MASTER

INVESTIGATION OF THE ATOMIC STRUCTURE AND THE NATURE
OF THE MAGNETISM IN SEVERAL MAGNETIC GLASSES

by

H. O. Hooper
Department of Physics
Wayne State University
Detroit, Michigan 48202

Final Progress Report

for

Contract: AT(11-1)-1700

U. S. Atomic Energy Commission

September, 1970

LEGAL NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

TABLE OF CONTENTS

	Page
I. Introduction.....	1
II. Iron Containing Sodium Borate Glasses.....	3
A. Glass Preparation- Fe_2O_3 - Na_2O - B_2O_3	3
B. Magnetization Results.....	3
C. Conductivity Measurements.....	9
D. NMR Measurements.....	13
E. Mossbauer Investigation and Summary.....	15
III. $\text{XO-Al}_2\text{O}_3$ - SiO_2 Glass Systems.....	18
IV. High Temperature Material.....	19
V. Personnel.....	33
VI. List of Publications.....	34
VII. References.....	36

I. INTRODUCTION

During the past three years under the support of the U.S. Atomic Energy Commission substantial progress has been made in the determination of the atomic structure, magnetic properties and electrical properties of several amorphous materials. Both highly paramagnetic and permanently magnetic glass samples have been prepared. The structures and properties of these materials have been studied by techniques such as powder x-ray analysis, nuclear magnetic resonance, electron spin paramagnetic resonance, Mossbauer resonance, magnetization, magnetic susceptibility, and electrical conductivity. It has been found that highly paramagnetic samples of the system $\text{Fe}_2\text{O}_3\text{-Na}_2\text{O-B}_2\text{O}_3$ can be prepared up to about 25 weight % Fe_2O_3 . At higher concentrations the materials prepared are paramagnetic glasses or glassy materials which contain very small particles of crystalline material, apparently Fe_2O_3 . These samples containing fine particles of Fe_2O_3 indicate antiferromagnetic type ordering at about 100°K. The electrical conductivity of the samples of the iron-sodium borate system appears to be related to the magnetic behavior. Both semiconducting and insulating glasses have been prepared.

The glass systems $\text{XO-Al}_2\text{O}_3\text{-SiO}_2$ have been examined first to investigate the glass forming region. (X is a heavy metal oxide.) Most success was realized in the system $\text{CoO-Al}_2\text{O}_3\text{-SiO}_2$ in which glasses of very high CoO content have been prepared. Amorphous samples of this system appear to have a good antiferromagnetic transition at very low temperatures and at very high CoO concentration with the ordering temperature increasing as the CoO concentration is reduced.

In addition to these glass samples, extensive NMR studies have been made of samples of the vanadium phosphate semi-conducting glass system. This work was reported in previous progress report (December 1968) and has recently been published¹.

In order to extend the Mossbauer studies to other glass systems, a series of antimony borate glasses has been prepared (see previous progress report December 1968) and the boron NMR has been studied to determine the environment of the boron atoms. Mossbauer studies have yet to be carried out on these materials.

Besides these amorphous systems considerable effort was devoted to an NMR investigation of powder samples of the interstitial materials² NbN_x and of the compounds of niobium and berillium³. Structural information and information concerning the conductivity of these compounds has been obtained from this work. In addition, through these studies a measure of the magnitude of the vanadium quadrupole moment has been obtained⁴.

The details of much of this work have been published but a brief summary of the results appear in this report. Work which has not been published is outlines in greater detail in this report.

II. IRON CONTAINING SODIUM BORATE GLASSES

A. Glass Preparation - Fe_2O_3 - Na_2O - B_2O_3

Glass samples were prepared in the system Fe_2O_3 - Na_2O - B_2O_3 from appropriate weights of the chemicals sodium carbonate, boric acid and ferric oxide. These reagents were mixed and then heated in a 20 ml platinum crucible. Samples were prepared usually with an air-gas mixture, however, some samples were heated with a gas-oxygen mixture at higher temperatures. Samples were quenched by pouring the fused melt into an aluminum mold or when necessary (at high iron concentrations) by squashing the melt between two flat aluminum plates. The properties of the glass samples were sensitive to the conditions of glass preparation procedures even for samples of identical composition. Considerable effort was devoted to the development of preparation procedures so that glass samples with specific magnetic and electrical properties could be reproduced.

Glass samples were prepared containing varying amounts of iron oxide (Fe_2O_3). A base glass containing no Fe_2O_3 was chosen to be of composition 1/3 mole % Na_2O + 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 . Glasses readily form from 0 to 24 weight percent Fe_2O_3 . Considerable effort was spent preparing glasses containing 25 to 40 weight percent Fe_2O_3 . These latter glasses were examined in some detail during the past year.

B. MAGNETIZATION RESULTS

Two different systems were employed to obtain the magnetization measurements for the glass system Fe_2O_3 - Na_2O - B_2O_3 . One system was a vibrating sample magnetometer designed after the Foner magnetometer⁵. The other system was a mutual induction bridge arrangement⁶. The magnetization

was measured as a function of applied magnetic field for some samples of the $\text{Fe}_2\text{O}_3\text{-Na}_2\text{O-B}_2\text{O}_3$ glass system. These measurements were made at room temperature using the vibrating sample magnetometer. The low iron concentration samples, below 18.2 weight % Fe_2O_3 gives a linear magnetization vs. field dependence, characteristic of a simple paramagnetic substance. All of the other samples of higher iron concentration give a non-linear curve, suggesting that saturation is occurring in these samples. 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 I. Note that the magnetization values, reported above, are given as per gram of the glass sample.

The differential (ac) magnetic susceptibility of the glass samples was measured using the mutual induction method. The ac susceptibility, χ , values (in phase, inductive component) for some samples taken at room temperature are given in Table II. No applied magnetic field was used to make these measurements. The susceptibility values are given as per gram of the glass sample. The susceptibility values for the samples are large and in general increase with increasing iron concentration.

The susceptibility of the glass samples was measured as a function of temperature. The temperature dependence of the susceptibility for most of the samples was measured to liquid helium temperature. The susceptibility of a few samples was measured to about 1.8°K. The susceptibility of the samples with room temperature values under about 600×10^{-6} emu/gm increases with decreasing temperature at low temperature.

