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STRUCTURAL EFFECTS ON ELECTRICAL PROPERTIES IN AMORPHOUS SEMICONDUCTORS

D. L. Kinser, et al

Vanderbilt University

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7/1/72 - 12/31/72

Structural Effects on Electrical Properties in Amorphous Semiconductors

School of Engineering
Vanderbilt University
Nashville, Tennessee 37235

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School of Engineering

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Date Submitted: January 31, 1973

ABSTRACT

During this report period, work has continued on a survey was made of the structure, electrical and magnetic properties of transition metal oxide phosphate glasses and glasses of the As_2Te_3-As_2Se_3 system. Results of magnetic and electrical observations in several transition metal phosphate glasses have revealed a high degree of magnetic and structural order. The magnetic properties of the manganese phosphate glass system have been studied and interpreted in terms of the glass structure. A theoretical model band on the Weiss molecular field theory is developed which explains the downward curvature of the inverse susceptibility as a function of temperature for these glasses.

Examination of a representative group of transition metal phosphate glasses in a Cobalt 60 radiation source has revealed a pronounced effect upon the DC conductivity of these glasses. The DC conductivity is increased by a factor of 10^3 over ambient by a gamma flux or 10^6 R/hr. This result is contrary to initial reports of radiation insensitivity in amorphous systems.

Detailed studies of the conduction process in copper phosphate glasses have revealed a mixed conduction mechanism of ionic and electronic mechanisms. This mixed conduction changes to exclusively electronic with thermal treatments which slightly densify the glass.

Statement of Problem

The device potential in amorphous semiconducting materials is a largely unexploited area, despite extensive research in this area. This is the result of a lack of systematic structure-property oriented research in these materials. A fundamental understanding of the structural features of this class of materials will allow rational interpretation and control of relationships between glass preparation variables and important electrical and magnetic properties.

Electronic conduction in amorphous solids has become the subject of interest to a number of theoreticians and has been reviewed by Mott[1,2] Gubanov[3] and numerous others. Virtually all of these works have begun with an assumption that amorphous solids are uniformly random, even though they recognize glasses are generally heterogeneous. These theoreticians have developed analytical descriptions of several systems which have been experimentally verified in some cases. Attempts to extend this approach to microscopically heterogeneous systems have had notably little success. There remains a considerable body of experimental results, including Hall and Seebeck coefficients, which are not rationalized by present theory.

Pearson[4] has suggested that heterogeneous structure in these materials may explain these anomalies if the separated phase is crystalline. It appears that heterogeneous transport analysis similar to that of Volger[5] or Bube[6] is required to ascertain the transport behavior in each phase.

Another important anomaly between theory and observation concerns the theoretically predicted insensitivity of amorphous semiconductors to doping. Early experimental observations by Kolimets, et al.[7], conformed to the theoretical predictions, but recent work by Mackenzie[8] clearly conflicts with the theory and the early work. It appears that the above anomalies are the result of inadequate structural characterization, rather than fundamental theoretical problems.

Further evidence that structural heterogeneities lie at the root of these anomalies can be inferred from work by Kinser, et al.[9], in K_2O-P_2O_5-V_2O_5 glasses. This work has shown that marked changes in dielectric behavior occur during thermal treatments customarily used to stress relieve glasses. These changes have been shown to be the result of structural changes involving precipitation of small amounts of crystals.

Wilson and Kinser[10] have observed similar, but somewhat more complex, behavior in FeO-P_2O_5 glasses after thermal treatments corresponding to annealing. Electron spin resonance (ESR) results have shown the onset of structural changes during thermal treatment prior to their observation by other commonly employed techniques[11,12].

It is thus apparent that homogeneous glasses, semiconducting or otherwise, are the exception rather than the rule.

General Methodology

The electrical and magnetic property changes accompanying structural modifications during glass processing are of prime interest in the present work. The above questions can only be answered with detailed structural characterization of representative glasses from the oxide and chalcogenide groups. The initial oxide glasses examined were the FeO-P_2O_5, V_2O_5-P_2O_5, CuO-P_2O_5, TiO_2-P_2O_5 and MnO-P_2O_5 systems. The chalcogenide glasses are from the As_2Te_3-As_2Se_3 system.

TRANSITION METAL PHOSPHATE GLASSES

Manganese Phosphate Glass

The magnetic properties of manganese phosphate glass system have been studied and interpreted in terms of the glass structure. A theoretical model which explains the downward curvature of the inverse susceptibility behavior of amorphous antiferromagnets at low temperatures has been proposed. Details of this work are contained in a doctoral thesis by Dr. E. J. Friebele, a copy of which is contained in this report.

The manganese phosphate system has proven ideal for magnetic property characterization. Microstructurally homogeneous glasses were made over the glass forming region from 30 to 55 mole % MnO; the ratio of divalent to trivalent manganese in these glasses is approximately 1500 to 1. Glasses in the 30 to 50 Mole % MnO range soften between 475 and 490°C and the 55-45 glass softens between 495 and 510°C.

The high temperature inverse susceptibility of all glasses obeys an antiferromagnetic Curie Weiss law. The projected antiferromagnetic Curie temperatures and the Curie constants of the glasses in the 30 to 50 mole % MnO range vary linearly with composition, and the effective field coefficient is constant in this range. The changes in magnetic properties which occur in this range are the result of inserting divalent manganese ions into the vacant octahedral holes created by the nesting of the phosphate tetrahedra. When the glass composition is 50-50 mole % $MnO-P_2O_5$, the matrix is saturated with metaphosphate structural units; further addition of manganese causes part of the matrix to form manganese pyrophosphate clusters. The resulting magnetic properties of the 55-45 glass are similar to those of crystalline manganese pyrophosphate.

The electron spin resonance spectra of the glasses consists of a broad symmetric singlet centered at $g' = 1.97$. The linewidth of the spectrum narrows as the concentration of manganese is increased due to exchange narrowing effects, and there is a slight decrease in g' value. The ESR line intensity relative to a paramagnetic standard and the ESR linewidth both increase as the temperature is decreased. The former is the result of Boltzmann depopulation of the $S = 5$ spin manifolds, and the latter occurs because spin pairs experiencing stronger interactions couple antiferromagnetically at higher temperatures. The ESR linewidth vs. temperature plot deviates from linearity near 40°K -- one indication that there is a magnetic transition below this temperature.

Low temperature susceptibility studies have detected the antiferromagnetic transition at 13°K. Below this temperature, the inverse susceptibility decreases as the temperature is decreased. Magnetization studies carried out a 1.9 and 4.83°K show no saturation in magnetization as the magnetic field is increased. There is a slight curvature in the magnetization plot at 1.9°K, however, which may indicate the presence of fine grained superantiferromagnetic particles in the 50-50 glass.

The Weiss molecular field theory was chosen as a basis for a model of amorphous antiferromagnetism. The randomness of the glass structure was introduced into the calculations by assuming a Gaussian distribution in spontaneous magnetization below the Néel temperature. Although the resulting mean susceptibility was larger than that of the crystalline susceptibility, the temperature dependence was identical. A downward curvature in the inverse susceptibility plot was obtained by adding a fractional paramagnetic component to the total susceptibility. This paramagnetic component could arise either from structurally isolated ions in the glass matrix or from fine grained superantiferromagnetic particles.

These results will be reported by the 1973 General Meeting of the American Ceramic Society in Cincinnati, Ohio.

Radiation Effects on Conduction in Transition Metal Phosphate Glasses

The effect of gamma radiation on the DC conductivity in several transition metal phosphate glasses has been examined using a Cobalt 60 source. Generally speaking the glasses with high conductivity have been observed to be insensitive to radiation when irradiated at room temperatures. The more insulating glasses such as the manganese and cobalt phosphate are quite sensitive to the gamma flux and the effect is linearly related to the gamma flux. The rise time and decay time of the effect in these glasses at room temperature is less than one second and no permanent after affect was noted. This work is continuing with studies in progress at lower temperatures.

Copper Oxide Phosphate Glass Studies

The studies of this system have been in progress for some time and have been complicated by the appearance of an ionic contribution to the conduction process. This effect has been most elusive and has caused considerable problem as to reproducibility. We have at this point discovered that the degree of oxidation and annealing cause a transition from mixed ionic and electronic to wholly electronic. We have observed a monotonically decreasing resistivity with increasing Cu^{2+}/Cu^{total} thus it appears that the Cu^{1+} is the charge carrier in the as cast unannealed glasses. This dependence is presently being examined in the annealed glasses where preliminary data indicates a behavior similar to other transition metal phosphate glasses. It is anticipated that these glasses will be stabilized with a third component calcium oxide in order to eliminate the ionic conduction.

Titanium Phosphate Glass

In order to study the magnetic and structural properties of the titanium oxide-phosphate glass system it was necessary to provide an accurate and rapid quantitative determination of the oxidation states of the titanium ions. Such a technique has been developed. This technique permits accurate calculation of the oxidation states from the oxygen uptake when a sample is measured in a pure oxygen environment. The development and application of this analysis procedure will be presented at the 1973 General Meeting of the American Ceramic Society. An abstract of this paper is contained in this report.

CHALCOGENIDE GLASSES

Magnetic Susceptibility Studies of the As_2Te_3-As_2Se_3 Glass System

The magnetic susceptibility of a series of As_2Te_3 - As_2Se_3 glasses over the composition range 40 tp 80% As_2Te_3 has been measured as a function of temperature. At high temperatures the susceptibility is negative and independent of temperature. The diamagnetic susceptibility at 300°K varies from 0.52×15^{6} to 0.72×10^{-6} emu/g for amorphous As_2Se_3. The low temperature behavior of the susceptibility indicated the presence of a paramagnetic impurity which is believed to be Fe^{3+} from electron spin resonance studies.

RECOMMENDATIONS

1. Our principal recommendation is to continue the present program in its present direction to allow the synthesis of each of the results in a unified theory along the lines which are now clear in the chalcogenide system.

2. As in our previous recommendations, we continue to recommend the survey preparation of new glasses. We anticipate that the transition metal oxide-phosphate, silicate, borate and germanate survey presently in progress will be continued.

3. The Mössbauer studies should be continued to examine 57 Fe and the system presently under examination using other techniques. This will significantly aid in atomic structure model development in these systems as an addition to the present tools.

4. We recommend that the far infrared "conductivity loss spectra." This will allow the loss behavior to be explicitly attributed (31) to each mechanism thus reinforcing both atomic and microstructural analyses.

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A REVIEW OF VANADIUM-PHOSPHATE GLASS ELECTRICAL PROPERTIES

D. L. Kinser and L. K. Wilson

The extensive electrical property studies in vanadium-phosphate have been reviewed and are presented in terms of a ternary VO_2-V_2C_5-P_2O_5 system rather than the usual binary V_2O_5-P_2O_5 system. Extensive electron microstructural studies on representative glasses throughout the ternary system have revealed extensive glass-glass immiscibility in the system. An examination of the electrical properties presented on the basis of a ternary system and the corresponding representative microstructures indicates that the previously observed conductivity maxima in this system in a consequence of microstructural as well as electronic behavior of this system. There is evidence for the existence of a second conductivity maxima near the $V^{4+}=V^{5+}$ composition although glasses in this composition range are difficult to prepare in the amorphous state. It thus appears that this system exhibits two conductivity maxima. Of these two maxima one is the result of microstructural segregation while the second is a consequence of the hopping conduction mechanism. It is thus the conclusion of this work that the anomalous behavior of this system is in fact not anomalous in an electronic sense, but is a consequence of microstructural features of the system.

Research sponsored by U. S. Army Research Office - Durham, N.C.

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Time on Program:

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Title: (Please Double Space) (See Instructions) Magnetic Properties of Manganese Phosphate Glasses

Author(s), Company, Address: (Please Double Space) (See Instructions) E. J. Friebele*, D. L. Kinser and L. K. Wilson; School of Engineering, Vanderbilt University, Nashville, Tennessee 37235

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Abstract (*Please Double Space*)

Magnetization studies of essentially monovalent glasses of the manganese phosphate system are reported over the composition range 30 MnO - 70 P_2O_5 to 55 MnO - 45 P_2O_5. The high temperature susceptibility of these glasses obeys a Curie-Weiss law with C and θ values that are interpreted by a molecular field approximation. The reciprocal susceptibility of the glasses exhibits a downward curvature at low temperature which is qualitatively explained by the existence of a small fraction of isolated ions in an otherwise antiferromagnetically coupled glassy matrix. The field dependence of the magnetization as a function of temperature is also reported.

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(See Instructions)

Author(s), Company, Address: E. J. Friebele*, D. L. Kinser and L. K. Wilson; School of Engineering, Vanderbilt University, Nashville, Tennessee 37235
(Please Double Space)
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Abstract *(Please Double Space)*

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Title: *(Please Double Space)* *(See Instructions)* **Quantitative Analysis of Oxidation States for Some Transition Metal Oxides in Phosphate Glass**

Name, Company, Address: *(Please Double Space)* *(See Instructions)* C. H. Perry*, L. K. Wilson and D. L. Kinser; School of Engineering, Vanderbilt University, Nashville, Tennessee 37235

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3. [illegible] all capital letters, [illegible] these [illegible]

Abstract *(Please Double Space)*

A routine technique has been developed which allows rapid and accurate quantitative determination of oxidation states of iron, copper, vanadium and titanium in phosphate glass. The method is generally applicable when the oxides of only one reduced metal are present in the glass. The sample is heated in a pure oxygen environment and the oxygen uptake is measured. This allows an accurate calculation of the oxidation states present in the glass.

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Title: Surface Crystallization of Silicate Glasses
(Please Double Space)
(See Instructions)

Authors, Company, Address: D. L. Kinser, G. Cutler and R. MacEachron*; Materials Science and Metallurgical Engineering, School of Engineering, Vanderbilt University, Nashville, Tennessee 37235
(Please Double Space)
(See Instructions)

Abstract *(Please Double Space)*

Surface crystallization morphology and kinetics were examined in the soda-silica, lithia-silica and borosilicate glass systems. Specific glass compositions were subjected to a series of thermal treatments at several temperatures and times to determine the morphology and kinetic behavior of surface crystallization. Scanning electron microscopy, petrographic microscopy and X-ray diffraction techniques were used to characterize the surface crystallization product. The pronounced preferred orientation in crystal growth was related to compositional and other crystallization process variables.

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Title: *(Please Double Space)* *(See Instructions)* Low Temperature Magnetic Studies of Iron-Phosphate Glasses

Author(s), Company, Address: *(Please Double Space)* *(See Instructions)* L. K. Wilson, J. H. Dayani* and D. L. Kinser; School of Engineering, Vanderbilt University, Nashville, Tennessee 37235

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Abstract *(Please Double Space)*

The temperature dependent magnetic susceptibility of a series of iron-phosphate glasses has been measured over the temperature range 2.0°to 300°K. The high temperature susceptibility of these glasses obeys a Curie-Weiss law with a negative Curie temperature indicating antiferromagnetic advising. The compositional dependence of the exchange constant is considered over the range 20 to 80 mole percent FeO. The low temperature inverse susceptibility shows a downward curvature typical of amorphous antiferromagnetism. Anomalous behavior of the susceptibility of some glasses below 10°K is examined in terms of possible microcrystalline inclusions in the glass and field dependance of the susceptibility is considered at low temperature.

(Research sponsored by the U. S. Army Research Office-Durham.)

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Title: *(Please Double Space) (See Instructions)* Mössbauer Effect Spectroscopy of Iron Phosphate Glasses

Author(s), Company, Address: *(Please Double Space) (See Instructions)* J. G. Vaughan*, L. K. Wilson and D. L. Kinser; School of Engineering, Vanderbilt University, Nashville, Tennessee 37235

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Abstract *(Please Double Space)*

The coordination states and magnetic structure of iron in several different compositions of iron phosphate semiconducting glasses containing variable Fe 3^+ / Fe_{total} ratios were studied using Mössbauer Effect Spectroscopy at 77°K and 300°K. Room temperature values for the isomer shift and magnetic quadrupole splitting indicate octahedral coordination. Magnetic hyperfine structure at 77°K was interpreted as evidence of short-range magnetic ordering. Glasses subjected to various heat treatments showed precipitation of at least two crystalline phases.

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Title: (Please Double Space) (See Instructions) Radiation Effects on Electrical Conduction in Transition Metal Phosphate Glasses

Author(s), Company, Address: (Please Double Space) (See Instructions)

D. L. Kinser, D. Fite* and L. K. Wilson; School of Engineering,
Vanderbilt University, Nashville, Tennessee 37235

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Abstract (Please Double Space)

Several transition metal phosphate glasses including the highly insulating $MnO-P_2O_5$ and the higher conductivity $FeO-P_2O_5$ glasses have been examined for radiation enhancement of conductivity. It has been observed that the Co^{60} - gamma flux significantly increases the in situ DC conductivity of the MnO and CoO systems but not in the FeO system. This effect is mathematically described by a linear radiation flux-conductivity equation over several orders of magnitude of flux change. At room temperature the more conductive glasses do not exhibit the effect while the more insulating glasses show a pronounced sensitivity.

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MAGNETIC PROPERTIES OF AN AMORPHOUS ANTIFERROMAGNET: MANGANESE PHOSPHATE GLASS

By

EDWARD JOSEPH FRIEBELE

Dissertation
Submitted to the Faculty of the
Graduate School of Vanderbilt University
in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

in

Electrical Engineering

May, 1973

Nashville, Tennessee

Approved:

Date:

18-A

To McG and Ed
With Whom It All Began

ACKNOWLEDGEMENTS

There are many people who have made significant contributions to this dissertation over the course of the past five years, and I am extremely grateful to all of them. I would like to thank Dr. Larry K. Wilson, my advisor, for his help, guidance, and friendship through five years of development, and for running the low temperature magnetization measurements; Dr. Donald L. Kinser for the knowledge of glass structure that he imparted to me; Dr. Robert A. Weeks, Solid State Division, Oak Ridge National Laboratories, and Dr. Israel S. Jacobs, General Electric, for their frequent consultations; the other members of my Ph.D. committee, Dr. Robert Nash, Dr. Ernest Jones and Dr. Charles V. Stephenson, who have helped in the final preparation of this dissertation.

I would also like to thank the many friends who have helped me, Dr. James Nelson, Dr. Richard Manning and Dr. Harry Sanders for their patient help with the computational problems of a relative novice; Mr. Jack Cannon for his loyal technical assistance; Mr. Charles Perry, Mr. Andrew Dozier, Mr. John Dayani, Mr. Robert Jennings, and Mr. Lee Buchanan for their concern and encouragement. I would like to especially thank my wife, Elaine, for her personal and financial support for the past two years, for her resolution of the optical spectra into Gaussian bands, and for her help in preparing the final copy of the dissertation.

The financial support of Vanderbilt University and the Army Research Office - Durham is gratefully acknowledged.

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CHAPTER I

INTRODUCTION

Interest in the magnetic properties of glasses containing paramagnetic constituents was stimulated by Sands in 1955 (1). He reported results of electron spin resonance (ESR) studies of a series of alkali-silicate glasses doped with various transition metal ions. In addition to a ubiquitous spectrum, which was later identified as the crystal field resonances of trivalent iron, he observed hyperfine splittings of known dopants such as vanadium, manganese, chromium, molybdenum, and copper.

Subsequent studies of the magnetic properties of amorphous materials have been classified into two general areas: studies of isolated paramagnetic ions in glassy hosts, and studies of exchange coupled ions in highly doped, "magnetic" glasses. The studies of isolated ions have been concerned with identifying the site symmetry of the paramagnetic ions and observing changes in glass structure using the paramagnetic ions as a probe. The studies of magnetic glasses have been directed towards an understanding of the nature of the exchange interaction which occurs between the magnetic ions in an effort to explain the anomalous magnetic behavior at low temperature. In addition, magnetic glasses have been studied by magnetic resonance techniques to determine the microstructural dependence of the magnetic properties of the glass.

In spite of the extensive investigations of the magnetic properties of amorphous materials, there are still many unanswered questions. The purpose of this chapter is to briefly review these previous studies, focusing on glasses containing manganese and iron. Some of the disparities between investigations and some of the unanswered questions will be discussed in order to establish a basis for the present program of research. The purpose of this research is to advance new experimental and theoretical results in order to further a unified theory of the magnetic properties of non-crystalline solids.

Background

Determination of Site Symmetry. In Sands' pioneer work (1) he reported resonance lines at g' = 4.3 and 6 in the ESR spectra of his glasses. His suggestion that these might be due to impurity-level iron ions in the base glass led to a series of ESR investigations of iron doped glasses. It was desired to correlate the presence or absence of the various Fe^{3+} absorptions, which occur at g' = 0.86, 2, 4.28, 6, and 11, with the site symmetry of the iron ion in the glassy matrix.

The Hamiltonian, which gives rise to ESR absorptions, may be solved by solving the eigenvalue problem, $H\Psi_n = E_n \Psi_n$, where H is the spin Hamiltonian, Ψ_n are the wave functions of the electrons, and E_n are the energy levels of the system. In general, the Hamiltonian in the ESR experiment may be written (2)

$$H = \mu\bar{S}\cdot\vec{g}\cdot\bar{H} + \bar{S}\cdot\vec{D}\cdot\bar{S} + \bar{S}\cdot\vec{T}\cdot\bar{I} + \bar{I}\cdot\vec{P}\cdot\bar{I}. \qquad (1.1)$$

The tensors $\vec{g}$, $\vec{D}$, $\vec{T}$, and $\vec{P}$ have the symmetry of the crystalline field of the paramagnetic ion and represent the interaction of the electrons with the applied magnetic field, the crystal field, the nucleus, and the interaction between nuclei, respectively. $\overline{S}$ and $\overline{I}$ are the electron and nuclear spin operators, respectively. The derivation of this Hamiltonian and its application to ESR in solids in given by Low (3).

Because of the random orientation of the spins in glasses, the anisotropic effects of the tensor operators of the spin Hamiltonian are averaged over all angles. They may then be reduced to two terms -- one parallel to the d.c. magnetic field, and one perpendicular to it. In the case where there are no hyperfine or quadrupole interactions, the third and fourth terms of the spin Hamiltonian vanish. The second term may be expanded in terms of the components of the $\overline{S}$ vectors as

$$H = g\mu\overline{H}\cdot\overline{S} + D[S_z^2 - \frac{1}{3}S(S+1)] + E[S_x^2 - S_y^2] \tag{1.2}$$

where the constants D and E represent the intermixing of energy levels in the presence of crystalline field components of axial and orthorhombic symmetry respectively (4). Determination of these constants may give an indication of the possible site configuration of the paramagnetic ion and the strength of the zero field splitting parameter.

A limit on D can be determined by comparing the ESR spectra obtained at different frequencies. The frequency at which crystal field resonances become weak or disappear is equal to $|D|/h$. If a line which is observed at a lower frequency is absent at a higher frequency, it can be said that $|D|<h\nu$, where ν is the higher frequency. This technique has been applied to chromium-phosphate glasses by Landry (4,5) and Fournier (6) and to iron-phosphate glasses by Friebele, et al. (7).

More accurate methods of determining D and E consist of solving the eigenvalue problem for each transition over a wide range of D and λ =

E/D values. A graphical technique for determining D and λ values from a given ESR spectrum was developed by van Reijan (8) for Cr^{3+} and was extended to Fe^{3+} by Barry (9), Downsing and Gibson (10), and Aasa (11).

Other investigators have solved the spin Hamiltonian in more specific cases in order to interpret the ESR spectra which they had obtained. Castner and his co-workers (12) pioneered the study of Fe^{3+} in glasses by solving the spin Hamiltonian for Fe^{3+} in a sodium silicate glass. To perform the solution they assumed that the crystalline effects dominated the Zeeman term, and hence the magnetic field could be treated as a perturbation. They also assumed that $D = 0$ to first order and that any contribution from the D term was exhibited in the broadness of the resonance line.

