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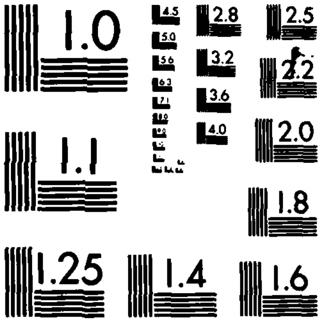

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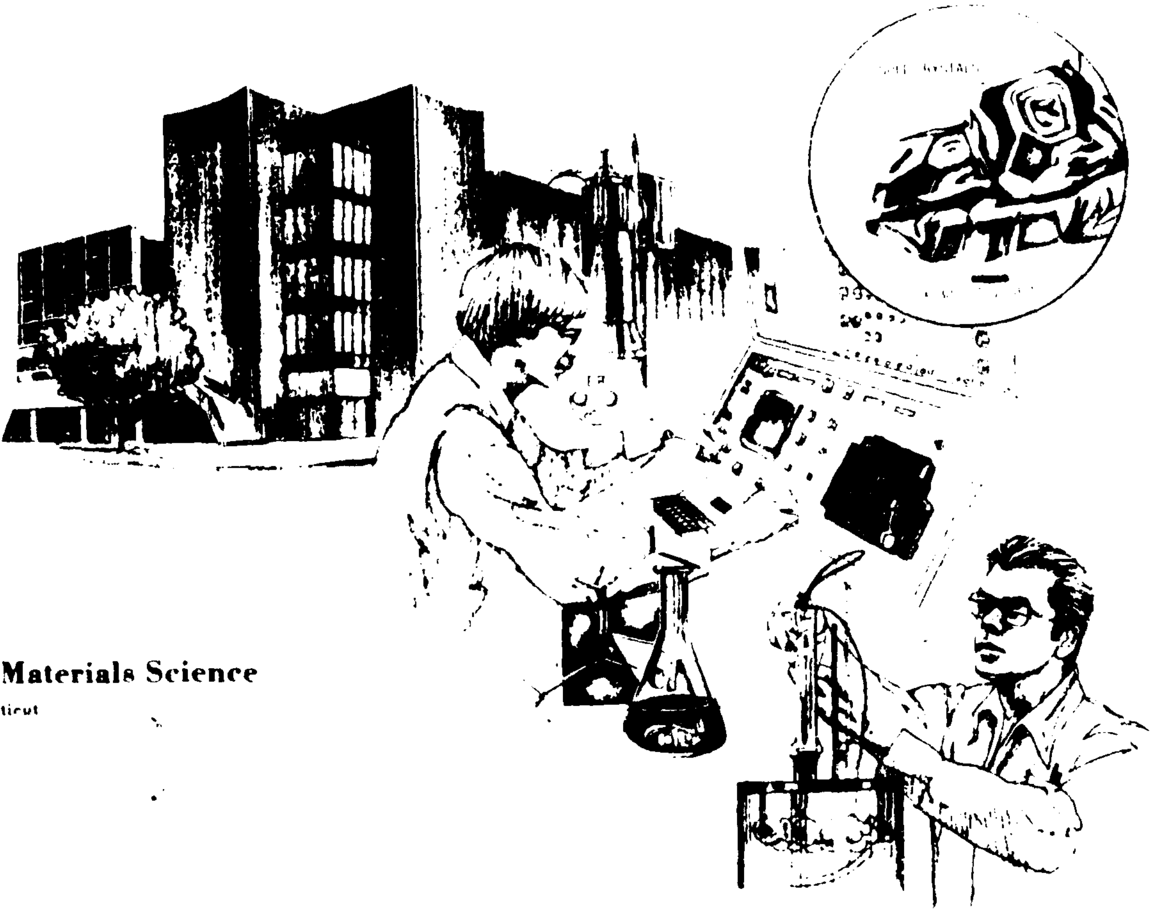

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METALLIC GLASSES: INVESTIGATION OF THE ELECTRONIC STRUCTURE AND ITS RELATIONSHIP TO PHYSICAL PROPERTIES

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Grant Number: AFOSR 80-0030

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November 30, 1984

Final Scientific Report: October 1, 1983 to September 30, 1984

METALLIC GLASSES: INVESTIGATION OF THE ELECTRONIC STRUCTURE AND ITS RELATIONSHIP TO PHYSICAL PROPERTIES

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

This report summarizes the work which was completed during the first four years of the research program (October 1, 1979 to September 30, 1983). Included are: (1) a NMR and magnetic susceptibility study of several rapidly quenched Ni-Pd-P, Ni-Pt-P and Ni-P metallic glasses, (2) a magnetization study of the $RE_{100-x}Al_x$ amorphous alloys (where RE is a rare earth element), (3) a NMR, magnetization and x-ray diffraction study of crystalline $Fe_{3-x}Ni_xSi$ and Metglas 2605 CO ($Fe_{67}Co_{18}B_{14}Si_1$), (4) a NMR and magnetic susceptibility study

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SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered) of the $Ca_{100-x}Al_x$ metallic glass system, (5) a magnetization study of some Co-Nb-B and Fe-Nb-B metallic glasses, (6) an EXAFS study of Metglas 2605 CO and (7) a XANES study of the $(Ni_{0.50}Pt_{0.50})_{75}P_{25}$ metallic glass system. In addition, this report describes in complete detail the progress during the past year (October 1, 1983 to September 30, 1984) which includes: (1) a spin-echo NMR study of the atomic environment in the $Fe_{100-x}B_x$ metallic glass system and (2) a low field magnetization study of the magnetic anisotropy in Metglas 2605 CO ribbons. Abstracts from this work follow.

In order to investigate the near-neighbor atomic environments, we have measured the ^{11}B spin-echo NMR spectra for the melt-spun $Fe_{100-x}B_x$ metallic glass system ($14 \leq x \leq 22$) at 4.2 °K over the frequency range 26-46 MHz. The addition of B to $Fe_{100-x}B_x$ shifts the peak in the hyperfine field distribution to smaller values by adding intensity to the low field portion of the distribution while leaving the high field portion unchanged. These results, along with ^{57}Fe hyperfine field measurements from Mössbauer experiments are being used to establish a model relating hyperfine fields and structural changes.

In order to investigate the magnetic anisotropy, low field magnetization measurements have been carried out on various samples of magnetically annealed Metglas 2605 CO. The as-fabricated material exhibits a magnetic anisotropy with the easy axis along the ribbon length. By using the magnetic annealing treatment which yields an enhanced value for the magnetomechanical coupling factor, a magnetic anisotropy is induced with the easy axis in the plane of the ribbon and perpendicular to the length. A value of $K = 4.3 \times 10^3$ erg/cm^3 is calculated for the induced anisotropy energy constant at room temperature. Using a model based on simple domain rotation, a value of $\lambda_s = 25 \times 10^{-6}$ is estimated for the corresponding saturation magnetostriction. The anisotropy increases 37% when the temperature is reduced to 77 °K. Values are presented for the saturation magnetization, domain magnetization, coercive field, and initial permeability.

Finally, this report describes the status of experiments currently in progress which includes: (1) optical properties of the $Ni_{100-x}P_x$ metallic glasses and (2) Mössbauer study of the Metglas 2605 CO system.

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I. INTRODUCTION

During the past decade, materials scientists and solid state physicists have devoted considerable research activity to amorphous materials such as magnetic glasses, amorphous semiconductors and amorphous metallic alloys[1-3]. This is due to a combination of a desire for a re-examination of some fundamental concepts of solids as well as the possibility for a variety of technological applications[4]. Our research effort has focused principally on the class of amorphous materials known as "amorphous metallic alloys" or "metallic glasses"; materials which possess all the properties normally associated with metals but are not spatially periodic. For the most part, we have studied metallic glass systems with the general form $TM_{100-x}G_x$, where TM is a transition metal (or combination of transition metals) such as Ni, Pd, Pt, Fe, Co or Nb; and G is a high valence metalloid (or combination of metalloids) such as B, Si or P. Although there are several methods of preparation, these amorphous alloys are typically prepared by rapid quenching ($\sim 10^5$ to 10^7 °C/sec) from the liquid state and possess metalloid compositions ranging from $x = 15$ to 30 at. %. Recently, because of their special significance, we have included systems of the form $RE_{100-x}M_x$ and $M^1{}_{100-x}M^2{}_x$, where RE is a 4f rare earth element such as Ce, Pr or Dy; and M is a simple metal such as Ca or Al. Our research program has utilized the techniques of nuclear magnetic resonance (pulse and steady state), magnetization, specific heat, optical spectroscopy, x-ray diffraction and x-ray absorption (XANES and EXAFS), in the study of: (1) the electronic structure, (2) the amorphous (glassy) structure, (3) the crystallization and (4) the bonding, glass forming tendency and structural stability of metallic glasses. This in turn leads to a better understanding of the electronic, magnetic and mechanical properties for these materials. In particular, our primary concern was a determination of the electronic structure (e.g., density of states) and its relationship to the technically useful physical properties. Finally, nuclear magnetic resonance and magnetization experiments were used to investigate (5) the occurrence and size of localized moments, the degree of spin polarization, the magnetic moment interactions (applied field, exchange and anisotropy), and the nature of any magnetic ordering. The results are being compared with existing theories of magnetism in amorphous materials.

The Air Force Office of Scientific Research (AFOSR) commenced sponsorship of this program on October 1, 1979. This Final Scientific Report describes generally the progress and achievements which occurred during the entire five years of the supported program with specific emphasis on this past final year (October 1, 1983 to September 30, 1984). The progress is discussed in the context of our proposed objectives. In all, thirteen journal articles, ten abstracts and twenty oral presentations can be credited to the AFOSR support of this program.

Sections IIA, IIB and IIC consist of concise one page statements which describe the "Objectives of Program", "Methods of Approach" and "Statement of Work", respectively. Such summary statements were contained in the previous proposal. Section III summarizes the scientific progress achieved during the first four years of the research program. Section IV ("Spin-Echo NMR Study of the Atomic Environment in the $Fe_{100-x}B_x$ Metallic Glass System") and Section V ("Low Field Magnetic Anisotropy in Metglas 2605 CO Ribbons") and Section VI ("Other Work") describe in detail the achievements of the past year. Section VII lists all of the journal articles, abstracts and oral presentations which can be credited to AFOSR support while Section VIII indicates all of the scientific personnel associated with the research program.

