ESR experiments it has been concluded that Mn^{2+} substitutes directly into the cation site in $\text{Mg}_2\text{P}_2\text{O}_7$. X-ray studies indicated that $\text{Mn}_2\text{P}_2\text{O}_7$ and β $\text{Mg}_2\text{P}_2\text{O}_7$ are isostructural with bond distances and bond angles nearly identical in the two structures. No phase transition has been found in $\text{Mn}_2\text{P}_2\text{O}_7$ above -150°C . This leads one to speculate on how Mn^{2+} changes the environment found in α $\text{Mg}_2\text{P}_2\text{O}_7$. One might expect that the Mn^{2+} impurities, because of their greater propensity for the β phase, would form nucleation centers for the

transition. The ESR results show considerable line broadening, indicating an inhomogeneous environment of the Mn^{2+} ions. This inhomogeneity would imply a distribution of transition temperatures at the various nucleation sites and could explain the increase in the diffuse nature with increasing manganese concentration. This would also be consistent with the decrease in the enthalpy of transition with added Mn^{++} . Unfortunately, at present, it is not possible to determine the detailed environment of the Mn^{2+} in $\alpha \text{Mg}_2\text{P}_2\text{O}_7$.

It is enlightening to discuss some of the crystallographic changes that constitute the phase transition. In $\text{Cu}_2\text{P}_2\text{O}_7$ the transformation is known (Robertson and Calvo, 1966) to be a one-dimensional disordering of layers parallel to the b-c plane. The disordering can be described by the sense of displacement of the central oxygen atom of the P-O-P group along the b axis. The β phase in $\text{Cu}_2\text{P}_2\text{O}_7$ appears to result from a random disordering of this displacement. Thus, a one-dimensional Ising model, as proposed by Tobolsky et al., can provide a basis for the discussion of the α - β $\text{Cu}_2\text{P}_2\text{O}_7$ transition. As was already noted, in $\text{Mg}_2\text{P}_2\text{O}_7$ the transition has been monitored, using a hot-stage microscope, by observing the index of refraction discontinuities in a single crystal as the crystal transforms. These discontinuities move parallel to the b-c plane as the temperature

is changed, suggesting a relationship with the transformation in $\text{Cu}_2\text{P}_2\text{O}_7$. The reduction in symmetry involved in the phase transition of $\text{Cu}_2\text{P}_2\text{O}_7$ allows it to be classified as a second order one in the Landau theory: the stacking faults that appear gradually and temperature dependently along the a^* axis provide a good example for a continuous change of state transition. While the transition in $\text{Mg}_2\text{P}_2\text{O}_7$ is related to that in $\text{Cu}_2\text{P}_2\text{O}_7$, it cannot be classified as of second order because the two symmetries differ by two irreducible representations (Calvo, 1967). The discontinuities that one has in a first order transition are caused on a microscopic level by the creation of additional bonds by Mg^{2+} in the α phase. That the state of the system does not change in a continuous way is testified to by the two sets of ESR lines that appear in the work of Leung et al.: the lines characteristic of the β phase do not grow out of those of the α phase, but rather appear separately.

3. Conclusions.

The α - β phase transition in $\text{Mg}_2\text{P}_2\text{O}_7$ is confirmed to be a diffuse first order phase transition. The transformation has been shown to depend, in a very sensitive manner, on the presence of manganese impurities. The addition of manganese depresses the transition temperature of $(\text{Mg}_{1-x}\text{Mn}_x)_2\text{P}_2\text{O}_7$ by

about 9°C/mole % for $0 < x < 0.02$. The existence of a dependence on the method of preparation has been shown but is not understood. It is suggested that the Mn^{2+} ion distorts the cation environment in the α phase of $\text{Mg}_2\text{P}_2\text{O}_7$ and that these distortions nucleate the α to β phase transition.

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