Many attempts have been made to infer the coordination and site symmetry of the Fe^{3+} ion from its ESR spectra in various materials. In particular, several investigators have attempted to correlate the presence of the resonance at $g' = 4.28$ with Fe^{3+} on a tetrahedral site (12-16). However, Griffith (17) showed that a rhombohedral site could give rise to the $g' = 4.28$ line, and Kurkjian and Sigety (18) concluded after correlation of ESR, optical and Mössbauer data, that the presence of the $g' = 4.28$ line cannot be used as an indication of the coordination of the Fe^{3+} in glass. In spite of the fact that Fe^{3+} in a strong tetragonal field gives rise to a resonance at $g' = 4.28$, the converse is not true.

In general, the presence or absence of certain resonance lines in the ESR spectra cannot be used to identify the site symmetry of the Fe^{3+} ion. However, a determination of D and λ from these lines may indicate possible site configurations based on the symmetry of the crystal field.

In recent years Mössbauer effect spectroscopy (MES) has been used in conjunction with ESR, nuclear magnetic resonance (NMR) and nuclear quadrupole resonance (NQR) to more precisely identify the site configuration of Fe^{3+} in glass. Because nuclear energy levels are extremely sensitive to changes in the electronic cloud through electron-nuclear interactions, any method which detects nuclear transitions is valuable in studying the nature of the bonding of an ion. Although information obtained from MES is similar to that obtained by NQR and NMR, the difference lies in the fact that the quadrupole moments of excited states as well as ground states may be observed. Thus the valence and coordination of isotopes such as Fe^{57}, which has no ground state quadrupole moment, may be studied.

Several investigators have studied the coordination of iron in phosphate and silicate glasses (19-21) and have interpreted their results by comparison with stochiometric crystalline iron compounds. In general it has been determined that both the trivalent and divalent ions occupy octahedral sites in phosphate glasses and tetrahedral sites in silicate glasses. In addition, the width of the absorption line has been used as a measure of site to site variation of the iron sites. An excellent review of MES studies of glasses has been written by Kurkjian (22).

In conclusion, the study of the site symmetry of paramagnetic ions in glassy hosts by conventional crystalline techniques is complicated by the random orientation of the ion sites. This results in an averaging of the angular dependent quantities in the spin Hamiltonian and a subsequent loss of precise quantitative information. It is through use of several different techniques that the site symmetry of the ion can be uniquely determined. An excellent report of the advantages of using both NMR and MES techniques has been written by Feldmann (23).

Studies of Glass Structure. One of the primary difficulties in the study of iron-containing glasses is the fact that the spin Hamiltonian for iron contains only the electron Zeeman and crystal field terms since iron has no nuclear spin. Hence, the additional information about bonding in the glass which might be obtained through an ESR study of the hyperfine interaction or an NMR study is not available. For this reason, other transition metal ions such as Mn^{2+} (I=5/2), Cu^{2+} (I=3/2), V^{4+} (I=7/2), Cr^{3+} (I=3/2) and Ti^{3+} (I=5/2, 7/2) have been used as dopants in glasses to serve as monitors of glass structure.

Early NMR studies centered on the alkali-borate glass system since there is a change in boron coordination which occurs with the addition of alkali ions to the glass -- the so-called boron anomaly.

Since B^{11}, which has a nuclear spin of 3/2, is 81.17% naturally abundant, extensive NMR investigations of borate glasses were conducted. It was determined by comparison of the NMR data with crystalline borate compounds that the boron atom can exist in two different coordinations in the glass. By observing the intensity of the NMR absorptions from three and four-fold boron atoms, the relative concentration of three and four coordinated boron as a function of alkali concentration was determined. The results from NMR data were in accord with previous observations of the boron anomaly in the range of 16 to 20% alkali concentration. The boron atoms in borate glass are triangularly coordinated at low alkali concentrations, but become predominately tetragonally coordinated as the alkali concentration is raised above about 20%. A saturation of four-fold boron concentration occurs at about $n_4 = 0.7$. Park (24) has recently published results of an NMR study of the strontium borate system, and a comprehensive review of early NMR studies has been written by Bray (25).

Subsequent investigations of alkali borate glasses have been performed by doping manganese into the glass and studying the resulting ESR spectra as a function of alkali concentration and microwave frequency. de Wijn and van Balderen (26), who studied manganese-doped potassium borate glasses, solved the spin Hamiltonian for the spectra based on an assumption of axially symmetric crystalline fields. From the value of the hyperfine splitting, they were able to determine that the Mn^{2+} ion was strongly ionic in the glass.

Tucker (15) considered two types of manganese sites which gave rise to absorptions at $g' = 4.3$ and $g' = 2$. Of course, since Mn^{2+} is isoelectronic with Fe^{3+}, these site assignments are applicable to all $S = 5/2$ systems. Tucker's Site I is extremely regular and has a special symmetry (12), and his Site II has randomly distributed zero field splittings.

Griscom and Griscom (27) studied manganese doped lithium borate glasses and explained the observed spectra on the basis of orthorhombic crystalline fields. Although they were unable to definitively assign a coordination number to the manganese ion, their work agreed with the site assignments of Tucker. By comparing the ESR spectra of their glasses with the spectra of analogous lithium borate crystals, they concluded that there existed extensive short range order in the glass with sufficient lattice deformation at long distances to account for the amorphous nature of the matrix.

Loveridge and Parke (28) examined a series of iron, manganese and chromium doped soda borate and soda silicate glasses and were able to interpret the spectra for manganese on the basis of the work of Griscom and Griscom. Taylor and Bray (29) studied the manganese doped strontium borate crystals and glasses and were able to fit the observed ESR spectra by assuming that the fine structure and hyperfine terms of the Hamiltonian acted as perturbations on the crystal field terms. The results were in agreement with the two site assignments of Tucker, where the two sites were those occupied by the manganese ion in two of the strontium-borate crystalline compounds.

Another glass system which has received considerable attention because of its semiconducting properties is the vanadium-phosphate system. Because of its excellent glass-forming properties, it is possible to prepare vanadium-phosphate glasses with as much as 95 mole % V_2O_5 by conventional techniques. In an effort to understand and clarify the conduction mechanism in these glasses, several investigators have turned to magnetic resonance methods. France and Hooper (30) used NMR techniques to derive an empirical relationship between the concentration of V^{4+} and the total vanadium concentration in the glass. They were able to successfully explain the high resistivities observed in glasses with high vanadium content as being due to the low concentration of V^{4+} in these glasses. Landsberger and Bray (31) employed ESR techniques to determine the V^{4+} concentration. They interpreted the NMR data in terms of two types of vanadium sites in the glass: one similar to the VO_5 site in crystalline V_2O_5, and the other similar to the VO_5 with a PO_4 group substituted for the apex oxygen. Lynch and his co-workers (32) measured the ESR lineshape and intensity as a function of temperature and found that the concentration of carriers was constant. This result is in disagreement with the work of Friebele (33). Other ESR studies by Nagiev (34) and Nagano et al. (35) have confirmed that the V^{4+} ion occupies a distorted tetrahedral site such as the VO_5 site, in vanadium-phosphate glasses. However, not all investigators have observed hyperfine structure in the V^{4+} ESR spectra of these glasses. A possible explanation for these disparate results is that there are microstructural differences in the glasses studied by different workers arising from different sample preparation techniques (33).

The general conclusions of these studies of glass structure as well as the studies of manganese-doped silicate, fluoroberyllate, and phosphate glasses (36-38) have been as follows:

1. There exists a high degree of short range order in the glasses. The local structural units in the glass are distorted versions of the structural units in stochiometric crystals of the same composition. Glasses of intermediate composition between two stoichiometric crystals contain a mixture of structural units of both crystals.

2. The transition metal ion site symmetry cannot be unequivocally assigned on the basis of ESR data. However, it is believed that manganese and iron occupy primarily octahedral sites in phosphate, borate, and fluoroberyllate glasses and tetrahedral sites in silicate glasses.

3. The manganese ion has been used as a monitor of local structural changes in the glass, such as the boron anomaly. Results from these ESR studies have agreed with previous observations of the boron coordination change.

4. The assignment by Tucker (15) of two different ion sites experiencing essentially two different crystalline fields has been verified in numerous glass systems.

5. The manganese-liqand bond becomes progressively more covalent in the order fluoroberyllate, phosphate and sillicate glass systems.

Several investigators have used the transition metal ion in glasses to monitor changes which occur with heat-treatment. Barry and Lay (39) monitored the devitrification of a lithia-alumina-silicate glass containing titanium by comparing the ESR spectra of the glasses doped with vanadium with the spectra of vanadium-doped standard phases. In this way they were able to monitor the Ti^{4+} coordination during crystallization. Friebele, et al. (7) and Kinser et al. (40) used ESR techniques to study a concentrated iron-phosphate glass during devitrification. They observed the onset of devitrification with the appearance of a sharp singlet centered at g' = 2 in their ESR spectra. Further heat treatment resulted in sufficient growth of the crystalline phases that they could be identified by conventional X-ray techniques. Garif'yanov and Tokareva (13) studied the crystallization of two silicate glasses by observing the spectra of titanium and chromium which they had doped into the matrix. They were able to observe the glass proceed to a more ordered and symmetrized state as the crystallization progressed.

Chatelain and Weeks (41) studied manganese-doped $ZnCl_2$ crystals and glasses and found that both ESR spectra could be fit to the same Hamiltonian with different D and E values. By heat treatment of the glass they observed the devitrification ordering processes and determining that first a short-range and then a subsequent long-range process were in effect. Subsequent vitrification disordering by irradiation also showed the existence of two separate short and long-range processes which operate sequentially.

An additional structural effect which has recently been the subject of some investigation is the changes in magnetic behavior which occur with liquid-liquid phase separation. Friebele et al. (33), who have studied the intensity of the V^{4+} ESR absorption in vanadium-phosphate glass, observed the appearance of a hysteresis in the intensity-temperature plot in samples which were microstructurally phase separated into two amorphous phases (42). In addition, they were able to observe weak antiferromagnetic coupling between V^{4+} pairs and between V^{3+} pairs.

Other investigators have used magnetic susceptibility techniques to observe the changes in magnetic behavior that occur with devitrification and phase separation during heat treatment of the glasses. O'Horo and Steinitz (43) studied an alumino-borosilicate glass containing 12 mole % Fe_2O_3, and found that heat treating the glass caused precipitation of Fe_3O_4 and Fe_2O_3. In the first stages of devitrification they detected typical superparamagnetic behavior whereas the as-cast glass behaved paramagnetically. Subsequent heat treatment caused the saturation magnetization to increase as the amount of ferromagnetic precipitate increased. They concluded that the progress of devitrification could be followed by observing the saturation magnetization.

Fahmy et al. (44) heat treated an iron containing barium borate glass and observed first an increase and then a decrease in magnetic moment per unit mass. The magnetization vs. H/T curves deviated substantially from Langevin behavior due to the presence of a distribution of magnetic moments in the precipitated phases. They determined that the precipitated phases consist of an inner ferrimagnetic core surrounded by an antiferromagnetic skin, and they observed this "grapefruit" morphology directly by electron microscopy.

Janakirama Rao (45) has studied a complete series of alkali borosilicate glasses containing various transition metal and rare earth ions. By calculating the specific susceptibility at infinite field strength, he was able to avoid the effect of possible ferromagnetic impurities when comparing the data from different glasses. He concluded that the internal glass structure, the microstructure, and the metal ion concentration had profound effects on the magnetic properties of the glass. In general, the molar susceptibility of the glasses was quite high at low metal ion concentrations and then decreased as the metal concentration was increased. The first effect was attributed to a high degree of ionization of the ion in the glass, and the latter was the result of mutual interactions between the ions and quenching of the orbital moment.

Extensive ESR studies of radiation damaged glasses have been carried out in order to determine the type of damage and to further elucidate the internal structure of the glass. No treatment of the magnetic properties of glasses would be complete without a thorough discussion of this topic. However, because of the vastness of the subject and because it has no direct bearing on the research reported in this dissertation, the author would like to merely cite a comprehensive review by Lell (46), a recent article by Griscom (47), and the references contained therein.

Studies of Antiferromagnetic Glasses. In 1960 Gubanov reported the theoretical possibility of cooperative magnetic phenomena in noncrystalline materials (48). This paper aroused interest in a study of alloys and glasses containing exchange coupled metal ions. Gubanov's prediction was soon verified, and since that time extensive experimental and theoretical effort has been generated in an effort to explain and study amorphous ferromagnetism. For a comprehensive review article, the reader is referred to Hasegawa (49).

The study of amorphous antiferromagnetism was pioneered by Schinkel and Rathenau, who in 1964 reported a magnetic susceptibility investigation of potassium borate glasses containing up to 45 mole % MnO (50). The inverse susceptibility of these glasses obeyed a Curie-Weiss law in the high temperature region and possessed an antiferromagnetic Curie temperature which decreased in temperature as the concentration of manganese was increased. This behavior was explained on the basis of a molecular field approximation. The manganese ions were assumed to be randomly distributed in the octahedral sites of a face-centered cubic lattice of oxygen atoms. The high symmetry which was assumed for the manganese sites is in accord with the subsequent ESR investigations of de Wijn and Balderen (26) and Griscom and Griscom (27). In fact, the work of Schinkel and Rathenau was the motivation for the work of Griscom and Griscom, and the samples used in both studies were identical.

The susceptibility data of Schinkel and Rathenau indicated the existence of antiferromagnetic exchange interactions between manganese ions. However, the low temperature behavior of the inverse susceptibility of the glasses differed radically from the behavior of antiferromagnetic crystals. Rather than displaying an increase in inverse susceptibility below the Néel temperature, the inverse susceptibility of the glasses decreased towards the origin. This anomalous decrease in susceptibility at low temperature will be seen later to be one hallmark of amorphous antiferromagnetism.

The existence of exchange interactions between transition metal ions in glass has been previously observed. Several investigators (13, 16, 22, 28, 38) observed changes in the ESR spectra of manganese and iron containing glasses as the transition metal ion concentration was raised above the dopant level. The broadening of the manganese hyperfine peaks and the appearance of a strong iron resonance at g' = 2 were attributed to the onset of exchange coupling between metal ions.

A thorough investigation of the temperature dependence of the ESR line intensity of a heavily doped chromium phosphate glass has been carried out (4, 5, 6) and the Cr^{3+} ions were determined to be antiferromagnetically coupled in the glass. By comparing the observed intensity with the intensity predicted by a model of exchange coupling based on the Landé interval rule, the above workers were able to determine the average value of the exchange integral, J. In addition, they were able to propose a Cr^{3+} pair structure which would give rise to the observed value of J and the observed values of the fine structure constants.

An ESR study of the iron phosphate glass system has revealed the existence of extensive antiferromagnetic coupling between trivalent and divalent iron ions (7). Exchange coupling between aliovalent ion pairs gives rise to exchange broadening (51), and in the case of iron phosphate glass, ESR linewidths greater than 10,000 Gauss have been observed. Heat treatment of this glass caused devitrification of the glass into crystalline phases in which the antiferromagnetic coupling was observed between Fe^{3+} ions.

Antiferromagnetic ordering has also been observed in the vanadium phosphate glass system (33). By measuring the ESR line intensity as a function of temperature, ordering temperatures for V^{4+} and V^{3+} ion pairs in the glass have been determined, and the effects of microstructure on the magnetic properties have been studied.

Mather et al. (52) have studied a lithia-silicate glass containing 40 wt. % Fe_2O_3 and have found that the glass is superparamagnetic. They determined that the magnetic phase was amorphous and consisted of antiferromagnetically aligned regions of about 100 Å in diameter.

Hooper and his co-workers (53) have examined a series of alkaliborate and aluminosilicate glasses containing large amounts of iron, cobalt and manganese ions and have found various types of magnetic behavior: paramagnetic, superparamagnetic and antiferromagnetic. Although some of the magnetic behavior is due to precipitated crystallites in the glass matrix, other totally amorphous glasses exhibit antiferromagnetic behavior, with transition temperatures that depend upon glass composition and preparation.

Various attempts have been made to theoretically explain the anomalous low temperature susceptibility behavior of amorphous antiferromagnetic films and glasses. Lucas (54) observed antiferromagnetic behavior in yttrium iron alloy films which had been oxidized. The susceptibility behavior was explained using a Weiss molecular field model which assumed that the random distribution in bond lengths and angles which occurs in an amorphous material would result in a Gaussian distribution in the effective field experienced by the magnetic ions. He assumed that the distribution was centered at $H_{eff} = 0$, which is equivalent to assuming predominately uncoupled, and hence paramagnetic, ions in the alloy. In addition, Lucas made the assumption that there existed a finite probability that some of the magnetic ions in the amorphous alloy would be totally surrounded by nonmagnetic atoms due to the random nature of the matrix. Then, the total susceptibility of the amorphous alloy would be the sum of a paramagnetic component due to these "isolated" ions and an antiferromagnetic component based on the Gaussian distribution of effective field:

$$\chi_t = f\chi_{ex} + (1-f)\chi_{para} \tag{1.3}$$

where χ_{ex} is the antiferromagnetic component of the susceptibility, χ_{para} is the paramagnetic component, and f represents the fraction of exchange coupled or "unisolated" ions. The results which Lucas obtained correctly predicted the downward curvature of the inverse susceptibility vs. temperature plot and predicted a decrease in the Néel temperature of the amorphous material from that of the crystalline compound. Lucas' derivation was subsequently repeated by Simpson (55), who assumed that there would be no correlation between spins of neighboring magnetic ions.

The results Simpson obtained were identical with those of Lucas, and were used to explain the susceptibility data obtained from a series of oxidized yittrium-iron thin films, (55, 56).

Another model for amorphous antiferromagnetism was advanced by Kobe and Handrich (57) based on a Heisenberg theory of amorphous ferromagnetism (58). The model assumes that the magnetic ions are located on a finite body-centered cubic lattice with periodic boundary conditions. The amorphous nature of the material is introduced by assuming that the exchange interaction between neighbors is a function of random numbers obeying an arbitrary distribution. Thus, the amorphous nature of the material can be simulated without knowing the functional dependence of the exchange interaction on the interatomic distance and without a detailed knowledge of the internal glass structure. The results which were obtained disagreed with the work of Simpson and Lucas in that the predicted Néel temperature was greater than that of the corresponding crystal. In addition, the low temperature inverse susceptibility did not decrease. Rather, the parallel susceptibility increased below the Néel temperature and the perpendicular inverse susceptibility continued linearly and became constant near T = 0°K. The model also predicted that the magnetization of the amorphous material was less than that of the crystalline material.

A further refinement of the Kobe and Handrich model was proposed by Hasegawa (59) who assumed that the amorphous material could be divided into pairs of antiferromagnetically aligned ions. By applying this modification of the two-sublattice model and summing the interactions over nearest and second nearest neighbor interactions, he obtained three results: depending upon the relative distribution widths of the first and second nearest neighbor interactions, the parallel susceptibility of the amorphous material could either be greater than, equal to or less than the parallel susceptibility of the ordered crystalline material; the Néel temperature was found to be greater than of the ordered state; and the inverse susceptibility increased below the Néel temperature in agreement with Kobe and Handrich (57) but in disagreement with Simpson (54) and Lucas (55).

At this point, the reader is no doubt anxious to learn which, if any, of these three theoretical models correctly predicts the experimental behavior of amorphous antiferromagnetic materials. To his dismay, the answer is that all three correctly predict the behavior of some materials. As was pointed out earlier, the Lucas model correctly predicts the behavior of oxidized yittrium-iron films (56), the Hasegawa model agrees with data which he has obtained on amorphous manganese-phosphorous-carbon alloys (60). Recent papers by Wilson et al. (61) and Egami et al. (62) which have reported studies of transition metal phosphate glasses have shown that data on manganese, cobalt and copper phosphate glasses is in agreement with the Simpson-Lucas theory, whereas data on iron phosphate glasses agrees with the theories of Kobe and Handrich.

A possible explanation of the behavior of the iron glass can be found in the work of Friebele et al. (7), who found the existence of both valence states of iron in the glass and extensive coupling between aliovalent iron ions. Apparently, the transition metal ions in the other glass systems exist predominately in one valence state.

No doubt the justification for further research in the field of amorphous antiferromagnetism is obvious. Although some work has been done, there is no one unified explanation for the behavior of these materials. Both ESR and magnetic susceptibility have been shown in this chapter to be valuable tools in the study of amorphous magnetic materials. As will be shown in subsequent chapters, it is the intention of the author to apply these tools in quest of an understanding of the manganese phosphate glass system.

Purpose of the Research

It has been shown that there has been considerable interest in the magnetic properties of glasses, and yet the characterization of these properties has been difficult. Conventional techniques of studying crystalline materials are unable to completely characterize glassy materials due to the site-to-site variation in the metal ion sites, the random orientation of the ions throughout the glass, the existence of microstructural inhomogeneities in the glass, and the possibility of multiple valence states of the transition metal ion. The present program of research was undertaken in order to characterize the magnetic properties of a magnetic glass more completely than had been previously realized, and to offer a possible explanation for the observed magnetic behavior.

One of the difficulties encountered in previous investigations of magnetic glasses was the large number of parameters which affected the magnetic properties of the glass under study. Examples include microstructural inhomogeneity, such as liquid-liquid phase separation or devitrification, the existence of multiple valence states of the magnetic ion, difficulty in determining precise glass composition, deliquescence, magnetic clustering and difficulty in the glass-making procedure resulting in unreproducible samples. The manganese phosphate glass system was chosen for the present study because many of the above parameters could be eliminated, and the magnetic properties of the glass could be more quantitatively interpreted. Specifically, the glasses were reproducibly prepared over a fairly large range of compositions which included superphosphates and a composition approaching that of the only known divalent manganese phosphate crystal, manganese pyrophosphate ($Mn_2P_2O_7$). As will be shown later, almost all of the manganese ions in the glass are in the divalent state, so that the magnetic data can be interpreted in terms of either isolated divalent manganese ions or exchange coupled divalent manganese ions. Finally, although microstructural inhomogeneity has been reported in a 55-45 mole % MnO-P_2O_5 heat treated glass (63), homogeneous stable glasses can be prepared over the composition range of 30-70 to 55-45 mole % MnO-P_2O_5.

In detail, the purpose of this research program is as follows:

1. To study and characterize the magnetic behavior of the manganese phosphate glass system; to explain this behavior in terms of internal glass structure; and to compare the behavior of the concentrated glasses with that of manganese pyrophosphate.

2. To propose a model of amorphous antiferromagnetism which explains the downward curvature of the inverse susceptibility observed at low temperatures; to compare the results of the present study with

those of other experimental and theoretical studies of amorphous antiferromagnetism.

CHAPTER II

EXPERIMENTAL METHODS

Glass Preparation

The glass samples were prepared by melting a physical mixture of x mole % MnO_2 and (1-x) mole % P_2O_5, where x = 20, 30, 40, 50, 55, and 60. Each mixture was melted in air in a silica crucible at 1300°C for one hour and then quenched to room temperature on water-cooled copper plates or in a water-cooled steel die. The 60-40 melt spontaneously crystallized, and the 55-45 glass showed some evidence of surface crystallization. The other glasses showed no tendency to crystallize. However, the melt of the 20-80 glass was extremely inhomogeneous in spite of stirring with a graphite rod at 10 minute intervals during the melting. The melt composition varied between 35-65 and 15-85 mole % MnO_2-P_2O_5; therefore this melt was discarded. All subsequent measurements were performed on the 30-70, 40-60, 50-50, and 55-45 (glassy phase) mole % MnO_2-P_2O_5 glasses.

Glasses in the as-cast state were highly strained and tended to fracture into small pieces. Approximately half of the samples of each melt were subjected to a strain anneal of one hour at 300°C. After the anneal the glasses could be cut and ground without spontaneous fracture.

All glass samples were examined for crystallinity in a vacuum Guinier deWolff X-ray camera using Mo Kα radiation. This technique permits detection and identification of as little as 0.1 wt % crystal for crystals larger than about 0.05μ. The crystalline phase on the surface of the 55-45 glass samples and the crystallization product of the 60-40 melt were identified as manganese pyrophosphate by this method. No evidence of crystallinity was found in any of the as-cast or annealed glasses other than the small surface crystallization of the 55-45 glass. However, no evidence of crystallinity was found in the glassy phase of this glass.