The samples with room temperature susceptibilities over about 600×10^{-6} emu/gm have a decrease in their susceptibilities with decreasing temperature in the vicinity of 100°K. This latter temperature dependence indicates the

TABLE I
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

TABLE II
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}

occurrence of an antiferromagnetic-type ordering which appears to be due to the presence of fine particles of Fe_2O_3 as indicated from Mossbauer studies and discussed else where in this report. These latter samples also have an increase in their susceptibility as the temperature is decreased below the transition temperature. The inverse susceptibility vs temperature of the samples was also plotted. These curves for several of the samples, are not a continuous straight line but have 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 $\alpha\text{-Fe}_2\text{O}_3$ with a distribution of particle sizes; the susceptibility of the very fine particles becoming dominant as the temperature is lowered. The slope of their curves in the lower temperature region is found and the effective magnetic moments μ_{eff} calculated. The results are given in Table III. The effective magnetic moments calculated from the inverse susceptibility curves for several of the samples are lower than that obtained for a free ferric ion in a paramagnetic salt. This can possibly 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. The inverse susceptibility curves, 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 its Neel temperature of $X = C/(T-\theta)$, where θ is a negative constant. The other interpretation, 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 $X = C/T$ or $X = C/(T-\theta)$, where θ is a positive constant.

TABLE III
MAGNETIZATION RESULTS FOR Fe_2O_3 - Na_2O - B_2O_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

Susceptibility measurements were also made in an applied magnetic field for some of the samples. The magnetic field was aligned parallel to the axis of the coil. For those samples that had a decrease in their susceptibilities as the temperature decreased in zero field, in an applied magnetic field of about 1000 gauss there was no decrease or just a very small decrease in their susceptibility.

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 $\text{Fe}_2\text{O}_3\text{-Na}_2\text{O-B}_2\text{O}_3$ glass system are given in Table IV. 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 $\text{CoO-Al}_2\text{O}_3\text{-SiO}_2$ and $\text{Fe}_2\text{O}_3\text{-Li}_2\text{O-Na}_2\text{O-B}_2\text{O}_3$ 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 polarization⁷. The resistance of the samples was measured at room temperature under an applied dc voltage of 200 volts for a period of about 24 hours. The resistance of sample number 101 (25% Fe_2O_3) increases by a factor of about 50 during the 24 hour period. The sample number 104 (28% Fe_2O_3) 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%) change 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

TABLE IV
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

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. 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. 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% Fe_2O_3) and number 112 (35% Fe_2O_3) the resistivity increases by a factor greater than 10^4 as the temperature is lowered to 77°K. The log of the 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 in Table V.

TABLE V
ACTIVATION ENERGY

	Temperature Region (°K)	Activation Energy (eV)
Sample 108 (30 wt% Fe_2O_3)	176→133	0.18
	133→ 77	0.0078
Sample 112 (35 wt% Fe_2O_3)	300→133	0.18
	133→105	0.05
	105→ 77	0.0096

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 0.0097eV. The activation energies below 113°K obtained for samples number 108 and number 112 are, respectively, 0.0078eV and 0.0097eV. 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.⁸ 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 ^{11}B nucleus was studied for glass samples of the system $\text{Fe}_2\text{O}_3\text{-Na}_2\text{O-B}_2\text{O}_3$. The ^{11}B NMR spectrum in sodium borate glasses consists of two lines⁹. 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 ^{11}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 ^{11}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. These spectra were taken at a frequency of 13.1 MHz with a modulation magnetic field of amplitude 6.8 gauss peak to peak. 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 a function of the iron concentration is given in Table IV. 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 cannot be made by measuring the separation between the peaks. A graph of the line width vs. the Fe_2O_3 concentration is very similar to a graph of the susceptibility of the samples vs. their Fe_2O_3 concentration. Thus, the ^{11}B NMR line width of a sample corresponds closely with the magnetic susceptibility of the sample.

E. MOSSBAUER INVESTIGATION AND SUMMARY

The Mossbauer effect has been employed to investigate the oxidation state, coordination, and magnetic behavior of the iron in the samples of the $\text{Fe}_2\text{O}_3\text{-Na}_2\text{O-B}_2\text{O}_3$ glass system. Earlier work was devoted to the identification of crystalline material in the samples¹⁰. This work was published and has been extended to a much more detailed study of the structure of the samples.

The glass samples exhibit a quadrupole doublet at room temperature which depends upon the oxidation state of the iron in the glass. Good glasses, i.e. those found to be amorphous by x-ray studies, exhibit only a quadrupole doublet with most of the samples having about identical quadrupole doublet with an isomer shift characteristic of trivalent iron. A wider quadrupole doublet characteristic of iron 2^+ has been observed in some samples and its presence appears to depend upon the glass making procedure, particularly upon the temperature used in the melting process.

Low temperature magnetic susceptibility measurements made on these glasses which showed this quadrupole doublet at room temperature showed

TABLE VI

^{11}B NMR LINE WIDTH FOR $\text{Fe}_2\text{O}_3\text{-Na}_2\text{O-B}_2\text{O}_3$ 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

no signs of magnetic ordering down to 4°K even for samples of good glass containing as much as 35 wt.% Fe_2O_3 . However, the Mossbauer data for the divalent iron glasses showed low temperature splitting. It is concluded that the appearance of rather complex hyperfine structure for the divalent iron is due to an increase in the paramagnetic relaxation time. No low temperature splitting was observed for the good glass samples containing the trivalent iron.

For some samples with iron concentrations between 30 to 40 weight % Fe_2O_3 the low temperature susceptibility data indicate an antiferromagnetic type ordering near 100°K. These susceptibility data are described in Section II B, of this report. In these samples the Mossbauer spectra at room temperature indicate the presence of hyperfine lines corresponding to $\alpha\text{-Fe}_2\text{O}_3$. The x-ray studies also indicate the presence of $\alpha\text{-Fe}_2\text{O}_3$. Some of the Mossbauer spectra also show small amounts of other hyperfine structure, but no evidence was seen in the x-ray data for crystalline material other than ferric oxide. However, it appears that these extra hyperfine lines do not play a role in the magnetic transition we observe. The Mossbauer spectra taken at lower temperatures both above and below the transition temperature obtained from susceptibility data are qualitatively the same. The intensity of the hyperfine structure increases somewhat relative to the quadrupole doublet as the temperature is lowered, but this change is gradual and cannot be associated directly with the change in susceptibility. A more subtle change in the spectra, however, is a reversal of the sign of the quadrupole splitting in the ferric oxide which is characteristic of the Morin transition. This is a spin-flip transition, above which ferric oxide is weakly ferromagnetic, and below which it is antiferromagnetic. The transition occurs in bulk ferric oxide at about 260°K. However, it is known that the Morin transition temperature is strongly dependent upon particle

size. The large transition observed in the susceptibility data occurs at a temperature which could indicate that $\alpha\text{-Fe}_2\text{O}_3$ particles of from two to three hundred angstroms in dimension are responsible for the transition. Furthermore, the magnitude of the transition is related to the intensity of the $\alpha\text{-Fe}_2\text{O}_3$ hyperfine lines observed in the Mossbauer spectra. It appears that the magnitude of the transition in the susceptibility is due to a cooperative interaction between weakly ferromagnetic particles of $\alpha\text{-Fe}_2\text{O}_3$ and the highly paramagnetic glassy matrix. When the small particles of $\alpha\text{-Fe}_2\text{O}_3$ become antiferromagnetically ordered this cooperative interaction ceases and the sample returns to a lower susceptibility characteristic of the paramagnetic glass.

