MAGNETIZATION AND ELECTRICAL CONDUCTIVITY
STUDIES OF SOME TRANSITION METAL OXIDE GLASSES

by

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CHAPTER I

INTRODUCTION

Solid state physics theory has been concerned mainly with explaining the properties of solids with simple models based on the regular periodic arrangements of atoms and molecules in a crystal lattice. For instance, the concepts of allowed and forbidden energy bands in solids are based directly on the idea of electrons moving in a potential having the periodicity of a perfect crystal lattice. However, experimentally many of the physical properties of materials are found to be not very sensitive to the periodicity and long-range order in the distribution of its atoms. Crystalline solids usually have structural imperfections and impurities that disturb the regular arrangement of atoms. Most metals and a few semiconductors are observed to retain their electrically conductive properties when melted. There also exist several kinds of amorphous materials that are semiconductors. The theories on magnetic ordering, also, generally consider only crystals. However, the exchange interaction is considered only to be large for nearest or next nearest neighbor atoms, and strict periodicity in the distribution of atoms does not seem essential. Nevertheless, in the molecular field theory, for example, all the exchange inter-

actions in the material are replaced by an effective field, which is assumed to be the same on the average at each lattice site. Thus, it is assumed that the system has long-range order.¹

This dissertation is concerned with investigating magnetic ordering and electrical conduction in amorphous materials, namely glasses. An amorphous solid is composed of atoms distributed in a random network. There are no symmetrical and repeating patterns as in crystals. Glasses are amorphous solids that may be heated to a viscous liquid and then cooled to a solid without crystallization occurring. In an amorphous material, because of the lack of periodicity, no two atoms are structurally equivalent. Thus, no unit cell, containing a few atoms, can be chosen to characterize the whole network. There are two general theories for the structure of glass.² One proposed by Levedev suggests that glass consists of crystallites, small regions with an ordered distribution of atoms, separated from one another by an amorphous phase. The other model, proposed by Zachariasen, pictures glasses as a continuous, irregular network of atoms. A given atom may have a regular distribution of neighbors, but the network as a whole has atoms randomly oriented and distributed. X-ray diffraction patterns consist of curves with several broad maxima and cannot distinguish between the two models.

In the _a investigations described here glasses containing large concentration of transition metal ions were prepared. The specific systems studied were iron-sodium borate ($\text{Fe}_2\text{O}_3 - \text{Na}_2\text{O} - \text{B}_2\text{O}_3$), cobalt-aluminium silicate ($\text{CoO} - \text{Al}_2\text{O}_3 - \text{SiO}_2$) and iron-lithium-sodium borate ($\text{Fe}_2\text{O}_3 - \text{Li}_2\text{O} - \text{Na}_2\text{O} - \text{B}_2\text{O}_3$) glasses. Bulk magnetization, nuclear magnetic resonance, and dc electrical conductivity studies were performed on the glasses. The idea behind this research effort was that in a system containing a high concentration of magnetic ions, magnetic ordering might occur even if the ions were in a glass network. The conductivity studies were performed to see if there was any correlation with the magnetic properties; a dependence between electrical conductivity and magnetic ordering is often found in transition-metal oxide materials.

CHAPTER II

MAGNETISM

A. Introduction

There are several types of magnetic behavior. The types commonly observed are diamagnetism, paramagnetism, ferromagnetism, antiferromagnetism, and ferrimagnetism. The magnetic properties of a material can be classified by the response of the material to an applied magnetic field. This response is characterized by the magnetic susceptibility, χ , defined by

$$\vec{M} = \chi \vec{H}_0$$

where $\vec{M}$ is the magnetization and $\vec{H}_0$ is the applied field. The susceptibility is in general a function of magnetic field and temperature.

Diamagnetic materials have a negative susceptibility which is independent of temperature. The magnitude of χ for these materials is small and is of the order of 1×10^{-6} e.m.u./gm. The diamagnetic susceptibility arises from the orbital motion of the electrons in the material and such materials are considered non-magnetic substances. The atoms in a diamagnetic material have no magnetic moments and all the spins are tightly paired. All materials, including those which exhibit other forms of magnetism, have a diamagnetic contribution to their susceptibility, but it

is small compared to the total and can usually be neglected. Paramagnetism is a type of magnetic behavior that only occurs in materials having atoms that possess permanent magnetic moments. In transition metal ions, for example, the magnetic moment arises from an unfilled shell of 3d-electrons. The susceptibility of this kind of material is positive and of the order of 100×10^{-6} e.m.u./gm. at room temperature. It is electronic paramagnetism that is considered here. There also exists a nuclear paramagnetism due to the nuclear moments. The nuclear moments are about 2000 times smaller than the electronic moments, and nuclear susceptibilities are approximately 10^6 times smaller than electronic susceptibilities. A paramagnetic material when placed in an applied magnetic field, experiences two opposing effects. One effect is the tendency of the field to orient the moments along the direction of the field, and the other is the tendency of the thermal agitation to cause a random orientation of the magnetic moments. Some substances, because of interactions between their magnetic atoms, acquire a spontaneous magnetization in the absence of an applied field, if they are cooled to low enough temperatures. The common types of these substances are classified as being ferromagnetic, antiferromagnetic, or ferrimagnetic. For ferromagnetic materials the interaction between atoms is such as to favor a parallel alignment of magnetic moments. At absolute zero the

the alignment is complete. The susceptibility of ferromagnetics is very large, about 1×10^2 e.m.u./gm. In antiferromagnetism the interaction between magnetic moments favors an antiparallel alignment of moments. The atoms of antiferromagnetic materials can generally be divided into two interpenetrating sublattices. The moments of the sublattices are of equal magnitude and become spontaneously magnetized in opposite directions. The susceptibility of these materials is generally on the order of 1×10^{-6} e.m.u./gm. In ferrimagnetism there is also an antiparallel alignment of magnetic moments. However, the moments on different sublattices are not equal, and the system has a net magnetization. The susceptibility of ferrimagnets is on the order of 1×10^{-3} e.m.u./gm.

B. Magnetic Theory

One common method, used to distinguish between the different types of magnetic behavior and to study magnetic materials, is to study the thermal variation of the susceptibility or some other magnetic property of a material. The theories that will be used to interpret the magnetization results are based on elementary statistical mechanics and simple molecular field theory. The following discussion of these theories will be applicable mainly to magnetic insulators. The discussion will be concerned primarily with paramagnetism and antiferromagnetism.

A simple paramagnetic is a system of non-interacting magnetic moments. Such a system can easily be treated by statistical mechanical procedures.³⁻⁶ Consider a system of N identical magnetic atoms having a total angular momentum, J , and a magnetic moment, μ . The Hamiltonian for the interaction of one atom with an applied magnetic field $\vec{H}_0$ is

$$\mathcal{H} = - \vec{\mu} \cdot \vec{H}_0 .$$

If we take $\vec{H}_0$ to be along Z -axis, then

$$\mathcal{H} = - \mu_z H_0 .$$

The eigenvalues of $\mathcal{H}$ are then

$$E_m = -g \mu_B m H_0 ,$$

where μ_B is the Bohr magneton, g is the Landé g -factor or gyromagnetic ratio, and the magnetic quantum number $m = J, J-1, \dots, -J$. The partition function for N atoms is

$$Z = \left\{ \sum_m e^{-E_m/kT} \right\}^N = \left\{ \sum_{m=-J}^J e^{g \mu_B m H_0 / kT} \right\}^N .$$

The Helmholtz free energy, F , is given by

$$F = -kT \ln Z .$$

Then the average component of magnetic moment along the applied field, H_0 , is given by

$$M = - \left(\frac{\partial F}{\partial H} \right)_T .$$

Thus

$$M = kTN \frac{d}{dH} \left[\ln \sum_{m=-J}^J e^{g \mu_B m H_0 / kT} \right],$$

and it is found that

$$M = Ng \mu_B J \left[\frac{2J+1}{2J} \coth \left(\frac{2J+1}{2J} X \right) - \frac{1}{2J} \coth \frac{X}{2J} \right] \quad (1)$$

or

$$M = Ng \mu_B J B_J (X) \quad (2)$$

where

$$X = \frac{g \mu_B J H_0}{kT},$$

and k is Boltzmann's constant. For the case $X \ll 1$, equation (1) reduces to

$$M = Ng \mu_B J \left[\frac{J+1}{3J} X \right], \quad X \ll 1$$

or

$$M = \frac{N g^2 \mu_B^2 J (J+1)}{3kT} H_0. \quad (3)$$

The susceptibility is given by $\chi = \frac{M}{H_0}$, thus

$$\chi = \frac{C}{T}, \quad (4)$$

where

$$C = \frac{N g^2 \mu_B^2 J (J+1)}{3k}. \quad (5)$$

Equation (4) is known as Curie's law for paramagnetic susceptibility, and C is Curie's constant. The

effective magnetic moment is defined by

$$\mu_{\text{eff}} = g \left[J (J + 1) \right]^{\frac{1}{2}}. \quad (6)$$

This quantity can be obtained from experimental data of the temperature dependence of the susceptibility of a material. The experimental value is given by

$$\mu_{\text{eff}} = \left(\frac{3 k C}{N \mu_B^2} \right)^{\frac{1}{2}}. \quad (7)$$

The paramagnetic susceptibility, $\chi = \frac{C}{T}$, is independent of field for small fields and vanishes for zero applied field.

However, many paramagnetic materials do not obey Curie's law, because there are interactions between their magnetic atoms. If the interaction between an atom and its neighbors is replaced by a magnetic field equal to $N_w M$, then Curie's law can be written as ⁷

$$M = \frac{C}{T} (H_0 + N_w M).$$

Thus,

$$M = \frac{C}{T - CN_w} = \frac{C H_0}{T - \theta},$$

and

$$\chi = \frac{C}{T - \theta} \quad (8)$$

The relation (8) is the Curie-Weiss law. Many

paramagnetic materials have susceptibilities that follow this relationship. The number, θ , is a positive constant and is called the paramagnetic Curie temperature.

In ferromagnetic materials the magnetic moments of the atoms are all aligned parallel at absolute zero. The spontaneous magnetization of these materials decreases, as the temperature is increased, until it is zero at a characteristic temperature called the Curie temperature. Above this temperature the material behaves as a paramagnetic. The susceptibility above the Curie temperature obeys the equation

$$\chi = \frac{C}{T - \theta}$$

where θ is a positive constant.

In an antiferromagnetic material at high temperatures where the effects of thermal agitation predominate, the susceptibility is similar to a paramagnet. The moments, however, start to become polarized below a temperature called the Neel temperature, T_N , and the susceptibility decreases as the temperature is lowered to absolute zero. The theory of antiferromagnetism will be treated by the molecular field approach.⁸

In the molecular field theory the interaction between magnetic moments is approximated by considering

one magnetic atom and replacing its interaction with the other atoms by an effective field. The effective field is assumed proportional to the average net magnetic moment of the material and is called the molecular field. The effective field is thus given by

$$\vec{H}_e = \gamma \vec{M}, \quad (9)$$

where γ is a constant. In some materials, especially elements of the transition series, the interaction between atoms arises from an exchange interaction between spins of electrons on neighboring atoms. The atoms have magnetic moments given by

$$\vec{\mu} = g \mu_B \vec{S}, \quad (10)$$

where $\vec{S}$ is the spin angular momentum. The Hamiltonian for interaction between the atoms and with an applied magnetic field is

$$\mathcal{H} = -2 \sum_{i < j} J_{ij} \vec{S}_i \cdot \vec{S}_j - g \mu_B H_0 \sum_i S_{iz}, \quad (11)$$

where the first term on the right is the Heisenberg interaction energy and the second term is the Zeeman energy in an applied field, H_0 , directed along the Z axis. J_{ij} is the exchange integral and is negative for antiferromagnetism. If only one kind of interaction is considered, the single atom Hamiltonian for the exchange interaction is

$$\mathcal{H} = -2J \vec{S}_i \cdot \sum_{j=1}^z \vec{S}_j, \quad (12)$$

where the sum is over the z nearest neighbors of the i th atom. If the interaction in the above equation is replaced by an effective magnetic field have

$$\mathcal{H} = -g \mu_B \vec{S}_i \cdot \vec{H}_e.$$

Thus,

$$\vec{H}_e = \frac{2J}{g \mu_B} \sum_{j=1}^z \vec{S}_j.$$

Assuming that $\vec{S}_j$ can be replaced by its average value $\langle \vec{S}_j \rangle$, the total magnetic moment of the material is

$$\vec{M} = N g \mu_B \langle \vec{S}_j \rangle.$$

Then

$$\vec{H}_e = \frac{2zJ}{g \mu_B} \langle \vec{S}_j \rangle = \frac{2zJ}{N g^2 \mu_B^2} \vec{M}.$$

Thus,

$$\gamma = \frac{2 z J}{N g^2 \mu_B^2}. \quad (13)$$

In an applied field the total field acting on an atom is

$$H = H_0 + H_e.$$

The the one-atom Hamiltonian is

$$\mathcal{H} = -g \mu_B S_z H$$

which has eigenvalues

$$E_m = -g \mu_B m H$$

where $m = S, S-1, \dots, -S$. Note that this Hamiltonian is of the form used for the case of a paramagnet.