Prior to annealing or heat treating any of the glass samples, dilatometric measurements were made to determine the softening points of all as-cast glasses. Characterization of these softening points was essential since heat treating or annealing the glasses in or near the softening range could result in liquid-liquid separation or crystallization. These dilatometric measurements were performed on an Orton recording dilatometer using one inch fragments of the as-cast glass samples in a silica sample holder.

Physical Property Studies

Electron Microscopy Studies. Microstructural imhomogeneity has been observed in the vanadium phosphate glass system (see references in 33), so direct replica electron microscopy studies of the manganese phosphate glass samples were performed. Both etched and unetched freshly fractured surfaces of the glass were used for the study. A portion of the samples were etched for varying lengths of time in 0.1 N. HCl. Both the etched and unetched samples were then shadowed with platinum-rhodium and coated with a layer of carbon. The carbon replicas were then examined in a Phillips EM 300 electron microscope under high magnification. However, despite varying the etching times, no evidence of microstructural heterogeneity was found in any of the as-cast glass samples.

Optical Absorption Measurements. Optical absorption measurements were performed on samples from each glass melt to determine the composition of the glass since no convenient chemical technique for measuring manganese concentration was known. The absorption bands of both divalent and trivalent manganese lie in the visible and near infrared regions of the spectra so that Gaussian resolution of the optical spectra results in a determination of the total concentration of manganese in the glass and the relative concentration of divalent and trivalent manganese.

Annealed glass samples were cut, ground, and polished to approximately 0.05 inch thickness. The optical spectra over the range 350-650 mμ were obtained using a Bausch and Lomb Model 503 spectrophotometer. Spectra from 650-1000 mμ were obtained using Hitachi Perkin-Elmer spectrophotometer. Both instruments were recording and dual beam.

The spectra were then resolved into their component Gaussian bands, and these bands were identified by comparison with published results of Mn^{2+} in calcium phosphate glass (64) and Mn^{3+} in alkali borate glasses (65). Although a quantitative determination of the Mn^{2+} concentration was not possible because the extinction coefficients of the absorption bands were not known, the $^4E(G)$, $^4A_1$ absorption band was used to make a qualitative determination as follows: Assuming that Bier's law is valid, the absorbance A is equal to the product of the sample thickness, t, the ion concentration, c, and the extinction coefficient for the band, e. It was assumed that the product ce = A/t would be a smoothly varying function of the nominal melt composition if the concentration of divalent manganese was the same in both the glass and the melt charge. If substantial deviations from smooth behavior were observed, the approximate divalent manganese concentration in these glasses could be determined by comparison with the A/t vs. nominal composition curve for the "well behaved" glasses.

The relative concentration of Mn^{2+} and Mn^{3+} in each glass was determined by measuring the absorbance of the resolved $^4E(G)$, A_1 band of divalent manganese and the $^5T_2(G)$ band of trivalent manganese. The extinction coefficients of divalent and trivalent manganese in identical soda-borate glasses can be found in the works of Bingham and Parke (64) and Paul (65). Assuming that the relative extinction coefficient, e(III)/e(II), in soda borate glass is approximately the same as the relative extinction coefficient in the present glass, the approximate relative ion concentration can be determined from

$$\frac{c(III)}{c(II)} = \frac{A(III)}{A(II)} \cdot \frac{e(II)}{e(III)} .$$

Magnetic Property Studies

Electron Spin Resonance Measurements. Electron Spin Resonance (ESR) studies were made on the glasses using a laboratory spectrometer consisting of a Varian VA217H klystron with a Hewlett Packard 718B klystron power supply, a PAR HR-8 lock-in amplifier tuned to 100 KHz., and a modified Triconix model KSLP integral plus proportional 70 KHZ.

A.F.C. system. A Varian V4531 rectangular cavity with 100 KHz. modulation operating in the TE_{102} mode was used. The d.c. magnetic field was supplied by a Varian nine-inch magnet, and the magnetic field strength was determined by means of an Alpha Scientific Laboratories proton resonance Gaussmeter. The frequency output of the Gaussmeter was electronically divided by 100 and fed into a Beckman 6020A preseteput counter so that a direct reading of the magnetic field at proton resonance was obtained. The klystron frequency was measured with a Systron-Donner 1017 hetrodyne frequency counter, which permitted actual counting of the microwave frequency. Variations in experiment temperature were obtained using a Varian V4540 variable temperature controller and a hydrogen Cryotip.

In order to study the relative intensity of the ESR resonance as a function of experiment temperature, a small quantity of diphenylpicrylhydrazil (DPPH) was introduced into the sample tube with the powdered glass sample. By dividing the intensity of the glass resonance by the intensity of the DPPH resonance, it was possible to factor out the temperature dependence of the sensitivity of the spectrometer. The ESR line intensity relative to a paramagnetic standard was thus obtained.

Magnetic Susceptibility Measurements. Static magnetic susceptibility measurements were performed over the temperature range 77 to 600°K using conventional Faraday techniques. A Cahn electrobalance was employed to measure the weight of the sample in and out of the magnetic field. The magnetic field factor, $2H\frac{dH}{dz}$, was determined by measurement of two samples of known susceptibility, Cr_2O_3

($x = 25.5 \times 10^{-4}$cgs) and Hg[Co(SCN)$_4$] ($x = 16.44 \times 10^{-4}$ cgs). The agreement between the two standards was very good.

Variations in experiment temperature between 300 and 600°K were obtained by surrounding the sample with a heating coil. Temperatures between 200 and 300°K were obtained by passing dry nitrogen gas through a heat exchanger containing liquid nitrogen and then passing a constant mass flow of this gas across the sample. Temperatures between 80 and 200°K were obtained by surrounding the sample with a dewar of liquid nitrogen. Magnetization and susceptibility measurements were made in the temperature range of 1.9 to 77°K by cooling the sample with liquid helium and using a vibration coil magnetometer.

CHAPTER III

EXPERIMENTAL RESULTS

Preliminary Studies

Preliminary studies of various physical properties of the manganese phosphate glass system were undertaken so that the various physical parameters which might affect the magnetic behavior could be characterized. These studies included X-ray analysis, electron microscopy, dilatometry and optical absorption studies.

One result of these preliminary studies is that the glasses of the manganese phosphate system are microstructurally homogeneous. No evidence of crystallinity was detected by X-ray analysis in any of the as-cast glasses, except for the previously mentioned surface crystallinity in the 55-45 mole % $MnO-P_2O_5$ glass. No evidence of liquid-liquid phase separation was found in any of the as-cast glasses although a 55-45 glass which had been heat treated for one hour at 300°C showed a droplet morphology, as shown in Figure 1. However, samples heat treated at higher temperatures showed no evidence of phase separation.

The results of the dilatometric studies are summarized in Table I. It can be seen that the softening ranges of the 30-70, 40-60, and 50-50 glasses are identical, whereas the softening range of the 55-45 glass is slightly higher. The linear expansion coefficients of all the glasses identical and equal to 0.005 %/°C.

The optical absorption studies have established that the glasses

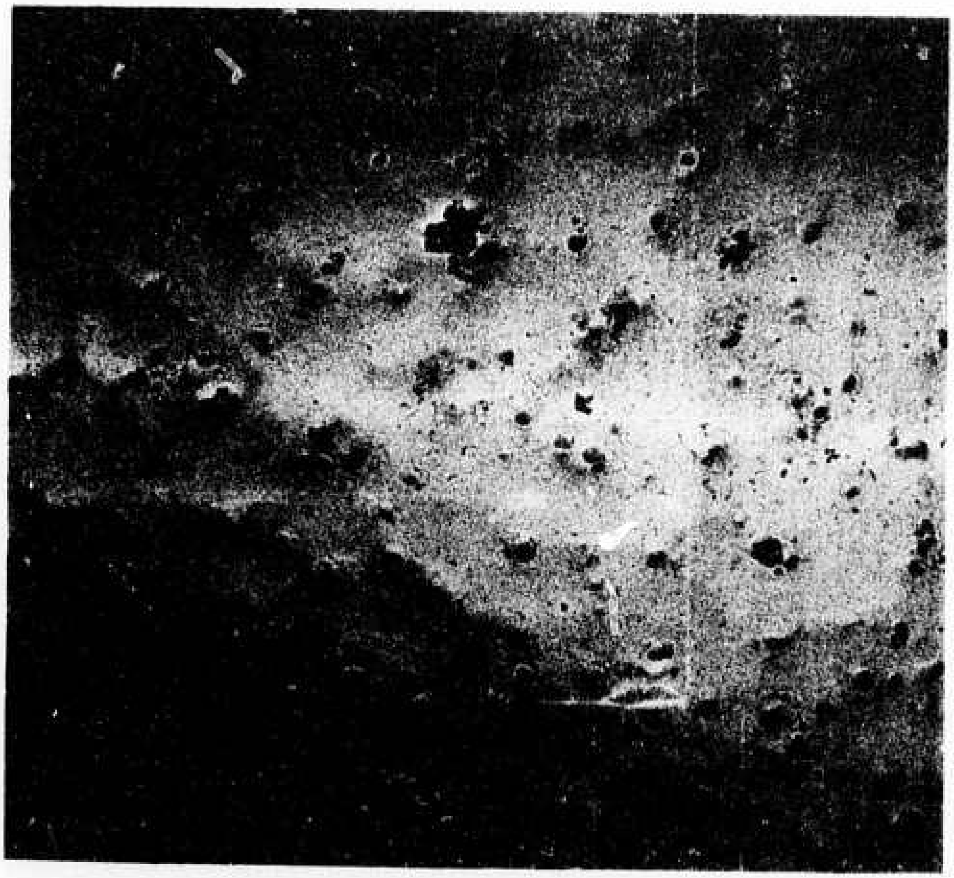


FIGURE 1. Electron Micrograph of a 55-45 Mole % MnO-P_2O_5 Glass Heat Treated for One Hour at 300°C. Magnification is 40,000.

TABLE I

Softening Ranges of the Manganese Phosphate Glass System

Composition	Softening Range (°C)
30-70	475-490
40-60	475-490
50-50	475-490
55-45	495-510

contain predominately divalent manganese in spite of the fact that they were prepared from MnO_2 -- an oxide of Mn^{4+}. This is not surprising since MnO_2 decomposes into MnO and oxygen at 535°C. In addition, these studies have established that the composition of the glasses is identical with that of the melt charge.

A typical optical absorption spectrum is shown in Figure 2 together with the resolved Gaussian bands, and a summary of the resolved spectra appears in Table II. The manganese phosphate glasses have a purple color, which is due to the presence of the trivalent ion (64, 65). However, the absorption by the trivalent ion is much more intense than that of the divalent ion because the latter arises from forbidden transitions. The strongest absorption by the trivalent ion arises from the $^5E(G) \rightarrow {}^5T_2(G)$ transition, which is spin-allowed. Whereas the extinction coefficient of the $^5T_2(G)$ band of trivalent manganese in 29-71 mole % Na_2O-B_2O_3 glass is 425 $(\text{mole-cm})^{-1}$, the extinction coefficient of the $^4E(G)$, $^4A_1$ peak of divalent manganese in an analogous 20-80 soda-borate glass is only 0.24 $(\text{mole-cm})^{-1}$ -- a ratio of 1,770 to 1. Thus, it is apparent from the optical absorption spectra of the 50-50 manganese phosphate glass shown in Figure 2 that although there is definitely some trivalent manganese in the glass, the concentration is very small. In fact, since the peak heights of absorptions due to divalent $[^4E(G), {}^4A_1]$ and trivalent $[^5T_2(G)]$ manganese are approximately the same, the concentration ratio of divalent to trivalent manganese is on the order of 1500 to 1. Such a small concentration of trivalent manganese could still give the glasses a purplish color.

The very large divalent to trivalent ion ratio has a pronounced

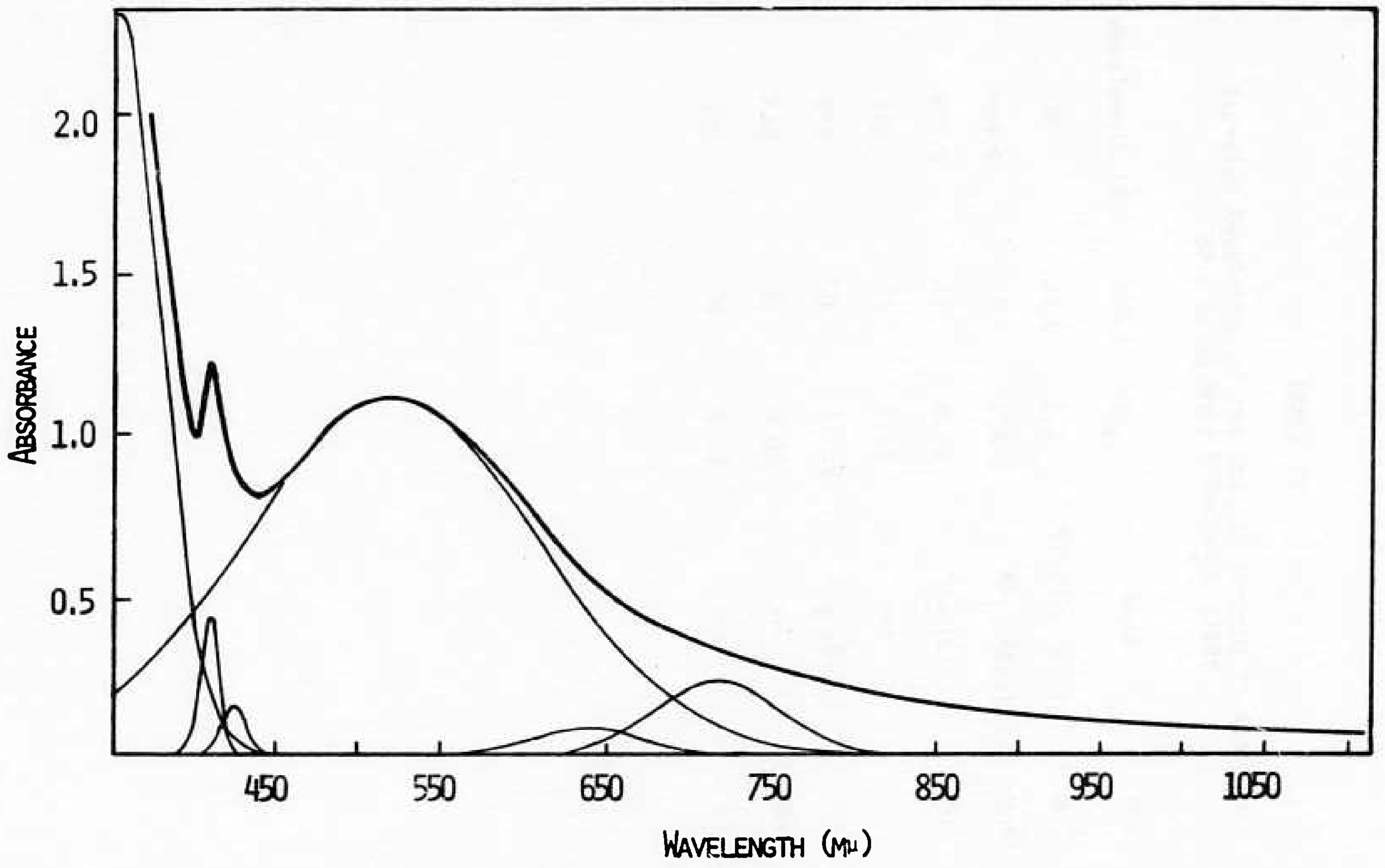


FIGURE 2. Optical Absorption Spectrum of a 50-50 Mole % $MnO-P_2O_5$ Glass (Heavy Line) and its Gaussian Resolution (Light Lines).

TABLE II

Gaussian Resolution of the Optical Absorption Spectrum of a 50-50 Mole % MnO-P_2O_5 Glass

Wavelength (Mμ)	Δ(Mμ)	y_{max}	Band	Ion
350	38.5	2.3	$^4T_2(D)$, $^4E(D)$	Mn^{2+}
409.5	8	0.445	$^4A_1$, $^4E(G)$	Mn^{2+}
423.5	11	0.16	$^4T_2$ (G)	Mn^{2+}
445	15	0.25	---	---
519	128	1.109	$^5T_2$ (G)	Mn^{3+}
640	45	0.09	---	Mn^{3+}
718	56	0.23	---	---

effect on electrical conductivity of manganese phosphate glasses. Friebele et al. (63) determined that the d.c. electrical conductivity of a 55-45 MnO_2-P_2O_5 glass was less than 7 x 10^{-15} (ohm-cm)$^{-1}$ at room temperature. Sayer and Mansingh (66), who studied a 50-50 mole % Mn_3O_4-P_2O_5 glass, were unable to observe any conductivity at room temperature. They determined the conductivity to be 10^{-14} (ohm-cm)$^{-1}$ at 400°K, and the activation energy of polaronic conduction to be 1.24 eV. It thus may be concluded that although there is a finite concentration of trivalent manganese in manganese phosphate glasses, the concentration is very small.

Because the concentration of trivalent manganese in the glass is negligible, the absorbance of the $^4E(G)$, $^4A_1$ peak of divalent manganese can be used as an indication of total manganese in the glass. A plot of the absorbance of the $^4E(G)$, $^4A_1$ peak divided by sample thickness as a function of the composition of the melt charge appears in Figure 3. It can be seen from the plot that the absorbance divided by the thickness is a smoothly varying function of manganese concentration. Thus, it may be concluded that the compositions of the manganese phosphate glasses are identical with that of the melt charges.

Magnetic Susceptibility Measurements

In order to study the bulk magnetic properties of the manganese phosphate glass system, magnetic susceptibility measurements were made. As shown in Figure 4, the high temperature inverse susceptibility of all glasses obeyed a Curie-Weiss law with a negative temperature axis intercept. A plot of the antiferromagnetic Curie temperature and Curie

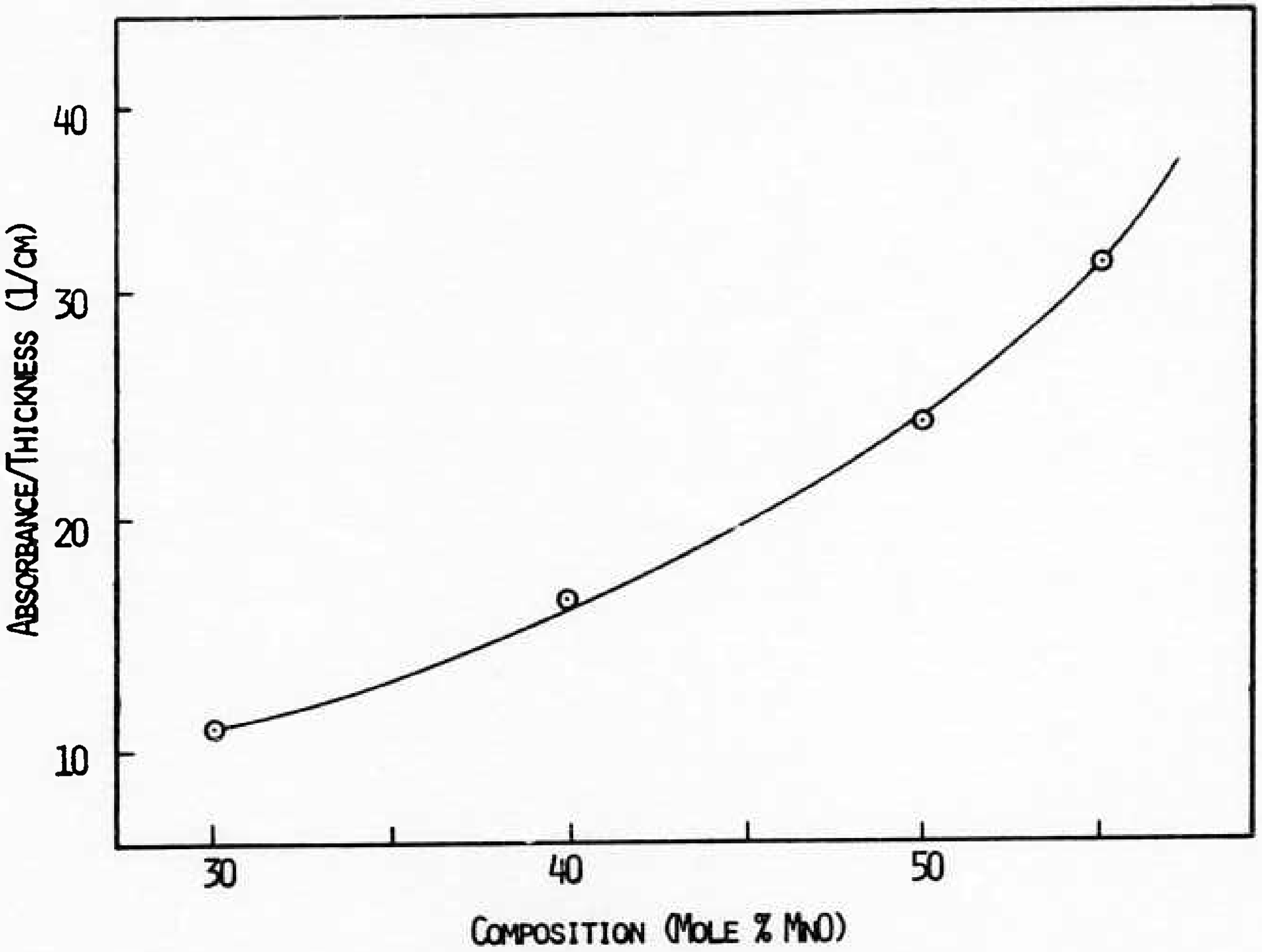


FIGURE 3. Absorbance/Thickness vs. Composition of Manganese Phosphate Glasses.

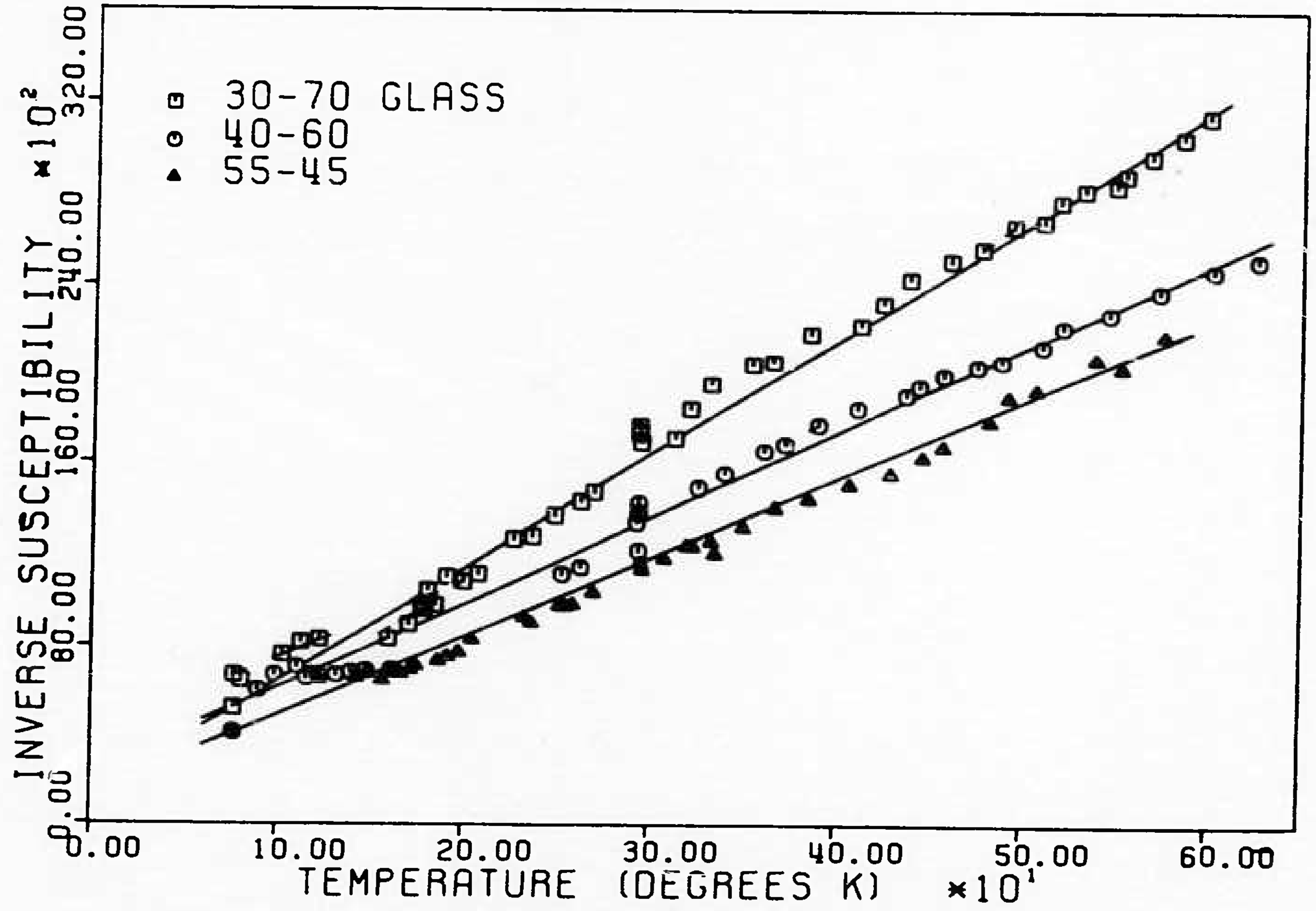


FIGURE 4. Inverse Susceptibility vs. Temperature of Manganese Phosphate Glasses.

constant as a function of composition is shown in Figure 5. The magnitude of the Curie temperature and the Curie constant increases as the manganese concentration is increased up to 50 mole % MnO, but then both decrease and approach the values of Θ and C of manganese pyrophosphate, as determined by Fowlis and Stager (67). It is interesting to note that in spite of the fact that MnO has a Néel temperature of 120°K, no transition is observed in the inverse susceptibility plots of any of the glasses down to 77°K. Table III contains a summary of the effective magnetic moment, the effective field coefficients, and the exchange integral of the manganese ions in the glass. The effective moment decreases as the manganese content is increased. The exchange integral increases up to 50 mole % MnO_2, and then decreases in the 55-45 glass and in manganese pyrophosphate.