III. $\text{XO-Al}_2\text{O}_3\text{-SiO}_2$ GLASS SYSTEMS

Some effort has been devoted to the preparation of silicate glasses which contain large amounts of iron-group ions. The system $\text{XO-Al}_2\text{O}_3\text{-SiO}_2$ where X is Co, Ni, Mn or Fe has been examined to determine the glass forming region. The region of composition of interest has been that region from 40 to 90 mole percent heavy metal oxide. These glasses are highly paramagnetic at room temperature and recent experimental evidence indicates that at least the $\text{CoO-Al}_2\text{O}_3\text{-SiO}_2$ glasses order antiferromagnetically at low temperatures. The preparation of glasses in these systems has been disappointing, primarily because of rather slow quenching due to the restrictions of the experimental apparatus. These glasses are prepared in a carbon arc-image furnace constructed from a 5 ft. diameter search light. The glasses are prepared in air in clay crucibles at temperatures from 1500°C to 2000°C . Glass samples in the $\text{CoO-Al}_2\text{O}_3\text{-SiO}_2$ system containing from 40 mole % to 85 mole % CoO have been prepared easily with this furnace. At the present time attempts are being made to prepare good glasses in the $\text{Fe}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-SiO}_2$ system

with the use of a smaller arc image furnace so that the samples can be more readily quenched and thereby increase the amount of glass formed from a melt.

Experiments have been carried out only on the $\text{CoO-Al}_2\text{O}_3\text{-SiO}_2$ glasses since all of the samples appear to be good amorphous materials. Powder x-ray analysis of the samples indicates no absorption lines.

The room temperature magnetic susceptibility values for the glass system $\text{CoO-Al}_2\text{O}_3\text{-SiO}_3$ are given in Table VII. The susceptibilities of these glasses were measured to 1.8°K. 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.

These results are extremely interesting and additional magnetization measurements will be made on new samples of various compositions in this system.

IV HIGH TEMPERATURE MATERIALS

Through our studies of the magnetic and semiconducting glasses and in particular our studies of the vanadium phosphate glasses¹ it has become apparent to us that both the niobium and vanadium nuclei are excellent nuclei for NMR investigations primarily because these nuclei have large knight shifts and/or large quadrupole interactions under their usual bonding

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

SAMPLE	WT% CoO	χ e.m.u./gm. sample
506	42.7	26×10^{-6}
525	61.4	45×10^{-6}
527	73.3	51.5×10^{-6}
528	85.2	51.2×10^{-6}

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

SAMPLE	WT% CoO	$T_N(^{\circ}\text{K})$	$\theta(^{\circ}\text{K})$	μ_{eff}
526	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

configurations. We completed studies of the niobium nucleus in NbV_x powders and this work has been published². In this work we employed NMR to determine the environment of the Nb nuclei in several samples of varying composition throughout the range of composition in this interstitial system. The γ , δ , and ϵ phases of the NbN_x system were identified by NMR by examining six NbN_x powder samples containing varying amounts of the phases mixed together. The relative amounts of the phases present were determined from the NMR line intensities. The type of bonding has been identified by an interpretation of the quadrupolar broadening and splittings of the NMR lines obtained for the niobium in different sites in the phases present in the samples. The niobium NMR from all samples showed no measurable chemical shift or knight shift indicating no conduction electrons were present.

We have extended our NMR study to the intermetallic compounds of the system NbBe_x . These compounds are of interest because they have high strength, strength retention at elevated temperatures and thermal-shock resistance. These refractory compounds also possess high melting points, low specific gravity and show good oxidation resistance. The compounds investigated were NbBe_2 , NbBe_3 , $\text{Nb}_2\text{Be}_{17}$ and NbBe_{12} . The x-ray analysis has been performed¹¹ and the results were of use in interpreting our NMR data. Because of the similarity of the NMR of the ^9Be nucleus in these compounds most of our effort was devoted to studies of the ^{93}Nb nucleus since the NMR of the ^{93}Nb nuclei was vastly different for each compound. The results of this work appear in Dr. Robert Bennett's Ph.D. Dissertation and in summary form have been submitted for publication.

Briefly the data obtained can be summarized as follows. The ^{93}Nb NMR from NbBe_2 is a single unsplit line with no quadrupole coupling constant

of $eqQ/h = 0\text{MHz}$, $24.2 \pm 0.2\text{ MHz}$, $30.1 \pm 0.3\text{ MHz}$ and corresponding Knight shifts of $0.693 \pm 0.03\%$, $0.724 \pm 0.03\%$, $0.532 \pm 0.03\%$. The first of these lines is identified as a less than 2% impurity of NbBe_2 . The other two resonances can be attributed to the two Nb sites which have been identified in the NbBe_3 crystal lattice. The ^{93}Nb NMR of $\text{Nb}_2\text{Be}_{17}$ exhibits a quadrupole constant, $eqQ/h = 5.93 \pm 0.15\text{ MHz}$, and an anisotropic Knight shift, $K_{\text{axial}} = 0.014\%$ and $K_{\text{isotropic}} = 0.34 \pm 0.02\%$. The ^{93}Nb resonance from NbBe_{12} was split by a very large quadrupole interaction yielding $eqQ/h = 21.73 \pm 0.3\text{ MHz}$ with a Knight shift of $0.552 \pm 0.2\%$. These data all appear reasonable if the x-ray structural data are considered. The study illustrates the varied environments of the Nb nuclei in these compounds. It would be of interest to compare the Knight shift values obtained for these compounds with magnetization and electrical conductivity measurements. Such a comparison would no doubt assist in the understanding of the electronic configuration existing in these materials.

PERSONNEL

During the third year of this contract in addition to the principal investigator, four graduate students, and a visiting associate professor have carried out work in areas described in this report. The extent of their participation is noted below. It should be noted that Dr. George Beard and particularly, Dr. Patrick Kenealy of the staff of the Department of Physics have devoted a large fraction of their research effort to the Mossbauer studies in these glasses.