Using the results for the simple paramagnet, we have

$$M = N g \mu_B S B_S(y) \quad (14)$$

$$\text{where } y = \frac{g \mu_B S H}{kT}$$

Consider the case of a simple antiferromagnet, consisting of two interpenetrating sublattices A and B, and assume that the A atoms interact only with B atoms and vice versa. Further, if it is assumed that the two different molecular fields, H_{eA} and H_{eB} , act respectively on the A and B sublattices, then

$$\vec{H}_{eA} = \frac{2 z J}{\left(\frac{N}{2}\right) g^2 \mu_B^2} \vec{M}_B = 2 \gamma \vec{M}_B$$

$$\vec{H}_{eB} = \frac{2 z J}{\left(\frac{N}{2}\right) g^2 \mu_B^2} \vec{M}_A = 2 \gamma \vec{M}_A$$

(Note $J < 0$ for antiferromagnetic interaction).

The total fields acting on the A and B atoms are thus

$$\vec{H}_A = \vec{H}_O + 2\gamma \vec{M}_B$$

$$\vec{H}_B = \vec{H}_O + 2\gamma \vec{M}_A$$

This results in

$$M_A = \left(\frac{N}{2}\right) g \mu_B S B_S(y_A)$$

and

$$M_B = \left(\frac{N}{2}\right) g \mu_B S B_S(y_B)$$

which are two coupled equations. Consider the case of the high temperature approximation, $y_A \ll 1$ and $y_B \ll 1$. Then

$$B_S(y) = \frac{S+1}{3S} y$$

Thus

$$M_A = \frac{N}{2} g \mu_B \frac{S(S+1)}{3S} \frac{g \mu_B S H_A}{kT} = \frac{\frac{1}{2} C}{T} (H_O + 2\gamma M_B), \quad (15)$$

and

$$M_B = \frac{N}{2} g \mu_B \frac{S(S+1)}{3S} \frac{g \mu_B S H_B}{kT} = \frac{\frac{1}{2} C}{T} (H_O + 2\gamma M_A), \quad (16)$$

where it has been assumed that at high temperatures the sublattice magnetizations are in direction of $\vec{H}_O$. The total magnetic moment is then

$$M = M_A + M_B$$

$$M = \frac{CH_0}{T} + \frac{\gamma C}{T} (M_A + M_B)$$

$$M = \frac{C}{T - \gamma C} H_0 = \frac{C}{T - \theta} H_0$$

Thus

$$\chi = \frac{C}{T - \theta} \quad (17)$$

where

$$C \gamma = \theta = \frac{2 Z J S (S + 1)}{3k} \quad (18)$$

Note that since $J < 0$, the constant θ is a negative number. The above relation for χ is the susceptibility above the transition temperature. To find the transition temperature, T_N , set $H_0 = 0$ in equations (15) and (16) and then find the non-zero solutions for M_A and M_B . Choose the solution

$$M_A = -M_B, \quad \frac{C \gamma}{T_N} = -1$$

Thus,

$$T_N = -C \gamma = -\theta \quad (19)$$

The above system gives a value of $\left| \frac{\theta}{T_N} \right|$ equal to unity, however most antiferromagnetic

materials have values that differ greatly from unity. One reason for this discrepancy is that most materials cannot be divided into the simple two-sublattice arrangement. Another reason is linked to θ , which depends on the exchange interactions, for a material may have several kinds of exchange interactions occurring among its atoms. A generalized molecular field theory exists which can be applied to more complicated sublattices and which considers distant neighbor exchange interactions.⁹ However, this theory still just considers systems where the magnetic atoms are translationally equivalent. Nevertheless, if one wanted to consider a random network of atoms as in an amorphous material, this theory may be a fair, if not a good, approximation.

In the generalized molecular field treatment the system is divided into n sublattices. The number, n , is made large enough so that an atom has no interactions with neighbors on its own sublattice. The total field acting on an atom on the i th sublattice is

$$\vec{H}_i = \vec{H}_0 + \sum_{j=1}^n \gamma_{ij} M_j,$$

where the summation is the molecular field exerted on an atom on the i th sublattice by its neighbors on the j th sublattice. This results in

$$\gamma_{ii} = 0$$

and

$$\gamma_{ij} = \frac{n (2 Z_{ij} J_{ij})}{N g^2 \mu_B^2}, \quad i \neq j$$

where Z_{ij} is the number of j neighbors of an i atom, and J_{ij} is the exchange interaction between the i atom and one of its j neighbors. Then by analogy with the two sublattice system, one obtains

$$\chi = \frac{C}{T - \frac{C}{n} \sum_{j=1}^n \gamma_{ij}} = \frac{C}{T - \theta}$$

where

$$\begin{aligned} \theta &= \frac{C}{n} \sum_{j=1}^n \gamma_{ij} = C \sum_{j=1}^n \frac{2 Z_{ij} J_{ij}}{N g^2 \mu_B^2} \\ &= \frac{2 S(S+1)}{3k} \sum_{j=1}^n Z_{ij} J_{ij} \end{aligned}$$

This can be written in the form

$$\theta = \frac{2 S(S+1)}{3k} \sum_{m=1}^{N'} Z_m J_m \quad (20)$$

where Z_m is the number of m th nearest neighbors of a given atom, J_m is the exchange interaction between m th neighbors, and N' is the number of sets of neighbors for which $J_m \neq 0$. Thus the θ - value is proportional to the sum of all the exchange interactions acting on a given atom.

Ferrimagnetic materials are materials having non-equivalent magnetic sublattices or magnetic atoms or both. Application of molecular field theory to ferrimagnetism can lead to rather complicated equations. The magnetizations of the sublattices can be of different magnitudes and directions, and the sublattice magnetizations can have different temperature dependences. These facts cause ferrimagnetism to give rise to some unusually shaped magnetization curves.

C. Fine-Grained Magnetic Particles

In finely divided antiferromagnetic or ferromagnetic material the anisotropy energy, signifying energy variations associated with varying orientations of the magnetization, of a particle may become comparable to the thermal energy kT .¹⁰ The magnetic behavior of an assemblage of such particles, whose magnetic moments are randomized by thermal fluctuations, is similar to that of atomic paramagnetism. The moment for a fine ferromagnetic particle, which will be single domain and will contain several atoms coupled ferromagnetically, is much larger than for the same atom in a paramagnetic salt. Thus, such particles are called superparamagnetic. Fine-grained antiferromagnetic particles of diameter under about $50 \text{ \AA}$ are expected to have a random distribution of atoms between the two antiferromagnetic sublattices and, thus, possess a small permanent moment resulting from an imperfect compensation of the magnetic sublattices.^{10,11} Above a certain blocking temperature such grains show a superparamagnetism with a Curie constant a little inferior to that of the corresponding free ions. By cooling in a magnetic field down below the blocking temperature, the grains obtain a thermo-remanent magnetization of high stability. When the diameter of the grains becomes larger than about $100 \text{ \AA}$ crystalline faces must appear. If a grain has faces containing atoms of the same sublattice, its magnetic

properties depend on the number of lattice planes, parallel to this face, contained in the grain. If the number is odd the grain is superparamagnetic as for the very fine-grained particles, if the number is even the antiferromagnetic susceptibility has a value twice as large as that of the corresponding antiferromagnetic material measured in the bulk. This latter phenomenon is called superantiferromagnetism.¹¹

In an assemblage of grains of different sizes the blocking temperature can vary from the Curie point for large grains to absolute zero for very small grains. For fine enough particles and low temperatures the superparamagnetic contribution may surpass the antiferromagnetic one by an order of magnitude. This is due in part to the Curie law $1/T$ dependence of the superparamagnetic magnetization compared to the relative temperature independence of the antiferromagnetic contribution. At low temperatures these very fine particles have magnetization curves which are weakly concave toward the field axis. For slightly larger particles the susceptibility increases with decreasing temperature, but passes through a maximum below which it decreases slowly.¹⁰ The temperature of this maximum decreases with decreasing particle size.

For a dilute assembly of randomly orientated superparamagnetic particles, the initial slope of the magnetization curve is given by the expression¹²

$$\frac{I}{H} = \frac{4\pi I_s^2 r^3}{9kT} \quad (21)$$

where I is the intensity of magnetization per unit volume and I_s is its saturation value. This relation allows an estimation of the particle size to be made. If there is a distribution of particle sizes the initial slope favors the larger particles, whose moments are more easily aligned, while the approach to saturation is influenced more by the smaller particles.

Alternatively, the particle size can be estimated from the Curie constant obtained from susceptibility measurements on the superparamagnetic particles.¹³

If each particle of magnetic moment μ is composed of n ions of magnetic moment μ_o , then it is assumed that

$$\mu = n \mu_o$$

The susceptibility of a particle is given by

$$\chi_p = \frac{n^2 \mu_o^2}{3kT} = \frac{C_p}{T}$$

where C_p is the Curie constant. The apparent susceptibility χ_a of an ion in the particle is equal to

$$\frac{n \mu_o^2}{3kT}$$

with an apparent Curie constant of

$$C_a = \frac{n \mu_o^2}{3k}$$

The susceptibility χ of the same ion when uncoupled

to its neighbors may be determined from measurements on one of its paramagnetic salts and is

$$\chi = \frac{\mu_o^2}{3kT} = \frac{C}{T}$$

where C is the Curie constant of an uncoupled ion.

The apparent Curie constant, C_a per ion, for an assemblage of small single-domained grains is n times as large as C for the same ion in a paramagnetic salt and therefore the apparent magnetic moment per ion is

$$\mu_a = n^{\frac{1}{2}} \mu_o$$

Thus, the number of ions per particle can be determined from the ratio C_a/C (or μ_a^2 / μ_o^2). Then the particle size can be calculated if the lattice dimensions of the bulk material are known.

CHAPTER III

ELECTRICAL CONDUCTIVITY

A. Electrical Conduction in Amorphous Semiconductors

The present quantum electron theory of crystalline solids is based on the periodicity of the potential and the presence of long-range order in the distribution of atoms. In crystalline materials the band structure of a material is expressed through the density of states $N(E)$. The lattice has a large effect upon the wave-functions of the electrons and on the density of states. In crystals the lattice produces the energy gaps. In some non-crystalline materials an energy gap must also exist; otherwise optical glass would not be transparent.¹⁴ Gubanov¹⁵ has shown theoretically that when long-range order disappears but short range order still exists that the energy spectrum retains its band structure. However, the allowed bands are broadened and there is spreading of their edges. Further Mott¹⁴ suggests that in amorphous materials the gap either persists or is replaced by a minimum, which is called a pseudogap. For energies in the pseudogap or near the edges of the conduction and valence bands, the electron wave-functions become localized. An electron in a localized state is described as being trapped; it cannot move unless thermal energy frees it. The absence of crystalline order produces a

high density of traps. If the Fermi energy lies in the energy range where states are localized, at $T = 0^\circ\text{K}$ there is no conductivity. At a finite temperature, as the electron moves it gains or loses energy from or to phonons. This process of conduction is called "thermally activated hopping". The idea of traps, due to impurities or defects, is common in the treatment of crystalline semiconductors. What is not familiar is the idea that a continuum of energy levels can exist, and in each of these levels the electron is trapped and unable to move. The theory on this suggests that the mobility μ of an electron with energy E in the localized region of energies is of the form

$$\mu = \mu_0 e^{-W(E)/kT}$$

If E_c denotes the energy separating the range in which states are localized and the range in which they are not, then $W(E)$ tends to zero at the energy E_c . If the Fermi energy lies in the localized energy region, conductivity is possible by two processes: ¹⁶

- A) Excitation to a higher energy state.
- B) Hopping from one localized state to another. This involves an activation energy because each localized state has its own quantized energy value. It may also involve tunnelling. The latter process

requires a smaller activation energy than the first and thus is predominant at low temperatures.