An inverse susceptibility vs. temperature plot for the 50-50 glass from 1.9 to 600°K is shown in Figure 6. It is apparent that there is a downward curvature at low temperature. The inverse susceptibility in the low temperature region is plotted in Figure 7, and the downward curvature is shown more clearly. The deviation from linear behavior occurs at about 13°K, and the inverse susceptibility approaches the origin at absolute zero.

A study of the magnetization of the 50-50 glass as a function of magnetic field was carried out in order to determine if the saturation which is characteristic of superparamagnetism existed. As seen in Figure 8, no saturation occured in measurements at 1.9 or 4.83°K. up to 21,000 Gauss.

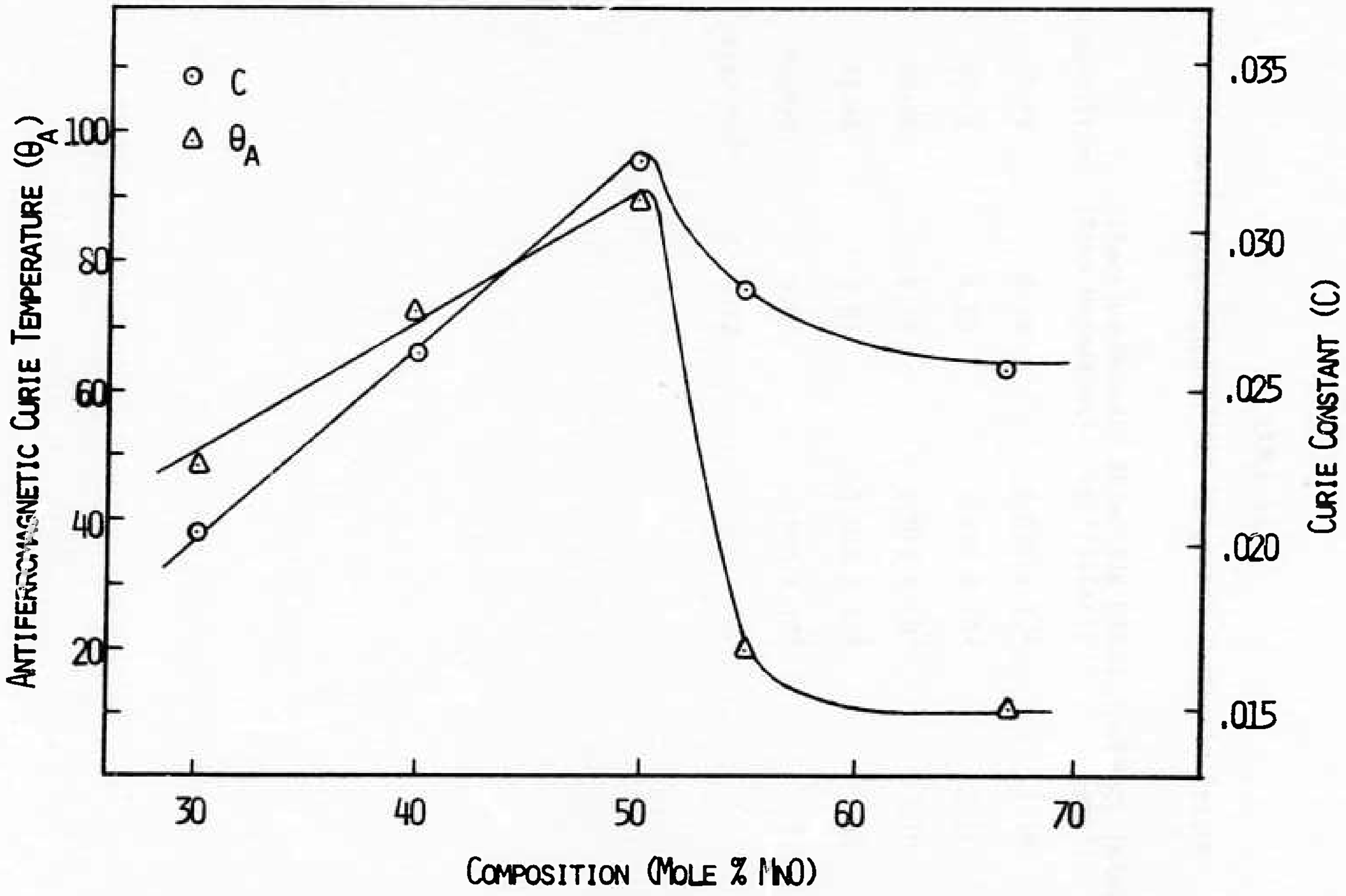


FIGURE 5. Antiferromagnetic Curie Temperature and Curie Constant vs. Composition for Manganese Phosphate Glasses and $Mn_2P_2O_7$ (Plotted at 67 Mole % MnO).

TABLE III

Magnetic Properties of the Manganese Phosphate System

Composition	Effective Monent (Bohr Magnetons)	Effective Field Coefficients	Exchange Integral (cm^{-1})
30-70	4.99	2.829×10^3	1.58
40-60	4.65	2.807×10^3	2.27
50-50	4.40	2.812×10^3	3.10
55-45	3.85	1.087×10^3	1.40
$Mn_2P_2O_7$	5.90	$.506 \times 10^3$	1.41
Free Mn^{2+}	5.92		

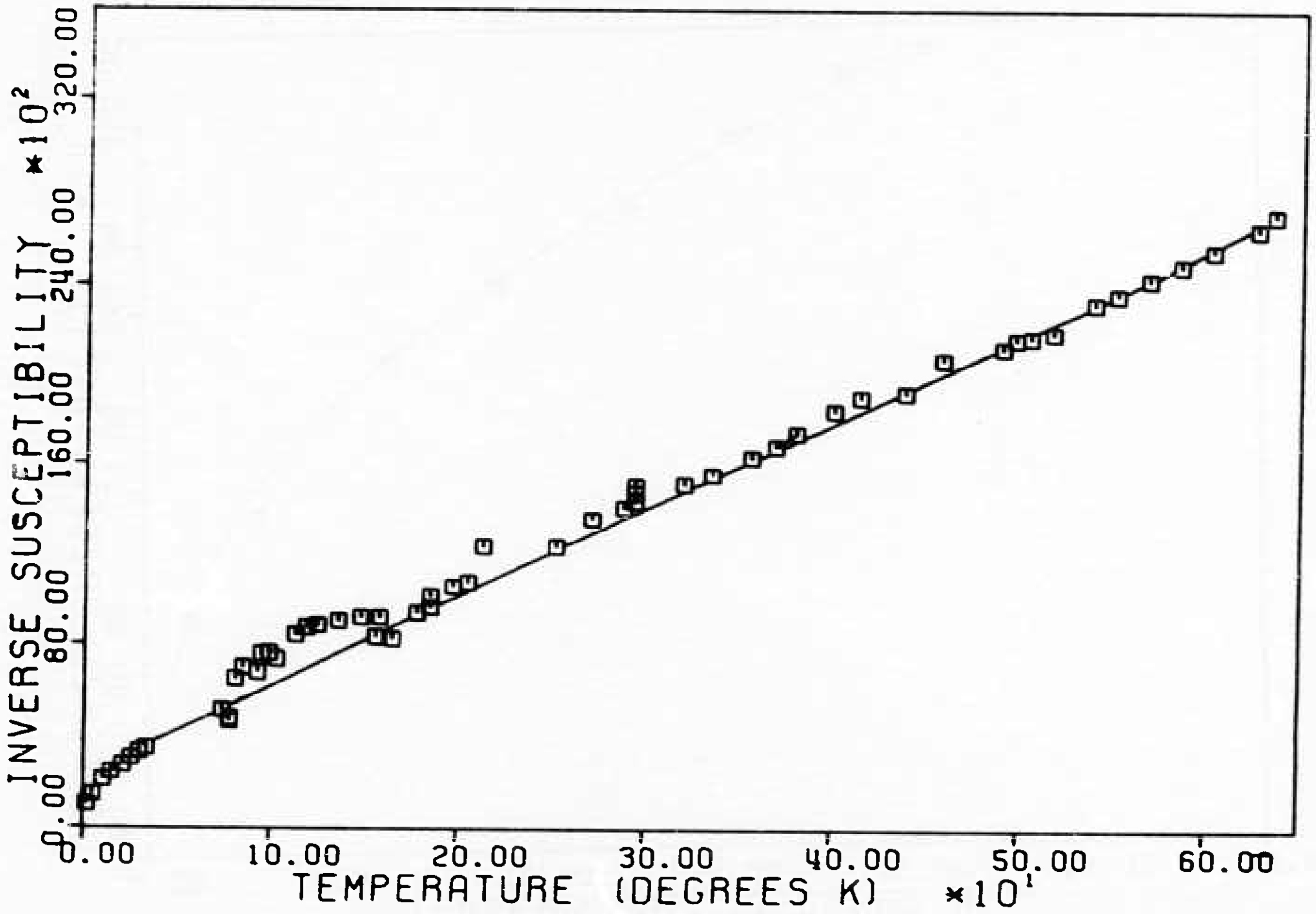


FIGURE 6. Inverse Susceptibility vs. Temperature of a 50-50 Mole % MnO-P_2O_5 Glass.

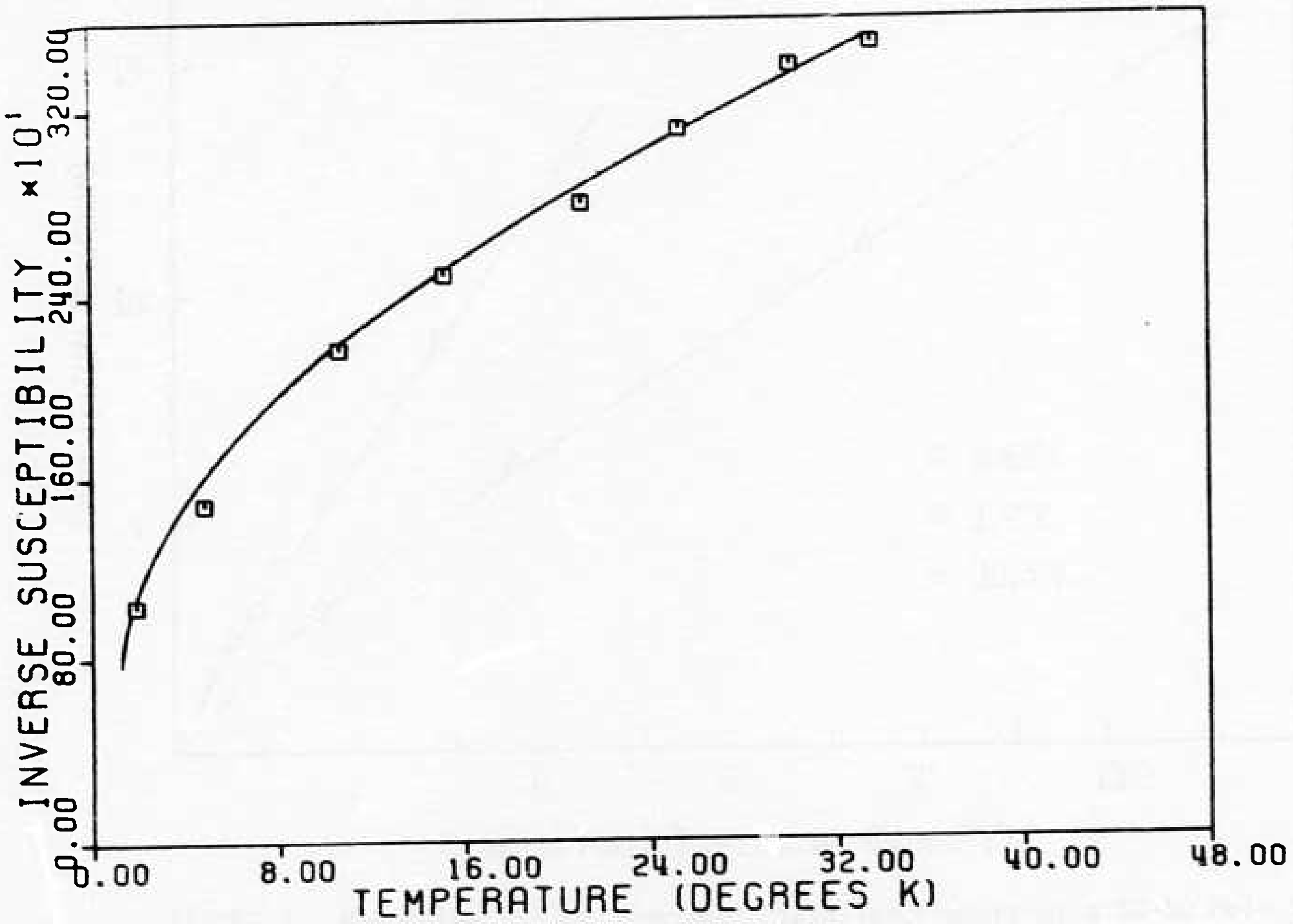


FIGURE 7. Inverse Susceptibility vs. Temperature for a 50-50 Mole % MnO-P_2O_5 Glass.

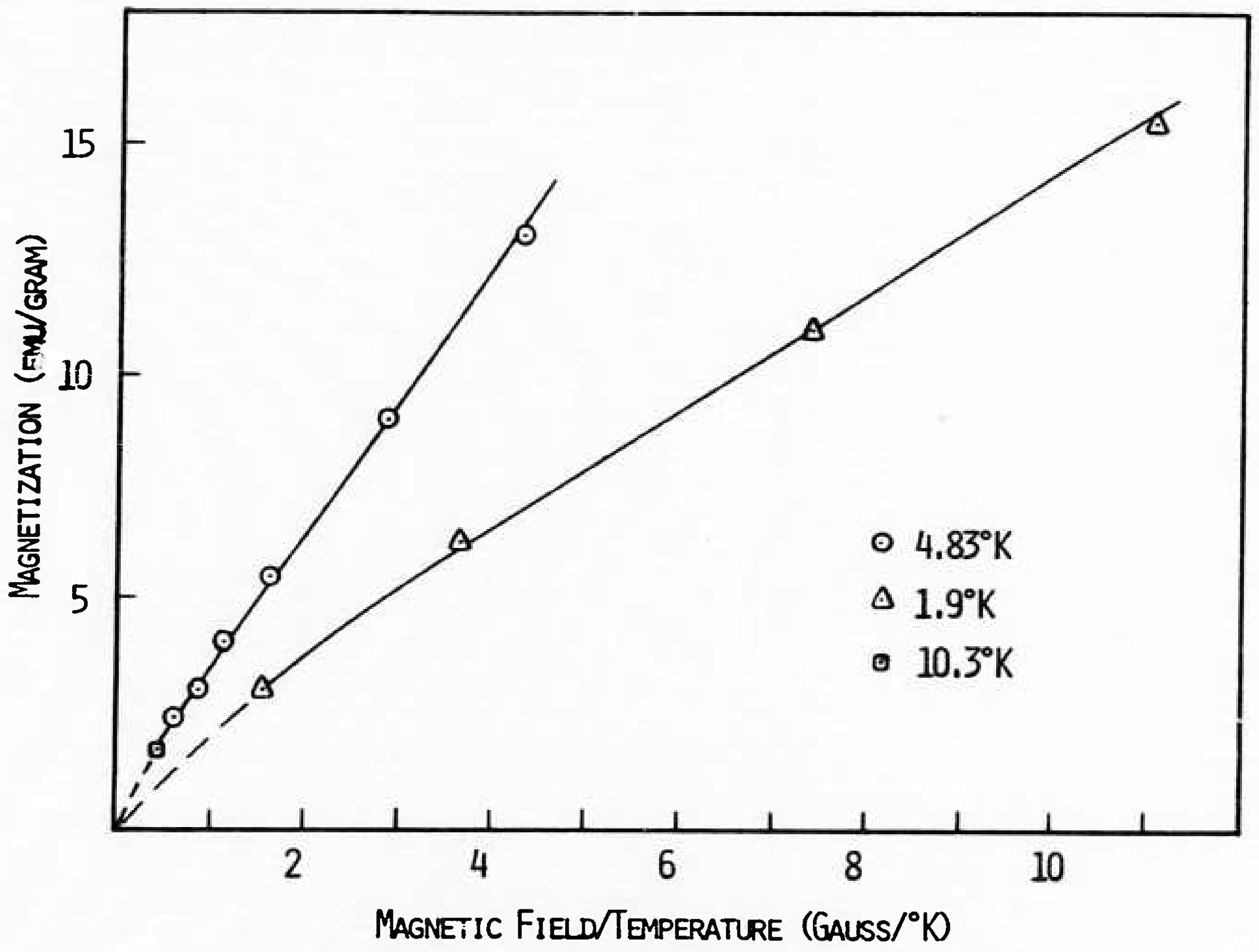


FIGURE 8. Magnetization vs. Magnetic Field/Temperature of a 50-50 Mole % $MnO-P_2O_5$ Glass.

ESR Measurements

The ESR spectra of all glasses studied consisted of a slightly asymmetric singlet centered at g' = 1.96 ± 0.01, as shown in Figure 9. It can be seen that the linewidth of the resonance in the glasses decreases as the manganese concentration increases. In spite of the fact that crystal field resonances of isoelectronic Fe^{3+} have been observed in 55-45 $FeO-P_2O_5$ glass (7), no crystal field resonances were observed in the spectra of any of the glasses, or of $Mn_2P_2O_7$.

Attempts were made to numerically integrate the spectra of the glass samples and of a calibrated pitch sample in order to determine the spin density in the glass. However, as may be seen in Table IV, the results obtained were an order of magnitude or more greater than the concentration of manganese in the melt charge. This will be discussed in a later chapter, but it is important to note that the ratio of apparent spin concentration for the 30-70, 40-60 and 50-50 glasses is identical to the ratio of the manganese concentration in these glasses.

It may also be seen in Table IV that the g' values of the resonances of all glasses are very nearly identical and decrease slightly as the manganese concentration is increased. The linewidths of the resonances decrease sharply as the manganese concentration in the glasses is decreased due to increased exchange narrowing effects.

Variable temperature ESR studies were carried out in order to further investigate the temperature dependence of the magnetic properties of the glass system. Representative ESR spectra of the 50-50 glass at

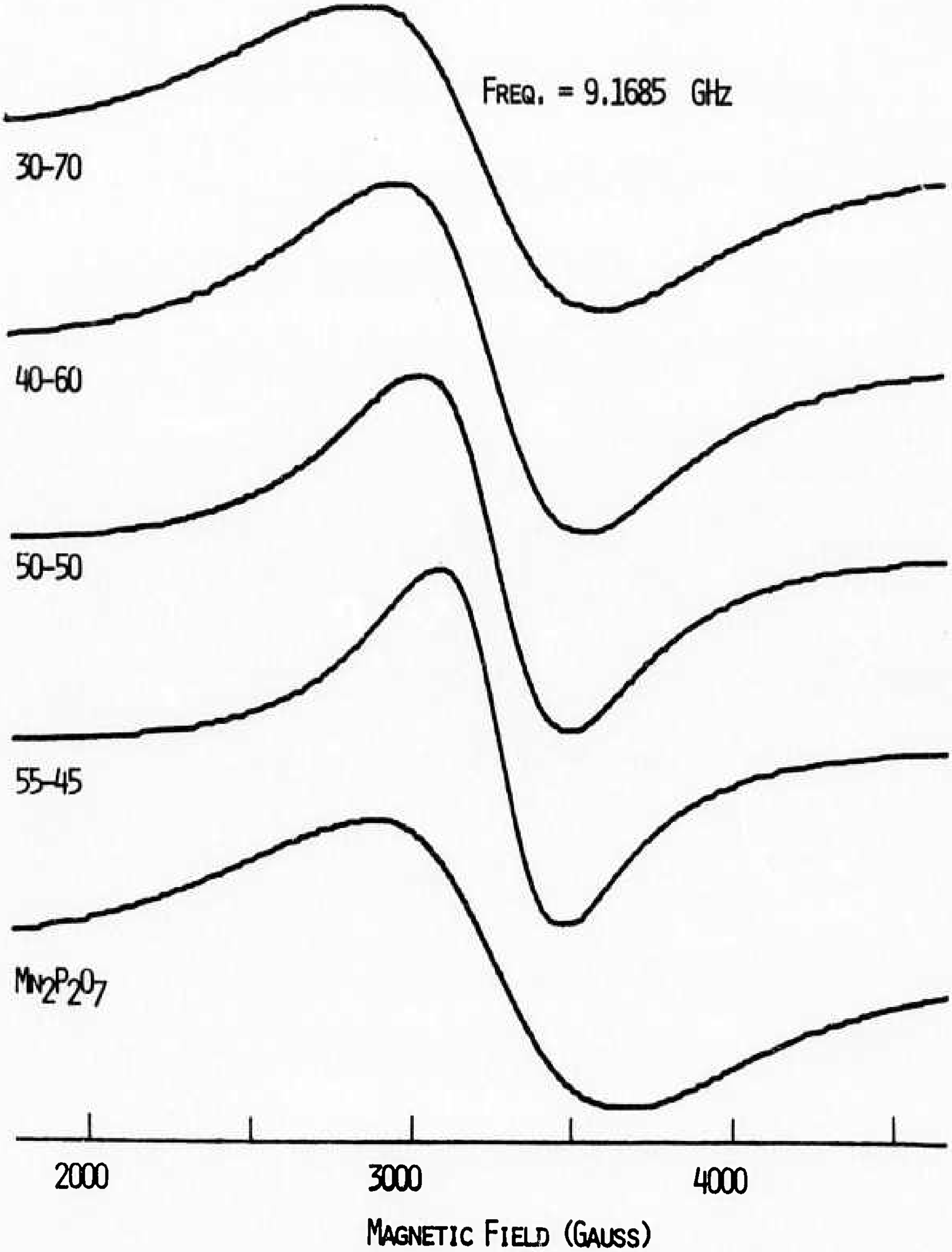


FIGURE 9. Electron Spin Resonance Spectra of Manganese Phosphate Glasses and Manganese Pyrophosphate, T = 300°K.