Dr. George O'Keefe spent the nine month academic year (September 1969-June 1970) working in our laboratories on studies of glass systems. He spent considerable effort preparing $\text{Fe}_2\text{O}_3\text{-Li}_2\text{O-Na}_2\text{O-B}_2\text{O}_3$ glasses which are now being studied by the Mossbauer Technique and Magnetic Susceptibility measurements.

Dr. Robert Bennett received support from this contract during the Spring Quarter of 1969 at which time he was completing his work on the NbBe_x compounds.

Mr. Richard Bukrey has worked and is continuing to work on the Mossbauer Investigations of the iron containing glasses. He has been supported by a fellowship.

Dr. Robert Catchings has devoted his total research efforts to the studies of the iron alkali borate glasses and the cobalt alamino-silicate glasses. Dr. Catchings has received his Ph.D. degree and much of his work is yet to be submitted for publication.

Mr. Roger Verhelst was supported by this contract during the Summer of 1969. Mr. Verhelst has continued to work in the area of the studies of the structure of glass and some of his effort has been devoted to the magnetic glass systems.

VI. LIST OF PUBLICATIONS

Listed below are publications in which work carried out under this contract is described.

PUBLICATIONS:

- "NMR Study of the Niobium-Nitrogen System NbN", Robert A. Bennett, U. Roy and H. O. Hooper, J. Appl. Phys. 40, 2241^x (1969).
- "Study of Structure and Crystalline Formation in the Glass System $\text{Fe}_2\text{O}_3\text{-Na}_2\text{O-B}_2\text{O}_3$ by Use of the Mossbauer Effect," R. R. Bukrey, P. F. Kenealy, G.B. Beard, and H. O. Hooper, J. Appl. Phys. 40, 4289 (1969).
- "Nuclear Magnetic Resonance Study of Semiconducting Vanadium Phosphate Glass", P. W. France and H. O. Hooper, J. Phys. Chem. Solids, 31, 1307 (1970).
- "Asymmetric Nuclear Magnetic Resonance Line Shapes Due to Nuclear Quadrupole and Anisotropic Shift Interactions", P. W. France and H. O. Hooper, J. Phys. Chem Solids (August 1970).
- "The Magnitude of the Vanadium Quadrupole Moment", Robert A. Bennett and H. O. Hooper, J. Chem. Phys. 52 5485 (1970).
- "Nuclear Magnetic Resonance Study of the Crystalline Compounds of the NbBe_x System", Robert A. Bennett and H. O. Hooper (submitted to J. Appl. Phys.)

PAPERS AT MEETINGS:

- "Magnetic Resonance Studies of Paramagnetic and Derromagnetic $\text{Fe}_2\text{O}_3\text{-Na}_2\text{O-B}_2\text{O}_3$ Glasses", H. O. Hooper and R. M. Catchings, Bull. Am. Phys. Soc. II, 11, 188 (1966).
- "NMR Study of the Crystalline Phases of NbN", Robert A. Bennett and H. O. Hooper, Bull. Am. Phys. Soc. 14, 332 (1969).
- "NMR Study of $\text{V}_2\text{O}_5\text{-P}_2\text{O}_5$ Glasses", P. W. France and H. O. Hooper, Bull. Am. Phys. Soc. 13, 90² (1968).
- "Bulk Magnetization and Mossbauer Investigation of the $\text{Fe}_2\text{O}_3\text{-Na}_2\text{O-B}_2\text{O}_3$ Glass System", Robert M. Catchings, Richard R. Bukrey, Patrick F. Kenealy and H. O. Hooper, Bull. Am. Phys. Soc. II, 14, 427 (1969).
- "Magnetic Glasses", H.O. Hooper, Amer. J. Phys. 1969.
- "Research Participation for High School Teachers--Reactions of a Project Director and a Participant," H. O. Hooper and James Fenner, Am. J. Phys., April, 1969.
- "Mossbauer Effect in Iron-Rich $\text{Na}_2\text{O-B}_2\text{O}_3\text{-Fe}_2\text{O}_3$ Glass", Richard R. Bukrey, Robert M. Catchings, H. O. Hooper and Patrick F. Kenealy, Bull. Am. Phys. Soc., 15, 108 (1970).

THESES:

"The Study of the Structure and Magnetic Properties of Ferric-Sodium Borate Glasses by Magnetic Resonance Methods" Robert M. Catchings, III M.S. Thesis, June 1966.

"Nuclear Magnetic Resonance Study of Semiconducting Vanadium Phosphate Glass" Peter W. France, Ph.D. Dissertation, June 1967.

"Nuclear Magnetic Resonance Study of The Crystalline Phases of NbN and NbBe and Supplement on Acoustic Nuclear Magnetic Resonance" Robert A^x Bennett,^x Ph.D. Dissertation, June 1969.

"Magnetization and Electrical Conductivity Studies of Some Transition Metal Oxide Glasses" Robert M. Catchings III, Ph.D. Dissertation, June 1970.

"D. C. Conduction in Glasses," William J. Ponke, Masters Essay, June 1967.

VII. REFERENCES

1. P. W. France and H. O. Hooper, J. Phys. Chem. Solids
P. W. France and H. O. Hooper, J. Phys. Chem Solids (to be published August 1970)
2. R. A. Bennett, U. Roy and H. O. Hooper, J. Appl. Phys. 40, 2441 (1969).
3. Robert A. Bennett and H. O. Hooper, Submitted for publication - J. Appl. Phys. and Robert A. Bennett Ph.D. Dissertation, Wayne State University June 1969.
4. Robert A. Bennett and H. O. Hooper, J. Chem. Phys. 52 5485 (1970).
5. S. Foner, Rev. Sci. Inst., 30, 548 (1959).
6. E. Maxwell, Rev. Sci. Inst. 36, 553 (1965), and D. deKlerk and R.P. Hudson, J. Research National Bureau of Standards, 53, 173 (1954).
7. J. D. Mackenzie, Modern Aspects of the Vitreous State, (Butterworth & Co. London, 1964) Vol. 3. Chap. 5.
8. N. B. Hannay, Semiconductors, (Reinhold Pub. Corp., New York, 1959) p. 40.
9. P. J. Bray and A. H. Silver, Modern Aspects of the Vitreous State, (Butterworths, London 1969) Vol. I.
10. R. R. Bukrey, P. F. Kenealy, G. B. Beard and H. O. Hooper,, J. Appl. Phys. 40, 4289 (1969).
11. D. E. Sands, A. Zalkin and O. H. Krikorian, Acta Cryst. 12, 461 and 713 (1959). F. W. VonBatchelder and R. F. Raeuchle, Acta Cryst. 10, 648 (1957).