II. SUMMARY STATEMENTS

A. Objectives of Program

The goals of the proposed work were to determine the electronic structure of metallic glasses and to investigate its relationship to the physical properties. In particular, the first objective was to quantitatively investigate the nature of the electronic density of states for metallic systems which have no long range crystallographic order. The experiments will distinguish between various approaches, ranging from liquid metal theories (which involve the nearly free electron approximation and pseudopotential techniques) to near neighbor environment models, as well as determine the applicability of rigid band ideas. Secondly, it was proposed to test certain features of the dense random packing model or, perhaps, support an alternative model (e.g., the random packing of microcrystalline units) for the atomic structure of metallic glasses. The experiments will determine the role of atomic size and electronegativity in such a structure. Thirdly, it was the objective of the proposed work to investigate the process of crystallization. In addition to identifying the resulting phases, the experiments will determine how near neighbor environments are affected by the thermal, magnetic and mechanical history. Fourthly, it was proposed to investigate the nature of bonding, structural stability and glass forming tendency for metallic glasses in the light of current theoretical descriptions. Such descriptions include an ionic-like charge transfer, directional covalent bonding and a lowering of the density of states. Finally, it was proposed to examine existing theories of magnetism in amorphous materials concerning the occurrence and size of localized moments, spin polarization, magnetic interactions (applied field, exchange and anisotropy), and magnetic ordering. All of this will lead to a better understanding of the electronic, magnetic and mechanical properties for metallic glasses.

B. Approaches and Techniques

During the course of the research program, the experimental approach utilized the tools of nuclear magnetic resonance (pulse and steady state), magnetization, specific heat, optical spectroscopy, x-ray diffraction and x-ray absorption (XANES and EXAFS) in the study of metallic glasses having the general forms $TM_{100-x}G_x$ and $M^1{}_{100-x}M^2{}_x$. Above, TM represents a transition metal (or combination) such as Ni, Pd, Pt, Fe, Co or Nb; G represents a high valence metalloid glass former (or combination) such as B, Si or P; and M represents a simple metal such as Ca or Al. These alloys possess favorable NMR species and are readily available in the amorphous state with compositions which can be systematically varied. Also, the magnetic properties of an additional system of the form $RE_{100-x}Al_x$, where RE represents a 4f rare earth element, were included.

Initially, the NMR Knight shift, NMR spin-lattice relaxation rate and magnetic susceptibility were heavily exploited since they provide a direct picture of the electronic structure. Later, the research program was expanded to include specific heat, specular reflectivity and XANES experiments which not only support the NMR results, but also provide a quantitative calculation for the s- and d-band densities of states. The description of the electronic structure which was obtained will enable an understanding of several physical properties (e.g., structural stability). Furthermore, NMR linewidth, EXAFS and x-ray diffraction measurements provided information concerning the near neighbor environment and, hence, can be utilized to understand the atomic structure and how it is affected by thermal, magnetic and mechanical processes. By using systematic variations in composition, the roles of atomic size and electronegativity were studied. Finally, magnetization measurements provided information concerning the size and occurrence of localized moments, degree of spin polarization, magnetic interactions, and nature of magnetic ordering; all of which can be compared with existing theories of magnetism in amorphous materials.

C. Statement of Work

This program consisted of a systematic and detailed investigation of the electronic structure of metallic glasses and its relationship to the physical properties. The techniques that were utilized included nuclear magnetic resonance, magnetization, specific heat, optical spectroscopy, x-ray diffraction and x-ray absorption. This section constitutes a statement of specific research work that was carried out by the Principal Investigator during the course of the supported program. Using the tools outlined above, the Principal Investigator:

(1) determined the nature of the electronic structure for metallic glasses, including a quantitative evaluation for the s- and d-band densities of states and hyperfine coupling constants,

(2) investigated the applicability of such approaches as the nearly free electron models, liquid metal theories, near neighbor models and rigid band ideas to the electronic structure for metallic glasses,

(3) determined the relationship between the electronic structure for metallic glasses and such physical properties as bonding, structural stability and glass forming tendency,

(4) investigated the nature of the atomic structure for metallic glasses (in the light of dense random packing and microcluster models) and determined the role played by such parameters as atomic size and electronegativity,

(5) determined how near neighbor atomic environments are affected by the thermal, magnetic and mechanical history, and investigated the phases resulting from crystallization,

(6) investigated the occurrence and size of localized moments, degree of spin polarization, magnetic interactions (applied field, exchange, anisotropy), and nature of magnetic ordering; compared the results with existing theories of magnetism in amorphous materials.

This experimental research program, which has just concluded, will lead to a better understanding of the electronic, magnetic and mechanical properties for metallic glasses.

III. PROGRESS AND ACHIEVEMENTS (First Four Years of Research Program)

This section summarizes the general progress achieved during the first four years of the research program (October 1, 1979 to September 30, 1983). A list of publications resulting from the program is provided in Section VII. Preprints and reprints of the publications have been submitted to the AFOSR under separate covers.

A. NMR and Magnetic Susceptibility Study of the Ni-Pd-P, Ni-Pt-P and Ni-P Metallic Glass Systems

During the initial phase of the research program, extensive NMR and magnetic susceptibility experiments were carried out on several rapidly quenched metallic glasses from the transition metal + metalloid family. By systematically varying the composition in the Ni-Pd-P, Ni-Pt-P and Ni-P metallic glasses, a preliminary qualitative description of the electronic structure was obtained. Publications A1, A3, A4 and B1 (see Section VII) describe in detail the NMR and magnetic susceptibility work which was carried out on the systems above. Here, we will summarize the important scientific conclusions from the work on these systems which have implications for the $TM_{100-x}G_x$ metallic glass systems in general. The metalloid (^{31}P) Knight shift and spin-lattice relaxation rate for all of these systems depend only on the P concentration, x, and not the relative transition metal composition (i.e., what fraction of Ni atoms are replaced by Pd or Pt). The ^{31}P Knight shift and spin-lattice relaxation rate are attributed solely to the direct contact hyperfine interaction. On the other hand, the transition metal (^{195}Pt) Knight shift has contributions arising from both the direct contact hyperfine and core polarization interactions, and depends on both the metalloid concentration and relative transition metal composition. The results are discussed in terms of a rigid two-band picture with estimates being made for the s- and d-band densities of states and hyperfine coupling constants. Relative to the Fermi energy, the d-states associated with Ni are higher in energy (and, therefore, the number of d-holes is greater), than those for Pd and Pt. Consistent with the DRP model, there is evidence of a transfer of charge from the P metalloid atoms to the transition metal d-states in these systems. For the $(Ni_{0.50}Pd_{0.50})_{100-x}P_x$ system, these states become full for x $\overset{\sim}{\sim}$ 20. Since the rigid band model predicts that if all of the P electrons go into the d-states, the filling would be complete for x $\overset{\sim}{\sim}$ 11, we conclude that slightly more than half of the P electrons go into the conduction band. There is no evidence of any minimum in the density of states as predicted by Nagel and Tauc[5]. Finally, we note that the various ^{31}P Knight shift and relaxation rate values satisfy Korringa relationships, with the value of the experimental Korringa constant decreasing as the P concentration increases. The values range from two to three times the free-electron value.

B. Magnetization Study of the $RE_{65}Al_{35}$ Metallic Glass Systems

Because of the existence of highly localized magnetic moments, the magnetic properties of rare earth + simple metal metallic glasses are of particular interest. Measurements of the bulk magnetization have been made as a function of temperature and magnetic field for three amorphous alloys from the $RE_{100-x}Al_x$ series: $Ce_{65}Al_{35}$, $Pr_{65}Al_{35}$ and $Dy_{65}Al_{35}$. Publication A6 describes this work in detail with the following scientific conclusions. $Dy_{65}Al_{35}$ and $Pr_{65}Al_{35}$ demonstrate a behavior which is characteristic of ferromagnetic ordering, without the implication of a strictly parallel alignment of moments. The onset of hysteresis and relaxation effects below the ordering temperature, as well as the lack of saturation, provides evidence of strong local anisotropy. Such behavior has been described by Ferrer and Zuchermann[6] using a random magnetic anisotropy model. Evidence for a RKKY interaction comes from the negative Curie-Weiss value for

$Ce_{65}Al_{35}$. This result appears to contradict the work of Buschow[7] on amorphous Gd alloys in which it was concluded that the RKKY interaction was of minor importance.

C. NMR, Magnetization and X-Ray Diffraction Study of the $Fe_{3-x}Ni_xSi$ Crystalline and $Fe_{67}Co_{18}B_{14}Si_1$ Metallic Glass Systems

Spin-echo NMR, magnetization and x-ray diffraction studies on the crystalline $Fe_{3-x}Ni_xSi$ system have enabled us to correlate magnetic moment formation and hyperfine field interactions with local (short range) environment configurations. Such studies on crystalline binary and ternary systems based on Fe_3Si are relevant to $TM_{100-x}G_x$ metallic glasses due to similarities in the atomic and electronic structures. The NMR results demonstrated that Ni selectively replaces the Fe in one of the two Fe-sites inherent in the Fe_3Si structure[8] and, consequently, a local environment model relating the hyperfine fields with the magnetic moments previously developed for such systems can be applied[9]. When one uses this model, a subdivision of the observed internal fields into contributions arising from the 4s spin polarization transferred from neighboring moments and the polarization resulting from the on-site moments is obtained. This work is described in detail in publication A2.