TABLE IV

Results of ESR Studies of the Manganese Phosphate Glass System

Composition	ΔH(Gauss)	g'	Apparent Spin Concentration	Ratio	Manganese Concentration	Ratio
30-70	720	1.977	6.32×10^{18}	1	1.44×10^{18}	1
40-60	573	1.972	8.78×10^{18}	1.39	2.00×10^{18}	1.38
50-50	453	1.958	12.20×10^{18}	1.93	2.63×10^{18}	1.83
55-45	387	1.958	20.5×10^{18}	3.24	2.96×10^{18}	1.86
$Mn_2P_2O_7$	793	1.974	$113. \times 10^{18}$	17.87	3.82×10^{18}	2.65

+100 and -180°C are shown in Figure 10. It is apparent that the intensity and linewidth of the resonance increase as the temperature decreases, but there is no significant change in the g' value of the resonance. In order to determine whether or not the intensity increases more rapidly than the paramagnetic Boltzmann factor, exp(-hν/kT), the intensity of the glass resonance line was divided by the intensity of a paramagnetic standard, DPPH. These results appear in Figure 11. It is apparent that the temperature dependence of the relative intensity of all glasses is quite similar. At low temperatures, the intensity increases more rapidly than the paramagnetic Boltzmann factor; this will be discussed in more detail in the following chapter. The relative intensity of manganese pyrophosphate resonance increases much more rapidly than that of the glasses as the temperature is decreased.

Figure 12 is a plot of the linewidth of ESR resonances of the glass and crystal as a function of temperature. It is seen that the linewidth of the glass resonances increases as the temperature is decreased, where whereas the linewidth of the $Mn_2P_2O_7$ resonance is essentially constant. The temperature dependence of the linewidths of all glass resonances is similar.

Figure 13 is a plot of the normalized intensity of the 50-50 glass resonance over the temperature range of 21-300°K. It is apparent that the relative intensity increases as the temperature decreases but that there is a change in the intensity-temperature behavior near 120°K. A linewidth vs. temperature plot for this glass is shown in Figure 14. The linewidth increases linearly as the temperature decreases, but the corresponding change in the linewidth-temperature behavior occurs near 40°K.

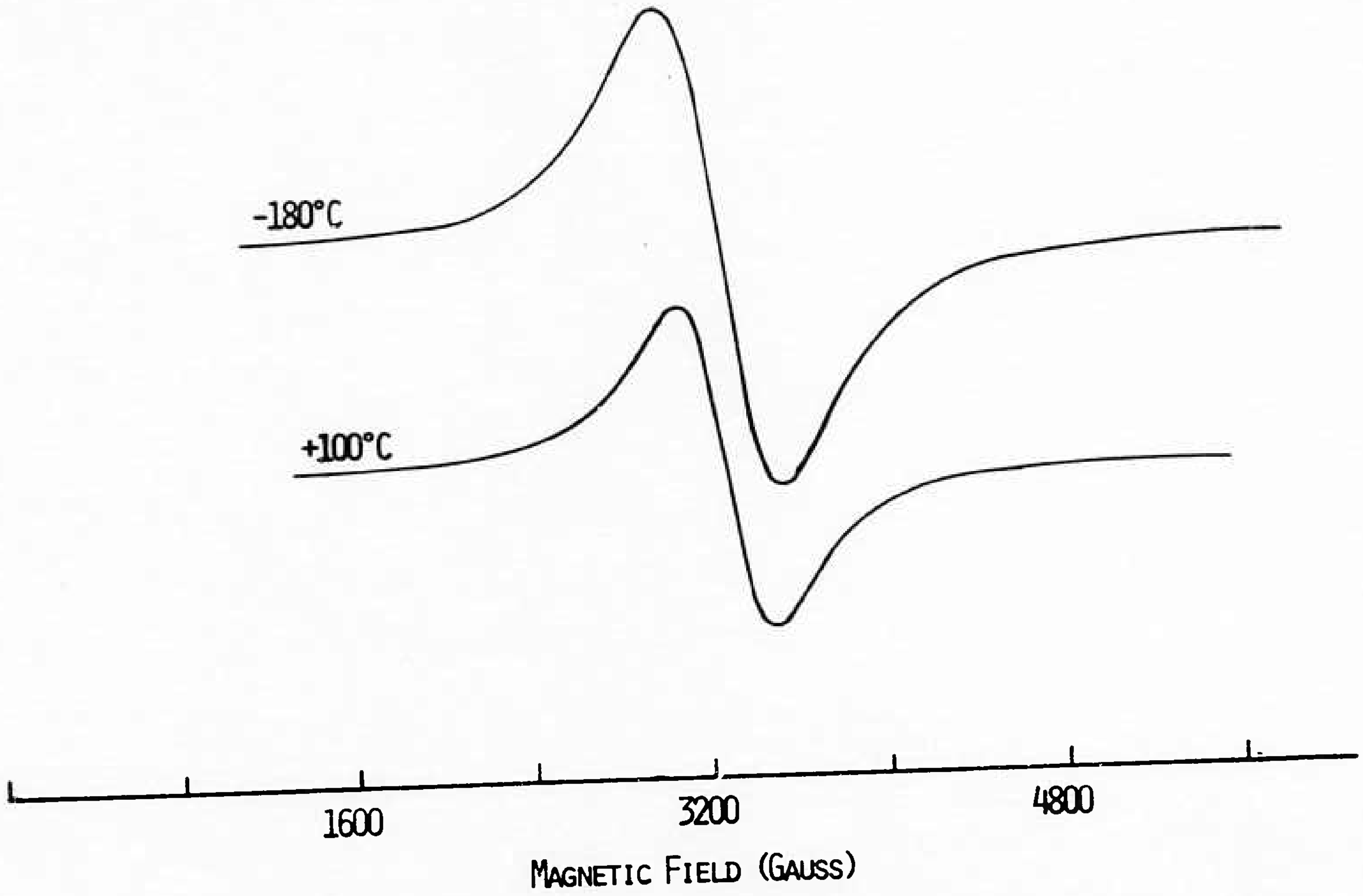


FIGURE 10. Electron Spin Resonance Spectra of a 50-50 Mole % MnO- P_2O_5 Glass at -180 and +100°C.

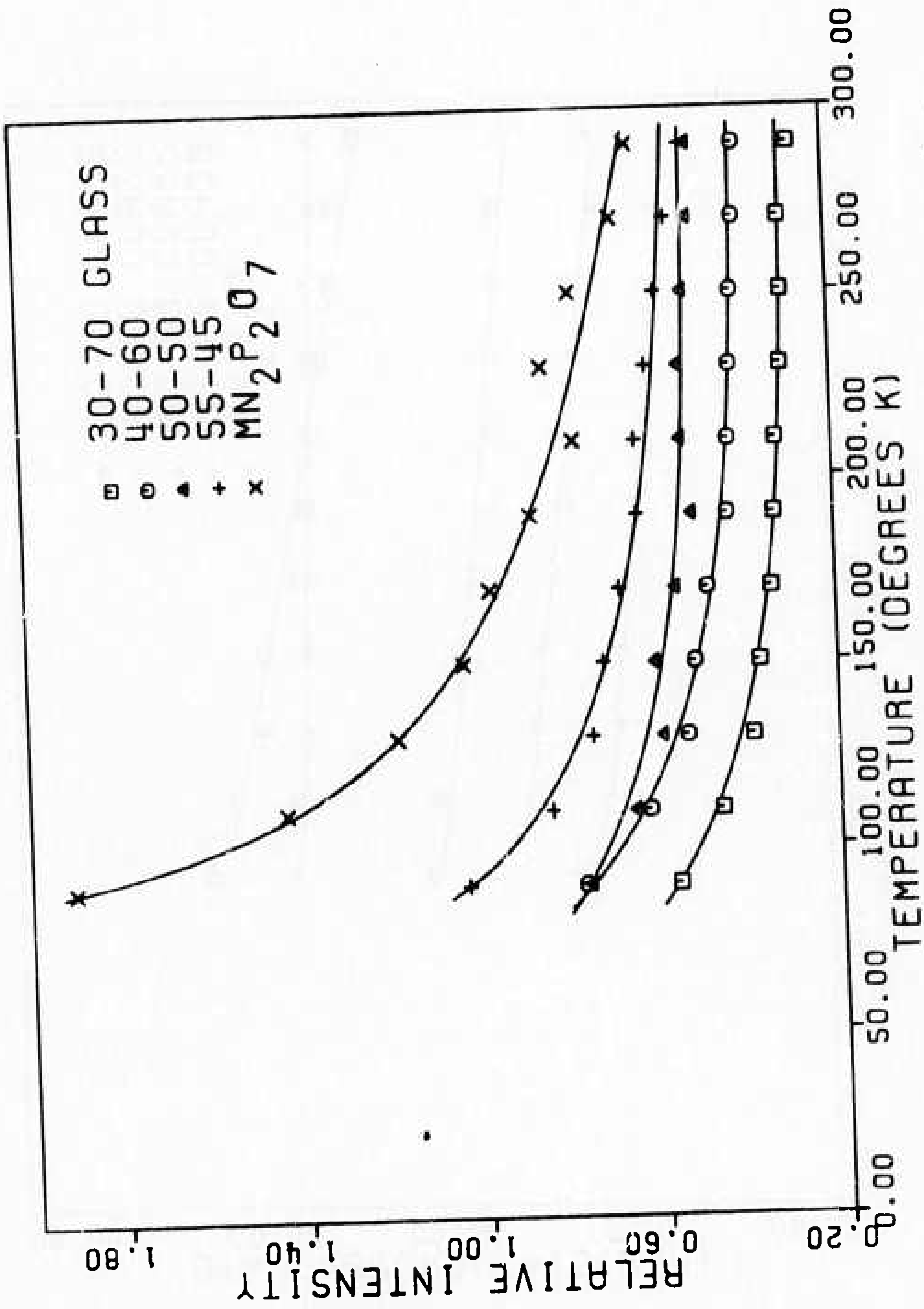


FIGURE 11. Relative ESR Intensity vs. Temperature of Manganese Phosphate Glasses and Manganese Pyrophosphate.

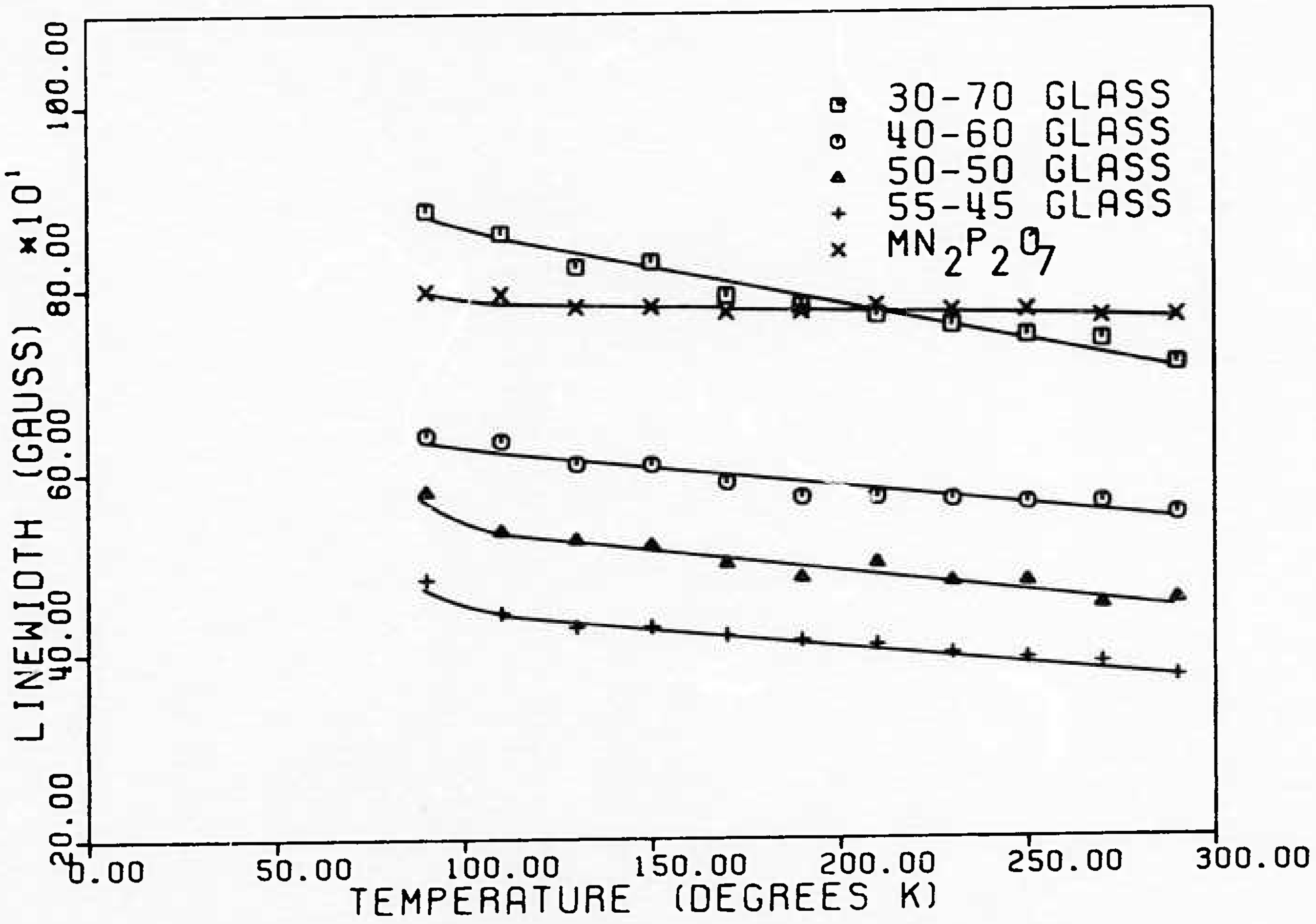


FIGURE 12: ESR Linewidths vs. Temperature of Manganese Phosphate Glasses and Manganese Pyrophosphate.

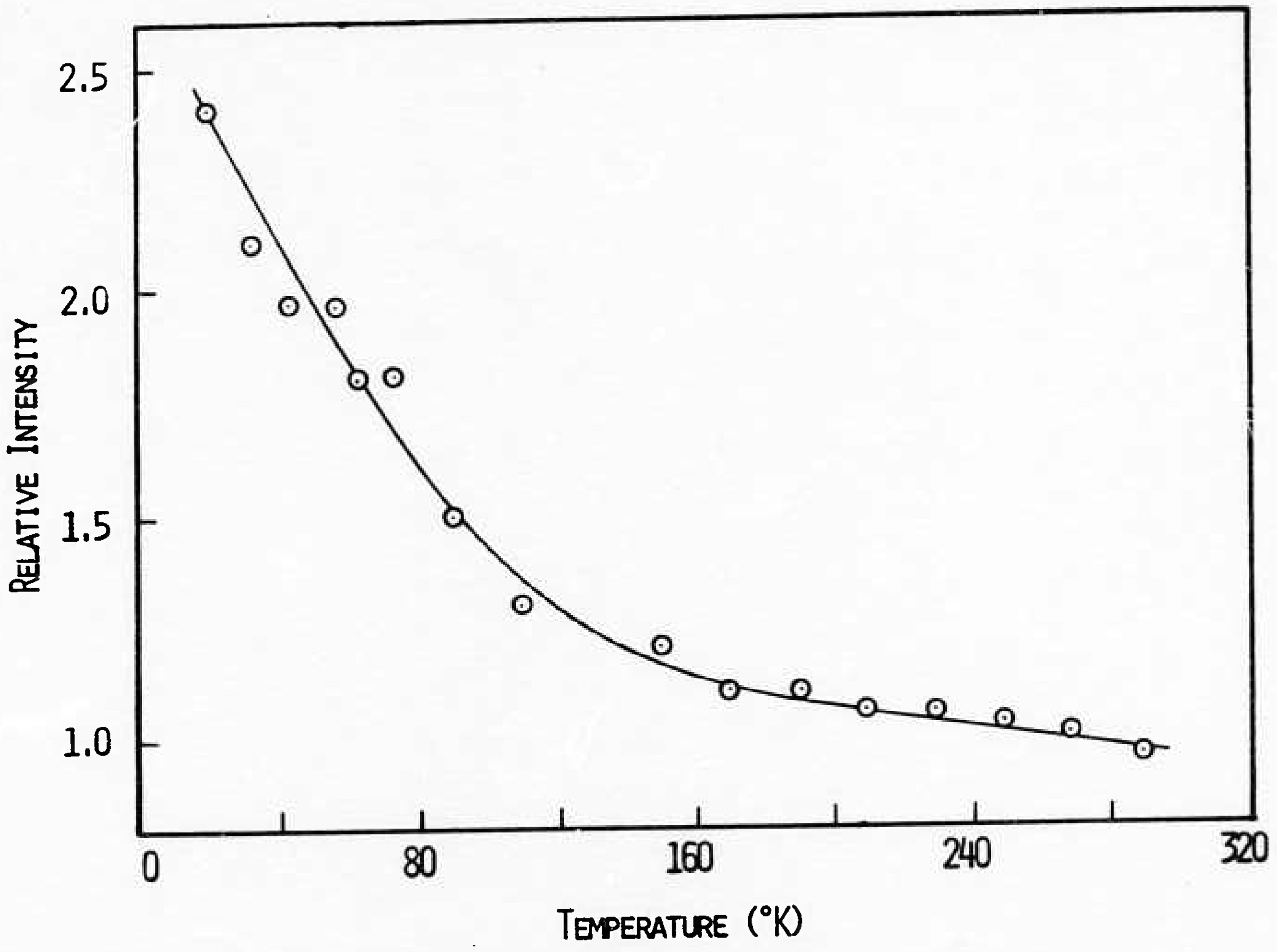


FIGURE 13. Relative ESR Intensity vs. Temperature of a 50-50 Mole % MnO-P_2O_5 Glass.

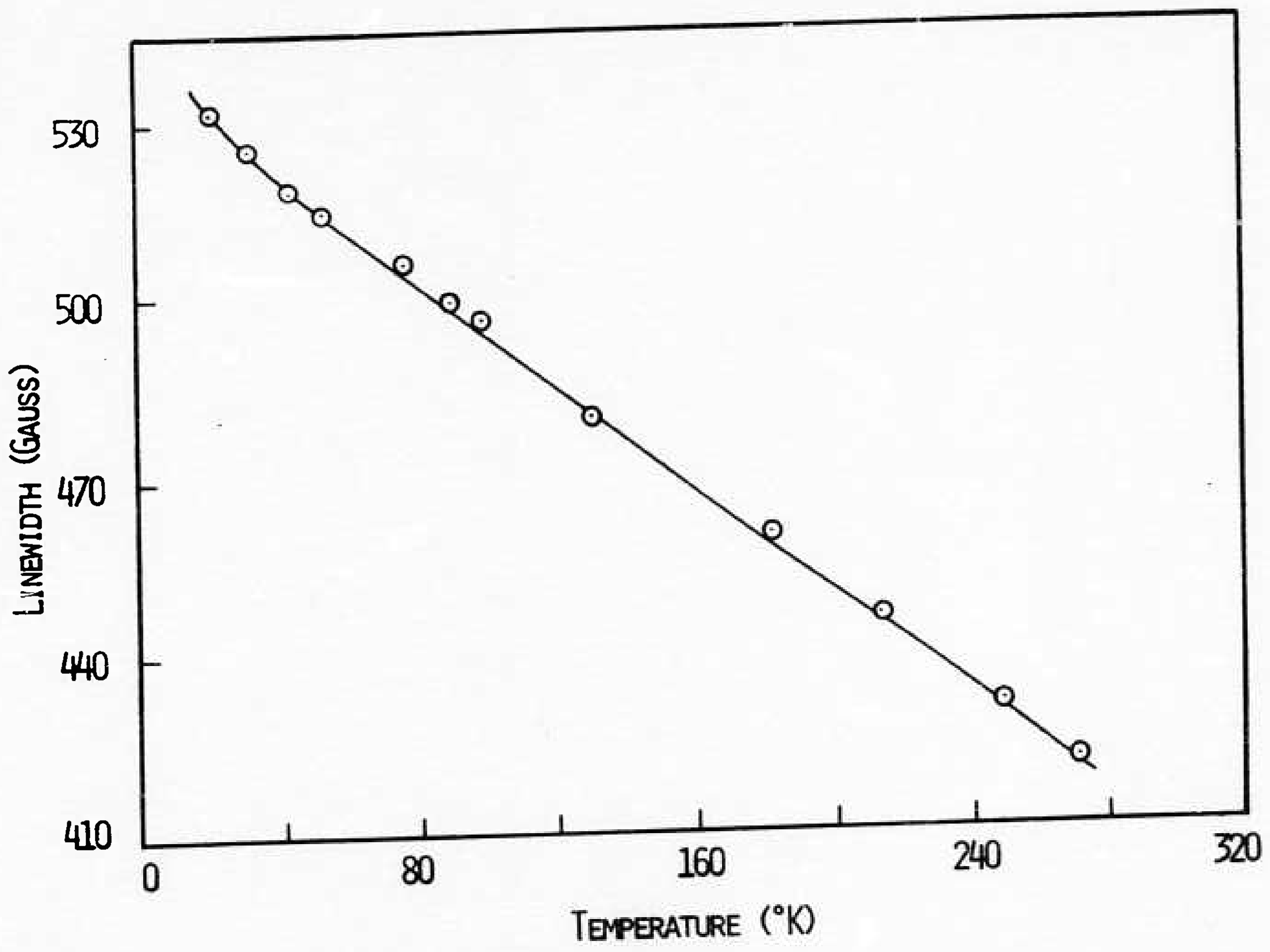


FIGURE 14. ESR Linewidth vs. Temperature of a 50-50 Mole % $MnO-P_2O_5$ Glass.

CHAPTER IV

DISCUSSION

As previously stated, the purpose of this research program is to chaterize the magnetic properties of manganese phosphate glass and offer a theoretical explanation for the observed low temperature susceptibility behavior. Preliminary property studies have established that the manganese phosphate glass system is ideal for this research because many of the physical parameters affecting magnetic behavior are constant. In particular, the fact that the glasses are microstructurally homogeneous as determined from X-ray and electron microscopy studies, and the fact that the glasses contain primarily one valence state of manganese as shown from the optical absorption studies mean that the interpretation of the magnetic data is relatively straightforward. The observed magnetic behavior can thus be the result of exchange coupled manganese ions and/or isolated, paramagnetic ions in a homogeneous glass.

Characterization of Magnetic Behavior

Compositional Effects. The magnetic properties of the manganese phosphate glass system are primarily the result of antiferromagnetically exchange coupled divalent manganese ions in the glassy matrix. Since the report by Gubanov (48) of the theoretical possibility of cooperative magnetic phenomena in non-crystalline materials, many workers have observed magnetic behavior in glassy systems arising from antiferromagnetically exchange coupled metal ions (see references in Chapter I). Although the strength and nature of the exchange interaction has varied from system to system, the magnetic behavior of all heavily doped transition metal glass systems studied to date has been the result of predominately antiferromagnetically coupled ions. It is not surprising, therefore, that all of the magnetic studies conducted during the present research program also show the existence of either antiferromagnetically coupled or isolated divalent manganese ions in the glass.

As shown in Figure 4 the inverse susceptibility of all glasses of the manganese phosphate system obeys a straight line relationship to temperature in the high temperature region (above the Néel temperature). Since the projected inverse susceptibility of all glasses intercepts the temperature axis in the negative temperature region, the data has been fit to the antiferromagnetic Curie-Weiss relationship

$$\chi = \frac{C}{T - \Theta_a} \qquad (4.1)$$

by least squares fitting techniques. These results are shown in Figure 5.