INVESTIGATION OF THE ATOMIC STRUCTURE AND THE NATURE
OF THE MAGNETISM IN SEVERAL MAGNETIC GLASSES

by

H. O. Hooper
Department of Physics
Wayne State University
Detroit, Michigan 48202

Final Progress Report

for

Contract: AT(11-1)-1700

U. S. Atomic Energy Commission

September, 1970

TABLE OF CONTENTS

	Page
I. Introduction.....	1
II. Iron Containing Sodium Borate Glasses.....	3
A. Glass Preparation- Fe_2O_3 - Na_2O - B_2O_3	3
B. Magnetization Results.....	3
C. Conductivity Measurements.....	9
D. NMR Measurements.....	13
E. Mossbauer Investigation and Summary.....	15
III. $\text{XO-Al}_2\text{O}_3$ - SiO_2 Glass Systems.....	18
IV. High Temperature Material.....	19
V. Personnel.....	33
VI. List of Publications.....	34
VII. References.....	36

I. INTRODUCTION

During the past three years under the support of the U.S. Atomic Energy Commission substantial progress has been made in the determination of the atomic structure, magnetic properties and electrical properties of several amorphous materials. Both highly paramagnetic and permanently magnetic glass samples have been prepared. The structures and properties of these materials have been studied by techniques such as powder x-ray analysis, nuclear magnetic resonance, electron spin paramagnetic resonance, Mossbauer resonance, magnetization, magnetic susceptibility, and electrical conductivity. It has been found that highly paramagnetic samples of the system $\text{Fe}_2\text{O}_3\text{-Na}_2\text{O-B}_2\text{O}_3$ can be prepared up to about 25 weight % Fe_2O_3 . At higher concentrations the materials prepared are paramagnetic glasses or glassy materials which contain very small particles of crystalline material, apparently Fe_2O_3 . These samples containing fine particles of Fe_2O_3 indicate antiferromagnetic type ordering at about 100°K . The electrical conductivity of the samples of the iron-sodium borate system appears to be related to the magnetic behavior. Both semiconducting and insulating glasses have been prepared.

The glass systems $\text{XO-Al}_2\text{O}_3\text{-SiO}_2$ have been examined first to investigate the glass forming region. (X is a heavy metal oxide.) Most success was realized in the system $\text{CoO-Al}_2\text{O}_3\text{-SiO}_2$ in which glasses of very high CoO content have been prepared. Amorphous samples of this system appear to have a good antiferromagnetic transition at very low temperatures and at very high CoO concentration with the ordering temperature increasing as the CoO concentration is reduced.

In addition to these glass samples, extensive NMR studies have been made of samples of the vanadium phosphate semi-conducting glass system. This work was reported in previous progress report (December 1968) and has recently been published¹.

In order to extend the Mossbauer studies to other glass systems, a series of antimony borate glasses has been prepared (see previous progress report December 1968) and the boron NMR has been studied to determine the environment of the boron atoms. Mossbauer studies have yet to be carried out on these materials.

Besides these amorphous systems considerable effort was devoted to an NMR investigation of powder samples of the interstitial materials² NbN_x and of the compounds of niobium and berillium³. Structural information and information concerning the conductivity of these compounds has been obtained from this work. In addition, through these studies a measure of the magnitude of the vanadium quadrupole moment has been obtained⁴.

The details of much of this work have been published but a brief summary of the results appear in this report. Work which has not been published is outlines in greater detail in this report.

II. IRON CONTAINING SODIUM BORATE GLASSES

A. Glass Preparation - Fe_2O_3 - Na_2O - B_2O_3

Glass samples were prepared in the system Fe_2O_3 - Na_2O - B_2O_3 from appropriate weights of the chemicals sodium carbonate, boric acid and ferric oxide. These reagents were mixed and then heated in a 20 ml platinum crucible. Samples were prepared usually with an air-gas mixture, however, some samples were heated with a gas-oxygen mixture at higher temperatures. Samples were quenched by pouring the fused melt into an aluminum mold or when necessary (at high iron concentrations) by squashing the melt between two flat aluminum plates. The properties of the glass samples were sensitive to the conditions of glass preparation procedures even for samples of identical composition. Considerable effort was devoted to the development of preparation procedures so that glass samples with specific magnetic and electrical properties could be reproduced.

Glass samples were prepared containing varying amounts of iron oxide (Fe_2O_3). A base glass containing no Fe_2O_3 was chosen to be of composition $1/3$ mole % Na_2O + $2/3$ 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 . Glasses readily form from 0 to 24 weight percent Fe_2O_3 . Considerable effort was spent preparing glasses containing 25 to 40 weight percent Fe_2O_3 . These latter glasses were examined in some detail during the past year.

B. MAGNETIZATION RESULTS

Two different systems were employed to obtain the magnetization measurements for the glass system Fe_2O_3 - Na_2O - B_2O_3 . One system was a vibrating sample magnetometer designed after the Foner magnetometer⁵. The other system was a mutual induction bridge arrangement⁶. The magnetization

was measured as a function of applied magnetic field for some samples of the $\text{Fe}_2\text{O}_3\text{-Na}_2\text{O-B}_2\text{O}_3$ glass system. These measurements were made at room temperature using the vibrating sample magnetometer. The low iron concentration samples, below 18.2 weight % Fe_2O_3 gives a linear magnetization vs. field dependence, characteristic of a simple paramagnetic substance. All of the other samples of higher iron concentration give a non-linear curve, suggesting that saturation is occurring in these samples. 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 I. Note that the magnetization values, reported above, are given as per gram of the glass sample.

The differential (ac) magnetic susceptibility of the glass samples was measured using the mutual induction method. The ac susceptibility, χ , values (in phase, inductive component) for some samples taken at room temperature are given in Table II. No applied magnetic field was used to make these measurements. The susceptibility values are given as per gram of the glass sample. The susceptibility values for the samples are large and in general increase with increasing iron concentration.

The susceptibility of the glass samples was measured as a function of temperature. The temperature dependence of the susceptibility for most of the samples was measured to liquid helium temperature. The susceptibility of a few samples was measured to about 1.8°K. The susceptibility of the samples with room temperature values under about 600×10^{-6} emu/gm increases with decreasing temperature at low temperature.