Cohen (and others)¹⁷ describe a band model for amorphous semiconducting alloys. They suggest that as a result of disorder the sharpness of the band edges disappears and localized states tail into the band gap. The tails of the valence and conduction bands overlap. The empty valence-band tail states give rise to a random distribution of localized positive charges neutralized on the average by a corresponding distribution of an equal number of localized negative charges which are associated with occupied conduction-band tail states. These charge states above and below the Fermi energy act as trapping centers for electrons and for holes, respectively. They suggest that the transition from the extended band states to localized gap states occurs at an energy E_v for the valence band and E_c for the conduction band (ignoring the spatially varying potential caused by the randomly distributed charged gap states). They propose that the mobility drops sharply at E_c and E_v , because here the conduction process changes from a low-mobility band transport with finite mobility at $T = 0$ to a thermally activated hopping between localized gap states which disappears at $T = 0$. The presence of the "mobility edges" near E_c and E_v explains why a well-defined activation energy is observed for the conductivity despite the

lack of sharp band edges.

B. Magnetic Structure and Electrical Conductivity

When the same electrons are involved in the electrical and magnetic properties of a material, the electrical conductivity of the substance should be dependent on its magnetic structure. The magnetic¹⁸ and electrical^{18,19} properties of magnetite have been studied and shows a dependence between the two properties. Such a correlation is often found in transition-metal-oxide materials, because the d electrons are responsible for both the magnetic and electrical properties. A drop in the conductivity and also the magnetization is observed upon cooling below about 119°K for magnetite. Verway¹⁹ related his conductivity results to an electron ordering on the octahedral sites. Thus to fully understand the magnetic and electrical properties of a material, it is important to know the character of the magnetic state and how it is related to the electronic states.

In many antiferromagnetic materials (and ferrites) the metal ions are separated by negatively charged anions which are diamagnetic. The distance between the metal ions is usually too great for a direct exchange interaction to be possible.²⁰ What has been proposed to describe the magnetic interaction in these materials is an indirect exchange inter-

action, called superexchange because of the large distances over which the exchange effects acts.

In superexchange the wave functions of the non-magnetic ions are modified by the presence of magnetic ions, and this modification of the wave functions has a magnetic character which can give exchange interactions with the other ions.²¹ The simplest such modification is the transfer of one of the electrons of the diamagnetic ion into the 3d shell of the magnetic ion. The electron must enter an empty d orbital and its spin will be parallel to the resultant moment if the shell was less than half occupied, otherwise it will be antiparallel (Hund's rule). The remaining electron can interact with another metal ion as in the hydrogen molecular bond.²⁰ This process is illustrated below²¹

I Ionic configuration

II The "excited" configuration

Thus the superexchange interaction gives rise to configurations of mixed valence states. The magnetic

coupling arising from the electron transfer gives rise to ferromagnetism if the cation has less than five electrons in the d shell and to antiferromagnetism if five or more electrons are in the d shell. The superexchange interaction is strongly dependent upon the angle made by the two cations with the anions as the apex.²² The interaction is strongest when the angle is equal to 180° and weakest at 90° .

The relation of superexchange to conductivity will now be considered. Consider the antiferromagnetic system below²²

The transition from this ionic configuration to the excited configuration is effected by the movement of an electron from the O^{--} ion to a neighboring cation. Under the influence of an applied electric field, one of the O^{--} p electrons can travel down the line of atoms; the only requirement being that vacancies be present in the p shells of the appropriate O^{--} ions. The electron can transfer to atom II and to the oxygen ion to the right of II if a vacancy exists in its P shell. However, the electron cannot go on to atom III as this would violate the Pauli principle. Thus, conduction by means of deviation from perfect ionic character

is forbidden in an antiferromagnetic lattice at 0°K. However, at a finite temperature some reversed spins exist in the lattice making conduction possible. The system thus should have a negative temperature coefficient of resistivity (the resistivity decreases with increasing temperature). This model suggests that anomalies might occur in the conductivity at the magnetic ordering temperature.

The dependence of the electrical conductivity on the magnetic ordering by considering the structure of the d band is discussed in a paper by Bulaevskii and Khomskii.²³ They show that in the localized-electron model, because of the Pauli principle the electron and the hole bands are much narrower in the ordered state. A strong broadening of the bands and a decrease in the energy gap occurs above the Neel temperature. They also suggest the possible occurrence of a band splitting due to the exchange interaction below the antiferromagnetic ordering temperature.

Conduction in the antiferromagnets $\alpha\text{-Fe}_2\text{O}_3$ and NiO has been studied by Morin.²⁴ He found that the mobility varies with the impurity ion concentration and increases exponentially with temperature. A low mobility is found in both Fe_2O_3 and NiO having an apparent activation energy of 0.1 ev. He explains this behavior as due to the concept of "wavy bands." These are potential fluctuations produced by crystal

imperfections and inhomogeneous distribution of impurities. These fluctuations give rise to an activation energy for the motion of holes and electrons. The residual activation energy of 0.1 eV may be the energy required for the transfer process, that is the energy required to transfer a carrier from the potential well of one cation to that of the next. Also the transfer may be related to the anti-ferromagnetic exchange energy kT_N . Yamashita²⁶ explains that the strong temperature dependence of the mobility deduced by Morin cannot be explained in terms of the motion of electrons (or holes) alone, because of the small mass of the electron. He suggests that it must be a thermally activated process and that phonons are intimately involved in the jumping process. He assumes that the wave function of the electron is localized closely around an ion and that the motion of the electron is so slow that lattice polarization is induced around the electron. The polarization moves with the electron (hole), and the change in polarization can give rise to an activation energy. He gives a theoretical treatment of this problem. In many transition metal oxides such as NiO and Fe_2O_3 the 3d band is extremely narrow, and thus the 3d charge carriers can be considered to occupy energy levels localized on the cations. The narrowness of the band means a high effective mass and low

mobility for charge carriers in the band. These oxides are insulators when pure at room temperature. In order for conduction to occur there must be ions of mixed valence states present. However, these excited states can only occur at high temperatures. Conduction is possible at room temperature, if the mixed valence states are introduced into the lattice by either a departure from stoichiometry or the substitution of impurity ions.²⁷ The transport is then expected to involve an activation energy associated with self trapping of the charge carriers.

Thus the conduction processes suggested for amorphous semiconductors and some of the transition-metal oxides have similar properties. Also, the electrical conductivity is expected to be dependent on the magnetic structure of the material.

CHAPTER IV

NMR IN MAGNETIC INSULATORS

The subject of observing nuclear magnetic resonance in magnetic materials will be considered. The discussion is based on the treatment given by Jaccarino.²⁸

The Hamiltonian for the interaction of a nucleus, having a magnetic dipole moment, $\vec{\mu}$, and total angular momentum $\vec{I}\hbar$, with an external field H_0 is

$$\mathcal{H} = - \gamma \hbar \vec{I} \cdot \vec{H}_0$$

where γ is the nuclear gyromagnetic ratio. The difference between adjacent eigenvalues of this Hamiltonian gives the following separation between the nuclear energy levels

$$\Delta E = \gamma \hbar H_0$$

The condition for resonance absorption if a perturbing oscillatory magnetic field of frequency ω is applied perpendicular to H_0 is

$$\omega = \gamma H_0$$

The dynamic aspects of a nuclear spin system, subject to interactions between the individual spins and between the spins and their environment, while undergoing resonance absorption, are given

by the Bloch equations:

$$\begin{aligned}\frac{dM_z}{dt} &= \gamma (\vec{M} \times \vec{H})_z + \frac{M_0 - M_z}{T_1} \\ \frac{dM_x}{dt} &= \gamma (\vec{M} \times \vec{H})_x - \frac{M_x}{T_2} \\ \frac{dM_y}{dt} &= \gamma (\vec{M} \times \vec{H})_y - \frac{M_y}{T_2}\end{aligned}$$

where $\vec{M}$ is the nuclear magnetization, M_0 is the equilibrium magnetization, T_1 is the longitudinal or spin-lattice relaxation time and characterizes the rate at which energy is transferred from the nuclear spin system to its environment, T_2 is the transverse relaxation time.

In magnetic materials electronic dipolar fields are 10^3 times larger than the corresponding nuclear dipole fields, and the atomic hyperfine fields of magnetic ions possible 10^6 times larger. If the instantaneous local field, H_{loc} , at each nucleus scaled proportionately, nuclear resonance would be unobservable in magnetic materials. The rapid fluctuations of the electronic spins resulting from dipolar, spin lattice, and exchange interactions causes the nuclei to see a static field which is proportional to the time average of the individual electronic spin moment $\langle \vec{S} \rangle$. This is related

to the magnetization per unit volume $\vec{M}_0$ by

$$\vec{M}_0 = N g \mu_B \langle \vec{S} \rangle$$

where g is the electronic gyromagnetic ratio and μ_B the Bohr magneton. The internal fields at the nucleus depends on the nature of the atom in the magnetic solid. For nuclei of nonmagnetic atoms the interaction Hamiltonian is for the k th atom

$$\begin{aligned} \mathcal{H}_k &= -\gamma \hbar \vec{I}_k \cdot \left[\vec{H}_0 - g \mu_B \sum_n r_n^{-3} (\langle \vec{S}_n \rangle - \frac{3 \vec{r}_n (\vec{r}_n \cdot \langle \vec{S}_n \rangle) }{r_n^2}) \right] \\ &= -\gamma \hbar \vec{I}_k \cdot [\vec{H}_0 - \vec{H}_D] \end{aligned}$$

where $\vec{H}_D$ is the dipolar field produced by all the electronic spins in the solid; the summation extends over spins $\vec{S}_n$ that are at a distance r_n from the k th atom. A material can have more than one physically equivalent site for like atoms, so that like atoms can have different dipolar fields. Thus in crystals having a number of inequivalent like atoms, the above Hamiltonian gives a number of different allowed transitions that vary in frequency as a function of the angle between $\vec{H}_0$ and the crystal axes. $\vec{H}_0$ and $\vec{H}_D$ may not be parallel, especially at temperatures below the ordering temperature of the material. The nuclei of paramagnetic atoms will be subjected to the intense hyperfine fields produced by electronic spin and orbital moments.