Similar experiments were carried out on the $Fe_{67}Co_{18}B_{14}Si_1$ (Metglas 2605 CO) metallic glass which yielded information concerning the near neighbor atomic environment and how it is affected by magnetic annealing. Spin-echo NMR spectra obtained from both metalloid (^{11}B) and transition metal (^{59}Co) nuclei detected no significant difference between an as-fabricated sample and a sample which has undergone the appropriate magnetic annealing for yielding the extremely high magnetomechanical coupling constants found in these systems[10]. Hence, it was concluded that any anisotropic atomic rearrangement which occurs during such magnetic annealing processes must involve a relatively small number of atoms, or be so subtle, that no significant change occurs in the broad NMR spectra obtained from amorphous materials. This is consistent with the prediction of Graham and Egami[11]. We note, however, that very recent and carefully done EXAFS experiments on similar samples of Metglas 2605 CO do indicate a slight atomic rearrangement resulting from the magnetic annealing treatment (see publication B7 and Section IIIF in this report). Careful x-ray diffraction studies indicate that a thin crystalline surface layer, which extends into the ribbon $\lesssim 3\ \mu m$, occurs on only the substrate wheel side of the as-fabricated ribbon. Most of the crystallites consist of an α-Fe phase and are preferentially oriented in a fiber texture configuration; the fiber axis being a mixture of the [100] and [110] directions, and normal to the ribbon surface. The crystalline surface layer does not appear to influence the high value of the magnetomechanical coupling factor obtained through magnetic annealing. This work is described in detail in publications A5, A9, B6 and B9.

D. NMR and Magnetic Susceptibility Study of the $Ca_{100-x}Al_x$ Metallic Glass System

Steady state NMR and magnetic susceptibility experiments have been carried out on a new metallic glass system consisting of "simple" metals only (see publication A7). Due to the existence of a nuclear quadrupole moment and differences in valence, $Ca_{100-x}Al_x$ ($15 \leqq x \leqq 45$ at. %) is ideal for studies of both the atomic and electronic structures. ^{27}Al NMR spectra were observed at room temperature as a function of resonance frequency for the various compositions. A consideration of the intensity, shape and frequency dependence indicates that the line is due to the central component only, or $+1/2 \longleftrightarrow -1/2$ transition, with the other transitions being far removed from the line due to the first order quadrupole interaction. Furthermore, both the ^{27}Al Knight shift and linewidth remain unchanged as the composition is varied throughout the entire glassy regime. Since both the average electronic concentration and average atomic volume change appreciably, these results provide evidence that certain features of the nearest neighbor atomic environment and electronic structure remain fixed as the composition is varied (i.e., some form of short range order). We note that for the transition metal + metalloid systems studied (see Section IIIA), the (^{31}P) metalloid Knight shift decreases dramatically as the electronic concentration is increased. Also, for the same $TM_{100-x}G_x$ systems, the linewidth is very sensitive to composition. Finally, an analysis of the composition dependence for the room temperature magnetic susceptibility indicates that estimates based on the free electron model are inadequate.

In order to investigate further the atomic and electronic structures, pulse NMR experiments were carried out on ^{27}Al in the $Ca_{100-x}Al_x$ metallic glass system as well as the related crystalline compounds. To our knowledge, this is the first such work in a simple metal system. Panissod, et al.[12,13] have observed the spin-echo NMR spectra in a series of transition metal + metalloid systems and demonstrated that, independent of the preparation technique, the electric field gradient surrounding the metalloid atoms in these amorphous alloys possessed the same local symmetry as the corresponding crystalline compounds. This adds to the increasing evidence for the existence of short range order in the transition metal + metalloid metallic glasses. As of this writing, the situation for the $Ca_{100-x}Al_x$ simple metal system is not as definitive. It is striking that, although the Al concentration varies by a factor of three, the qualitative features of the observed spectra remain unchanged throughout the entire glass regime. The observed quadrupole spectra for the metallic glasses indicate that there is considerable distribution in the electric field gradient surrounding an Al atom and the local symmetry is non-uniaxial. This is also the case for the compositionally closest phase, Ca_3Al, which is not identified at this time. However, significant differences in the spectra and spin-spin relaxation times exist between the $Ca_{100-x}Al_x$ metallic glasses and Ca_3Al.

Finally, the experimental results indicate that the ^{27}Al Knight shift, measured in the steady state NMR experiments described above, and spin-lattice relaxation time, measured in the pulse NMR experiments described here, remain constant throughout the entire glassy regime. In addition, the small value for the Knight shift and, correspondingly, the long spin-lattice relaxation time indicate that the local Al-site density of s-electron states at the Fermi energy is small. These results are consistent with recent ultraviolet photoemission spectroscopy experiments as well as augmented-spherical-wave band structure calculations by Nagel, et al.[14] This work is part of a Ph.D. thesis by A. Paoluzi (see publications A10 and B4). A recent reprint (publication A10) is included at the end of this section.

E. Magnetization Study of the Co-Nb-B and Fe-Nb-B Metallic Glass Systems

Measurements of the saturation magnetization (and hence, Co or Fe magnetic moment) as well as the Curie temperature have been carried out on several new amorphous metallic alloys based on Co or Fe and stabilized with up to 10 at. % B and 14 at. % Nb. These new systems show attractive soft ferromagnetic properties, similar to those of the familiar transition metal + metalloid systems, while offering improved thermal stability despite the reduced metalloid content. This work is described in detail in publications A8, B2 and B3.

F. EXAFS Study of the $Fe_{67}Co_{18}B_{14}Si_1$ Metallic Glass System

K-shell extended x-ray absorption fine structure (EXAFS) data has been very carefully obtained and thoroughly analyzed on two thinned ribbon samples of $Fe_{67}Co_{18}B_{14}Si_1$ (Metglas 2605 CO): (1) as-fabricated and (2) magnetically annealed to obtain the enhanced magnetomechanical coupling constant. Spectra have been obtained and analyzed for both the Fe and Co absorbers, with x-ray polarizations both parallel and perpendicular to the length of the ribbon length, and at both room and liquid nitrogen temperatures. The first conclusion is that, in contrast to the work by Cargill, et al.[15] on Fe-P metallic glasses, the metalloid atoms are not the primary source of the EXAFS in Metglas 2605 CO. The EXAFS data show that the average distance from an Fe absorber to the transition metal shell nearest neighbors is larger than that for the Co absorber, i.e., $R_{Co-Co} < R_{Co-Fe} = R_{Fe-Co} < R_{Fe-Fe}$. This result is clearly supported by corresponding XANES spectra. Furthermore, the amplitude of the Fe EXAFS is smaller than that for Co. The fitting results indicate that the average disorder about the Fe site is larger than that about the Co site, which can account for the reduced Fe EXAFS amplitude. These results are in qualitative agreement with Wong[16] and DeCrescenzi, et al.[17] on Fe-Ni-metalloid metallic glasses. One possible explanation for these results is the preference of Co and Ni to exist in a close-packed environment, with a coordination of 12 neighbors, while Fe prefers to exist in an 8 nearest neighbor bcc-like environment. Finally, there was some evidence for structural anisotropy in the second near neighbor shell, however, additional polarization studies are necessary to confirm this observation. This work was part of a Ph.D. thesis by G. H. Hayes, for which Prof. J. I. Budnick served as major advisor (see publication B7).

G. XANES Study of the $(Ni_{0.50}Pt_{0.50})_{75}P_{25}$ Metallic Glass System

New data on the Pt L_{III} and Pt L_{II} x-ray absorption edge near-in structure of the $(Ni_{0.50}Pt_{0.50})_{75}P_{25}$ metallic glass system has been obtained and compared with previous results on random solid solution crystalline alloys as well as other transition metal + metalloid metallic glasses. For the $(Ni_{0.50}Pt_{0.50})_{75}P_{25}$ system, it was found that the total number of 5d holes per Pt site is actually greater than that for pure crystalline Pt. This is particularly striking in that various experimental probes of the electronic structure, such as magnetic susceptibility, heat capacity and Knight shift, indicate that the density of d-states at the Fermi energy, $N_d(E_F)$, is sharply reduced in the metallic glass relative to the pure crystalline transition metal. In particular, the ^{195}Pt Knight shift and magnetic susceptibility results for $(Ni_{0.50}Pt_{0.50})_{75}P_{25}$ described in Section IIIA indicate that $N_d(E_F)$ is much smaller than that for Pt[18]. It is common practice to interpret such results in terms of a filling of the transition metal d-band due to a transfer of electronic charge from the metalloid. Such an explanation would appear to contradict the XANES results, however, a clever model developed by D. M. Pease has reconciled this dilemma. Because the core hole broadening is so much greater than the actual width of the unoccupied d-band, the height of the threshold peak in the XANES is sensitive only to the integrated number of d-holes and is insensitive to the details of the density of states near E_F. The moral to be drawn is that even if the addition of a metalloid to a transition-metal-based glassy alloy results in a lowering of $N_d(E_F)$, this observation by no means implies that the d-band is being filled in the process. This work is part of a Ph.D. thesis by M. Choi, for which Prof. D. M. Pease served as major advisor (see publications A11 and B10). A recent reprint (publication A11) is included at the end of this section.

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ATOMIC AND ELECTRONIC STRUCTURES OF THE Ca-Al METALLIC GLASS SYSTEM: A PULSE NMR STUDY*

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In order to investigate the atomic and electronic structures, pulse NMR experiments were carried out on ^{27}Al in the melt spun $Ca_{100-x}Al_x$ metallic glass system and the related crystalline compounds. The spin-echo quadrupole spectra indicate considerable distribution in the electric field gradient and non-uniaxial local symmetry for the Al atoms. Measurements of the spin-lattice relaxation time are consistent with a small density of s-electron states at the Al sites as predicted by recent band structure calculations.