The samples with room temperature susceptibilities over about 600×10^{-6} emu/gm have a decrease in their susceptibilities with decreasing temperature in the vicinity of 100°K. This latter temperature dependence indicates the

TABLE I
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

TABLE II
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}

occurrence of an antiferromagnetic-type ordering which appears to be due to the presence of fine particles of Fe_2O_3 as indicated from Mossbauer studies and discussed else where in this report. These latter samples also have an increase in their susceptibility as the temperature is decreased below the transition temperature. The inverse susceptibility vs temperature of the samples was also plotted. These curves for several of the samples, are not a continuous straight line but have 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 $\alpha\text{-Fe}_2\text{O}_3$ with a distribution of particle sizes; the susceptibility of the very fine particles becoming dominant as the temperature is lowered. The slope of their curves in the lower temperature region is found and the effective magnetic moments μ_{eff} calculated. The results are given in Table III. The effective magnetic moments calculated from the inverse susceptibility curves for several of the samples are lower than that obtained for a free ferric ion in a paramagnetic salt. This can possibly 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. The inverse susceptibility curves, 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 its Neel temperature of $X = C/(T-\theta)$, where θ is a negative constant. The other interpretation, 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 $X = C/T$ or $X = C/(T-\theta)$, where θ is a positive constant.

TABLE III
MAGNETIZATION RESULTS FOR Fe_2O_3 - Na_2O - B_2O_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

Susceptibility measurements were also made in an applied magnetic field for some of the samples. The magnetic field was aligned parallel to the axis of the coil. For those samples that had a decrease in their susceptibilities as the temperature decreased in zero field, in an applied magnetic field of about 1000 gauss there was no decrease or just a very small decrease in their susceptibility.

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 $\text{Fe}_2\text{O}_3\text{-Na}_2\text{O-B}_2\text{O}_3$ glass system are given in Table IV. 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 $\text{CoO-Al}_2\text{O}_3\text{-SiO}_2$ and $\text{Fe}_2\text{O}_3\text{-Li}_2\text{O-Na}_2\text{O-B}_2\text{O}_3$ 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 polarization⁷. The resistance of the samples was measured at room temperature under an applied dc voltage of 200 volts for a period of about 24 hours. The resistance of sample number 101 (25% Fe_2O_3) increases by a factor of about 50 during the 24 hour period. The sample number 104 (28% Fe_2O_3) 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%) change 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

TABLE IV
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

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. 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. 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% Fe_2O_3) and number 112 (35% Fe_2O_3) the resistivity increases by a factor greater than 10^4 as the temperature is lowered to 77°K. The log of the 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 in Table V.

TABLE V
ACTIVATION ENERGY

	Temperature Region (°K)	Activation Energy (eV)
Sample 108 (30 wt% Fe_2O_3)	176→133	0.18
	133→ 77	0.0078
Sample 112 (35 wt% Fe_2O_3)	300→133	0.18
	133→105	0.05
	105→ 77	0.0096

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 0.0097eV. The activation energies below 113°K obtained for samples number 108 and number 112 are, respectively, 0.0078eV and 0.0097eV. 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.⁸ 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 ^{11}B nucleus was studied for glass samples of the system $\text{Fe}_2\text{O}_3\text{-Na}_2\text{O-B}_2\text{O}_3$. The ^{11}B NMR spectrum in sodium borate glasses consists of two lines⁹. 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 ^{11}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 ^{11}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. These spectra were taken at a frequency of 13.1 MHz with a modulation magnetic field of amplitude 6.8 gauss peak to peak. 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 a function of the iron concentration is given in Table IV. 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 cannot be made by measuring the separation between the peaks. A graph of the line width vs. the Fe_2O_3 concentration is very similar to a graph of the susceptibility of the samples vs. their Fe_2O_3 concentration. Thus, the ^{11}B NMR line width of a sample corresponds closely with the magnetic susceptibility of the sample.

E. MOSSBAUER INVESTIGATION AND SUMMARY

The Mossbauer effect has been employed to investigate the oxidation state, coordination, and magnetic behavior of the iron in the samples of the $\text{Fe}_2\text{O}_3\text{-Na}_2\text{O-B}_2\text{O}_3$ glass system. Earlier work was devoted to the identification of crystalline material in the samples¹⁰. This work was published and has been extended to a much more detailed study of the structure of the samples.

The glass samples exhibit a quadrupole doublet at room temperature which depends upon the oxidation state of the iron in the glass. Good glasses, i.e. those found to be amorphous by x-ray studies, exhibit only a quadrupole doublet with most of the samples having about identical quadrupole doublet with an isomer shift characteristic of trivalent iron. A wider quadrupole doublet characteristic of iron 2^+ has been observed in some samples and its presence appears to depend upon the glass making procedure, particularly upon the temperature used in the melting process.

Low temperature magnetic susceptibility measurements made on these glasses which showed this quadrupole doublet at room temperature showed

TABLE VI
 ^{11}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

no signs of magnetic ordering down to 4°K even for samples of good glass containing as much as 35 wt.% Fe_2O_3 . However, the Mossbauer data for the divalent iron glasses showed low temperature splitting. It is concluded that the appearance of rather complex hyperfine structure for the divalent iron is due to an increase in the paramagnetic relaxation time. No low temperature splitting was observed for the good glass samples containing the trivalent iron.

For some samples with iron concentrations between 30 to 40 weight % Fe_2O_3 the low temperature susceptibility data indicate an antiferromagnetic type ordering near 100°K. These susceptibility data are described in Section II B, of this report. In these samples the Mossbauer spectra at room temperature indicate the presence of hyperfine lines corresponding to $\alpha\text{-Fe}_2\text{O}_3$. The x-ray studies also indicate the presence of $\alpha\text{-Fe}_2\text{O}_3$. Some of the Mossbauer spectra also show small amounts of other hyperfine structure, but no evidence was seen in the x-ray data for crystalline material other than ferric oxide. However, it appears that these extra hyperfine lines do not play a role in the magnetic transition we observe. The Mossbauer spectra taken at lower temperatures both above and below the transition temperature obtained from susceptibility data are qualitatively the same. The intensity of the hyperfine structure increases somewhat relative to the quadrupole doublet as the temperature is lowered, but this change is gradual and cannot be associated directly with the change in susceptibility. A more subtle change in the spectra, however, is a reversal of the sign of the quadrupole splitting in the ferric oxide which is characteristic of the Morin transition. This is a spin-flip transition, above which ferric oxide is weakly ferromagnetic, and below which it is antiferromagnetic. The transition occurs in bulk ferric oxide at about 260°K. However, it is known that the Morin transition temperature is strongly dependent upon particle

size. The large transition observed in the susceptibility data occurs at a temperature which could indicate that $\alpha\text{-Fe}_2\text{O}_3$ particles of from two to three hundred angstroms in dimension are responsible for the transition. Furthermore, the magnitude of the transition is related to the intensity of the $\alpha\text{-Fe}_2\text{O}_3$ hyperfine lines observed in the Mossbauer spectra. It appears that the magnitude of the transition in the susceptibility is due to a cooperative interaction between weakly ferromagnetic particles of $\alpha\text{-Fe}_2\text{O}_3$ and the highly paramagnetic glassy matrix. When the small particles of $\alpha\text{-Fe}_2\text{O}_3$ become antiferromagnetically ordered this cooperative interaction ceases and the sample returns to a lower susceptibility characteristic of the paramagnetic glass.