In this case the interaction Hamiltonian is

$$\mathcal{H}_k = -\gamma \hbar \vec{I}_k \cdot [\vec{H}_0 + \vec{H}_{kD}] + \vec{I}_k \cdot \tilde{\mathbf{A}} \cdot \langle \vec{S}_k \rangle$$

where the electron-nuclear hyperfine interaction is represented by a tensor $\tilde{\mathbf{A}}$; H_{kD} is the dipolar field at k th one. The hyperfine coupling can be considered as producing an additional field H_{HF} at the nucleus, where

$$H_{HF} = -(\gamma \hbar)^{-1} \tilde{\mathbf{A}} \cdot \langle \vec{S} \rangle.$$

At temperatures above the magnetic ordering transition temperature of the material the strong exchange interaction between electronic spins produces a rapid reorientation of the spin moments. If during the NMR observation period the local fields fluctuate very rapidly, their effects will average to zero. This observation period is the Larmor period T_L given by

$$T_L = (\gamma H_{eff})^{-1}$$

where H_{eff} is the time-averaged field due to the sum of the external field and constant components of the fields produced by the electronic spins. Transverse components of the fluctuating field at the Larmor frequency will induce transitions between the energy levels and will contribute to the relaxation times T_1 and T_2 , since each level is lifetime broadened. It is necessary to consider the frequency dependence of

the amplitude of the local field spectra $|H(\omega)|$. The amplitude of $|H(\omega)|$ will vary, depending on whether the field arises from hyperfine or dipolar coupling, but the frequency distribution will not. $|H(\omega_L)|$ will be much less than estimates based on the static hyperfine or dipolar field, because the integrated spectral density must remain constant and since exchange effects distribute the local field spectra over a large frequency range the low-frequency components are severely attenuated. A rough estimate of the necessary condition for observing resonance in a magnetic solid is given by the inequality

$$\frac{1}{T_{1,2-\min}} > \frac{(\gamma H_{\text{int}})^2}{\omega_e}$$

where $T_{1-\min}$ and $T_{2-\min}$ are the smallest values of the relaxation times for which resonance is observable, H_{int} is the static value of the perturbing field at the nucleus, and ω_e the exchange frequency. Note that the many other factors that enter into the observability of a NMR signal have been neglected. One important factor is the electric quadrupole interaction which can cause splitting of the energy levels and broadening of the resonance line.

Although the NMR signal of a material may be observed, the fluctuating fields due to the electron spins can affect the width of the resonance line.

The half width of the absorption curve at half intensity is $1/T_2$.²⁹ Thus $1/T_2$ is related to the resonance line width. The half width can be written as³⁰

$$\frac{1}{T_2} = \frac{1}{T_2'} + \frac{1}{2T_1}$$

where $1/T_2'$ is broadening due to the spread in the longitudinal field and $1/2T_1$ is broadening due to the finite lifetime of spin in an eigenstate as a result of spin-lattice relaxation.

CHAPTER V

EXPERIMENTAL EQUIPMENT AND PROCEDURE

A. Magnetization Measurements

1. Introduction

Several methods were employed in an effort to measure the bulk magnetization of the glass samples. A method was sought which was sufficiently sensitive to measure paramagnetic susceptibilities and which would allow measurements to be made easily at low temperatures. Both dc and ac methods were attempted. The ac methods proved to be the most successful, mainly because of the availability of good ac electronic detecting and amplifying systems. Generally, ac systems have greater resolution and stability and less zero drift than do dc systems. The ac electronic systems, which were used, employ equipment that are usually found in magnetic resonance laboratories.

2. DC Methods

In the dc methods two different types of magnetic flux sensors were used. Both are made by American Aerospace Controls, Inc. One was a Hall effect generator (model HA-12), and the other was a bismuth magnetic flux - sensitive resistor (MRA-12). A discussion of a Hall effect

magnetometer is given in an article by Viehmann.³¹ The experimental procedure for the two types of sensors are essentially the same. The main difference between these devices is that the Hall generator is a four-terminal device and the bismuth probe a two-terminal device. Two elements of a particular type sensor are used. The elements are connected in series opposition and placed in a homogeneous magnetic field. The sample is placed near to one of the elements. A diagram of the experimental arrangement is given in Fig. 1. The system is balanced in the absence of a sample to have a zero output. Circuit diagrams for the two systems are given in Figs. 2-3. The dipole field of the sample modifies the magnetic induction around the sensor, thus changing the balance of the system. This unbalanced dc signal, which is proportional to the magnetization of the sample, is then detected. For accurate results the samples should be of the same size and placed in the same position relative to the sensor element.

This experimental system failed to give reliable and reproducible results. The change in the null balance with temperature together with the drift in the zero point output makes accurate measurements difficult. Also the system lacked

FIG. 1
Experimental arrangement for magnetic flux sensors.

FIG. 2
Circuit diagram for Hall probes.

FIG. 3
Circuit diagram for Bismuth probes.

a high gain, stable dc amplifier, which is necessary to detect small changes in the signal.

3. AC Methods

a. Radiofrequency Method

When a sample is placed in a coil, which is part of the tank circuit of a high frequency oscillator, the inductance of the coil changes, thus, changing the frequency of the oscillator. This principle was used to make magnetization measurements. The oscillator used was a radio-frequency oscillator and detector (Pound-Knight-Watkins oscillator), which was usually a part of a NMR spectrometer. The frequency of the oscillator was measured with a Hewlett-Packard electronic counter (model 5245L). The stability of the oscillator is the limiting factor in making measurements. Also, temperature changes in the coil affect the oscillation frequency of the oscillator.

b. Vibrating - Sample Magnetometer

Successful magnetization measurements were obtained using a vibrating-sample magnetometer designed after the system described by Foner.³² In this system the sample is vibrated perpendicularly (Z-direction) to an applied uniform magnetic field (in X-direction). The oscillating dipole field of the vibrating sample induces a voltage in stationary detection coils.

This voltage, which is proportional to the magnetization of the sample, is then detected. Consider a fixed magnetic dipole M at the origin and pointing in the X -direction. Then its scalar potential is

$$U = \frac{M X}{r^3}$$

If M is vibrated in the Z -direction with a small amplitude a , then its time varying potential in the space is

$$\phi_o e^{i\omega t}$$

where

$$\phi_o = -a \left(\frac{\partial U}{\partial Z} \right) = \frac{3aMXZ}{r^5}$$

The flux pattern of the time varying field is given by $-\text{grad } \phi_o$. A diagram of this pattern is given in Fig. 4. Thus, if two detection coils are used, they can be placed along the horizontal direction (X -direction) of the magnetic field with their axes vertical. The coils must be connected series-opposing each other to obtain a net output signal.

A simplified version of the Foner magnetometer was actually used. A diagram of the system is given in Figs. 5 and 6. The sample was vibrated by means of a loudspeaker assembly. A teflon rod is glued to the loudspeaker and the sample is attached to the other end. The speaker must be placed at

FIG. 4

Diagram of time varying part of dipole field.

FIG. 5
Block diagram of vibrating-sample magnetometer circuit.

FIG. 6 (a)
Diagram of vibrating-sample magnetometer system.

FIG. 6 (b)
Detection coils

a sufficiently large distance from the detection coils so that the electromagnet in the loudspeaker assembly does not induce a signal in the coils. The coils are wound with several thousand turns of no. 40 copper magnet wire. The size and spacing of the coils are given in Fig. 6b. The signal from the detection coils is fed into a lock-in amplifier. The loudspeaker is driven at the same frequency as the reference frequency, which the lock-in is tuned to detect. A signal equal to this reference frequency is provided by the lock-in amplifier and sent to a modulation unit, which is a power amplifier used to drive the speaker. A small three inch electromagnet was used to provide the magnetic field. Fields up to 5000 gauss could be obtained. The sample is vibrated at a small amplitude. Vibration frequencies of 45 and 90 Hz were used. Frequencies of 60 Hz or multiples of this should be avoided. The system is calibrated by using a small sphere of nickel metal as a standard.

A serious problem which must be avoided is mechanical coupling between the vibrating system and the fixed detection coils. If the coils subtend a region of nonuniform magnetic field, the signal caused by this mechanical coupling will be field dependent. To eliminate this problem the apparatus was assembled in the basement of the Physics Research Building, where a pillar, which is isolated from the

the rest of the building, exists. The coils and magnet are placed on this pillar, and the loudspeaker assembly is attached to the walls of the building.

Magnetization measurements as a function of temperature were performed by allowing nitrogen gas, cooled by liquid nitrogen, to flow over the sample. A diagram of the cooling apparatus is given in Fig. 7. The temperature can be varied over the range from room temperature to 77°K by varying the flow rate of the nitrogen gas and by means of heater coils employed in the system. The temperature was monitored with a copper-constantan thermocouple. There were two serious problems connected with this arrangement. It was difficult to obtain good temperature control of the sample with this system. Another serious problem was the prevention of mechanical coupling between the flow system and the detection coils. By careful adjustment this coupling can be greatly reduced or eliminated. However, the system is not stable, and the coupling can occur again. Also, it should be noted that the thermocouple was not in direct contact with the sample, because wires could not be attached to the vibrating sample. This may cause some inaccuracy in determining the temperature of the sample. Nevertheless, it was possible to obtain good measurements with this system.

FIG. 7
Gas - flow cooling apparatus

c. Mutual Induction Method

The majority of the magnetization measurements were made using a mutual induction technique to measure the ac susceptibility of the samples. The method employs a mutual inductance bridge system designed after an arrangement described by E. Maxwell.³³ The bridge is a modification of the Hartshorn mutual inductance bridge, which is described in detail by de Klerk and Hudson.³⁴ The Hartshorn bridge uses a calibrated variable mutual inductor to cancel out the signal produced by the sample coils. In the Maxwell system a commercial decade autotransformer and a fixed mutual - inductor are used to replace the variable mutual inductor of the Hartshorn bridge. The autotransformer is connected across the secondary of the fixed mutual inductor and is adjusted to tap off the desired fraction of in-phase voltage. The autotransformer has high impedance and acts as a true voltage divider.

A diagram of the bridge system used is given in Fig. 8. The mutual inductance coils M_1 contain the sample, and these coils are placed in the Dewar. These coils are made by winding no. 40 copper magnet wire around a paper form. The coils are thus very close to the sample. The primary coil consists of about 1000 turns wound directly over the secondary coils. The secondary consists of two sections each of about 600 turns and wound in opposition to each other.

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FIG. 8 (a)

Diagram of mutual inductance bridge system.

FIG. 8 (b)
Sample mutual inductance coils, M_1

The mutual inductance of this coil arrangement with no sample is small, but not zero. The other part of the bridge consists of a fixed mutual inductance, M_2 , (Leed and Northrup, Fixed Inductor, #1540, 50 mh) and the decade autotransformer (Gertsch RT-60 Ratiotran). The primaries of the two inductors, M_1 and M_2 , are connected in series. The secondary of the fixed inductor, M_2 , is connected to the input of the autotransformer. The output of the autotransformer is connected to the secondary of the inductor M_1 containing the sample. It is connected so as to oppose the signal from the inductor M_1 . The bridge is balanced by adjusting the autotransformer, which takes a fraction of the in-phase voltage from the fixed inductor, M_2 , and adds it to the signal from the sample coils. For null detection a lock-in amplifier (Princeton Applied Research, model HR-8) was used. The lock-in amplifier puts out a dc signal proportional to the component of its input signal which is in phase with its reference frequency. Any component in the input signal not coherent with the reference frequency is averaged to zero. The modulation unit takes a signal at the reference frequency from the lock-in and amplifies it to drive the primaries of the inductance coils. A frequency of 4500 Hz was used in the experiment.

Generally, in most arrangements of the Hartshorn bridge, the primary of the coils containing the sample is kept at a constant temperature by placing the coils

in a liquid nitrogen bath. This arrangement was not possible with the Dewar available. Since the resistance of the coils changes with temperature, this factor as well as the change in susceptibility of the sample will cause the balance of the sample to change with temperature. However, it was possible to determine the unbalance as a function of temperature with no sample in the coils. Then the values obtained with a sample in place could be corrected. The system can be balanced by adjusting the autotransformer and using the lock-in as a null indicator, or the system can just be balanced at room temperature and continuous changes in the lock-in output signal recorded. This latter procedure was the method used to make measurements. Also in the Hartshorn bridge a variable potentiometer resistance is included in the circuit to compensate for the resistive voltage component of the susceptibility arising from phase shift in the secondary caused by ac losses in the sample. However, these changes in resistance are small. The potentiometer arrangement was not included in the present bridge system.