1. INTRODUCTION

In spite of the considerable research effort devoted to metallic glasses during the past decade, fundamental questions concerning the atomic and electronic structures remain unanswered. Nuclear magnetic resonance (NMR) is a very powerful tool for investigating the microscopic properties of liquids, and both amorphous and crystalline solids. In particular, information concerning the atomic structure can be obtained through the electric quadrupole interaction, while the hyperfine interaction is useful for electronic structure studies. With this in mind, measurements of the NMR Knight shift and linewidth, as well as the magnetic susceptibility, were recently carried out on the binary $Ca_{100-x}Al_x$ metallic glass system for $15 \leq x \leq 45$[1]. These initial measurements were carried out at room temperature using steady state (cw) NMR techniques. All of the observed spectra were attributed to the ^{27}Al central component, or $-1/2 \longleftrightarrow +1/2$ transition, with the other transitions being far removed from the line due to the first order quadrupole interaction. The most significant observation in the early study was that both the ^{27}Al Knight shift and linewidth remain unchanged within error throughout the entire range of composition. This occurs in spite of the fact that both the average atomic volume and average electronic concentration change appreciably. The initial results seem to suggest that some form of short range order exists in this simple metal system, similar to that observed for transition metal + metalloid metallic glasses. In order to

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Figure 1 shows the ^{27}Al spin-echo NMR spectra observed at 4.2 °K and 10.5 MHz for four representative compositions from the a-$Ca_{100-x}Al_x$ metallic glass system (x = 15, 25, 35 and 45). Except for signal intensity, the spectra observed for the other intermediate compositions are similar in every respect. All of the spectra are significantly broadened by the electric quadrupole interaction and consist of a characteristic peak associated with the central transition and wings extending over 2 kOe (2 MHz) associated with all other transitions. Although the Al concentration, x, increases by a factor of three over the glassy regime and, therefore, substantial changes in the electric field gradient would be expected, the observed qualitative features of the spectra remain unchanged. The observed signal intensity simply scales with the number of resonating ^{27}Al nuclei. The spectra indicate that there is a significant distribution in the electric field gradient surrounding an Al atom and the local symmetry is non-uniaxial.

Figure 2 shows the ^{27}Al spin-echo NMR spectra observed at 4.2 °K and 10.5 MHz for the three crystalline alloys, c-Ca_3Al, c-$Ca_{55}Al_{45}$ and c-$CaAl_2$, as well as the a-$Ca_{65}Al_{35}$ metallic glass. Only the c-$CaAl_2$ spectrum demonstrates the distinct features which are characteristic of a well-ordered environment for the Al atoms. The c-$CaAl_2$ spectrum is typical of those observed for $I = 5/2$ nuclei in a single type of site with uniaxial symmetry ($\eta = 0$) and $\nu_Q = 294$ kHz. There is essentially no distribution in the electric field gradient. This is expected as c-$CaAl_2$ is a member of the cubic Laves (AB_2) family; a class of compounds which crystallize with a cubic structure but possess atoms at sites of less-than-cubic symmetry. X-ray diffraction measurements on the c-$CaAl_2$ sample confirmed the Laves structure. The other two crystalline samples, c-Ca_3Al and c-$Ca_{55}Al_{45}$ demonstrate non-uniaxial symmetry for the local Al environment and considerable distribution in the electric field gradient similar to that observed for the a-$Ca_{100-x}Al_x$ metallic glasses. As of this writing, efforts based on x-ray diffraction have proved unsuccessful in identifying the c-Ca_3Al phase. c-$Ca_{55}Al_{45}$ is a two phase combination of c-Ca_3Al and c-$CaAl_2$.

Preliminary values for the spin-spin relaxation time, T_2, were obtained at 4.2 °K and 10.5 MHz in the conventional way by measuring the spin-echo amplitude as a function of the time delay between the $\pi/2$ and π pulses. As expected, the value for T_2 characteristic of the central peak is significantly shorter than the value characteristic of the wings. (For a-$Ca_{65}Al_{35}$, the values are 1.2 msec and 2.3 msec, respectively.) This fact was exploited in obtaining central peak T_2 values for selected samples (see Table I). Except for c-$Ca_{55}Al_{45}$, all of the samples demonstrated exponential behavior for the central peak echo versus time delay thereby yielding single values for T_2. c-$Ca_{55}Al_{45}$ possessed both long and short components to T_2, which are associated with Al in the two crystalline Al. We note that the ^{27}Al relaxation rate remains unchanged within the error over the entire range of Al concentration ($15 \leq x \leq 45$) and is about 22% that for crystalline Al. This behavior is consistent with the earlier Knight shift measurements[2], and is significant in that a change in the Al concentration would vary the average number of electrons per atom.

4. DISCUSSION AND CONCLUSIONS

This paper presents spin-echo quadrupole spectra for the $Ca_{100-x}Al_x$ metallic glass system and related crystalline compounds. To our knowledge, this is the first such observation in a simple metal system. Panissod, et al.[6] have observed the spin-echo spectra in a series of transition metal + metalloid systems: (i) ^{71}Ga in splat-cooled glassy $La_{75}Ga_{25}$, (ii) ^{11}B in sputtered amorphous $Mo_{70}B_{30}$ and in splat-cooled glassy $Mo_{48}Ru_{32}B_{20}$, and (iii) ^{11}B in glassy $Ni_{78}P_{14}B_8$ quenched from the melt. Their work demonstrated that, independent of the preparation technique, the electric field gradient surrounding the metalloid atoms in the amorphous alloys possessed the same local symmetry as the corresponding crystalline compounds, i.e., cubic La_3Ga, tetragonal Mo_2B and orthorhombic Ni_3B. In their analysis of the ^{11}B quadrupole spectra in $Ni_{100-x}B_x$ metallic glasses, Panissod, et al.[7] find that the symmetry of the electric field gradient for the x = 18.5 and 40.0 concentrations are similar to the compositionally closest nickel borides (Ni_3B and Ni_4B_3, respectively), and conclude that the local atomic structure is therefore similar. Furthermore, they suggest that the intermediate concentrations are related to an admixture of crystalline Ni_3B and Ni_4B_3. There is increasing evidence for the existence of short range order in the transition metal + metalloid metallic glasses. As of this writing, the

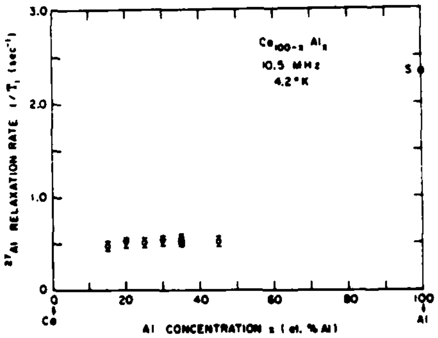

FIGURE 3
^{27}Al spin-lattice relaxation rate for $Ca_{100-x}Al_x$ metallic glasses

TABLE I

Sample	T_2 (msec)	T_2^* (μsec)	K (%)
a-$Ca_{65}Al_{35}$	1.2	13	0.042
c-Ca_3Al	1.7	58	-0.003
c-$Ca_{55}Al_{45}$	0.39 >1.2	22	0.033
c-$CaAl_2$	0.42	17	0.107

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ON THE DENSITY OF UNOCCUPIED d STATES IN TRANSITION METAL-METALLOID METALLIC GLASSES.*

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New data on the X-ray absorption edge near-in structure of the $(Ni_{0.50}Pt_{0.50})_{75}P_{25}$ system is compared with previous results on random solid solution alloys and other TM-M metallic glasses. Whereas experimental probes of the density of d states at the Fermi energy, $\rho_d(E_f)$, often indicate a sharp reduction in $\rho_d(E_f)$ due to the presence of metalloids or nontransition metals, absorption edge results usually indicate a negligible decrease in the total number of d holes per transition metal atom. In the $(Ni_{0.50}Pt_{0.50})_{75}P_{25}$ system the number of 5d holes per Pt site is actually found to be greater than for the case of pure Pt. A model is proposed which may reconcile the results of absorption edge measurements and $\rho_d(E_f)$ determinations.

1. INTRODUCTION

In studies of the electronic structure of transition metal-metalloid (TM-M) metallic glasses, it is often found that the density of d states at the Fermi level $\rho_d(E_f)$ is sharply reduced in the glass relative to the pure transition metal. Thus, photoemission, magnetic susceptibility, and specific heat measurements indicate that $\rho_d(E_f)$ is considerably lowered in several metallic glasses based on either a Pd or Ni transition metal matrix[1,2,3,4,5]. Platinum Knight shift results for the $(Ni_yPt_{1-y})_{75}P_{25}$ system show that the large negative core polarization contribution to the Knight shift in pure Pt is not present in the metallic glasses studied[6]. In these systems, the Pt Knight shift is nearly zero, indicating a low value of $\rho_d(E_f)$.

When a low value of $\rho_d(E_f)$ is observed in a metallic glass, it is a common practice to interpret this observation in terms of a filling of the transition metal d band. For instance, Riley, et al. interpret the photoemission results on amorphous $Pd_{0.81}\ Si_{0.19}$ in terms of a filling of the Pd 4d shell[4], and Hines, et. al. have interpreted their NMR data in terms of a filling of the Pt 5d holes in the $(Ni_yPt_{1-y})_{75}P_{25}$ system[6]. Results of saturation magnetic moment measurements are often considered a different form of evidence for d band filling in metallic glasses. Thus, Mizoguchi and Yamauchi interpret the changes in magnetic moment of the 3d transition metal in certain (TM-M) metallic

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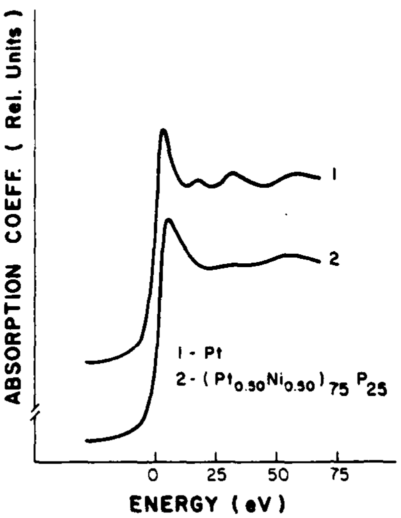

FIGURE 1
Pt L_{III} edges of pure Pt and $(Pt_{0.50}Ni_{0.50})_{75}P_{25}$

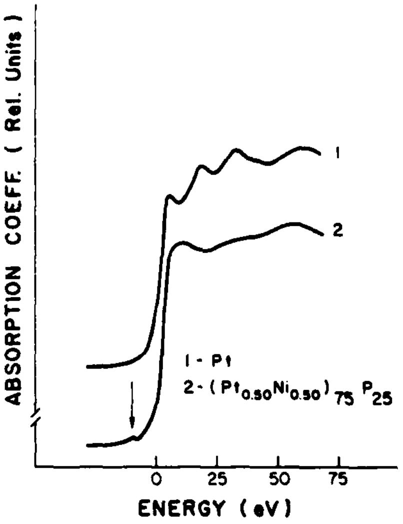

FIGURE 2
Pt L_{II} edges of pure Pt and $(Pt_{0.50}Ni_{0.50})_{75}P_{25}$. The arrow denotes the position of the pre-edge feature referred to in the text.

of this feature increasing systematically with Pt concentration, and the dip goes negative in a manner suggestive of the Fano effect[16]. However, until more synchrotron time becomes available so that it is possible to exhaustively reproduce this feature of the data, our emphasis will be on the d band occupancy of the single $(Ni_{0.50}Pt_{0.50})_{75}P_{25}$ composition.