III. $\text{XO-Al}_2\text{O}_3\text{-SiO}_2$ GLASS SYSTEMS

Some effort has been devoted to the preparation of silicate glasses which contain large amounts of iron-group ions. The system $\text{XO-Al}_2\text{O}_3\text{-SiO}_2$ where X is Co, Ni, Mn or Fe has been examined to determine the glass forming region. The region of composition of interest has been that region from 40 to 90 mole percent heavy metal oxide. These glasses are highly paramagnetic at room temperature and recent experimental evidence indicates that at least the $\text{CoO-Al}_2\text{O}_3\text{-SiO}_2$ glasses order antiferromagnetically at low temperatures. The preparation of glasses in these systems has been disappointing, primarily because of rather slow quenching due to the restrictions of the experimental apparatus. These glasses are prepared in a carbon arc-image furnace constructed from a 5 ft. diameter search light. The glasses are prepared in air in clay crucibles at temperatures from 1500°C to 2000°C . Glass samples in the $\text{CoO-Al}_2\text{O}_3\text{-SiO}_2$ system containing from 40 mole % to 85 mole % CoO have been prepared easily with this furnace. At the present time attempts are being made to prepare good glasses in the $\text{Fe}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-SiO}_2$ system

with the use of a smaller arc image furnace so that the samples can be more readily quenched and thereby increase the amount of glass formed from a melt.

Experiments have been carried out only on the $\text{CoO-Al}_2\text{O}_3\text{-SiO}_2$ glasses since all of the samples appear to be good amorphous materials. Powder x-ray analysis of the samples indicates no absorption lines.

The room temperature magnetic susceptibility values for the glass system $\text{CoO-Al}_2\text{O}_3\text{-SiO}_3$ are given in Table VII. The susceptibilities of these glasses were measured to 1.8°K. 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.

These results are extremely interesting and additional magnetization measurements will be made on new samples of various compositions in this system.

IV HIGH TEMPERATURE MATERIALS

Through our studies of the magnetic and semiconducting glasses and in particular our studies of the vanadium phosphate glasses¹ it has become apparent to us that both the niobium and vanadium nuclei are excellent nuclei for NMR investigations primarily because these nuclei have large knight shifts and/or large quadrupole interactions under their usual bonding

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

SAMPLE	WT% CoO	χ e.m.u./gm. sample
506	42.7	26×10^{-6}
525	61.4	45×10^{-6}
527	73.3	51.5×10^{-6}
528	85.2	51.2×10^{-6}

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

SAMPLE	WT% CoO	$T_N(^{\circ}\text{K})$	$\theta(^{\circ}\text{K})$	μ_{eff}
526	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

configurations. We completed studies of the niobium nucleus in NbV_x powders and this work has been published². In this work we employed NMR to determine the environment of the Nb nuclei in several samples of varying composition throughout the range of composition in this interstitial system. The γ , δ , and ϵ phases of the NbN_x system were identified by NMR by examining six NbN_x powder samples containing varying amounts of the phases mixed together. The relative amounts of the phases present were determined from the NMR line intensities. The type of bonding has been identified by an interpretation of the quadrupolar broadening and splittings of the NMR lines obtained for the niobium in different sites in the phases present in the samples. The niobium NMR from all samples showed no measurable chemical shift or knight shift indicating no conduction electrons were present.

We have extended our NMR study to the intermetallic compounds of the system NbBe_x . These compounds are of interest because they have high strength, strength retention at elevated temperatures and thermal-shock resistance. These refractory compounds also possess high melting points, low specific gravity and show good oxidation resistance. The compounds investigated were NbBe_2 , NbBe_3 , $\text{Nb}_2\text{Be}_{17}$ and NbBe_{12} . The x-ray analysis has been performed¹¹ and the results were of use in interpreting our NMR data. Because of the similarity of the NMR of the ^9Be nucleus in these compounds most of our effort was devoted to studies of the ^{93}Nb nucleus since the NMR of the ^{93}Nb nuclei was vastly different for each compound. The results of this work appear in Dr. Robert Bennett's Ph.D. Dissertation and in summary form have been submitted for publication.

Briefly the data obtained can be summarized as follows. The ^{93}Nb NMR from NbBe_2 is a single unsplit line with no quadrupole coupling constant

of $eqQ/h = 0\text{ MHz}$, $24.2 \pm 0.2\text{ MHz}$, $30.1 \pm 0.3\text{ MHz}$ and corresponding Knight shifts of $0.693 \pm 0.03\%$, $0.724 \pm 0.03\%$, $0.532 \pm 0.03\%$. The first of these lines is identified as a less than 2% impurity of NbBe_2 . The other two resonances can be attributed to the two Nb sites which have been identified in the NbBe_3 crystal lattice. The ^{93}Nb NMR of $\text{Nb}_2\text{Be}_{17}$ exhibits a quadrupole constant, $eqQ/h = 5.93 \pm 0.15\text{ MHz}$, and an anisotropic Knight shift, $K_{\text{axial}} = 0.014\%$ and $K_{\text{isotropic}} = 0.34 \pm 0.02\%$. The ^{93}Nb resonance from NbBe_{12} was split by a very large quadrupole interaction yielding $eqQ/h = 21.73 \pm 0.3\text{ MHz}$ with a Knight shift of $0.552 \pm 0.2\%$. These data all appear reasonable if the x-ray structural data are considered. The study illustrates the varied environments of the Nb nuclei in these compounds. It would be of interest to compare the Knight shift values obtained for these compounds with magnetization and electrical conductivity measurements. Such a comparison would no doubt assist in the understanding of the electronic configuration existing in these materials.

PERSONNEL

During the third year of this contract in addition to the principal investigator, four graduate students, and a visiting associate professor have carried out work in areas described in this report. The extent of their participation is noted below. It should be noted that Dr. George Beard and particularly, Dr. Patrick Kenealy of the staff of the Department of Physics have devoted a large fraction of their research effort to the Mossbauer studies in these glasses.