B. Conductivity Measurements

The bulk dc resistivities of the glass samples were measured using a two-probe pressure contact method. A voltage is applied across the sample and a standard resistor connected in series with the sample. The voltage drop across the standard resistor is then measured and the resistance of the sample calculated. A schematic diagram of the circuit is given in Fig. 9. The voltage drop across the standard resistor was measured with a Keithley microvolt-ammeter (model 150B). This microvolt meter has high internal impedance, so it can be assumed that the same current passes through the sample and the standard resistor. The resistance of the sample can be calculated from the relations

$$\frac{V_x}{R_x} = \frac{V_s}{R_s}$$

$$R_x = R_s \frac{V_x}{V_s} = R_s \frac{(V - V_s)}{V_s},$$

where R_s and V_s are, respectively, the resistance of the standard resistor and the potential drop across the standard resistor, R_x and V_x are the corresponding values for the sample, and V the applied voltage.

The resistivity ρ is given by $\rho = R_x \frac{A}{L}$, where A is the cross-sectional area of the sample and L is its length. Note that this definition of resistivity

FIG. 9

Schematic diagram of circuit for resistivity measurements.

assumes the sample to be uniform in its properties.

There are a number of problems involved with making measurements on semiconductors and insulators:

- 1) Contact resistance, which usually occurs when semiconductor-metal contacts are present,
- 2) Surface effects, such as surface conductivity, water vapor or other atmospherically induced surface effects, and oxidation at the surface of the sample occurring mostly during cooling when sample is prepared. These factors can cause the surface to have a higher or a lower resistivity than the bulk.

- 3) Shielding and interference problems from stray radiofrequency and 60 - cycle fields.

- 4) Noise due to fluctuations in the contacts.

In an effort to reduce errors due to contact resistance and surface effects a method described by G. G. Harman and T. Higier⁴⁵ was used. This method involves determining the resistance vs. voltage characteristics of the sample. The resistance of the metal-semiconductor surface barrier is reduced as the applied voltage is increased. The method essentially involves determining the high voltage region where the barrier resistance is negligible. A voltage in this region is then chosen to perform the resistance measurements. The samples were sanded lightly with light grade sand paper. Silver paint was then used as an electrical contact. The paint was applied to opposite faces of

the sample and was allowed to air dry at room temperature. Two copper electrodes were used as probes and were applied to the painted contacts. A diagram of the sample holder is given in Fig. 10. This two-terminal device was designed so that it could be attached to the Dewar sample support rod to allow low temperature measurements to be made. With the sample in place silver paint is then applied around the base of the probes and to the paint already on the sample in order to reduce pressure fluctuations in the contacts. A guard electrode system was employed in order to eliminate surface conductivity. A guard ring was painted around the mid-section of the sample with the silver paint, and a copper probe is allowed to touch this ring. The probe is then painted over. Fig. 9 shows how the guard system is employed.

C. Dewar System

For low temperature studies an Andonian Associates, Inc. three liter liquid helium Dewar (model MHD-3L-30N) was employed. This Dewar allows a continuous change in temperature from 1.3°K to 350°K . The sample is cooled by allowing helium gas to flow over it. The helium is admitted into the sample changer from the liquid helium storage well through a throttle valve, heat-exchanger, and diffuser. Over the range 4.2°K to 350°K flow from the helium well to the sample chamber is induced by slightly pressuring the helium well. By varying the

FIG. 10

Sample holder for resistivity measurements.

flow rate of the helium with the throttle valve and by means of heaters present in the Dewar, it is possible to vary the temperature of the sample from 4.2°K to 350°K . Temperatures below 4.2°K are obtained by vacuum pumping on the sample chamber through the off-gas line. For operation just between 77°K and room temperature liquid nitrogen can be used in the helium well.

D. Temperature Measurement

For temperature measurements over the range 4.2°K to room temperature a copper constantan thermocouple was used (For calibration tables and a discussion of thermocouple thermometry see: "Low-Temperature Thermocouple Thermometry", R. L. Powell, M. D. Bunch, and L.P. Caywood, CEL National Bureau of Standards, Boulder, Colorado). The ice point (273°K) was used as a reference junction. To measure the potential difference a Varian dual channel strip chart recorder (model #G-2020) was used. Also, below 77°K a Keithley Instruments, Inc. microvolt-ammeter (model #150B) was used. By means of the zero suppression control, the microvolt meter was adjusted to have a zero reading at 77°K , allowing 0.01 millivolts to be read. For measurements below 4.2°K a CryoCal, Inc. germanium resistance temperature sensor (model CR1000) was employed. This was calibrated against helium vapor pressure. The Keithley microvolt meter was used to measure the voltages. The circuit

diagram for these resistance measurement is given in Fig. 11. To avoid excessive Joule heating a current of $\approx 1 \mu$ a was put through the sensing element. This was obtained by producing a 7 mv voltage drop across the 6.98 K precision resistor.

E. NMR Measurements

The nuclear magnetic resonance signals of the glass samples were obtained with a Varian, Wide Line NMR Spectrometer (model V-4200B). The dc output NMR signal was recorded on a Varian strip chart recorder (model G-14). The magnetic field was provided by a Varian 9 inch electromagnet (model V-3400) with a Fieldial magnetic field regulator.

F. Glass Preparation

The majority of this research involved an investigation of glass samples of the system $\text{Fe}_2\text{O}_3 - \text{Na}_2\text{O} - \text{B}_2\text{O}_3$. A few samples from the systems $\text{CoO} - \text{Al}_2\text{O}_3 - \text{SiO}_2$ and $\text{Fe}_2\text{O}_3 - \text{Li}_2\text{O} - \text{Na}_2\text{O} - \text{B}_2\text{O}_3$ were also studied. The iron containing systems are prepared by a similar procedure. The silicate glasses were prepared in this laboratory with an arc image furnace by M. E. Forrest. The preparation of glasses of the system $\text{Fe}_2\text{O}_3 - \text{Na}_2\text{O} - \text{B}_2\text{O}_3$ is described below.

The glass samples are made using reagent grade chemicals. For the iron-sodium borate glasses the appropriate weights of the chemicals sodium carbonate,

64

R_T
 R_0
 R_1
 R_2 ($\sim 350\Omega$), R_3 ($\sim 720\Omega$)

FIG. 11

Circuit diagram for resistance temperature sensor.

Na_2CO_3 , boric acid, H_3BO_3 , and ferric oxide, Fe_2O_3 are mixed and then heated in a 20 ml platinum crucible. Most of the samples were heated over a Fisher Blast Burner using a compressed air and gas mixture. Some samples were made using the hotter flame of a Fisher Multi-Flame Burner, which uses a gas and oxygen mixture. The melt is heated for approximately an hour. After heating the melt is either poured into an aluminum mold and formed into a cylinder, or it is squashed between two flat aluminum plates and formed into thin flat disks. The sample is quenched faster by using the latter method. Often the samples of high iron concentrations will shatter or crack immediately after cooling. In an effort to prevent strains in the sample, several samples were allowed to quench slowly by pouring the melt into heated molds or on heated plates.

Samples prepared to have the same compositions, containing the same weights of batch chemicals, are often found to have different properties. This problem is common in the preparation of glass materials for their properties which are found to be very sensitive to various factors in their history of preparation. The temperature of the melt is a factor that can affect the final properties of a sample. In adjusting the flame of the burner there is no way to be sure that the same temperature is always obtained. Also, all parts of the crucible are not at the same temperature. Non-uniformity of the melt could seriously affect the

the final properties of a sample. Sometimes small incompletely dissolved proportions of sample mixture form on the sides of the crucible, usually near the upper, cooler parts of the crucible. In order to prevent this the position of the crucible was constantly changed to allow all parts to be near the hottest part of the flame. Also, the crucible was periodically swirled to mix the melt. The Multi-Flame burner, having the hotter flame, probably provided a more uniform and completely dissolved melt. The time of heating and rate of cooling of the melt are other factors that influence the characteristics of the sample.

In making calculations of the sample compositions only the following chemical reactions are assumed:

Therefore, the batch mixture is given by

The water and carbon dioxide are assumed to be completely boiled off during heating of the melt. The sample compositions are given either in mole percentages of the components Na_2O , B_2O_3 and Fe_2O_3 or as weight percent

Fe_2O_3 in the mixture $\text{Na}_2\text{O} + \text{B}_2\text{O}_3 + \text{Fe}_2\text{O}_3$. The glass containing no Fe_2O_3 was chosen to be of composition 1/3 mole % $\text{Na}_2\text{O} + 2/3$ mole % B_2O_3 . To make the iron containing glasses, varying amounts of Fe_2O_3 are added to the same amounts of Na_2CO_3 and H_3BO_3 , which give the above mole percentages of Na_2O and B_2O_3 . The experimental investigation was concerned mainly with high iron concentrated glasses, so all effort was concerned with making and studying glasses in the composition range of from 25 to 40 weight percent Fe_2O_3 .

In making the susceptibility measurements employing the mutual induction method, the samples in the shape of cylinders could be put directly in the coils. The flat samples were broken and crushed into a powder. Then the powder was put in cylindrical paper containers made to be of the same size as the cylindrical samples. For the vibrating sample magnetometer and the conductivity measurements, small beads and broken pieces of glass samples were used.

CHAPTER VI

EXPERIMENTAL RESULTS

A. Samples

The materials that were studied were glasses of the following systems: $\text{Fe}_2\text{O}_3 - \text{Na}_2\text{O} - \text{B}_2\text{O}_3$, $\text{CoO} - \text{Al}_2\text{O}_3 - \text{SiO}_2$, and $\text{Fe}_2\text{O}_3 - \text{Li}_2\text{O} - \text{Na}_2\text{O} - \text{B}_2\text{O}_3$. The compositions of the samples, investigated, are given in Tables I-III. The compositions are given in terms of weight percent of the transition metal oxide present and, also, in terms of molar percent of the various constituents present. These compositions are calculated from the weights of the batch chemicals used to prepare the glass samples. The samples of the system $\text{Fe}_2\text{O}_3 - \text{Na}_2\text{O} - \text{B}_2\text{O}_3$ can not be characterized uniquely by their batch percentages, for samples prepared to have the same composition were often found to have different properties. Not enough samples of the other systems were investigated to tell if this was true for them also.

B. Magnetization Results

The magnetization as a function of applied magnetic field was measured for some samples of the glass system $\text{Fe}_2\text{O}_3 - \text{Na}_2\text{O} - \text{B}_2\text{O}_3$. These measurements were made at room temperatures, using the vibrating sample magnetometer. The magnetometer was calibrated by using a small nickel

TABLE I
COMPOSITION OF Fe_2O_3 - Na_2O - B_2O_3 SAMPLES

SAMPLE	WT % Fe_2O_3	MOLAR %		
		Fe_2O_3	Na_2O	B_2O_3
90	18.2	8.5	30.6	60.8
91	24	11.9	29.3	58.7
92	24.5	12.2	29.2	58.5
93	25	12.4	29.1	58.3
94	28	14.2	28.5	57.1
95	28	14.2	28.5	57.1
96	30	15.4	28.1	56.3
101	25	12.4	29.1	58.3
102	26	13	28.9	57.9
103	27	13.7	28.7	57.5
104	28	14.2	28.5	57.1
105	28	14.2	28.5	57.1
106	29	14.8	28.3	56.7
107	29	14.8	28.3	56.7
108	30	15.4	28.1	56.3
109	30	15.4	28.1	56.3
110	30	15.4	28.1	56.3
111	33	17.4	27.5	55
112	35	18.6	27.1	54.2
113	35	18.6	27.1	54.2
114	37	20.1	26.6	53.2
115	40	22.2	25.9	51.8
	0	0	33.3	66.6

TABLE II
COMPOSITION OF $\text{CoO} - \text{Al}_2\text{O}_3 - \text{SiO}_2$ SAMPLES

SAMPLE	WT % CoO	MOLAR %		
		CoO	Al_2O_3	SiO_2
506	42.7	40	10	50
525	61.4	60	10	30
527	73.3	71.2	5.1	23.7
528	85.2	83	1.3	15.5

TABLE III
COMPOSITION OF Fe_2O_3 - Li_2O - Na_2O - B_2O_3 SAMPLES

SAMPLE	WT % Fe_2O_3	MOLAR %			
		Fe_2O_3	Li_2O	Na_2O	B_2O_3
568	18.7	7.9	15.3	15.3	61.4
567	21.7	9.69	15.05	15.05	60.2
581	25	11.4	14.75	14.75	59.06
587	30	14.16	14.3	14.3	57.23

sphere as a standard. The results of these measurements are given in Figs 12,13. The low iron concentration sample 90 gives a linear magnetization vs. field dependence. All of the other samples shown give a non-linear dependence. The initial susceptibility χ_0 , calculated from the initial slope of these curves, and an estimation of the saturation magnetization σ_s (when possible), obtained by extrapolation from these curves, are given in Table IV. The magnetization values are given in c.g.s. electromagnetic units (e.m.u.). Note that the magnetization values, reported above, are given as per gram of the glass sample.