Several methods have been proposed for quantifying XANES spectra in terms of d hole count[17,18,19]. Lytle suggests that an arctangent-like approximation to the continuum be removed in order to isolate the d hole contribution[17]. In Lytle's method, the inflection points of the absorption edge and arctangent are aligned. Brown, et. al., point out that both L_{II} and L_{III} edges must be compared, since these spectra are senstitive to $d_{3/2}$ and $d_{5/2}$ holes, respectively[18]. This consideration is particularly important for Pt XANES because of the relativistic effects in the Pt band structure[20]. One often overlooked point in discussions of how best to subtract the continuum contribution from the XANES is the difficulty of knowing how to align the energy scale of a presumed continuum state arctangent with the observed absorption edge. In Lytle's method, the inflection point of the arctangent is lined up with the inflection point of the experimental spectrum[17]. Traditionally, the inflection point of an absorpexperimental results of Cordts, et. al.[11], even though the calculated $\rho_d(E_f)$ is decreasing rapidly with increasing copper concentration, and the experimental results indicate no corresponding change in the integrated number of 3d holes per nickel site. The calculation shows the high energy tail of the unoccupied d states extending further above the Fermi energy as copper concentration increases. Thus, the calculated area corresponding to the total number of nickel 3d holes per nickel atom does not decrease, though $\rho_d(E_f)$ does decrease as copper concentration becomes larger. In a calculation more germane to the present discussion, Bisi and Calandra have calculated the partial density of Pt d states for crystalline Pt_2Si[27]. The value of $\rho_d(E_f)$ is quite low, though there is a large density of Pt 5d states split off from the main 5d band and peaking about 1 eV above E_f. Since the broadening of the Pt L_{III} core hole is roughly 5 eV,[28] XANES of this material would integrate the entire d hole region but be completely insensitive to the low $\rho_d(E_f)$. In conclusion, there is no real discrepancy between XANES and various probes of $\rho_d(E_f)$, for the presently studied system and others as well. The moral to be drawn is that even if the addition of a metalloid to a TM based glassy alloy results in a lowering of $\rho_d(E_f)$, this observation by no means implies that the d band is being filled in the process.

Finally, it should be mentioned that the present paper has not dealt with yet another potential conflict between XANES and other probes of alloy electronic structure; namely, the extinction of the TM saturation moment in systems for which no d hole filling is detected. There are schematic models of ferromagnetism in these systems which have potential for resolving this difficulty, such as the split band approach of Beeby[29] or the model of Corb, et. al.[30] The nature of the dependence of ferromagnetism on alloying is still a subject requiring considerable experimental and theoretical investigation.

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IV. SPIN-ECHO NMR STUDY OF THE ATOMIC ENVIRONMENT IN THE $Fe_{100-x}B_x$ METALLIC GLASS SYSTEM

There exists a number of studies concerning the bulk and local properties of the binary $Fe_{100-x}B_x$ metallic glass system[3]. These studies include composition dependent measurements of the magnetization[19] and nearest neighbor coordination[20], as well as Mössbauer studies of the Fe hyperfine field[21,22]. To our knowledge, no systematic study involving the composition dependence of the B hyperfine field in the stable glassy region for $Fe_{100-x}B_x$ has been reported. There does exist, however, a composition dependence study of the B hyperfine field for the mixed system $Fe_{79}P_{21-x}B_x$, in which B is substituted for P maintaining a constant Fe-to-metalloid ratio[23]. In addition, some results from systematic studies of the NMR relaxation rates in related systems have been reported[24].

In an effort to provide additional microscopic information concerning the binary $Fe_{100-x}B_x$ metallic glass system, we have undertaken a systematic study of the hyperfine field distribution at the B site for $14 \leqq x \leqq 22$, a composition region known to produce a stable glassy structure. The ribbons studied were fabricated by a melt spinning process, and examined by x-ray diffraction and differential thermal analysis[19]. Five NMR samples having compositions within the above concentration range were prepared by cutting and stacking the ribbons with alternate layers of 12 μm mylar foil. Spin-echo NMR spectra were obtained at 4.2 °K, over the frequency range 22 MHz to 46 MHz, using two approximately equal radio frequency pulses to excite the echo. The experimental techniques and calibration procedure have been described in detail elsewhere[25].

As expected from isotropic abundance and relative NMR sensitivity considerations, and demonstrated by Raj et al.[26], the principal contribution to the spectra at these frequencies arises from the ^{11}B nuclei and results from a hyperfine field transferred from the near neighbor Fe atoms. Thus, the B nuclei provide a sensitive probe for monitoring several things resulting from variations in the B-to-Fe ratio, including changes in the coordination number and near neighbor distance, as well as some longer-range effects which are usually difficult to separate.

In Fig. 1, we show the ^{11}B spin-echo NMR spectra, echo amplitude versus frequency, for the $Fe_{86}B_{14}$, $Fe_{82}B_{18}$, and $Fe_{78}B_{22}$ metallic glass compositions. The ^{11}B spectra for the intermediate compositions, $Fe_{84}B_{16}$ and $Fe_{80}B_{20}$, fall between the three shown in a consistent manner; however, they have been omitted to allow a clearer view of the compositional variation. Our results are in good agreement with a recent study by V. S. Pokatilov[27] on the $Fe_{82}B_{18}$ metallic glass. As the B concentration, x, is increased, intensity is added to the low field portion of the hyperfine field distribution with the high field components remaining essentially unchanged. As illustrated in Fig. 2, a plot of the peak location, or average hyperfine field, for increasing B concentration shows a smooth decreasing trend. This view of the data does not emphasize variations in the shape of the hyperfine field distribution. A recent analysis of the systematics of the Mössbauer results for the ^{57}Fe hyperfine field in $Fe_{100-x}B_x$ suggests that increasing the B concentration adds intensity at lower hyperfine fields with a less significant reduction in the high field contribution, similar to our preliminary results for ^{11}B (see ref. 28). Fig. 2 compares the composition dependence of the B hyperfine field obtained from our work with that for Fe obtained from the Mössbauer study[21,22]. Further analysis is in progress to establish a detailed model relating the hyperfine fields and structural changes.

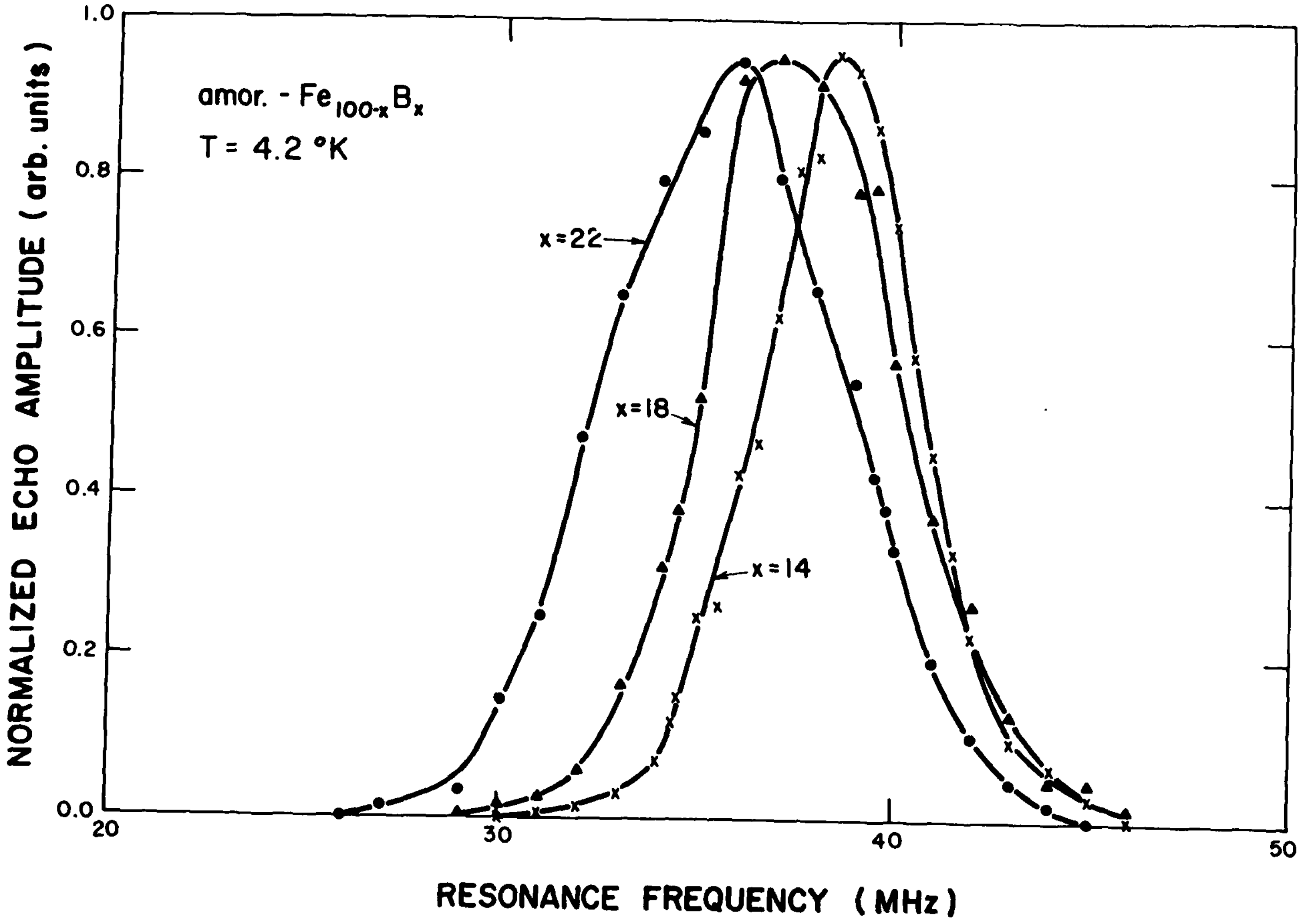

Fig. 1. Normalized NMR spin-echo amplitude (arbitrary units versus resonance frequency (MHz): crosses - $Fe_{86}B_{14}$, triangles - $Fe_{82}B_{18}$, and circles - $Fe_{78}B_{22}$. The spectra are attributed mainly to the metalloid ^{11}B nuclei.