The strength of the exchange interaction is a direct function of the distance between interacting ions and decreases rapidly as the distance between the ions increases. As the metal cations are added to the glass structure, they fill octahedral holes created by the nesting of the phosphate tetrahedra. The cationic separation of two ions in neighboring octahedral sites is fixed by the local structure of the glass and will vary in a distribution about a central value. In a glass containing few metal ions randomly distributed through the matrix, the average metal ion separation will be large, and the average exchange energy will be small. As the concentration of the ions increases, there is a higher probability that the ions will fill adjacent holes in the matrix, and assuming the internal structure of the glass does not change, the average cationic separation decreases. The average exchange energy thus increases. One result of this increased exchange interaction is increased exchange narrowing of the ESR line. This behavior, which is observed in the manganese phosphate system, as seen in Table IV, is further evidence that the manganese in the glasses exists primarily in one valence state. Van Vleck (51) has shown that exchange coupling between ions of the same valence state results in exchange narrowing, but exchange coupling between ions of different valence states results in exchange broadening. In the case of the iron phosphate glass system, exchange coupling between Fe^{3+} and Fe^{2+} results in ESR linewidths on the order of 10,000 Gauss (7). Another result of increasing the exchange interaction is to increase the magnetic susceptibility of the glass. This behavior is observed in Figure 4, where it is seen that the inverse susceptibility at a given temperature decreases as the concentration of manganese in the glass increases. Of course, any change in site symmetry of the magnetic ion or change in the internal structure of the glass would cause a corresponding change in the cation separation and the strength of the exchange interaction. This effect will be discussed in more detail at a later time.

Increasing the exchange interaction also lowers the antiferromagnetic Curie temperature, Θ_a. As more of the magnetic ions experience stronger exchange fields, it becomes more difficult for the thermal energy of the system to keep the ion pairs from aligning antiferromagnetically, thus the Néel temperature, the temperature at which the magnetization of an ion is opposite that of its neighbors, is increased.

Likewise, the antiferromagnetic Curie temperature, the imaginary temperature at which the susceptibility of the ions would go to infinity if the ions did not align themselves antiferromagnetically but remained paramagnetic, decreases. This behavior is observed in Figure 5. The antiferromagnetic Curie temperature of the 30-70, 40-60, and 50-50 glasses decreases as the concentration of manganese is increased. The anomalous behavior of the 55-45 glass and manganese pyrophosphate (plotted in Figure 5 at the 66 mole % MnO composition) is a result of structural changes in the glass that will be discussed later.

It may also be seen in Figure 5 that the Curie constant, C, increases as the concentration of manganese and the average exchange interaction increase in the 30 to 50 mole % manganese range. Once again, the anomalous behavior in the 55-45 glass and manganese pyrophosphate is a structural effect. It is interesting to note that both the Curie constant and the antiferromagnetic Curie temperature obey similar straight line relationships as functions of composition in the 30 to 50 mole % range. This similarity in relationship is to be expected, however, because

$$\Theta_a = C\gamma = \frac{2ZJS(S+1)}{3k} \qquad (4.2)$$

where Z is the coordination number of the manganese, J is the exchange integral, S is the spin and k is the Boltzmann constant. Gamma (γ) is the molecular field constant

$$\gamma = \frac{2ZJ}{Ng^2\beta^2} . \tag{4.3}$$

where β is the Bohr magneton and g is the gyromagnetic ratio, and N is the density of magnetic ions. As can be seen in Table III, the gyromagnetic ratio of the glasses in the 30 to 50 mole % MnO range is essentially constant. This implies that as the density of magnetic ions in the glass is increased, the average exchange energy increases in direct proportion. Furthermore, the structure of the glasses in this concentration range is constant since g is constant, as determined from the ESR data shown in Table IV. Optical absorption studies have established that divalent managnese occupies octahedral sites in phosphate glass (64); thus Z = 6. Using the values of g' obtained from ESR studies of these glasses as the values of g in equation 4.3, the density of the glass determined by the Archimedes method, and the mass concentration of manganese the value of the exchange integral can be calculated. Furthermore, the effective magnetic moment can be calculated from

$$\mu_{eff}^2 = \frac{3kC}{N\beta^2} . \tag{4.4}$$

The decrease in magnetic moment observed in Table III as the concentration of manganese in the glass increases is direct evidence of the antiferromagnetic coupling between ions. As the concentration increases, the average exchange integral increases, and more of the ions become less free to behave paramagnetically and independently of each other. The ions tend to align antiferromagnetically, and thus, the effective magnetic moment decreases from the free spin value of 5.92.

An interesting comparison can be made between the antiferromagnetic Curie temperature obtained in the present work and from the work of Schinkel and Rathenau (50). As can be seen in Figure 15, the values of Θ obtained in the present study of manganese in a phosphate glass are identical to the values obtained from their work on manganese in a potassium-borate glass. Furthermore, the functional dependence of Θ upon the composition in both cases is identical. These results are not unexpected, since manganese occupies octahedral sites in both glass systems (64). The slight deviation from $g' = 2.000$ in g' values of the ESR spectra of the present study indicates that the site symmetry of the manganese ion in the phosphate glasses is slightly lower than that in the potassium-borate glasses ($g' = 2.000$ in these glasses). There is a difference between the ionic radius of pentavalent phosphorous (0.34 Å) and trivalent boron (0.20 Å) but neither this difference nor the slightly lower symmetry creates a significant difference in the data from the two glass systems. Schinkel and Rathenau have interpreted their data on the basis of a molecular orbital model which assumes high short range order. The manganese ions were assumed to be randomly distributed over octahedral sites created by oxygen atoms arranged in cubic close packed lattice. The close agreement between the results of the two studies indicates that similar model is valid in

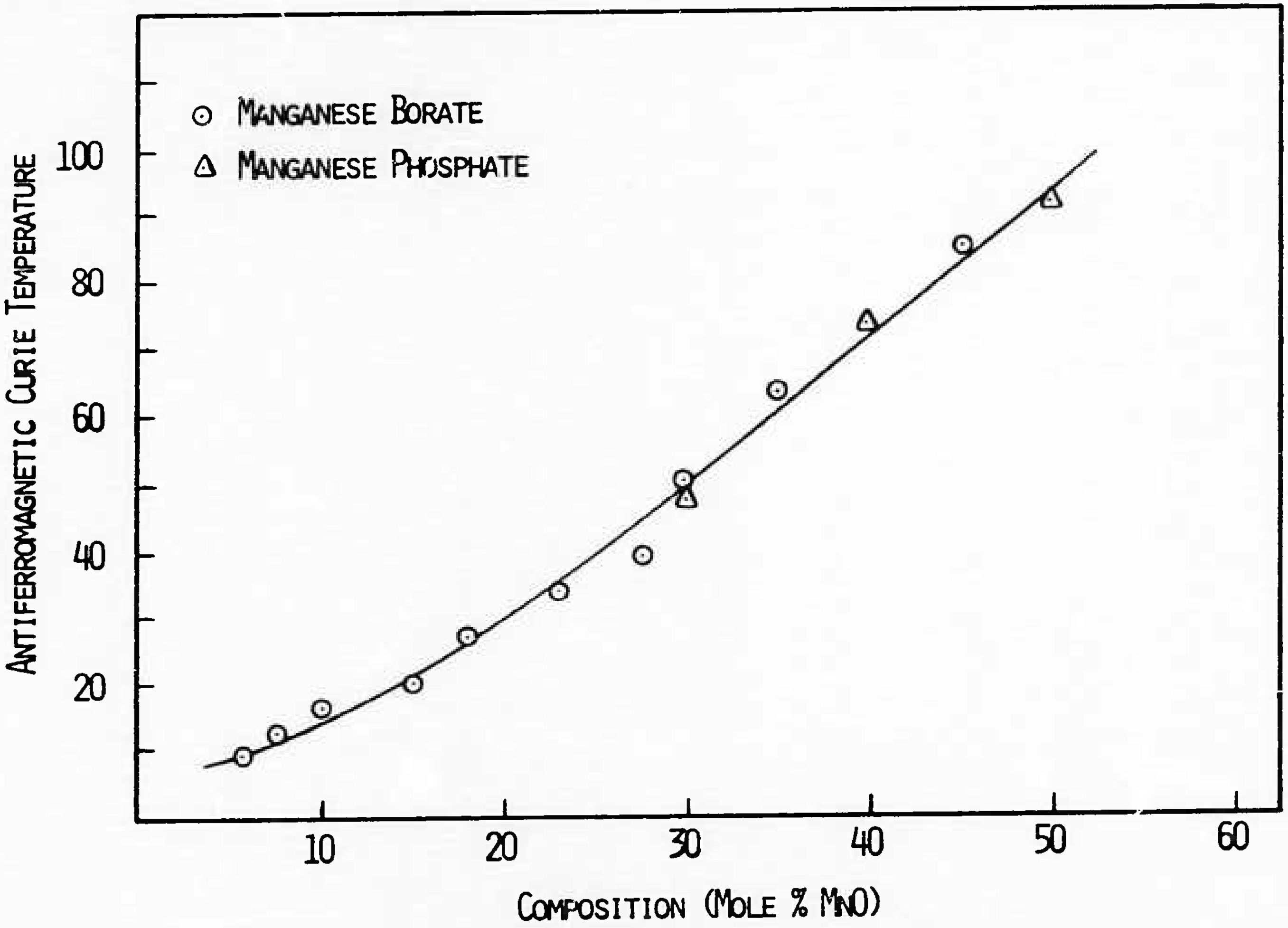


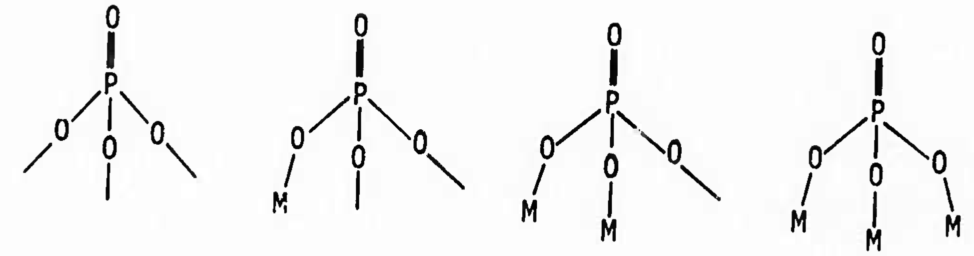
FIGURE 15. Antiferromagnetic Curie Temperature vs. Composition for Manganese Phosphate Glasses and Manganese Borate Glasses [After Schinkel and Rathenau (50)].

the manganese phosphate system. A high degree of short range order exists in the phosphate glass, and the manganese ions are distributed over highly symmetrical octahedral sites created by the oxygen matrix. Since the glass structure is constant in the 30 to 50 mole % MnO composition range, the strength of the average exchange interaction and resulting magnetic behavior are functions only of the concentration of manganese ions distributed in the glassy matrix.

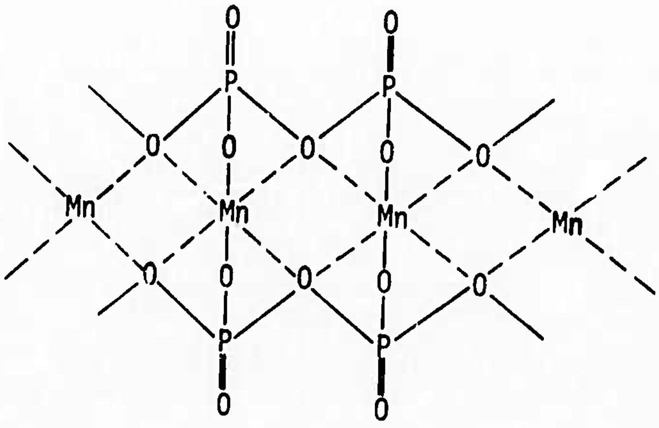
When the concentration of MnO is increased above 50 mole %, there are marked changes in the magnetic and physical properties of the glass. Both the Curie constant and the Curie temperature decrease drastically in the 50 to 55 mole % MnO range, as can be seen in Figure 5. The exchange integral decreases by a factor of two and the effective magnetic moment decreases sharply, as shown in Table III. In addition, the molecular field constant which had been constant in the 30 to 50 mole % composition range, decreases by almost a factor of three. As seen in Table IV there is a marked change in the apparent spin concentration data determined from measurements at this point. Whereas in the 30 to 50 composition range, the apparent spin concentration followed the ratio of manganese in the glass, there is a drastic increase in the apparent spin concentration of the 55-45 glass and in manganese pyrophosphate.

It is apparent that once the concentration of MnO in the glass exceeds 50 mole %, some type of structural change takes place in the glass matrix. The remarkable changes in the magnetic behavior cannot be simply the result of an increase of 5 mole % manganese. Further evidence of the structural change may be found in the dilatometric data in Table I. Whereas the glasses in the 30 to 50 composition range all soften between 475 and 490°C, the 55-45 glass softens at a slightly higher temperature range, 495 to 510°C.

Changes in internal glass structure as a function of composition have been discussed by Van Wazer (68). The pure P_2O_5 glass consists solely of the branching structures shown in Figure 16a. As a monovalent metal, M is added to the glass, middle or meta structures form (figure 16b). Then, as more metal is added, end or pyro structures, and ortho structures compose the glass (Figures 16c, d). For a glass of a given composition, the structures present depend upon the metal to phosphorous ratio and the equilibria that exist between the different types of structures. For monovalent metals in an ideal glass, $R = M_2O/P_2O_5 = 0$ corresponds to 100% branching structures, R = 1 to 100% middle, R = 2 to 100% end, and R = 3 to 100% ortho structures. For intermediate values of R, e.g. $1 < R < 2$, both middle and end structures will be present. In the case of divalent metals, the above limiting values of R must be divided by two. The result is that when $MO/P_2O_5 = 0.5$, the limit of middle structures has been reached. This is the case of the 50-50 glass, and the structural units which compose it are shown in Figure 16e. Because this is the limit of the middle structures, these are the only types of structural units that can exist in an ideal 50-50 glass. Of course, some of the P_2O_5 in the original melt may have bonded to water, and throughout the real glass matrix, there is a possibility of small numbers of other structural units. However, in the ideal 50-50 glass, only the structural units shown in Figure 16e are possible.



a. Branching b. Meta c. Pyro d. Ortho



e. Manganese Phosphate Glass Structure

FIGURE 16. Structural Units of Phosphate Glasses: a. Branching, b. Metaphosphate, c. Pyrophosphate, d. Orthophosphate, e. 50-50 Mole % $MnO-P_2O_5$ Glass.

When additional manganese is added to the glass matrix of the 50-50 glass, some type of structural rearrangement is necessary. All of the phosphorous in the glass is already used up in creating the manganese metaphosphate structural units, so the additional manganese forces part of the glass into the pyrophosphate structure, which is a stable crystalline structure. For this reason, the magnetic properties of the 55-45 glass, which is composed of randomly oriented, interconnected manganese metaphosphate units with interspersed manganese pyrophosphate clusters, are similar to those of $Mn_2P_2O_7$. The fact that surface crystallinity was observed only on glasses with $MnO/P_2O_5 > 0.5$ and the fact that liquid-liquid phase separation occurred only in the 55-45 glass is further evidence that the limit of stable metaphosphate glass formation if in the 50-50 composition.

The liquid-liquid separation of the heat treated 55-45 glass is an indication that the limit of miscibility of MnO and P_2O_5 in a glass is less than 55 mole % MnO. Levin and Block (69) have derived an expression for the limit of miscibility (N_x) of a glass former and a glass modifier based on the cation separation (s), the density of the limiting composition, (p), and the molecular weights of the glass former (G), and the glass modifier (M):

$$N_x = \frac{100G}{.602ps^3n + G-M} \qquad (4.6)$$

where n = 1 for a divalent metal and n = 2 for a monovalent metal. Substituting appropriate values, and assuming that the cation separation results from two manganese ions in contact with an intermediate oxygen ion, a value of $N_x = 62.75$ is obtained. However, if one assumes that the oxygen ions in the glass structural unit shown in Figure 16e constrain the manganese ions so that they are not in contact with the intermediate oxygen, the limiting composition is decreased. In fact, an 11% increase in the cationic separation, which is entirely plausible, is sufficient to decrease the limit of miscible glass formation to 50 mole % MnO.

The manganese pyrophosphate clusters which form in the glass matrix when Mn/P > 0.5 are not large enough to be detected by X-ray techniques. However, they are numerous enough to have a pronounced effect on the magnetic properties of the 55-45 glass. All magnetic properties of the system with the exception of ESR linewidth and effective magnetic moment change in the direction of the corresponding magnetic properties of manganese pyrophosphate as the concentration of manganese is increased from 50 to 55 mole %. The fact that the magnetic behavior of the 55-45 glass is so similar to that of manganese pyrophosphate is further evidence that the clusters in the glass are truly composed of $Mn_2P_2O_7$ unit cells.

Jacobs and Bean have reviewed the discussion by Néel of the theoretical magnetic properties of a material containing small antiferromagnetic clusters (70). Because the anisotropy energy of the cluster is comparable to the thermal energy, the direction of the antiferromagnetic axis of the cluster is no longer fixed with respect to an external field. The small cluster will possess a permanent magnetic moment resulting from imperfect compensation of the moments on the surface, and the strength of this moment would vary inversely as the size of the cluster. In very fine particles when the antiferromagnetism is mobile, the particle attains a paramagnetic behavior, a phenomena which Néel termed "superparamagnetism." The superparamagnetic contribution to the total susceptibility may exceed the antiferromagnetic contribution by an order of magnitude at low temperatures.

Another phenomena occurs when the size of the clusters is somewhat larger. There are fewer imperfections of the type that give rise to superparamagnetism, but there is a magnetostatic couple between the applied magnetic field and the surface ferromagnetic layer planes of the antiferromagnetic structure. This couple produces a rotation of the direction of surface antiferromagnetism towards the field, and hence the susceptibility of the particle is enhanced by a factor 20 below the Néel temperature of the particle. This effect has been termed "superantiferromagnetism."

Depending upon the size of the antiferromagnetic clusters in the 55-45 glass, either superparamagnetic or superantiferromagnetic behavior could result. Since the cluster size is below the detection limit of X-ray analysis and since no low temperature susceptibility or magnetization data is available, it is necessary to investigate the anomalously large apparent spin concentrations measured by ESR to obtain a clue to which phenomenon exists in the glass.

The intensity of an ESR absorption is a function of the number of atoms in a material whose electrons are undergoing a transition from the ground state to a spin state of higher energy. The eigenvalues of the spin Hamiltonian of the ESR experiment are functions of the angle the magnetic axis of an ion makes with the applied d.c. magnetic field.

In a powder sample of a crystal or in an amorphous material, the ions in the material are randomly oriented with respect to the applied magnetic field, and so many simultaneous transitions within the total sample are possible. In addition, if the spin state of the magnetic ion is greater than 1/2, such as Mn^{2+} with $S = 5/2$, multiple transitions within each of the spin manifolds are also simultaneously possible.

Below the Néel temperature, the spins of the manganese ions are coupled to form an $S = 5$ system. However, above this temperature thermal agitation disrupts the antiferromagnetic coupling, and there is a resultant moment for each pair of ions. The total of these resultant moments is greater than $S = 1/2$. Since the apparent spin concentration of the glasses and crystal of the manganese phosphate system was measured by comparing the intensity of the Mn^{2+} ion absorption with the intensity of a calibrated pitch sample with $S = 1/2$, the apparent spin concentration is much higher than the actual spin concentration. The fact that the ratio of apparent spin concentration in the glasses is identical with the ratio of divalent manganese concentration in the 30 to 50 mole % composition range is evidence that the multiple transitions in the spin manifolds of the manganese ion in the glass give rise to a constant error in the observed ESR intensity.

The anomalously large apparent spin concentrations observed in the 55-45 glass and in manganese pyrophosphate have their origin in the magnetic structure of $Mn_2P_2O_7$. As determined in the neutron diffraction studies by Collins et al. (71), the magnetic structure consists of sheets of manganese ions lying in the a - c plane of the unit cell. The ions in each sheet are aligned ferromagnetically and the moments of each sheet are aligned antiferromagnetically with those in neighboring sheets. The occluded antiferromagnetic clusters of manganese pyrophosphate in the 55-45 glass contain a large amount of surface area, and hence some of the ferromagnetic layer planes would lie on the surface. The resulting large moments would enhance the susceptibility and account for the large spin concentration measured for the 55-45 glass.

Likewise, in the polycrystalline sample of manganese pyrophosphate used for ESR measurements, there is a large amount of surface area. Furthermore, the crystal was grown by remelting and slowly cooling the crystalline material taken from a 60-40 melt. No X-ray study was made to determine if a single crystal resulted, and in all probability, there are extensive crystalline defects in the powder used for the ESR measurements. Both the surface area and the defects would result in uncompensated moments which would give rise to an anomalously large intensity.

It is apparent that the explanation of the large apparent spin concentration measured in the 55-45 glass and manganese pyrophosphate is a description of superantiferromagnetism. Both the uncompensated moments arising from both the exposed ferromagnetic layer planes and the crystalline defects produce superantiferromagnetic behavior, and this behavior in turn would enhance the susceptibility and the apparent spin concentration. However, before the definite existence of superantiferromagnetism can be established, it would be necessary to study the magnetization at very low temperatures. Certainly the evidence for superantiferromagnetism is present, but more data is necessary before an unequivocal statement can be made.

Temperature Effects. A characterization of the temperature dependence of the magnetic properties of the manganese phosphate glass system is essential to a complete understanding of its magnetic behavior. For this reason, variable temperature ESR, magnetic susceptibility, and magnetization studies were undertaken.

The results of the variable temperature magnetic susceptibility studies in the high temperature region shown in Figures 4 and 6 have been discussed in the preceeding section. It was concluded that since the inverse susceptibility of all glasses and of manganese pyrophosphate obeyed a Curie Weiss law with a negative temperature axis intercept, the Mn^{2+} ions in the glass and crystal experience negative exchange fields. These fields cause antiferromagnetic coupling between the ions, and give rise to the observed susceptibility behavior.

The temperature dependence of the ESR linewidth and normalized intensity shown in Figures 11 and 12 support the conclusion that the manganese ions are antiferromagnetically coupled.

Previous investigations of antiferromagnetically coupled chromium ions in chromium phosphate glass have been made by Landry et al. (4, 5) and Fournier et al. (6). In these works the temperature dependence of the normalized ESR intensity of the Cr^{3+} -Cr^{3+} pair spectrum obtained below the Néel temperature was used to determine the value of the exchange integral in the pair Hamiltonian

$$H_{pair} = J\, \bar{S}_1 \cdot \bar{S}_2 \ . \qquad (4.7)$$

Below the Néel temperature the spins of the Cr^{3+} ions ($S = 3/2$) combine to form a total spin of $S = 3$, which gives rise to spin manifolds of $S = 0, 1, 2, 3$ by application of the Landé interval rule. The separation between the manifolds was assumed to be greater than the microwave quantum of energy so that in an ESR experiment, transitions were induced only between M_S levels in the same manifold.

A similar situation exists in the manganese phosphate system. The Mn^{2+} ions, which in the paramagnetic state have $S = 5/2$, combine in the coupled state to give rise to a total spin of $S = 5$. The resulting spin manifolds of $S = 0, 1, 2, 3, 4$, and 5 are shown in Figure 17. As derived for the chromium phosphate system, the normal intensity relative to a paramagnetic standard of $S = 1/2$ is

$$\frac{I}{I_o} = \frac{\sum_{l=0}^{S} 2l \exp\left[-l(l+1)\, j/2\right]}{\sum_{l=0}^{S} (2l+1) \exp\left[-l(l+1)\, j/2\right]} \quad ; \; j = \frac{J}{kT} \, . \tag{4.8}$$

In the case of manganese with $S = 5/2$, this becomes

$$\frac{I}{I_o} = \frac{2e^{-j} + 4e^{-3j} + 6e^{-6j} + 8e^{-10j} + 10e^{-15j}}{1 + 3e^{-j} + 5e^{-3j} + 7e^{-6j} + 9e^{-10j} + 11e^{-15j}} \quad ; \; j = \frac{J}{kT} \, . \tag{4.9}$$

A plot of the theoretical temperature dependence of the normalized intensity below the Néel temperature of the pair spectrum of Mn^{2+} for various values of the exchange integral appears in Figure 18. It should be emphasized that this pair spectrum would be obtained only below the Néel temperature of the material.