The differential magnetic susceptibility of the glass samples was measured using the mutual induction method. To calibrate the mutual inductance bridge, manganese dioxide (MnO_2) and ferric ammonium sulfate ($\text{FeNH}_4(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$) were used as standards. For MnO_2 the room temperature susceptibility is $2280 \times 10^{-6} / \text{mole}$.³⁵ For $\text{FeNH}_4(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$ the Curie constant is 4.37 per mole. Both of these materials were used as standards for the room temperature susceptibility measurements. However, since ferric ammonium sulfate obeys Curie's law to low temperatures, it was used to calibrate the susceptibility vs. temperature measurements.

The room temperature susceptibility measurements were obtained by first balancing the bridge with no

FIG. 12

Magnetization vs. applied magnetic field for iron-sodium borate samples 90, 92, 93, 94, 96.

FIG. 13

Magnetization vs. applied magnetic field for iron-sodium borate sample 95.

TABLE IV
MAGNETIZATION VS. APPLIED FIELD RESULTS

SAMPLE	WT % Fe_2O_3	χ_o e.m.u./gm. sample	σ_s e.m.u./gm. sample
90	18.2	18.4×10^{-6}	-
91	24	154×10^{-6}	0.25
92	24.5	90×10^{-6}	> 0.25
93	25	430×10^{-6}	0.5
94	28	500×10^{-6}	> 0.65
95	28	3350×10^{-6}	7
96	30	150×10^{-6}	> 0.3

sample in the coil, then with the sample in the coil either balancing the bridge again or just measuring the recorder deflection. The main sources of error in this measurement result from slight movement of the coil during insertion of the sample, positioning of the samples in the coil, and the different sample shapes causing the filling factor to vary with the samples.

The ac susceptibility χ values for samples of the system $\text{Fe}_2\text{O}_3 - \text{Na}_2\text{O} - \text{B}_2\text{O}_3$, taken at room temperature, are given in Table V. No applied magnetic field was used to make these measurements. The ac susceptibility values are given as per gram of the sample. A plot of these susceptibility values vs. the Fe_2O_3 concentration is given in Fig. 14. In general there is an increase in the susceptibility with the Fe_2O_3 concentration. A few samples have values much greater than the majority of the other samples.

The susceptibility of the glass samples was measured as a function of temperature. The temperature of the sample was made to vary slowly, and the continuous change in the susceptibility was recorded. The resistance of the sample mutual induction coils changes with temperature, thus causing the balance of the system, with no sample, to change with temperature. A sensitivity of the apparatus had to be chosen to allow both for changes in the susceptibility of the samples to be

TABLE V
AC SUSCEPTIBILITY OF Fe_2O_3 - Na_2O - B_2O_3 SAMPLES

SAMPLE	WT % Fe_2O_3	χ e.m.u./gm.
101	25	25×10^{-6}
102	26	53×10^{-6}
103	27	238×10^{-6}
104	28	47×10^{-6}
105	28	136×10^{-6}
106	29	173×10^{-6}
108	30	778×10^{-6}
109	30	1536×10^{-6}
110	30	213×10^{-6}
112	35	2450×10^{-6}
113	35	496×10^{-6}
114	37	422×10^{-6}

FIG. 14
AC susceptibility vs. weight percent Fe_2O_3
for iron-sodium borate samples.

measured and for changes in the balance with no sample to be easily determined. This forced measurements to be taken with a sensitivity of about 25×10^{-6} e.m.u. although it was possible to detect changes in susceptibility of about 5×10^{-6} e.m.u.

The temperature dependence of the susceptibility for most of the samples has been measured to liquid helium temperatures. The susceptibility of a few samples was measured to about 1.8°K . The ac susceptibility vs. temperature curves for samples of the system $\text{Fe}_2\text{O}_3 - \text{Na}_2\text{O} - \text{B}_2\text{O}_3$ are given in Figs. 15(A)-21(A). The susceptibilities of the samples with room temperature values under about 600×10^{-6} e.m.u./gm. increases with decreasing temperature, similar to a temperature dependence of a paramagnetic material.

The samples with room temperature susceptibilities over about 600×10^{-6} e.m.u./gm. have a decrease in their susceptibilities with decreasing temperature. This latter temperature dependence indicates an antiferromagnetic type ordering. These last samples also have an increase in their susceptibility as the temperature is decreased below the transition temperature. The transition also occurs at slightly different temperatures when the sample is cooled and heated. This may be due to the fact that, even though the temperature is varied slowly, the sample as a whole does not come to complete thermal equilibrium. The values for the transition temperature obtained from the heating curve

FIG. 15

- (A) AC susceptibility vs. temperature
 (B) Inverse susceptibility vs. temperature for iron-sodium borate sample 102.

SAMPLE 105

FIG. 16

- (A) AC susceptibility vs. temperature.
(B) Inverse susceptibility vs. temperature for iron-sodium borate sample 105.

FIG. 17

- (A) AC susceptibility vs. temperature
(B) Inverse susceptibility vs. temperature for iron-sodium borate sample 110.

SAMPLE 113

(A)

Fig. 18

- (A) AC susceptibility vs. temperature.
 (B) Inverse susceptibility vs. temperature for iron-sodium borate sample 113.

FIG. 19

- (A) AC susceptibility vs. temperature.
(B) Inverse susceptibility vs. temperature for iron-sodium borate sample 114.

FIG. 20

AC susceptibility vs. temperature curves for iron-sodium borate samples 108 and 112 to 77°K and for sample 109 to 4.2°K .

FIG. 21

- (A) AC susceptibility vs. temperature for region 1.8-100 $^{\circ}\text{K}$.
 (B) Inverse susceptibility vs. temperature for iron-sodium borate sample 109.

are given in Table VI. A transition was also observed in sample 93 using the vibrating-sample magnetometer. This sample is also included in Table VI.

The inverse susceptibility vs. temperature of the samples was plotted. These curves are shown in Figs 15B-21B. From the slope of these curves the Curie constant C is found, and the effective magnetic moment μ_{eff} defined as

$$\mu_{\text{eff}} = \left(\frac{3kC}{N \mu_B^2} \right)^{\frac{1}{2}}$$

can be calculated. The Curie constant was converted to the value for a mole of iron atoms, and then Avogadro's number was used for N in the formula for

μ_{eff} . The results are given in Table VI. For the one sample (109) that had a slight increase in susceptibility above its transition temperature, the inverse susceptibility vs. temperature was plotted for this temperature region ($T > T_N$). It was found that the effective magnetic moment is 50 and that the paramagnetic Neel temperature θ is -520°K . The generalized molecular field theory predicts that θ is related to the sum of the exchange interactions acting on a given atom as follows

$$\theta = \frac{2S(S+1)}{3k} \sum_{m=1}^{N'} z_m J_m$$

If the value for θ is taken as -520 and the value $S = 5/2$ is assumed, it is found that

TABLE VI

MAGNETIZATION RESULTS FOR $\text{Fe}_2\text{O}_3 - \text{Na}_2\text{O} - \text{B}_2\text{O}_3$ SYSTEM

SAMPLE	WT % Fe_2O_3	T_N ($^{\circ}\text{K}$)	θ ($^{\circ}\text{K}$)	μ_{eff}
102	26			4.19
* 105	28			3.12
108	30	113		
109	30	126	-520	50 ($T > T_N$)
* 109	30			3.36 ($T < T_N$)
110	30			3.95
112	35	113		
* 113	35			5.6 (under 4°K)
113	35			7.3 (above 4°K , 3000 gauss)
* 113	35			10.5 (above 4°K , 0 gauss)
114	37			4.95
114	37			7.0 (6000 gauss)
93	25	~ 130		

* susceptibility measured to 1.8°K .

$$\sum_{m=1}^{N'} z_m J_m = -125 \times 10^{-16} \text{ erg.}$$

The inverse susceptibility is also plotted for the low temperature region where the samples show an increase in their susceptibilities. The curves for all the samples, when extended to zero temperature, intercept the positive inverse susceptibility axis. This can be interpreted in two ways. One way would be to assume that the susceptibility has the form for an antiferromagnetic material above the Neel temperature of

$\chi = C/(T-\theta)$, where θ is a negative constant. The other way, which is more probable, is to assume that the susceptibility is the sum of a temperature-independent susceptibility and a temperature-dependent paramagnetic susceptibility. The paramagnetic susceptibility can be of the forms $\chi = C/T$ or $\chi = C/(T-\theta)$, where θ is a positive constant.

Susceptibility measurements were also made in an applied magnetic field for some of the samples. The magnetic field was parallel to the axis of the coil. For those samples that had a decrease in their susceptibilities in zero field, in a magnetic field of 1000 gauss there was no decrease or just a very small decrease in the susceptibility. Fig. 22, shows the results for sample 109 in a field of 2000 gauss. Values of μ_{eff} for the 37% sample in a field of 6000 gauss and also in zero field are given in Table VI.

SAMPLE 109
(2000 GAUSS)

FIG. 22

AC susceptibility vs. temperature for iron-sodium borate sample 109 in a magnetic field of 2000 gauss.

The change in the ac susceptibility of the samples as a function of the applied magnetic field is given in Fig. 23. The samples having very high room temperature susceptibility values have a large decrease in their ac susceptibility with increasing field.

The room temperature magnetic susceptibility values for the glass system $\text{CoO} - \text{Al}_2\text{O}_3 - \text{SiO}_2$ are given in Table VII. The susceptibilities of these glasses were measured to liquid helium temperatures. The results are given in Figs. 24-27. The three higher percentage samples show an increase then a decrease in their susceptibility as the temperature is lowered. This dependence is characteristic of typical antiferromagnetic ordering. The transition temperatures are given in Table VIII. There seems to be a dependence on the transition temperature with glass composition. The lower percentage samples having a slightly lower transition temperature. The inverse susceptibilities of these glasses were plotted and their θ and μ_{eff} values determined. The results are given in Table VIII. The susceptibilities all show a $\chi = C/(T-\theta)$ dependence on temperature with the θ values negative.

The susceptibilities of these glasses seems to be independent of an applied magnetic field. Also the transition seems to be just affected slightly or unaffected to fields of 5000 gauss.

The room temperature ac susceptibilities for the glass system $\text{Fe}_2\text{O}_3 - \text{Li}_2\text{O} - \text{Na}_2\text{O} - \text{B}_2\text{O}_3$ are given in Table IX. These values are comparable to or larger than

FIG. 23

Relative change in ac susceptibility as a function of applied magnetic field for iron-sodium borate samples 105, 109, 113, and 114.

TABLE VII
AC SUSCEPTIBILITY OF $\text{CoO} - \text{Al}_2\text{O}_3 - \text{SiO}_2$ SYSTEM

SAMPLE	WT %	χ
	CoO	e.m.u./gm. sample
506	42.7	26×10^{-6}
525	61.4	45×10^{-6}
526	73.3	51.5×10^{-6}
528	85.2	51.2×10^{-6}

SAMPLE 506

(A)

FIG. 24

- (A) AC susceptibility vs. temperature
(B) Inverse susceptibility vs. temperature for cobalt aluminum silicate sample 506.

SAMPLE 528

(A)

FIG. 27

- (A) AC susceptibility vs. temperature.
(B) Inverse susceptibility vs. temperature for cobalt aluminum silicate sample 528.