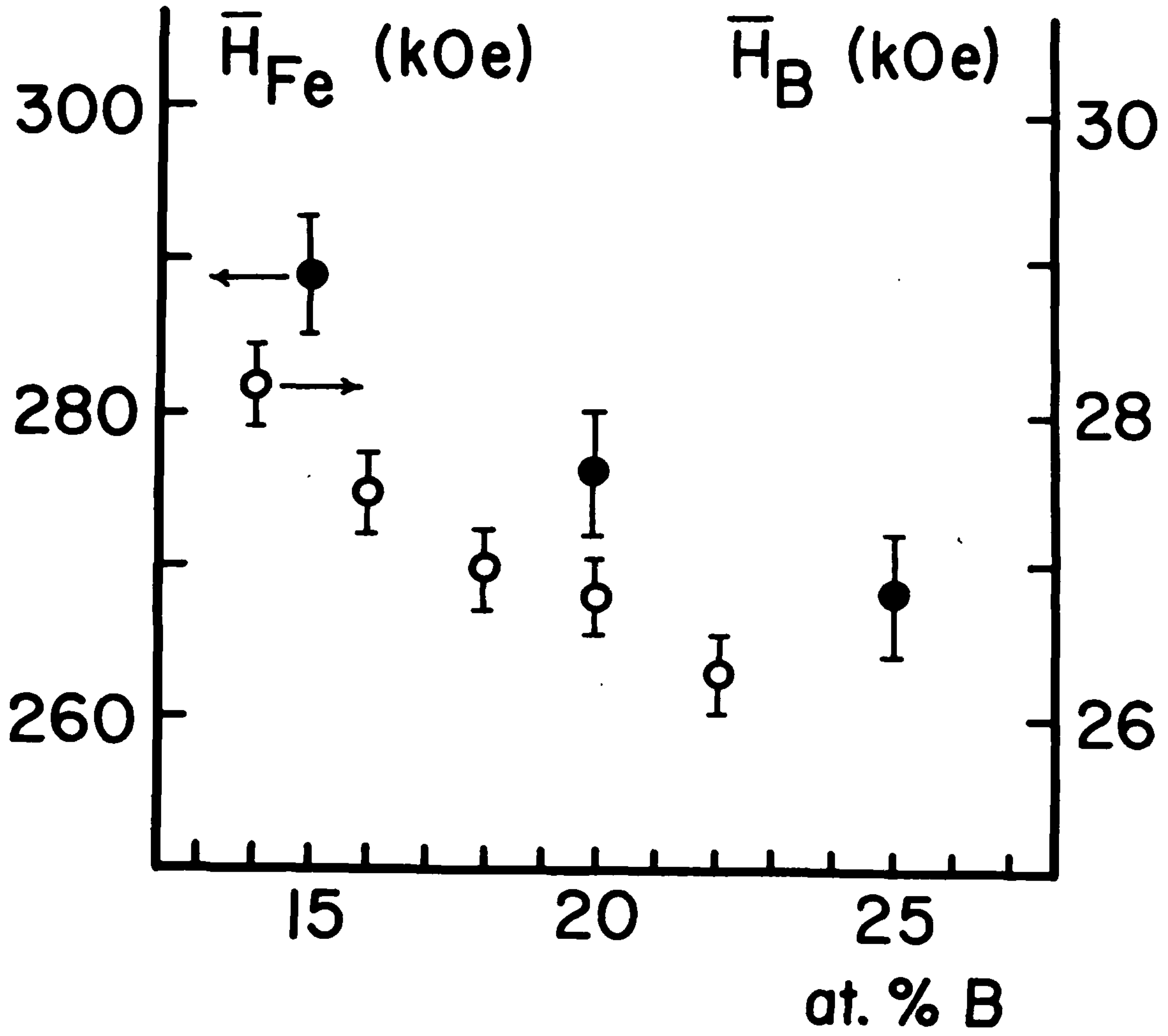

Fig. 2. Average hyperfine field, $\overline{H}$, in kOe, versus B concentration, x, in at. %, for the $Fe_{100-x}B_x$ metallic glass system: solid circles - ^{57}Fe from Mössbauer, refs. 21 and 22; and open circles - ^{11}B from NMR, this work.

V. LOW FIELD MAGNETIC ANISOTROPY IN METGLAS 2605 CO RIBBONS

A. Introduction

Recently, there has been considerable research interest concerning the enhanced magnetoelastic properties of certain iron-based metallic glasses. Such magnetoelastic properties include the magnetomechanical coupling factor, k_{33}, which is a measure of the conversion of magnetic energy into elastic energy. In particular, Metglas 2605 CO ($Fe_{67}Co_{18}B_{14}Si_1$) and Metglas 2605 SC ($Fe_{81}B_{13.5}Si_{3.5}C_2$) exhibit very high coupling factors (0.71 and ≥ 0.90, respectively) after undergoing specific magnetic annealing treatments[10]. In order to understand the origin and nature of this high coupling, we have carried out detailed low field magnetization measurements at room and liquid nitrogen temperatures on several samples of Metglas 2605 CO ribbons, which include as-fabricated, magnetically annealed, and non-magnetically annealed samples. This report presents magnetization data showing directly the magnitude of the anisotropy which exists in the as quenched ribbons due to the fabrication process, as well as that which is induced by magnetic annealing. In addition, values for the saturation magnetization, M_s, domain magnetization, M_d, coercive field, H_c, initial permeability, μ, anisotropy energy constant, K, and saturation magnetostriction, λ_s, are reported.

As indicated above, this report concerns the characterization of Metglas 2605 CO with regard to the bulk magnetic properties in general and magnetic anisotropy in particular. In addition to this work, a number of local studies on Metglas 2605 CO are currently in progress, which are aimed at determining the nature of the near neighbor atomic environments, how these environments are affected by the thermal, mechanical, and magnetic history, and the phases that result from crystallization. These studies include the techniques of NMR[29], EXAFS and XANES[30], Mössbauer[31], and x-ray diffraction[32]. One of the ultimate goals of these local studies is to understand the microscopic nature of the magnetic anisotropy which exists or is induced, in these systems.

B. Experimental Apparatus and Procedure

Ribbons of Metglas 2605 CO prepared by the "planar flow casting" process, 1.3 cm wide and 40 μm thick, are commercially available from the Allied Corporation. All the samples for the magnetization experiments were carefully cut into squares, 0.635 ± 0.005 cm on a side, such that the sides are parallel and perpendicular to the ribbon length. The magnetization measurements presented here were obtained with the externally applied magnetic field lying in the plane of the ribbon and having one of these two orientations (i.e., parallel or perpendicular to the ribbon length). As discussed in Section VC, the demagnetization contribution is significant in these experiments and, hence, a precise control of the sample geometry was required. Some of the samples were thinned using a metallography polishing wheel with various grades of alumina slurries.

Some of the samples used in this work were identical in preparation to those used in the local studies mentioned above[29,30,31,32] and have undergone the following heat treatments: (1) no annealing treatment after the initial fabrication, (2) annealing at 369 °C for 10 minutes in a magnetic field of 6.1 kOe lying in the plane of the ribbon perpendicular to its length, and (3) annealing at 425 °C for 15 minutes in a magnetic field of 6.1 kOe lying in the plane of the ribbon perpendicular to its length. The sample prepared from the original material [(1) above] was designated "as quenched". The sample prepared by process (2) represents a partially relaxed glassy state and was designated "annealed". The "annealed" sample yields a maximum value for k_{33} (0.71). The sample prepared by process (3) was designated "crystalline" and represents a partially crystallized two-phase situation in which an initial crystalline phase emerges leaving behind a residual amorphous phase with altered composition. The "crystalline" sample has a drastically reduced value of k_{33}. To avoid confusion, we have used the same sample designations here as used in the other studies. Two additional sample preparations with the following heat treatments were used in this work: (4) annealing at 350 °C for 10 minutes with no magnetic field present and (5) annealing at 580 °C for 15 hours with no magnetic field present. The sample prepared by process (4) was designated "non-magnetically annealed" and represents an attempt to eliminate the magnetic anisotropy induced by the fabrication process. The sample prepared by process (5) was designated "totally crystalline" and is composed of the terminal crystalline phases of the material.

The magnetization measurements were carried out on a P. A. R. Model 155 vibrating sample magnetometer, at room and liquid nitrogen temperatures, with the externally applied magnetic fields continuously variable (and reversible) up to 20 kOe. The magnetometer was calibrated against the known room temperature saturation magnetization for Ni (55.01 emu/gm), while the applied magnetic field was measured with a Hall probe gaussmeter. The sample temperature was controlled with a modified Varian Model V-6040 nitrogen gas flow system.

C. Experimental Results and Analysis

Figure 3 shows the room temperature magnetization (in emu/gm), M, as a function of the externally applied magnetic field (in Oe), H_{ext}, for the two orientations of H_{ext} in a typical "as quenched" sample of Metglas 2605 CO. As indicated above, the two orientations for H_{ext} (lying in the plane of the ribbon) are parallel and perpendicular to the ribbon length. As can be seen in Fig. 3, there exists a small magnetic anisotropy with the easy axis parallel to the ribbon length. The room temperature magnetizations for the two orientations saturate at a common value of $M_s = 189$ emu/gm.