It can be seen in Figure 7 that the inverse susceptibility of the

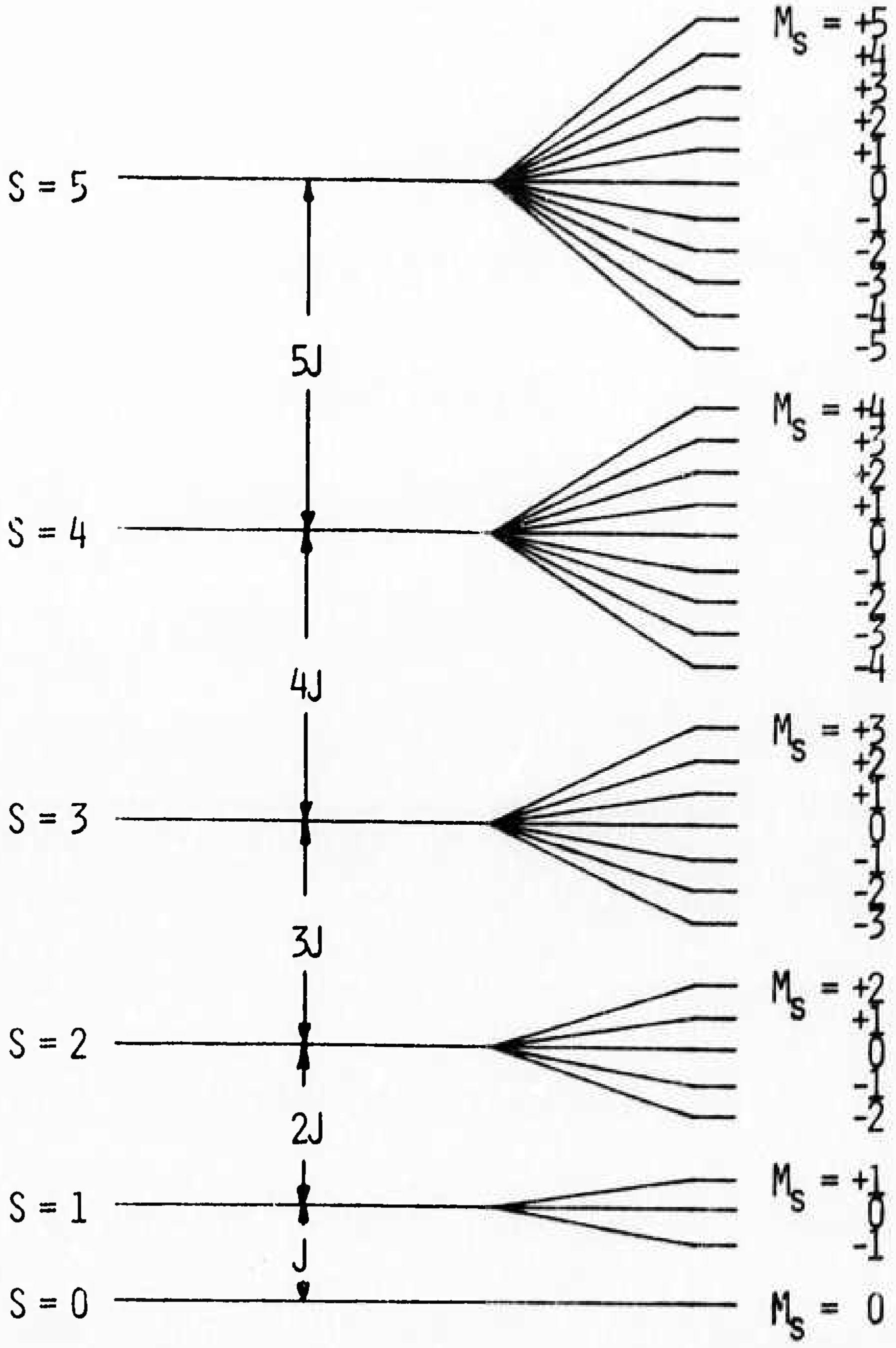


FIGURE 17. Spin Manifolds for an S = 5 Spin System.

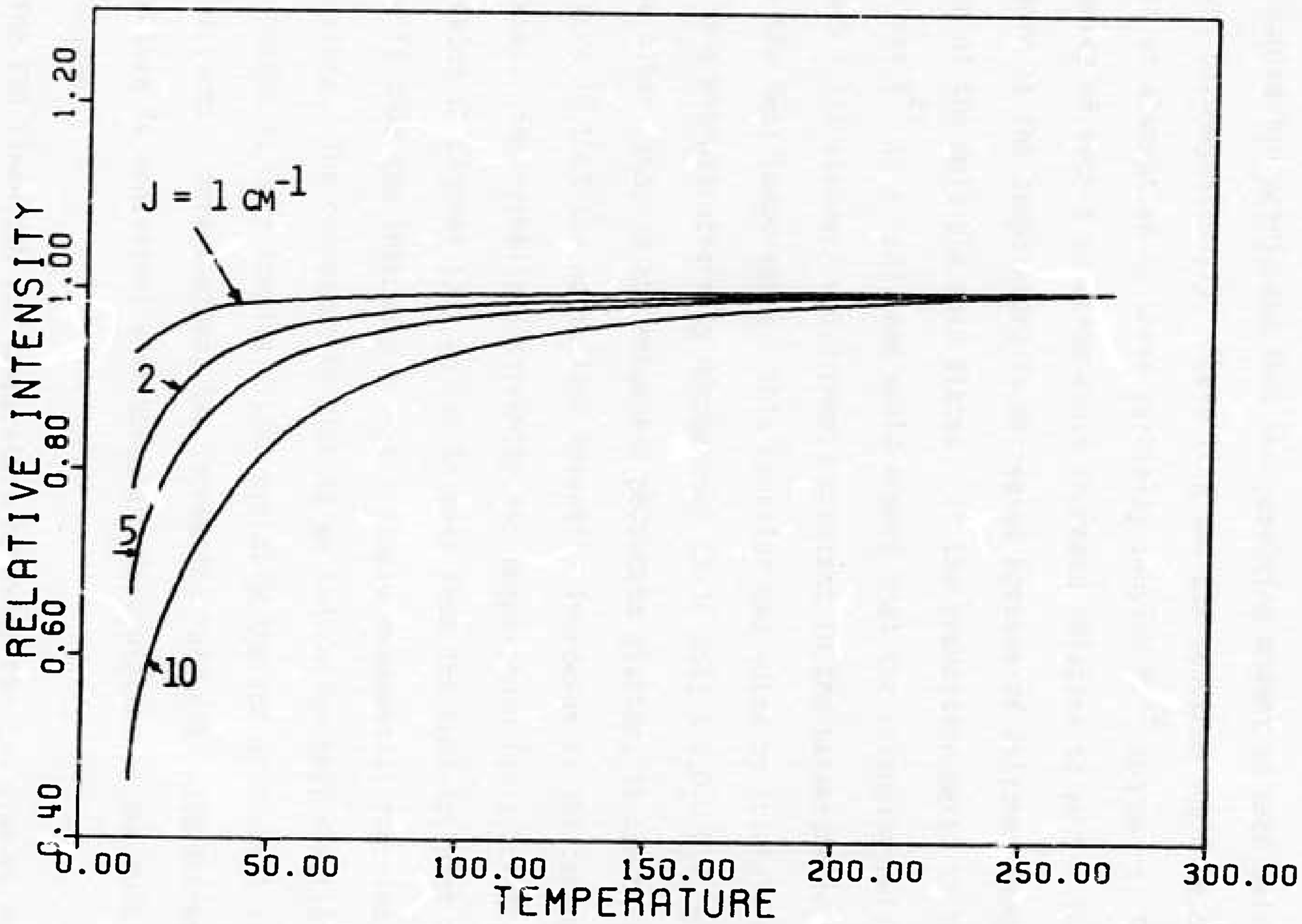


FIGURE 18. Theoretical Relative ESR Intensity vs. Temperature for Antiferromagnetically Coupled S = 5/2 Ions.

50-50 glass is a linear function of temperature above 13°K. It thus may be concluded that above this temperature, thermal energy disrupts the coupled ion pairs, and that the resulting moment of each pair behaves paramagnetically. Above 13°K the ESR spectrum would be the result of absorption by these partially coupled Mn^{2+} ion pairs. The intensity of such a spectrum would increase relative to an $S = 1/2$ standard as the temperature is decreased because of Boltzman depopulation of the multiple spin states. If the transition metal in the glass was V^{4+} ($S = 1/2$), one would expect that the intensity relative to an $S = 1/2$ standard would remain constant in the paramagnetic region above the Néel temperature. This behavior was noted by Friebele et al. (33) in a microstructurally homogeneous 65-35 mole % V_2O_5- P_2O_5 glass. On the other hand, in the manganese phosphate glasses, it can be seen in Figure 11 that the normalized intensity increases as the temperature decreases. The normalized intensity vs. temperature for a 50-50 glass is plotted in Figures 13. It can be seen from the semi-log plot in Figure 19 that the intensity is not a simple exponential function of temperature. The curvature in plot is an indication that functional relationship is more complex; it is probably the sum of several exponential terms. Nevertheless, the increasing intensity with decreasing temperature is consistent with Boltzmann depopulation of the multipled spin states.

The ESR linewidth vs. temperature behavior for the glasses and crystal is shown in Figures 12, and 14. There is a linear increase in linewidth in all cases as the temperature is decreased. This behavior can also be explained on the basis of antiferromagnetic exchange

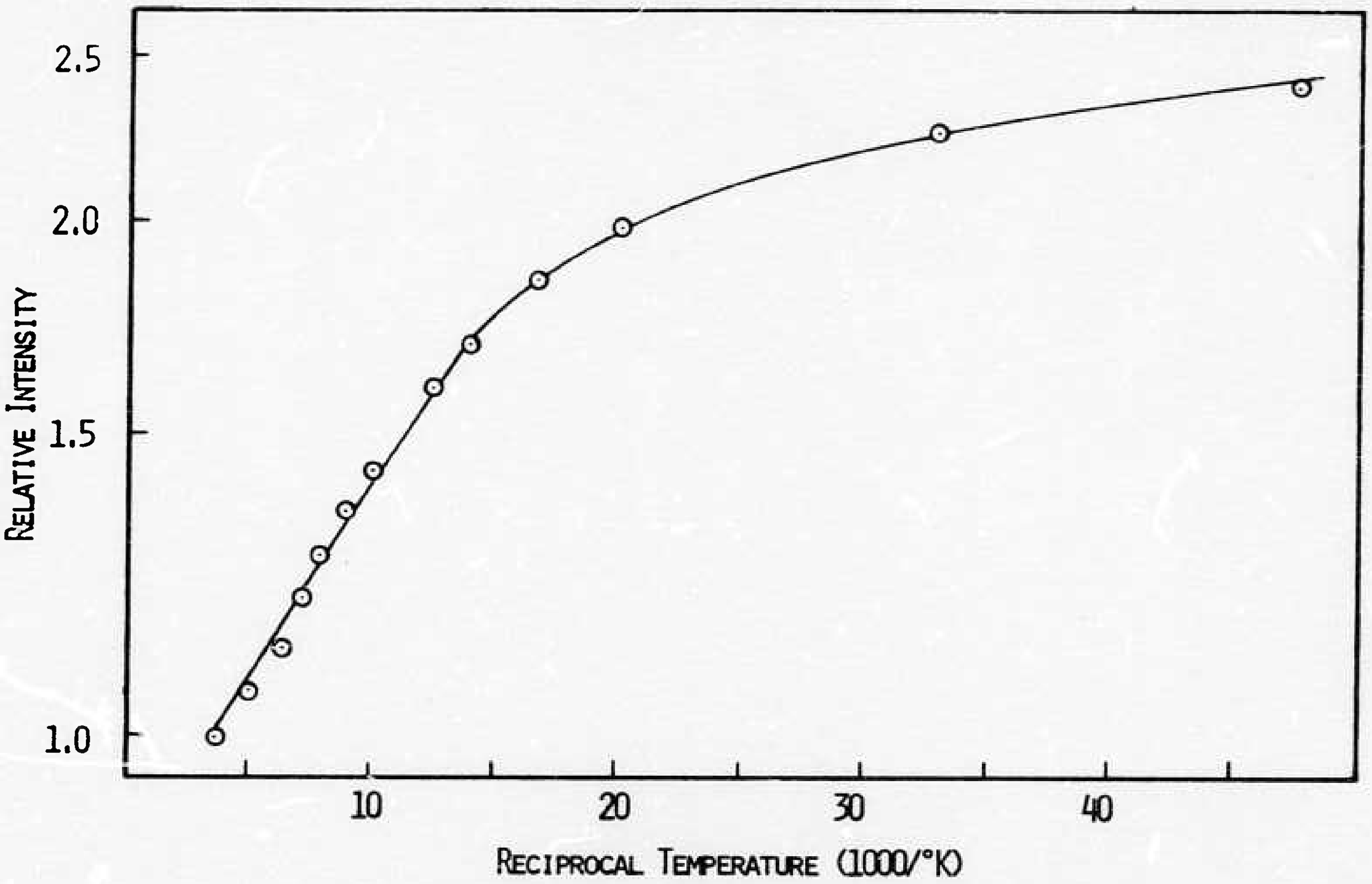


FIGURE 19. Logarithmic Relative ESR Intensity vs. Reciprocal Temperature of a 50-50 Mole % MnO-P_2O_5 Glass.

interactions between manganese ions. Because of the randomness of the glass matrix and the random orientation of the manganese metaphosphate structural units with respect to each other, there is a distribution in the distance between interacting manganese ions. This distribution creates a distribution in the exchange energy between the ions. The resonant packets corresponding to strong interactions are more narrow than those corresponding to weak interactions due to exchange narrowing effects (51). Thus, as the temperature decreases, the ions experiencing the stronger interactions will tend to align antiferromagnetically before the ions experiencing weak interactions. As the ions begin to couple antiferromagnetically, the resultant moment of the pair decreases, and the intensity of the resonant packet decreases. Since the ions in strong interactions begin to pair first as the temperature is decreased, the more narrow resonant packets decrease in intensity first. The result is that the total resonance line, which is composed of many packets of differing linewidth, appears to broaden as the temperature is decreased. Similar linewidth and intensity behavior has been observed in crystalline systems by Maxwell and McGuire (72).

One final conclusion that may be derived from the variable temperature ESR data is that the manganese ion is in a structurally stable site. As discussed in the first chapter, the g' value of the ESR resonance is highly sensitive to the site symmetry of the paramagnetic ion. The g' value of the ESR resonances of each of the glasses and the crystal remains constant over the temperature range of study. Since any temperature dependent structural transition would cause a marked change in the g' value of the resonance, it may be concluded that the manganese ion is in a stable site.

The magnetic susceptibility and magnetization of a sample of 50-50 mole % MnO-P_2O_5 glass were measured in the temperature range of 1.9 to 50°K in order to investigate the temperature dependence of these properties at and below the Néel temperature. The departure from linearity of the ESR linewidth vs. temperature plot shown in Figure 14 is an indication that the glass is approaching a magnetic transition below 20°K. Manganese pyrophosphate has a Néel temperature at 13°K (67), and although the internal glass structure is different from the structure of the crystal, the magnetic transition in the glass is also at 13°K as seen in Figures 6 and 7. Although the nature of the inverse susceptibility vs. temperature plot below 13°K is markedly different from that obtained from the crystal, there is definitely a transition at 13°K. A complete theoretical treatment of this downward curvature appears in the next section, and a comparison between the experimental and theoretical results of this study and other studies of amorphous antiferromagnetism appears in the next section.

Since there is a possibility of antiferromagnetic clusters in the manganese phosphate system, magnetization studies of the 50-50 glass were undertaken at 1.9 and 4.83°K. It has been previously discussed that there is some evidence that superantiferromagnetism exists in the 55-45 glass, and it was desirable to determine if either superparamagnetism or superantiferromagnetism existed in the 50-50 glass. The results of these studies appear in Figure 8. It can be seen that at neither temperature is there any saturation in magnetization -- a characteristic of superparamagnetic behavior. Although it may be concluded that no superparamagnetism exists in the 50-50 glass, the large magnetizations which are induced at these low temperatures could indicate the presence of superantiferromagnetism. If the superantiferromagnetic particles are small, the excess susceptibility follows a paramagnetic Curie law, and at low temperatures, the magnetization vs. H/T curves have a slight curvature towards the field axis (70). It will be shown in the next section that the observed inverse susceptibility behavior is the result of exchange coupled ions obeying an antiferromagnetic Curie-Weiss law and a component obeying a paramagnetic Curie law. On the basis of the susceptibility data, superantiferromagnetism is possible in the 50-50 glass. The fact that the magnetization curve at 1.9°K has a slight curvature is further evidence for its existence. If the superantiferromagnetic particles are larger, the susceptibility increases with decreasing temperature, and then passes through a maximum. Since this behavior is not observed, if superantiferromagnetism exists in the 50-50 glass, the cluster size must be very small.

A Model of Amorphous Antiferromagnetism

In order to explain the downward curvature of the inverse susceptibility of the manganese phosphase glasses at low temperature, a model of amorphous antiferromagnetism which result in similar behavior is proposed. The Weiss molecular field model of antiferromagnetism was chosen as a basis for the derivation. Although this model is not quantitatively accurate in predicting some of the low temperature magnetic phenomena observed in antiferromagnets, it is qualitatively accurate for many systems such as Cr_2O_3, MnO, and $Mn_2P_2O_7$. The calculations involved in dealing with this model are much more straightforward than those of the Heisenberg models, and it was felt that the ease in calculations far outweighed the quantitative inaccuracies. Furthermore, the calculations of Simpson (55) and Lucas (54) were based on the Weiss model, and it was desired to correlate the present derivation with their derivation. Since their calculations had resulted in a correct prediction of the downward curvature, the Weiss model was chosen for the present study. It should be pointed out that the Weiss model assumes a high degree of short range order, a fact established in many studies of glassy materials. The preliminary formulae for susceptibility in a crystalline material were taken from Smart (73), in which other models of antiferromagnetism, their advantages and disadvantages are discussed. Basically, the derivation may be divided into two parts -- one deriving the susceptibility of a totally antiferromagnetically exchange coupled system, and one deriving the susceptibility of an exchange coupled system with a small percent of paramagnetic ions present.

As derived in Smart, the parallel and perpendicular susceptibility are equal at the Néel temperature and equal to

$$\chi_{\perp}(T_N) = \chi_{\parallel}(T_N) = \frac{C\,\frac{3S}{S+1}\,B_s'(y_N)}{T_N - \frac{3S}{S+1}\,\theta\,B_s'(y_N)} \qquad (4.10)$$

where $B_s'(y_N)$ is the first derivative of the Brillouin function evaluated at T_N:

$$B_x(y_N) = \frac{2S+1}{2S}\coth\left(\frac{2S+1}{2S}\,y_N\right) - \frac{1}{2S}\coth\left(\frac{1}{2S}\,y_N\right) \qquad (4.11)$$

and

$$B_s\ (y_N) = -\left(\frac{2S+1}{2S}\right)^2 \operatorname{csch}^2\left(\frac{2S+1}{2S}\, y_N\right) + \left(\frac{1}{2S}\right)^2 \operatorname{csch}^2\left(\frac{1}{2S}\, y_N\right) \quad (4.12)$$

where

$$y_N = \frac{g\beta N}{2kC} M_j \ . \quad (4.13)$$

The perpendicular susceptibility remains constant below the Néel temperature and equal to its value at the Néel temperature. The parallel susceptibility below the Néel temperature is equal to

$$\chi_{\parallel} = \frac{C\,\frac{3S}{S+1}\,B_s'\ (y)}{T - \frac{3S}{S+1}\,\Theta\,B_s'\ (y)} \quad (4.14)$$

where

$$y = \frac{g\beta N\ T_N}{2kC\ T} M_j . \quad (4.15)$$

In order to take into account the distribution in exchange interactions arising from the distribution in distance between manganese ions, a Gaussian distribution was introduced into the spontaneous magnetization

$$P_\xi\ (M) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left[\frac{-(M-M_0)^2}{2\sigma^2}\right]. \quad (4.16)$$

For simplicity in this qualitative derivation, the spin of the ion was chosen as 1/2. The derivative of the Brillouin function thus becomes

$$B'_{1/2}\,(y) = B' = -4\ \mathrm{csch}^2\,(2y) + \mathrm{csch}^2\,(y). \tag{4.17}$$

In order to calculate the mean susceptibility of the amorphous system, it was first necessary to derive the probability density function of susceptibility. Now if a certain distribution function $P_\xi\,(M)$ is introduced for the variable M_j, the resulting distribution function for the susceptibility will be

$$P_\eta\,(\chi) = P_\xi\,(M)\left|\frac{dM}{d\chi}\right| = \frac{P_\xi(M)}{\left|\frac{d\chi}{dM}\right|} \tag{4.18}$$

if both $\chi = f(M)$ and $M = f'(\chi)$ are single valued functions (74,75). In the present case $\chi(M) = \chi(-M)$ because the hyperbolic cosecants are raised to an even power. Since $M = f'\,(\chi)$ is not single valued the probability density function $P_\eta\,(\chi)$ must become in this case

$$P_\eta\,(\chi) = \frac{P_\xi\,(-M)}{\left|\frac{d\chi}{dM}(-M)\right|} + \frac{P_\xi\,(M)}{\left|\frac{d\chi}{dM}\,(M)\right|} \tag{4.19}$$

where

$$\frac{d\chi}{dM} = \frac{CT\,\frac{dB'}{dM}}{(T - \Theta B')^2} \tag{4.20}$$

and

$$\frac{dB'}{dM} = 16A \operatorname{csch}^2(2y) \coth(2y) - 2A \operatorname{csch}^2(y) \coth(y) \qquad (4.21)$$

$$A = \frac{g\beta NT_N}{2kCT} \;. \qquad (4.22)$$

In order to calculate values of the probability density function $P_n(\chi)$ for various valued of M_j, it was necessary to determine the approximate value of y. From the susceptibility data of the 50-50 glass, the susceptibility at the Néel temperature equals

$$B' = \frac{\chi_N T_N}{\chi_N \Theta + C} = -4\operatorname{csch}^2(2y) + \operatorname{csch}^2(y). \qquad (4.23)$$

By trigonometric substitution

$$-4\operatorname{csch}^2(2y) + \operatorname{csch}^2(y) = 1 - \tanh^2(y). \qquad (4.24)$$

Then substituting $\chi_N = 4.021 \times 10^{-4}$, $T_N = 15$, $\Theta = 90$, and $C = .032$,

$$\tanh^2(y_N) = .912 \qquad (4.25)$$

$$y_N = \frac{g\beta N}{2kC} M_J^{\circ} \simeq 1.0 \qquad (4.26)$$

where M_J° is the center of the Gaussian distribution. The results of these calculations of $P_n(\chi)$ appear in Figures 20 and 21. The calculated probability density function has several interesting features. Although a symmetric Gaussian distribution was introduced into the

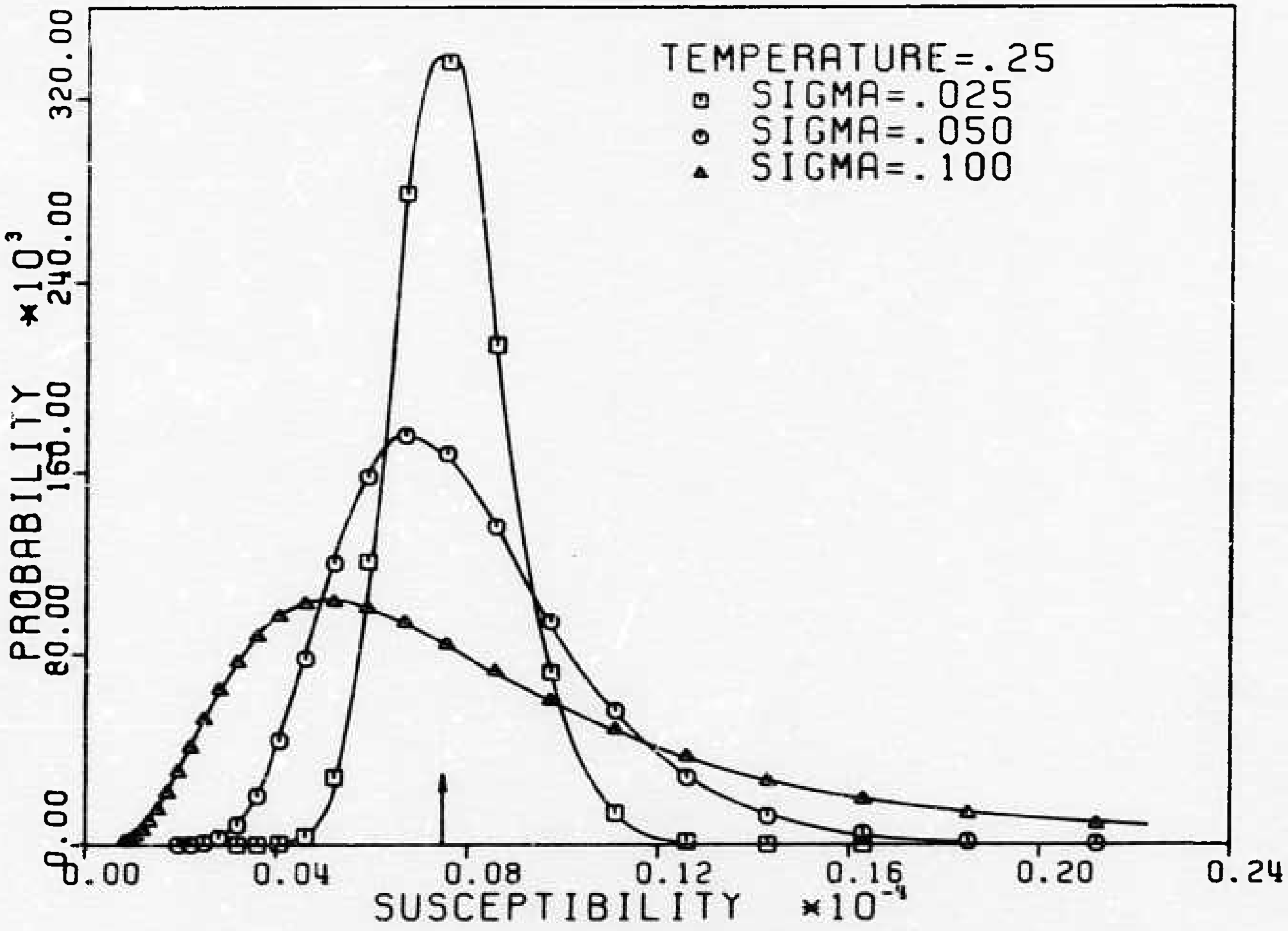


FIGURE 20. Theoretical Susceptibility Probability Density vs. Susceptibility for Relative Temperature (T/T_N) Equal to 0.25. The Arrow Indicates the Value of Crystalline Susceptibility.