SAMPLE 527

FIG. 26

- (A) AC susceptibility vs. temperature.
(B) Inverse susceptibility vs. temperature for cobalt aluminum silicate sample 527.

SAMPLE 525

(A)

$$\chi^{-1}$$

$$\left(\frac{\text{gm}}{\text{e.m.u.}} \right)$$

(B)

FIG. 25

- (A) AC susceptibility vs. temperature.
 (B) Inverse susceptibility vs. temperature for cobalt aluminum silicate sample 525.

TABLE VIII
MAGNETIZATION RESULTS FOR $\text{CoO} - \text{Al}_2\text{O}_3 - \text{SiO}_2$ SYSTEM

SAMPLE	WT % CoO	T_N ($^{\circ}\text{K}$)	θ ($^{\circ}\text{K}$)	μ_{eff}
506	42.7			5.6
525	61.4	4.2-6	-42	7.5
527	73.3	8 - 10	-32	4.8
528	85.2	8 - 10	-27	5.3

TABLE IX
AC SUSCEPTIBILITY OF $\text{Fe}_2\text{O}_3 - \text{Na}_2\text{O} - \text{Li}_2\text{O} - \text{B}_2\text{O}_3$ SYSTEM

SAMPLE	WT % Fe_2O_3	χ e.m.u./gm. sample
568	18.7	20×10^{-6}
567	21.7	916×10^{-6}
581	25	2650×10^{-6}
587	30	$10,675 \times 10^{-6}$

the $\text{Fe}_2\text{O}_3 - \text{Na}_2\text{O} - \text{B}_2\text{O}_3$ system. The temperature dependence of the susceptibilities for a few of these glasses has been studied. The sample 581 and 587 were found to have a decrease in their susceptibilities with decreasing temperature characteristic of an anti-ferromagnetic transition. The change in the ac susceptibility as a function of applied field for these two samples is given in Fig. 28.

C. Conductivity Measurements

The dc conductivities of the glass samples were measured using a two-terminal contact method. The resistivity values for some samples of the $\text{Fe}_2\text{O}_3 - \text{Na}_2\text{O} - \text{B}_2\text{O}_3$ glass system are given in Table X. These values were taken at room temperature and without a guard electrode. Some of the samples have low values of resistivity of the order of 10^4 to 10^6 ohm-cm. The glass samples of the systems $\text{CoO} - \text{Al}_2\text{O}_3 - \text{SiO}_2$ and $\text{Fe}_2\text{O}_3 - \text{Li}_2\text{O} - \text{Na}_2\text{O} - \text{B}_2\text{O}_3$ gave no measurable conduction. Thus, these samples must have resistivities of the order of 10^{12} ohm-cm. or higher.

A study was made of the time dependence of the electrical resistance of the iron-sodium borate glass samples, in order to determine whether or not the conduction mechanism is electronic or just ionic. If the conductivity is due to ions, the resistance of the material under a dc field will increase in time due to polarization.³⁷ The resistance of the samples was

FIG. 28
Relative change in AC susceptibility as a function
of applied magnetic field for iron-lithium-sodium
borate samples 581 and 587.

TABLE X

RESISTIVITY OF Fe_2O_3 - Na_2O - B_2O_3 GLASS SYSTEM

SAMPLE NUMBER	WT. % Fe_2O_3	RESISTIVITY ohm-cm	APPLIED VOLTAGE volts
101	25%	2.5×10^{10}	30
103	27%	8.8×10^9	30
104	28%	1.4×10^{10}	30
108	30%	9×10^5	30
111	33%	2.9×10^9	30
112	35%	2.3×10^5	30
113	35%	2.4×10^4	2
115	40%	1×10^4	2

measured at room temperature under an applied dc voltage of 200 volts for a period of about 24 hours. The results of these measurements are given in Figs. 29(A) and 29(B). The resistance of sample number 101 (25%) increases by a factor of about 50 during the 24 hour period. The sample number 104 (28%) shows a relatively small increase in resistance for about 4 hours and then its resistance remains fairly constant at the high value. The resistances of the glass samples number 108 (30%) and number 112 (35%) changes little from their low values during the 24 hour period. These results suggest that the glass sample number 101 is mainly an ionically conducting glass, and the sample numbers 108 and 112 are mainly electronic conducting.

The resistance versus applied voltage characteristics of the samples were measured in order to determine the voltage region where the resistance of the sample is ohmic. These results are given in Figs. 30(A) and 30(B). The high resistance samples are ohmic after about 5 volts. The low resistance glasses start becoming ohmic after about 25 volts.

The temperature dependence of the resistivity was studied from room to liquid nitrogen temperatures. The bulk resistivity of the sample was what was of interest, so a guard electrode was used in order to exclude the contributions from surface conductivity. The guard electrode did make a small difference in the value of the measured resistance. The resistance

(A)

(B)

FIG. 29

Resistance as function of time for some iron-sodium borate samples under an applied voltage of 200 volts.
(A) Samples 101 and 104. (B) Samples 108 and 112.

FIG. 30

Resistance vs. applied voltage characteristics for some iron-sodium borate samples.

(A) Samples 101, 103, 104, and 111. (B) Samples 108 and 112.

vs. voltage curves for two samples with and without a guard electrode are given in Figs. 31 (A) and 31 (B). In the temperature studies an applied voltage of 70 volts was used. The resistances of the high resistance glasses were too large for the apparatus to give clear results. For the samples number 108 (30%) and number 112 (35%) the resistivity increases by a factor greater than 10^4 as the temperature is lowered to 77°K . The results are shown in Figs. 32 and 33. These resistivity vs. inverse temperature curves consist of several straight line segments of different slope. The resistivity ρ , thus, appears to decrease exponentially with increasing temperature and can be assumed to follow a relation of the form

$$\rho = \rho_0 e^{E/kT}$$

where E is an activation energy for the motion of the current carriers. A change in the slope of the resistivity curve could correspond either to different conduction mechanisms or to different mobilities for the current carriers with differing activation energies. The values obtained for the activation energies of samples number 108 and number 112 are given on their resistivity curves in Figs. 32 and 33. The magnetization measurements for these two samples showed an antiferromagnetic type transition occurring at 113°K . The antiferromagnetic exchange energy kT_N calculated from $T_N = 113^\circ\text{K}$ is 0.0097 ev. The activation energies

(A)

SAMPLE 101

FIG. 31

Resistance vs. applied voltage curves with and without a guard electrode for sample iron-sodium borate sample. (A) Sample 101 (B) Sample 112

FIG. 32

Resistivity vs. inverse temperature curve for iron-sodium borate sample 108, including values for activation energy, E .

FIG. 33

Resistivity vs. inverse temperature curve for iron-sodium borate sample 112, including values for activation energy, E .

below 113°K obtained for samples number 108 and number 112 are, respectively, 0.0078 ev and 0.0096 ev. Thus, the number 112 (35%) sample gives an activation energy that closely corresponds with the exchange energy for ordering. The sample number 108 (30%) gives an activation energy that has a 20% deviation from the value for the exchange energy. However, the resistivity of sample number 108 is high in this temperature region, and there is a greater uncertainty in the measurements; also, there is greater scattering of points in this region and there is some question as to the best straight line to draw.

A rough thermoelectric power (Seebeck effect) measurement was performed on the number 108 and number 112 samples. In this measurement a temperature difference between the ends of a sample gives rise to an emf. The mobile charge carriers (electrons or holes) tend to diffuse from the hot to the cold junction, so that the cold junction acquires a potential of the same sign as the carriers.³⁸ In the actual experiment the sample was placed in the two-terminal probe, and one terminal was heated with a hot soldering iron. The resulting potential difference was measured with a Keithley microvolt ammeter (model 150B). The results indicated that the charge carriers are negative. The conductivity results, thus, indicate that the number 108 and number 112 samples are n-type semiconducting glasses.

D. NMR Measurements

The nuclear magnetic resonance spectra of the boron B" nucleus was studied for glass samples of the system $\text{Fe}_2\text{O}_3 - \text{Na}_2\text{O} - \text{B}_2\text{O}_3$. The B" NMR spectrum in sodium borate glasses consists of two lines.³⁹ One line is due to boron atoms bonded to three oxygen atoms. This is a planar configuration where the boron atoms form trigonal bonds with the oxygen atoms. The electric field gradient at the boron nucleus arises almost entirely from the bonding electrons in the boron-oxygen bonds. The nuclei of boron atoms in this configuration experience a large electric nuclear quadrupolar interaction from the field gradient which perturbs the magnetic energy levels and results in a very broad NMR line width in a powder or glass sample. The other resonance line is due to boron atoms bonded to four oxygen atoms. This is a tetrahedron configuration with the oxygen atoms at the four vertices of the tetrahedron and the boron atom at the geometric center. The boron nuclei in this configuration experience little or no quadrupolar interaction from the bonding electrons and, thus, have a narrow and unperturbed NMR line.

The B" NMR spectrum was studied in the iron-sodium borate glass system of high iron concentrations of 25 - 35 weight percent Fe_2O_3 . The B" spectra due to boron atoms in both the three and four-coordinated configurations could be observed in all the samples

from 25 - 28 weight percent Fe_2O_3 and also in the 30 weight percent sample 110. The boron resonance line due to the borons in the four-coordinated configuration was observed in all the glass samples. Some representative B" NMR spectra of the iron-sodium borate glass samples are given in Figs. 34 - 40. The NMR spectrometer provides the first derivative of the resonance adsorption curve. These spectra were obtained using different gain settings on the NMR spectrometer, and the samples are of different weights. However, the intensity of the resonance is not to be considered here, just the line width of the spectra is to be studied. These spectra were taken at a frequency of 13.1 MHz. A modulation magnetic field of amplitude 6.8 gauss peak to peak was used to observe resonance in these glass samples. However, the samples 109, 112, and 113 give lines that were so broad that they could barely be observed. A higher modulation field of amplitude 17 gauss peak to peak was used to detect the resonance lines in these samples. The line width was determined by measuring the separation in gauss between the two peaks of the first derivative curve. The spectrum of the four-coordinated boron nuclei is of special interest, because their line width should be less a function of the quadrupolar interaction with its bonding electrons and more a function of magnetic dipolar interactions with its environment. The line width of the four-coordinated boron line as

113

FIG. 34

B" NMR resonance line in iron-sodium borate sample 101.

114

FIG. 35

B" NMR resonance line in iron-sodium borate sample 102.

115

FIG. 36

B" NMR resonance line in iron-sodium borate sample 105.

116

FIG. 37

B" NMR resonance line in iron-sodium borate sample 105.

(A)

(B)

FIG. 38

B" NMR resonance line in iron-sodium borate
sample 109.

(A) Modulation field of 6.8 gauss peak to peak.

(B) Modulation field of 17 gauss peak to peak.

FIG. 39

B" NMR resonance line in iron-sodium borate sample 105.

119

(A)

(B)

FIG. 40

B" NMR resonance line in iron-sodium borate sample 113.

(A) Modulation field of 6.8 gauss peak to peak.

(B) Modulation field of 17 gauss peak to peak.

a function of the iron concentration is given in Table XI. In general, the line width increases with the iron concentration. The resonance lines for the samples 109, 112, and 113 are so broad that a good estimate of their line width really can not be made by measuring the separation between the peaks. A graph of the line width vs. the Fe_2O_3 concentration is given in Fig. 41. When this graph is compared to the plot of the susceptibility of the samples vs. their Fe_2O_3 concentration, given in Fig. 14, it is noted that the two graphs have a very similar distribution of points. Thus, the B" NMR line width of a sample corresponds closely with the magnetic susceptibility of the sample.

TABLE XI

B" NMR LINE WIDTH FOR Fe_2O_3 - Na_2O - B_2O_3 SAMPLES

SAMPLE	WT % Fe_2O_3	LINE WIDTH (gauss)
101	25	8.6
102	26	9.6
103	27	13.3
104	28	10.1
105	28	12.5
106	29	19.8
108	30	12.5
109	30	18
110	30	10.9
112	35	23
113	35	20

FIG. 41

B" NMR line width vs. Fe_2O_3 concentration.