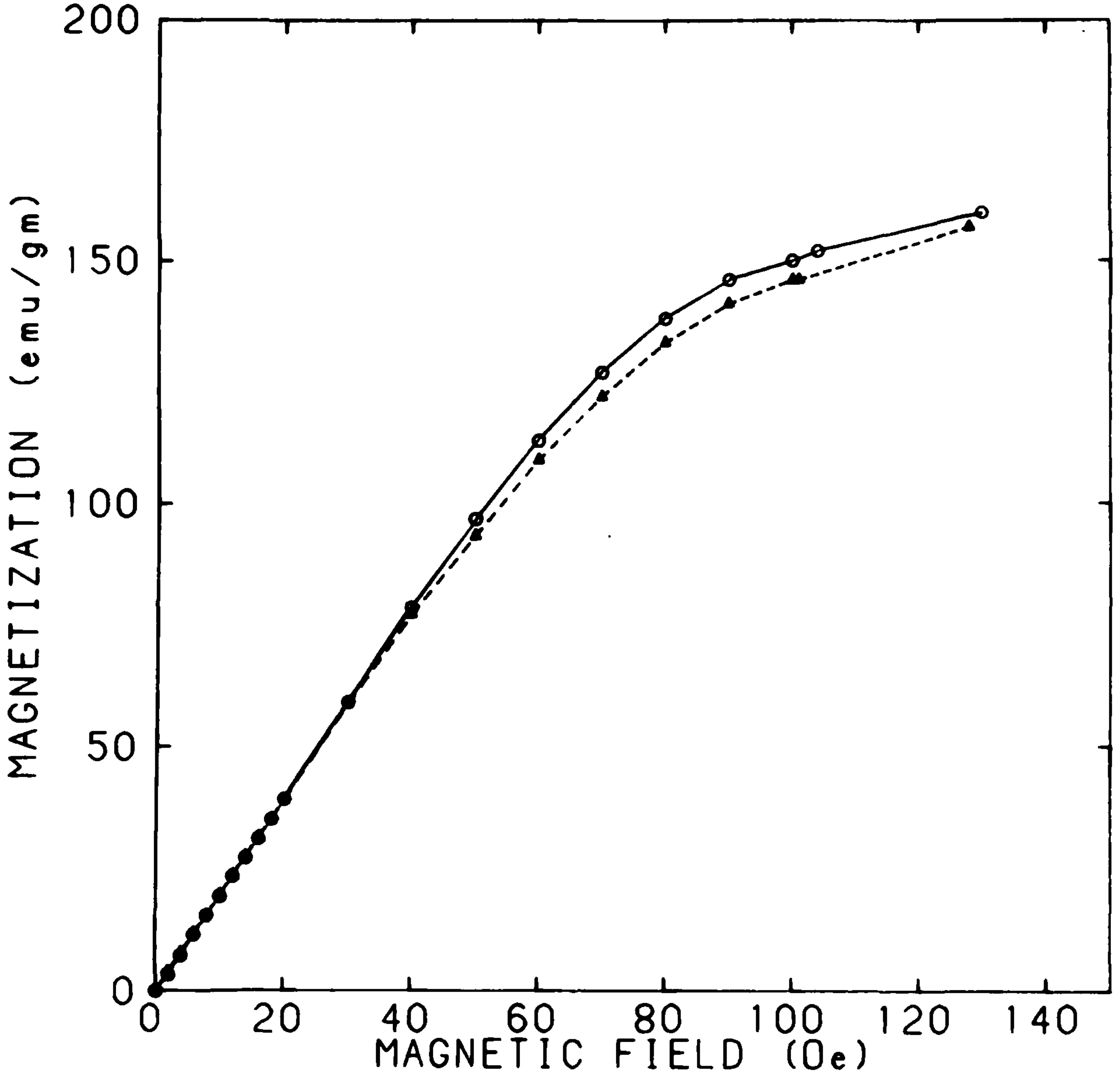

Fig. 3. The room temperature magnetization (in emu/gm), M, as a function of the externally applied magnetic field (in Oe), H_{ext}, for "as quenched" Metglas 2605 CO. The solid line with open circles represents H_{ext} parallel to the ribbon length and the dashed line with solid triangles represents H_{ext} perpendicular to the ribbon length.

Figure 4 shows M as a function of H_{ext} for the two orientations of H_{ext} in a typical "annealed" sample of Metglas 2605 CO. However, as illustrated in Fig. 4, the effect of the magnetic annealing treatment has been to induce a magnetic anisotropy with the easy axis now lying perpendicular to the ribbon length. The common saturation value of the room temperature magnetization obtained for both orientations of the "annealed" sample is $M_s = 192$ emu/gm. Within experimental error, the magnetization curves for both the "as quenched" and "annealed" samples of Metglas 2605 CO exhibit no coercivity (i.e., $H_c \leqq 0.5$ Oe).

As indicated earlier, the demagnetization effect is very important for the sample geometry used in these measurements. We note that using longer ribbon geometries in air core magnet systems usually eliminates the demagnetization problems[33], however, it is not as straightforward to measure the magnetization directly for two orientations on the same sample with such systems. For the magnetization measurements presented in this paper, it was essential to eliminate any anisotropy resulting from differences in the demagnetization factor, D, for the two orientations due to imperfections in sample geometry (square). We have estimated D for our sample geometry by two methods. The first method uses the expressions for the three demagnetization factors associated with a general ellipsoid which have been calculated by Osborn[34]. By approximating our samples as very flat prolate spheroids with the polar axis being normal to the ribbon plane and using the sample dimensions indicated above, we estimate $D = 6.0 \times 10^{-2}$ (Gaussian units). The second method approximates the "induced magnetic charge" or "poles" as a finite line of poles and calculates the corresponding demagnetization field in the interior of the sample. This results in an average value of $D = 6.3 \times 10^{-2}$. It should be noted that for our square samples of Metglas 2605 CO, the high initial permeability compensates for the small demagne-

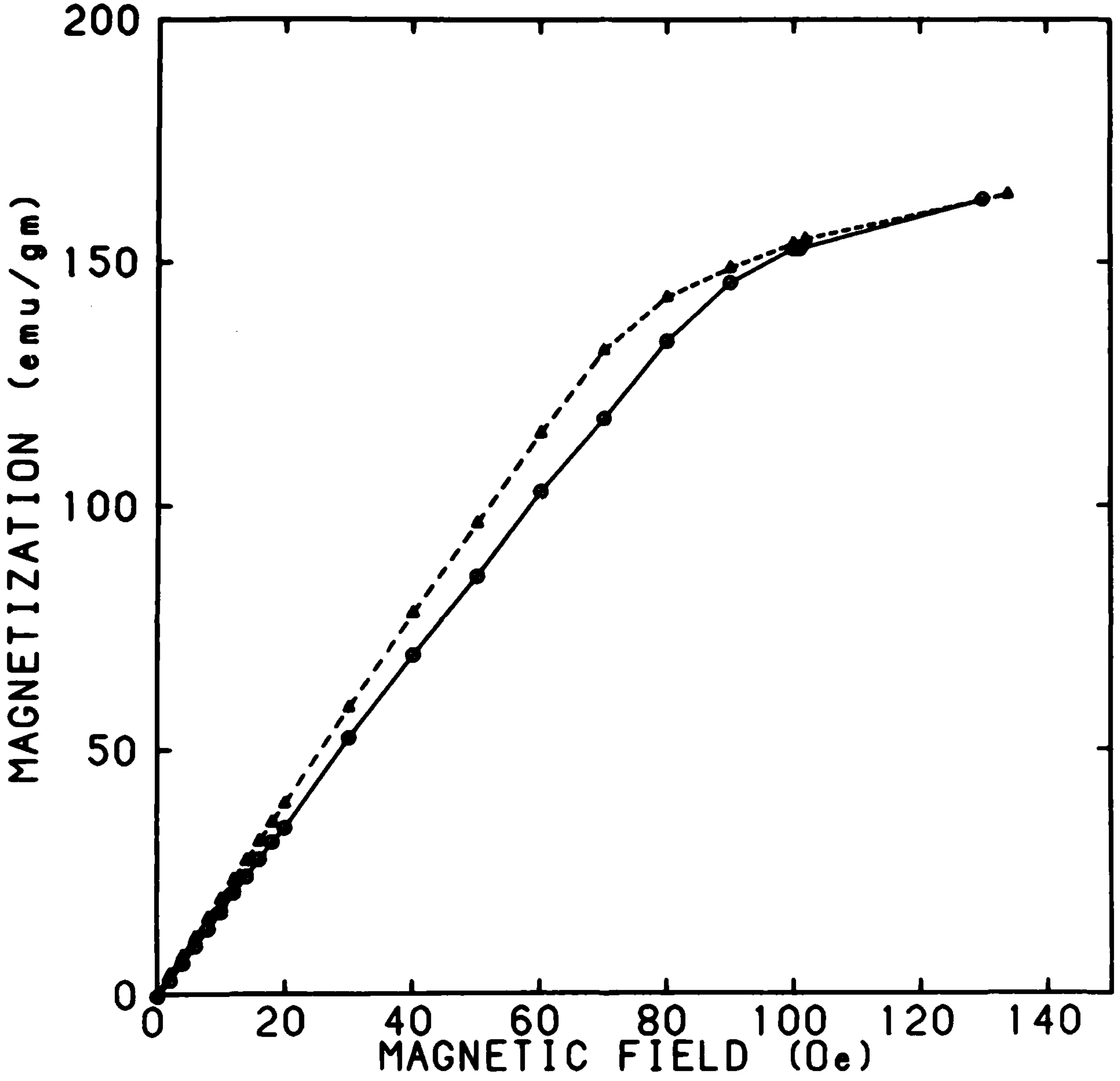

Fig. 4. The room temperature magnetization (in emu/gm), M, as a function of the externally applied magnetic field (in Oe), H_{ext}, for "annealed" Metglas 2605 CO. The solid line with open circles represents H_{ext} parallel to the ribbon length and the dashed line with solid triangles represents H_{ext} perpendicular to the ribbon length.

tization factor. In order to experimentally determine the contribution to the measured anisotropy associated with differences in D which arise from errors in cutting the samples, a series of samples whose three dimensions varied in a systematic way were prepared and measured. From the experiments on this series, it was determined that the samples could be cut with sufficient accuracy to insure that the observed anisotropy is truly characteristic of the bulk material and not a manifestation of differences in the demagnetization effect for the two orientations. Finally, the anisotropy in an "as quenched" sample of Metglas 2605 CO was measured and then remeasured in the same sample after it had undergone the same magnetic annealing treatment as the "annealed" samples. The change in the magnetic anisotropy for this sample is consistent with all the results obtained previously from separate "as quenched" and "annealed" samples.