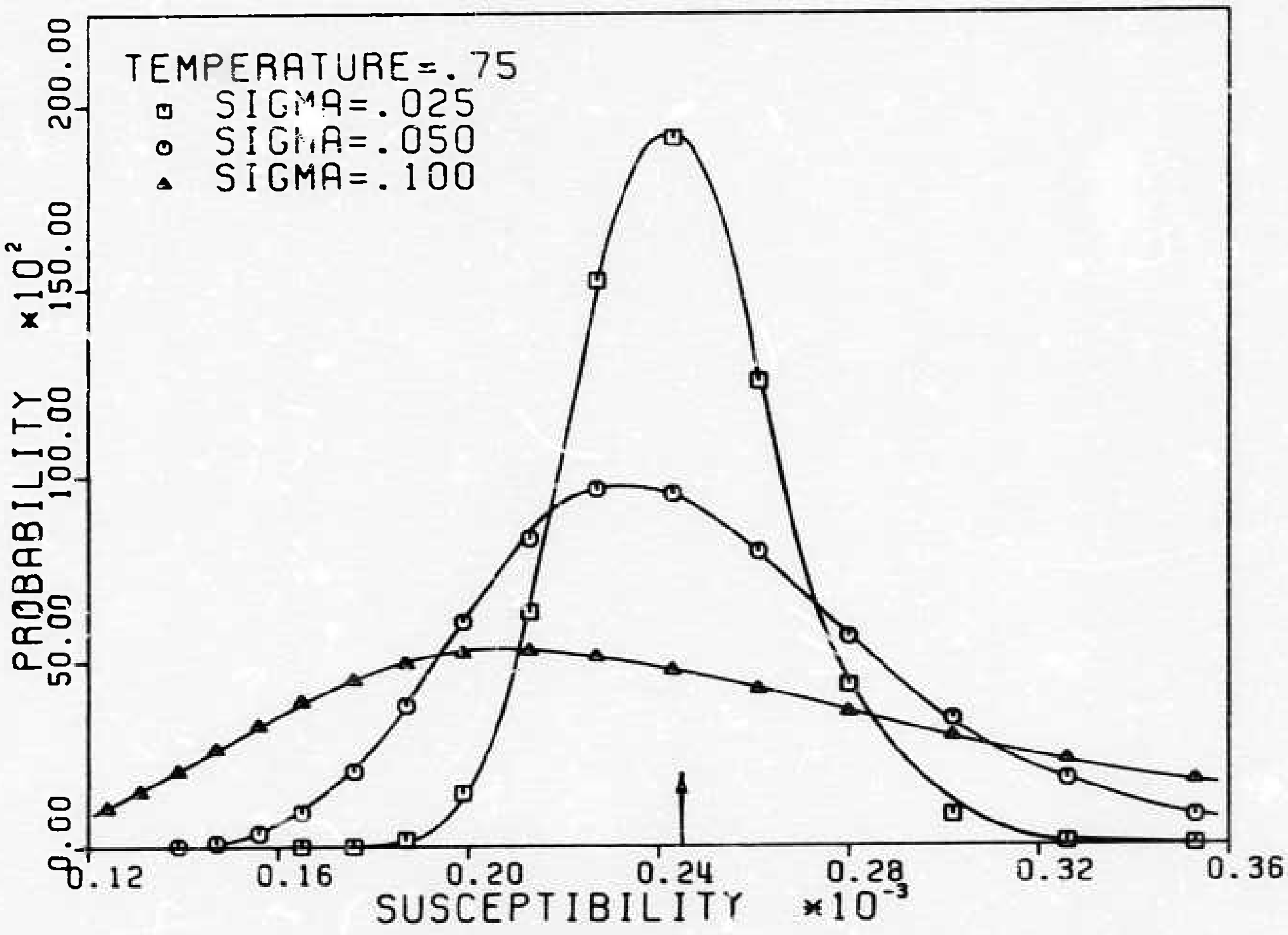


FIGURE 21. Theoretical Susceptibility Probability Density vs. Susceptibility for Relative Temperature (T/T_N) Equal to 0.75. The Arrow indicates the Value of Crystalline Susceptibility.

spontaneous magnetization, the peak in the susceptibility probability density in the positive susceptibility region is asymmetric. It will be seen later that this will give rise to a shift in the mean susceptibility from that of a regular crystalline lattice. Another feature of interest is that the widths and center of the probability density functions are dependent upon the standard deviation of the spontaneous magnetization distribution. This behavior is expected since the susceptibility probability density is a direct function of the magnetization probability density. Finally, it is seen that the probability density peaks shift towards zero susceptibility as the temperature is reduced. This behavior causes the mean susceptibility to decrease as the temperature is lowered, as will be seen in the next paragraph.

It is necessary to calculate the mean susceptibility for the system in order to investigate the temperature dependence of the model. The mean susceptibility is

$$\bar{\chi}\ (T) = \int_{\chi} \chi\, P_n(\chi)\ d\chi \qquad (4.27)$$

or equivalently,

$$\bar{\chi}\ (T) = \int_{M} \chi(M)[P_n(\chi(M))]dM\ . \qquad (4.28)$$

As a check of the accuracy of the numerical integration, the probability density function of M_J was integrated over the same limits. In all cases, the value of this integral was within 0.5% of 1.000, so the integration of the susceptibility can be assumed to have the same accuracy.

The resulting mean susceptibility as a function of reduced temperature (T/T_N) for three standard deviations in spontaneous magnetization is plotted in Figure 22. For comparison, the parallel susceptibility of a crystalline material with spontaneous magnetization M_j^o is also plotted in these figures. It can be seen that although the introduction of a distribution into the spontaneous magnetization increases the resulting susceptibility, the temperature dependence of the susceptibility is quite similar. It is important to note that the susceptibility at T = 0°K is still equal to zero. Thus, it may be concluded that the introduction of a Gaussian distribution into the spontaneous magnetization in the Weiss molecular field model of antiferromagnetism cannot account for the inverse susceptibility behavior observed in the 50-50 manganese phosphate glass. Furthermore, by induction it may be concluded that the distribution in exchange interaction that results from the distribution in cation separation cannot alone account for the downward curvature of the inverse susceptibility.

One origin of the downward curvature may be found in the internal structure of the glass. It will be recalled that the ideal 50-50 glass consists only of randomly oriented metaphosphate units, and that ideal glasses containing less than 50 mole % MnO consist of both metaphosphate and branching units. However, in real glasses, all types of structural units are possible.

If we first consider glasses with less than 50 mole % MnO, a possible structural arrangement is two manganese metaphosphate groups connected each to two branching phosphate units. In this case, since the branching units are not bonded to a metal ion, the manganese ion

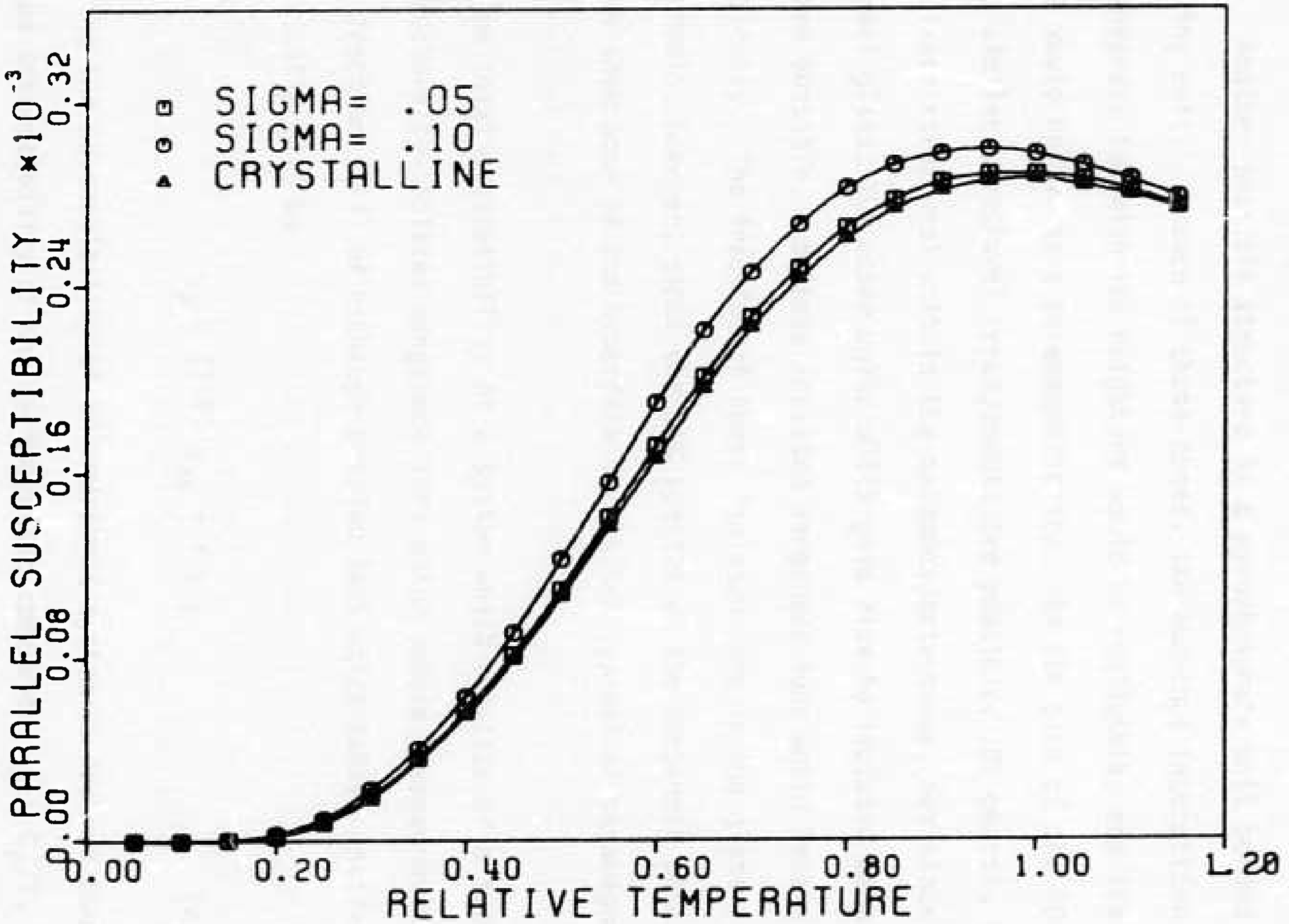


FIGURE 22. Parallel Theoretical Susceptibility vs. Relative Temperature (T/T_N) for the Amorphous and Crystalline Cases.

bonded to the metaphosphate groups would be sufficiently far away from neighboring manganese ions that any exchange interaction would be negligible. Another possible structure is a pyrophosphate unit bonded to a branching unit. In each of these cases, the exchange interaction of the manganese ion with its neighbors would be negligible, and the manganese would behave as a paramagnetic ion. In the case of the 50-50 glass, similar structural arrangements are possible. Of course, the predominate structural unit is the metaphosphate group, but since this is a real glass, the other units which give rise to isolated manganese ions are possible, and these isolated manganese ions would behave paramagnetically. The fraction of these isolated ions in the glass is quite small, however, since the ESR spectra of the manganese phosphate glasses show none of the hyperfine splittings typical of paramagnetic Mn^{2+}.

The total susceptibility of a system which consists of a fraction of structurally isolated manganese ions which behave paramagnetically and a fraction (1-f) of exchange coupled ions which behave antiferromagnetically will be

$$\chi_p = (1-f)\,\chi_{ex} + f\,\chi_p \qquad (4.29)$$

By using the susceptibility of an amorphous system as derived above and the susceptibility of the paramagnetic component, $\chi_p = C_p/T$, it is possible to calculate the net susceptibility of the amorphous system. For this calculation it is assumed that the manganese ions are in a cubic site so that

$$\chi_{ex} = 1/3\ \chi_{\perp} + 2/3\ \chi_{\parallel}. \tag{4.30}$$

This assumption is at least qualitatively correct. It can be seen in Figure 23 that the introduction of only 2% isolated paramagnetic ions gives rise to the observed susceptibility behavior. It is completely plausible that there will be at least 2% of the magnetic ions in a randomly oriented glassy system in uncoupled sites.

It should be emphasized that it is not the distribution in exchange interactions arising from the amorphous nature of the glass that causes the downward curvature of the inverse susceptibility plot. It is the possibility of a paramagnetic component of the total susceptibility that accounts for the behavior observed in the present system, in yittrium-iron thin films (56), in cobalt and copper phosphate glasses (62), and in manganese borate glasses (50).

The results of the present model are in qualitative agreement with the work of Simpson (55) and Lucas (54). As previously stated, the models used in those studies incorporated the distribution in exchange interaction into a distribution in effective field. Because both models assumed that the center of the distribution was at zero effective field rather than ± H_A, they neglect the possibility of short range order in the glass. It should be pointed out that the downward curvature of the inverse susceptibility plot is obtained in these models only when an additional paramagnetic term is added to the susceptibility. Furthermore, in these models it was assumed that the total susceptibility will be equal to the perpendicular susceptibility in the absence of any

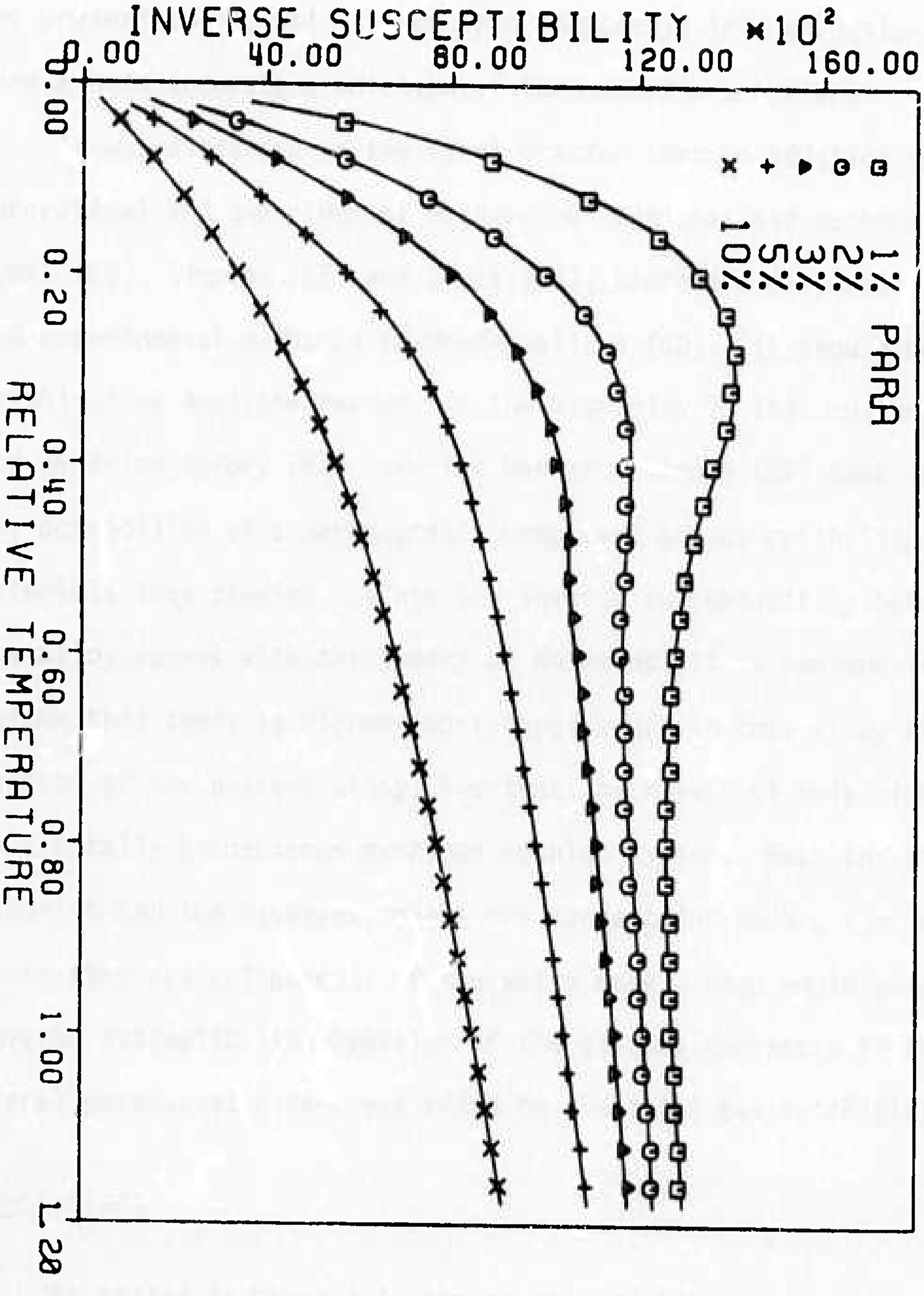


FIGURE 23. Theoretical Inverse Susceptibility vs. Relative Temperature (T/T_N) of an Antiferromagnetically Coupled System with a Fractional Paramagnetic Component.

anisotropy. However, because the axes joining the exchange coupled manganese ions are randomly oriented throughout the glass, there will be both parallel and perpendicular components of the susceptibility. The present model, which takes both components into account, is therefore a more accurate prediction of the magnetic behavior.

It was discussed in the first chapter that in addition to the theoretical and experimental evidence of Schinkel and Rathenau (50), Egami (62), Simpson (55) and Lucas (54), there are disparate theories and experimental evidence on Mn-P-C alloys (60). It should be apparent by this time that the reason for the disparity is that neither the Kobe and Handrich theory (57) nor the Hasegawa theory (59) took into account the possibility of a paramagnetic component of susceptibility in the materials they studied. Since the inverse susceptibility behavior of the alloy agrees with the theory of Hasegawa, it is reasonable to assume that there is higher short range order in this alloy than in the glasses of the present study, and that the result of this higher order is a totally homogeneous exchange coupled system. Both the Kobe and Handrich and the Hasegawa models are correct for such a system, and since they are refinements of the Weiss model, they would predict the inverse susceptibility behavior of the glasses correctly if the additional paramagnetic term was added to the total susceptibility.

Conclusions

As stated in Chapter I, the purpose of this research program was to characterize the magnetic behavior of the manganese phosphate system, to advance a theory of amorphous antiferromagnetism which would explain the anomalous low temperature susceptibility behavior, and to compare the results of this research with other experimental and theoretical studies of amorphous antiferromagnets.

The results of the present study have determined that glasses of the manganese phosphate system in the 30 to 50 mole % MnO composition range are microstructurally homogeneous. Glasses containing more than 50 mole % MnO contain dispersed antiferromagnetic clusters of manganese pyrophosphate which may give rise to superantiferromagnetic behavior. The manganese ions in all glasses studied exist primarily in the divalent state: the ratio of divalent to trivalent manganese is approximately 1,500 to 1.

Studies of the magnetic properties of glasses have established that the manganese ions are antiferromagnetically coupled. In the 30 to 50 mole % range, the effective field coefficient is constant indicating that the structure of the glass is stable and consists of metaphosphate and branching structural units. At the 50-50 composition, the glass is composed primarily of metaphosphate units, and when the manganese concentration is increased to 55 mole %, manganese pyrophosphate clusters form in the glassy matrix. The magnetic and structural properties of the glasses in the 30 to 50 mole % range vary continuously with composition, but there are discontinuities in the properties when the manganese concentration is increased to 55 mole %. The magnetic properties of the 55-45 glass are similar to those of crystalline manganese pyrophosphate, and there is evidence of superantiferromagnetic behavior in this glass although further experimental studies are necessary before an unequivocal statement can be made.

Low temperature studies of the 50-50 glass have revealed a downward curvature in the inverse susceptibility vs. temperature plot. A theoretical treatment of this behavior has been developed based upon introducing a Gaussian distribution into the spontaneous magnetization that an ion experiences below the Néel temperature. The results of this treatment have shown that in a totally exchange coupled system, variations in spontaneous magnetization arising from a distribution in cation separation cannot account for the decreasing inverse susceptibility below the Néel temperature. On the other hand, if a fractional paramagnetic component of susceptibility is added to the component arising from the exchange coupled ions, the downward curvature results. The fractional paramagnetic component can arise either from structurally isolated ions behaving paramagnetically in the glassy matrix, or from superparamagnetic or superantiferromagnetic cluster. The lack of saturation in the magnetization vs. field plot of the 50-50 glass indicates that there is no superparamagnetism in this glass. However, the slight curvature of the plot at 1.9°K is evidence that superantiferromagnetic clusters may exist.

The theoretical results of this study have shown that the origin of the downward curvature of the inverse susceptibility at low temperature lies in a paramagnetic component of the total susceptibility. This result explains the disparate results of other theoretical treatments appearing in the literature.

Although extensive experimental work has been conducted in this program of research, the characterization of the manganese phosphate glass system is by no means complete. Additional low temperature ESR, magnetic susceptibility, and magnetization studies of all glasses are necessary to investigate the possibility of clustering more thoroughly. The results of the present research have established an excellent foundation for additional work.

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