CHAPTER VII

DISCUSSION AND CONCLUSIONS

The outstanding properties observed for the glass samples are the antiferromagnetic type ordering observed in the three glass systems, the high susceptibilities of the $\text{Fe}_2\text{O}_3 - \text{Na}_2\text{O} - \text{B}_2\text{O}_3$ and $\text{Fe}_2\text{O}_3 - \text{Li}_2\text{O} - \text{Na}_2\text{O} - \text{B}_2\text{O}_3$ glass systems, and the low resistivities observed in some of the $\text{Fe}_2\text{O}_3 - \text{Na}_2\text{O} - \text{B}_2\text{O}_3$ samples.

The high susceptibilities of the $\text{Fe}_2\text{O}_3 - \text{Na}_2\text{O} - \text{B}_2\text{O}_3$ and $\text{Fe}_2\text{O}_3 - \text{Li}_2\text{O} - \text{Na}_2\text{O} - \text{B}_2\text{O}_3$ samples and the fact that some of the iron-sodium borate samples have magnetization curves showing saturation effects occurring at room temperature, suggests, at first, that these glasses might contain some small amount of ferromagnetic or ferrimagnetic material, such as magnetite (Fe_3O_4) or maghemite ($\gamma - \text{Fe}_2\text{O}_3$), possibly in a superparamagnetic state since no hysteresis was observed. These two magnetic substances could very possibly be formed during preparation of the samples by some reducing process occurring in the $\alpha - \text{Fe}_2\text{O}_3$ used in making the samples.⁴⁰ Obviously, there is also the possibility that there are some fine and superparamagnetic particles of $\alpha - \text{Fe}_2\text{O}_3$ present in the glasses, due to saturation in the glass melt and, thus, all the $\alpha - \text{Fe}_2\text{O}_3$ is not dissolved. However, the susceptibilities of most of the iron-sodium borate and iron-lithium sodium borate samples are much higher than would be expected to be caused by just individual $\alpha - \text{Fe}_2\text{O}_3$ particles. The room temperature susceptibilities of the samples 102, 112, 113, 95, and

587 are, respectively, 53×10^{-6} , 2450×10^{-6} , 496×10^{-6} , 3350×10^{-6} , and $10,675 \times 10^{-6}$ e.m.u./gm.

The susceptibilities of these samples per gram of Fe_2O_3 are respectively 200×10^{-6} , 7000×10^{-6} , 1420×10^{-6} , $11,960 \times 10^{-6}$, and $35,580 \times 10^{-6}$ e.m.u./gm. of Fe_2O_3 .

Assuming the presence of just superparamagnetic

α - Fe_2O_3 in the samples 93 and 95, the particle size (2r) calculated from the relation

$$\frac{I}{H} = \frac{4\pi I_s^2 r^3}{9 k T}$$

using the values obtained from the magnetization curves of Figs. 12 & 13 are respectively 262 Å and 206 Å. It should be noted that the relation used to determine the particle size is likely to give the average size of the larger particles present. Assuming that the magnetization curve for sample 95 is due to superparamagnetic magnetite of concentration 0.01 gm. for 1 gram of sample, the particle size of approximately 60 Å is obtained for magnetite. Magnetite of this size is single domain and would be superparamagnetic.⁴¹

The iron in the iron-sodium borate glasses were studied using the Mossbauer effect. These measurements were performed by R. R. Bukrey and Dr. P. F. Kenealy. At room temperature the majority of the glass samples show no magnetic hyperfine spectrum and their Mossbauer spectrum consists of just a quadrupole split doublet.

This spectrum is characteristic of iron in a paramagnetic state, where since the relaxation time for transitions between the electronic levels is short, the magnetic hyperfine field at the nucleus has a time average of zero. Most of these samples exhibited a doublet characteristic of the ferric ion (Fe^{+++}). The samples 113 and 115 exhibit additional lines, consisting of a wider doublet, characteristic of divalent iron (Fe^{++}). The sample 95 exhibited a hyperfine spectrum indicating the presence of magnetite in the sample. The Mossbauer spectra for the glass samples, having the antiferromagnetic type transition, all showed hyperfine lines corresponding to

$\alpha - \text{Fe}_2\text{O}_3$. It should be noted that the Mossbauer spectrum for $\gamma - \text{Fe}_2\text{O}_3$ is very similar to $\alpha - \text{Fe}_2\text{O}_3$, and if a small amount, relative to the $\alpha - \text{Fe}_2\text{O}_3$, were present it would be difficult to detect. Some of the spectra with the $\alpha - \text{Fe}_2\text{O}_3$ lines have a slight indication of added structure which could be due to $\gamma - \text{Fe}_2\text{O}_3$. The Mossbauer spectra of these iron samples, showing the $\alpha - \text{Fe}_2\text{O}_3$ lines, was studied at room and liquid nitrogen temperatures. A Morin transition was observed to have occurred in the $\alpha - \text{Fe}_2\text{O}_3$, although the exact temperature of the transition was not determined.

Hematite ($\alpha - \text{Fe}_2\text{O}_3$) is of rhombohedral structure.⁴¹⁻⁴³ It has an antiferromagnetic spin structure with spins aligned in basal plane, at room temperature and above, and along the triad axis below the Morin transition (250°K), the spin flipping temperature. Between the Morin transition and the Curie temperature (675°K), $\alpha - \text{Fe}_2\text{O}_3$ has a very weak ferromagnetism, caused by spin canting in the basal

plane. The weak ferromagnetism is generally believed to vanish below the Morin transition, and it decreases as the crystal size gets smaller. The spin flipping temperature (Morin transition) has been observed to decrease with decreasing particle size.⁴⁴ In sufficiently fine particles (250Å) the spin flipping was not observed to occur above liquid nitrogen temperature. It should be noted that the Mossbauer spectra of the glass samples having the anti-ferromagnetic type transition showed no indication of the presence of magnetite or divalent iron. This is important because bulk magnetite has a transition in the vicinity of 113°K where its magnetization decreases with decreasing temperature.¹⁸ It therefore appears unlikely that magnetite is responsible for the observed transition. It should be noted that the size of the α -Fe₂O₃ particles, observed to undergo a Morin transition in the vicinity of 150°K, was 350Å⁴⁴ which is just a little larger than the estimations of particle size (200 - 265Å) obtained from the magnetization curves of two samples.

All the Fe₂O₃ - Na₂O - B₂O₃ samples show an increase in susceptibility with decreasing temperature at low temperatures. However, the inverse susceptibility vs temperature curves for several of the samples is not a continuous straight line but has a change in slope under about 4°K. These results could possibly be explained, in part, by the presence of a combination of ferric ions and fine particles of α -Fe₂O₃ with a distribution of particle sizes. The susceptibility of the very fine particles becoming dominant as the temperature is lowered. The effective magnetic moments, calculated from the inverse susceptibility vs temperature

results, for several of the samples are lower than that obtained for a free ferric ion in a paramagnetic salt. This can be explained by the possibility of some of the fine particles being antiferromagnetic and having small or no effective moments. Also, it can be explained by the possibility of antiferromagnetic interactions occurring between some of the particles, causing their total effective moment to be smaller than that of the sum of all their individual ions. Such exchange interactions between particles are to be expected when there is a high concentration of particles and at very low temperatures. There was also evidence of a temperature-independent susceptibility being present. For sample 109 it is about 500×10^{-6} e.m.u./ gm sample. This is fairly large and cannot be assumed due to large α - Fe_2O_3 fine particles.

The Fe_2O_3 - Na_2O - B_2O_3 glass samples which have the antiferromagnetic type transition, also have other properties that distinguish them from the other samples of the system. The susceptibilities of these samples at room temperature are much larger than the other samples in the system. Their Mossbauer spectra show lines corresponding to α - Fe_2O_3 . Also these samples were found to be n - type semiconductors. The temperature dependence of the resistivity of these samples showed a change in activation energy to a value closely corresponding to the antiferromagnetic exchange energy of the sample, in the temperature region where the sample had the magnetic transition. The conductivity of samples could be explained by the presence of mixed valence states of plus two and plus three valent iron ions in the sample. However,

the Mossbauer spectra of these samples gave no or very little indication of the presence of divalent iron. The sample showing the presence of divalent iron did have a low value of resistivity, however. The Fe_2O_3 - Li_2O - Na_2O - B_2O_3 and CoO - Al_2O_3 - SiO_2 glass systems all had high values of resistivity. Thus there is evidence for the presence of superparamagnetic and possibly large fine particles of α - Fe_2O_3 in the Fe_2O_3 - Na_2O - B_2O_3 glass system. The room temperature susceptibility and the magnitude of the transition, observed in some of the samples, are too large to be expected from fine particles of pure α - Fe_2O_3 particles. However, possibly a small particle could become so deformed or changed, perhaps by the intervention of sodium ions or water particles, to possess a very large moment. Also, there may be exchange interactions between the particles and ferric ions in the glass network, and this could be causing the observed magnetic properties. The Morin transition observed in the α - Fe_2O_3 Mossbauer spectra could possibly be related to the antiferromagnetic transition observed in some of the glass samples.

Some samples of the CoO - Al_2O_3 - SiO_2 glass system were also observed to have an antiferromagnetic type transition. The transition temperature was slightly higher for the higher cobalt concentrated samples than for the sample a little less concentrated. The effective moments obtained for the glass samples, except for one

sample, are of the order found in bulk CoO of 5.1. The susceptibility curves for the $\text{CoO} - \text{Al}_2\text{O}_3 - \text{SiO}_2$ samples having the maximum in the susceptibility are of different shape than the iron glass susceptibility curves for the samples showing the decrease in susceptibility. The magnetization results for the $\text{CoO} - \text{Al}_2\text{O}_3 - \text{SiO}_2$ glass system could possibly be explained, in part, by the presence of fine CoO particles. However, no Mossbauer studies can be performed on the cobalt sample, but X - ray studies revealed no diffraction peaks. The ordering observed must then be due either to the glassy material as a whole or to very fine CoO particles.

There may be some question as to whether to classify an amorphous material containing fine particles, rather than just molecules and irons, as a glass. This question is probably equivalent to determining what size microcrystal separates a glass from a non-glass. Is an amorphous material, containing a "microcrystal" so small as to give very weak or no X - ray diffraction peaks, a glass? Is an amorphous material, containing fine $\alpha - \text{Fe}_2\text{O}_3$ particles so small as to give faint or no X - ray diffraction peaks but shows a Mossbauer hyperfine pattern, a glass? Is an amorphous material, containing just ultra-fine superparamagnetic $\alpha - \text{Fe}_2\text{O}_3$ particles a glass? The answer to these questions depends on how a glass is to be defined.

The transition metal oxide glass systems studied here, whether they can be considered glasses or not, are very interesting systems for they are amorphous

and electrical conduction and magnetic ordering was observed in some of the samples.

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ABSTRACT

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Magnetization and Electrical Conductivity Studies of Some Transition Metal Oxide Glasses

Bulk magnetization versus temperature studies, nuclear magnetic resonance studies, and dc electrical conductivity studies were performed on the glass systems: iron-sodium borate ($\text{Fe}_2\text{O}_3 - \text{Na}_2\text{O} - \text{B}_2\text{O}_3$), cobalt-aluminum silicate ($\text{CoO} - \text{Al}_2\text{O}_3 - \text{SiO}_2$), and iron-lithium-sodium borate ($\text{Fe}_2\text{O}_3 - \text{Li}_2\text{O} - \text{Na}_2\text{O} - \text{B}_2\text{O}_3$). The investigation was concerned with the study of magnetic ordering and electrical conduction in amorphous materials, namely glasses. Glass samples were prepared containing large concentrations of some transition metal ions. Magnetic transitions, that were characteristic of an antiferromagnetic type of ordering, were observed in some of the glasses of the three systems studied. Also, some glass samples of the iron-sodium borate system were found to be semiconductors. The possibility that the magnetic ordering arises from microcrystals in the

glass samples is examined in detail. In some instances it appears that the ordering may be caused by fine crystalline particles in the samples, and in other instances the magnetic ordering may be due to the amorphous material.