With the customary assumption of uniform internal magnetization, M, and magnetic field intensity, H, we can relate the internal magnetic field intensity to the externally applied magnetic field, H_{ext}, by

$$H = H_{ext} - DM. \tag{1}$$

(M is now expressed in emu/cm^3 by taking the density of Metglas 2605 CO to be $\rho = 7.56$ gm/cm^3.) Furthermore, the anisotropy energy density for a sample with a single easy axis is $E = K \sin^2\theta$, where K is the anisotropy energy constant and θ is the angle between the easy axis and the magnetization direction. Since the work required to change the magnetization from zero to M is just

$$W = \int_0^M HdM, \tag{2}$$

we can calculate K for an "annealed" sample by

$$K = \int_0^M H_{||}dM - \int_0^M H_{\perp}dM = \int_0^M [H_{ext}(||) - H_{ext}(\perp)]dM, \qquad (3)$$

which is just the area between the magnetization curves for the two orientations. Equation (1) has been substituted for H and, since D is the same for both orientations, the demagnetization terms cancel. From the room temperature magnetization data for all of the "annealed" samples, we find an average value of $K = (4.3 \pm 0.6) \times 10^3$ erg/cm^3. When the temperature is reduced to 77 °K, the anisotropy increases resulting in an average value of $K = (5.9 \pm 0.6) \times 10^3$ erg/cm^3. Correspondingly, the saturation magnetization increases to 201 emu/gm. As was the case at room temperature, there is no detectable coercivity at 77 °K for the "annealed" samples.

Finding the area between the magnetization curves for the two orientations of an "as quenched" sample was complicated by the occurrence of a long thin "tail" which obscured the point at which the two curves merge. Consequently, we report a lower limit for the average value of K, i.e., $K \geq 1.8 \times 10^3$ erg/cm^3 for "as quenched" Metglas 2605 CO. Furthermore, we note that the "non-magnetically annealed" sample exhibited essentially the same magnetic anisotropy as the "as quenched" samples, i.e., $K \geq 1.8 \times 10^3$ erg/cm^3, with the easy axis parallel to the ribbon length. However, the saturation magnetization for the "non-magnetically annealed" sample is the same as that for the "annealed" sample, i.e., 192 emu/gm.

Finally, the magnetization curves for the "crystalline" sample indicate an initial onset of coercivity (H_c = 4.2 Oe) and a saturation magnetization of 198 emu/gm. These values are common to both orientations of the "crystalline" sample; it appears that any anisotropy which might exist is masked by the effects of the coercivity. The magnetization curves for the "totally crystalline" sample exhibit H_c = 67 Oe, M_s = 205 emu/gm, and no detectable anisotropy.

D. Discussion and Conclusions

The low field magnetization measurements on as-fabricated Metglas 2605 CO indicate that a magnetic anisotropy exists with the easy axis along the ribbon length. It was not possible to eliminate this anisotropy by a non-magnetic annealing treatment below the crystallization temperature. By using a magnetic annealing treatment which yields an enhanced value for k_{33}, an anisotropy is induced with the easy axis in the plane of the ribbon and perpendicular to the length ($K = 4.3 \times 10^3$ erg/cm^3 at room temperature and 5.9×10^3 erg/cm^3 at 77 °K). Hernando, et al.[35] and Livingston, et al.[36] have directly observed the domain structure for "annealed" Metglas 2605 CO by a Bitter technique and scanning electron microscopy, respectively. Using a simple domain rotation model, Spano, et al.[33] calculate k_{33} by

$$k_{33} = [\ 1 + 8K^3/(9H_{bias}{}^2M_d{}^2\lambda_s{}^2E_m)\ ]^{-1/2}, \qquad (4)$$

where H_{bias} is the bias magnetic field, M_d is the domain magnetization, and E_m is Young's modulus. For "annealed" Metglas 2605 CO, Modzelewski, et al.[10] found a maximum value of k_{33} for H_{bias} = 10.5 Oe. Bucci, et al.[37] have determined the direction and spread of the magnetization in this material by using Mössbauer techniques. From their work, we can take $M_d = 0.75M_s$ = 143 emu/gm = 1090 emu/cm^3. Using the measured value of $E_m = 9.5 \times 10^{11}$ dyne/cm^2 from Meeks and Hill[38] along with the parameters above, we calculate $\lambda_s = 25 \times 10^{-6}$ from Eqn. (4). Finally, the various initial permeabilities can be calculated from the slopes of our magnetization curves ($S = \Delta M/\Delta H_{ext}$) by taking

$$\mu = 1 + 4\pi S/(1 - DS). \qquad (5)$$

In particular, we find a room temperature value of μ = 950 for "annealed Metglas 2605 CO parallel to the ribbon length. This value is in good agreement with that obtained by Modzelewski, et al.[10] using a long ribbon geometry in an air core system.

VI. OTHER WORK

A. Reflectivity Study of the $Ni_{100-x}P_x$ Metallic Glass System

In order to investigate the electronic structure of the $Ni_{100-x}P_x$ ($15 \leq x \leq 25$) metallic glass system, measurements of the specular reflectivity for near normal incidence have been carried out at room temperature over the energy range 0.52 eV to 6.2 eV on samples prepared by both rapid quenching and electroplating techniques. The measured reflectivity for rapidly quenched $Ni_{81}P_{19}$ decreases from 85% (0.52 eV) to 15% (6.2 eV), with structure occurring at approximately 4.0 eV. The reflectivity behavior is qualitatively similar to that observed for Au-Si metallic glasses, however, a plot of $-\ln R$ vs. $E^{1/2}$ for low energies does not follow the (linear) Drude form[39]. Calculations for the real part of the dielectric constant, ε_1, and optical absorption, ε_2/λ, carried out by the standard Kramers-Kronig analysis as well as a "time domain" method were consistent[40]. Similar measurements of the reflectivity have been made on various compositions of electroplated $Ni_{100-x}P_x$ and the results are being analyzed in terms of existing models for the electronic structure.

B. Mössbauer Study of the $Fe_{67}Co_{18}B_{14}Si_1$ Metallic Glass System

Motivated by the initial surface crystallinity study of $Fe_{67}Co_{18}B_{14}Si_1$ (see ref. 32), Prof. J. I. Budnick and Dr. G. Longworth carried out an investigation of the ^{57}Fe hyperfine field distributions associated with the various crystalline and amorphous phases. Using the techniques of transmission and conversion electron Mössbauer spectroscopy, they were able to examine both bulk and surface regions in as-fabricated, magnetically annealed and partially crystallized samples. The results indicate that the magnetically annealed sample, which exhibits a large magnetomechanical coupling factor, possesses an α-Fe phase in which 25 at. % Co is dissolved as well as an amorphous phase. Our interest has been to completely characterize the surface regions and bulk properties of this material by using a combination of the Mössbauer measurements and previously published NMR[29], EXAFS and XANES[30], and x-ray[32] data. Ultimately, we will present additional results on the identification of phases, preferred orientation in the near surface region and local environment descriptions for the Fe and Co sites.

VII. PUBLICATIONS ATTRIBUTED TO AFOSR SUPPORT

A. Journal Articles

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B. Abstracts

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C. Oral Presentations

1. Institute of Chemical Analysis, Northeastern University
Materials Science Seminar
November 7, 1979

2. Materials Research Society
   1979 Annual Meeting, Cambridge, Massachusetts
   November 28, 1979

3. Department of Physics, University of Connecticut
   Physics Colloquium
   February 1, 1980

4. American Physical Society
   New York Meeting
   March 25, 1980

5. Department of Physics, College of William and Mary
   Physics Colloquium
   April 16, 1980

6. Department of Physics and Physical Sciences, Virginia Commonwealth University
   Seminar and Colloquium Series
   April 17, 1980

7. 25th Annual International Magnetics Conference
   Boston, Massachusetts
   April 24, 1980

8. 26th Annual Conference on Magnetism and Magnetic Materials
   Dallas, Texas
   November 13, 1980

9. Naval Surface Weapons Center
   Solid State Seminar
   May 13, 1981

10. Department of Physics, University of Delaware
    Solid State Seminar
    May 14, 1981

11. 27th Annual Conference on Magnetism and Magnetic Materials
    Atlanta, Georgia
    November 10, 1981

12. 3rd Joint Intermag. - Magnetism and Magnetic Materials Conference
    Montreal, Quebec, Canada
    July 22, 1982

13. Institute of Chemical Analysis, Northeastern University
    Materials Science Seminar
    February 23, 1983

14. Department of Physics, Northeastern University
    Physics Colloquium
    February 23, 1983

15. American Physical Society
    Los Angeles Meeting
    March 24, 1983

16. 5th International Conference on Liquid and Amorphous Metals
    Los Angeles, California
    August 15, 1983

17. Institute of Materials Science, University of Connecticut
    Advisory Board Meeting
    October 31, 1983

18. Department of Physics, University of Rhode Island
    Physics Colloquium
    November 11, 1983

19. Department of Physics, Central Connecticut State University
    Physics Seminar
    May 1, 1984

20. 30th Annual Conference on Magnetism and Magnetic Materials
    San Diego, California
    November 28, 1984

VIII. SCIENTIFIC PERSONNEL AND COLLABORATORS

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INSTITUTE OF MATERIALS SCIENCE

The Institute of Materials Science (IMS) was established at The University of Connecticut in 1966 in order to promote academic research programs in materials science. To provide requisite research laboratories and equipment, the State of Connecticut appropriated $5,000,000, which was augmented by over $2,000,000 in federal grants. To operate the Institute, the State Legislature appropriates over $700,000 annually for faculty and staff salaries, supplies and commodities, and supporting facilities such as an electronics shop, instrument shop, a reading room, etc. This core funding has enabled IMS to attract over $2,500,000 annually in direct grants from federal agencies and industrial sponsors.

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