Dr. George O'Keefe spent the nine month academic year (September 1969-June 1970) working in our laboratories on studies of glass systems. He spent considerable effort preparing $\text{Fe}_2\text{O}_3\text{-Li}_2\text{O-Na}_2\text{O-B}_2\text{O}_3$ glasses which are now being studied by the Mossbauer Technique and Magnetic Susceptibility measurements.

Dr. Robert Bennett received support from this contract during the Spring Quarter of 1969 at which time he was completing his work on the NbBe_x compounds.

Mr. Richard Bukrey has worked and is continuing to work on the Mossbauer Investigations of the iron containing glasses. He has been supported by a fellowship.

Dr. Robert Catchings has devoted his total research efforts to the studies of the iron alkali borate glasses and the cobalt alamino-silicate glasses. Dr. Catchings has received his Ph.D. degree and much of his work is yet to be submitted for publication.

Mr. Roger Verhelst was supported by this contract during the Summer of 1969. Mr. Verhelst has continued to work in the area of the studies of the structure of glass and some of his effort has been devoted to the magnetic glass systems.

VI. LIST OF PUBLICATIONS

Listed below are publications in which work carried out under this contract is described.

PUBLICATIONS:

- "NMR Study of the Niobium-Nitrogen System NbN", Robert A. Bennett, U. Roy and H. O. Hooper, J. Appl. Phys. 40, 2241 ^x(1969).
- "Study of Structure and Crystalline Formation in the Glass System $\text{Fe}_2\text{O}_3\text{-Na}_2\text{O-B}_2\text{O}_3$ by Use of the Mossbauer Effect," R. R. Bukrey, P. F. Kenealy, G.B. Beard, and H. O. Hooper, J. Appl. Phys. 40, 4289 (1969).
- "Nuclear Magnetic Resonance Study of Semiconducting Vanadium Phosphate Glass", P. W. France and H. O. Hooper, J. Phys. Chem. Solids, 31, 1307 (1970).
- "Asymmetric Nuclear Magnetic Resonance Line Shapes Due to Nuclear Quadrupole and Anisotropic Shift Interactions", P. W. France and H. O. Hooper, J. Phys. Chem Solids (August 1970).
- "The Magnitude of the Vanadium Quadrupole Moment", Robert A. Bennett and H. O. Hooper, J. Chem. Phys. 52 5485 (1970).
- "Nuclear Magnetic Resonance Study of the Crystalline Compounds of the NbBe_x System", Robert A. Bennett and H. O. Hooper (submitted to J. Appl. Phys.).

PAPERS AT MEETINGS:

- "Magnetic Resonance Studies of Paramagnetic and Derromagnetic $\text{Fe}_2\text{O}_3\text{-Na}_2\text{O-B}_2\text{O}_3$ Glasses", H. O. Hooper and R. M. Catchings, Bull. Am. Phys. Soc. II, 11, 188 (1966).
- "NMR Study of the Crystalline Phases of NbN_x", Robert A. Bennett and H. O. Hooper, Bull. Am. Phys. Soc. 14, 332 (1969).
- "NMR Study of $\text{V}_2\text{O}_5\text{-P}_2\text{O}_5$ Glasses", P. W. France and H. O. Hooper, Bull. Am. Phys. Soc. 13, 90² (1968).
- "Bulk Magnetization and Mossbauer Investigation of the $\text{Fe}_2\text{O}_3\text{-Na}_2\text{O-B}_2\text{O}_3$ Glass System", Robert M. Catchings, Richard R. Bukrey, Patrick F. Kenealy and H. O. Hooper, Bull. Am. Phys. Soc. II, 14, 427 (1969).
- "Magnetic Glasses", H.O. Hooper, Amer. J. Phys. 1969.
- "Research Participation for High School Teachers--Reactions of a Project Director and a Participant," H. O. Hooper and James Fenner, Am. J. Phys., April, 1969.
- "Mossbauer Effect in Iron-Rich $\text{Na}_2\text{O-B}_2\text{O}_3\text{-Fe}_2\text{O}_3$ Glass", Richard R. Bukrey, Robert M. Catchings, H. O. Hooper and Patrick F. Kenealy, Bull. Am. Phys. Soc., 15, 108 (1970).

THESES:

"The Study of the Structure and Magnetic Properties of Ferric-Sodium Borate Glasses by Magnetic Resonance Methods" Robert M. Catchings, III M.S. Thesis, June 1966.

"Nuclear Magnetic Resonance Study of Semiconducting Vanadium Phosphate Glass" Peter W. France, Ph.D. Dissertation, June 1967.

"Nuclear Magnetic Resonance Study of The Crystalline Phases of NbN and NbBe and Supplement on Acoustic Nuclear Magnetic Resonance" Robert A^x Bennett,^x Ph.D. Dissertation, June 1969.

"Magnetization and Electrical Conductivity Studies of Some Transition Metal Oxide Glasses" Robert M. Catchings III, Ph.D. Dissertation, June 1970.

"D. C. Conduction in Glasses," William J. Ponke, Masters Essay, June 1967.

VII. REFERENCES

1. P. W. France and H. O. Hooper, J. Phys. Chem. Solids
P. W. France and H. O. Hooper, J. Phys. Chem Solids (to be published August 1970)
2. R. A. Bennett, U. Roy and H. O. Hooper, J. Appl. Phys. 40, 2441 (1969).
3. Robert A. Bennett and H. O. Hooper, Submitted for publication - J. Appl. Phys. and Robert A. Bennett Ph.D. Dissertation, Wayne State University June 1969.
4. Robert A. Bennett and H. O. Hooper, J. Chem. Phys. 52 5485 (1970).
5. S. Foner, Rev. Sci. Inst., 30, 548 (1959).
6. E. Maxwell, Rev. Sci. Inst. 36, 553 (1965), and D. deKlerk and R.P. Hudson, J. Research National Bureau of Standards, 53, 173 (1954).
7. J. D. Mackenzie, Modern Aspects of the Vitreous State, (Butterworth & Co. London, 1964) Vol. 3. Chap. 5.
8. N. B. Hannay, Semiconductors, (Reinhold Pub. Corp., New York, 1959) p. 40.
9. P. J. Bray and A. H. Silver, Modern Aspects of the Vitreous State, (Butterworths, London 1969) Vol. I.
10. R. R. Bukrey, P. F. Kenealy, G. B. Beard and H. O. Hooper, J. Appl. Phys. 40, 4289 (1969).
11. D. E. Sands, A. Zalkin and O. H. Krikorian, Acta Cryst. 12, 461 and 713 (1959). F. W. VonBatchelder and R. F. Raeuchle, Acta Cryst. 10, 648 (1957).