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**Study of Local Atomic
and
Electronic Structure in Glassy Metallic Alloys
Contract DE-AC02-79ER-10382**

Progress Report: December 1, 1979 to November 1, 1980

Prepared by

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Prepared for

**Office of Basic Energy Sciences
U. S. Department of Energy
Washington, D. C. 20545**

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1. Introduction

This report is a summary of progress made during the period December 1, 1979 to November 1, 1980 under contract DE-AC02-79ER-10382 entitled "Local Atomic and Electronic Structure in Glassy Metallic Alloys" from Department of Energy, Division of Basic Energy Sciences, Materials Science Program.

2. Theoretical Work

During the first reporting period, March 1, 1979 - December 1, 1979, small clusters such as Fe_4 , Ni_4 , Ni_2Fe_2 alone and containing the metalloid atoms P and B were investigated. The effect of P and B on the magnetic moment of the clusters was investigated and found to parallel the known experimental trend. Significant metal-metalloid bonding was found in all the clusters studied.

During the present reporting period a detailed analysis of the bonding in these small clusters was carried out. As a result of this detailed analysis a very significant conclusion has been reached: there are preferential metal-metalloid interactions which are predicted on the basis of the calculations. Specifically it has been found that in FeNi clusters there is a preferential bonding of P to Fe and B to Ni. This has been described in two papers which are in press and preprints are included with this summary.

This specificity of bonding interactions is consistent with preliminary EXAFS measurements on Fe-Ni-B-P glasses by Wong et al. Also quite recently, Mossbauer results have been communicated to us by two European groups both of whom maintain that the analysis of the hyperfine fields in these glasses strongly support our theoretical conclusions.

Because of this unexpected finding regarding specificity of bonding interactions, we have pursued a somewhat different course in our calculations for this year than originally anticipated. We have completed calculations on the following clusters during this reporting period: Ni_6 , Ni_6B , Fe_6 and Fe_6B in O_h and D_{3h} symmetries (two different local environments of a B atom with 6 nearest neighbor metals) and of $\text{Ni}_3\text{Fe}_3\text{B}$ in C_{3v} symmetry. A similar series of calculations with a P atom as the metalloid are in progress, as are calculations using Ni_4B_2 and Ni_9B_2 clusters to investigate metalloid-metalloid interactions.

Although these calculations should be completed in about two months time, the analysis of the results will probably require an additional two months.

3. Experimental Work

Room temperature extended x-ray absorption fine structure (EXAFS) spectra above the K absorption edge of metal constituents in the following metal-metalloid and metal-metal glasses have been measured in the February and June 1980 runs at Stanford Synchrotron Radiation Laboratory: $\text{Fe}_{1-x}\text{B}_x$, $(\text{FeNi})_{1-x}\text{B}_x$, $\text{Ni}_{1-x}\text{B}_x$; $\text{Zr}_{1-x}\text{M}_x$ (M- Fe, Co, Ni and Cu) and $\text{Nb}_{1-x}\text{Ni}_x$. The data were Fourier transformed to yield structural information in real space about the central absorbing metal atoms in the glass structure. In addition a Fourier filtering technique has been used to isolate backscattering contribution from selected regions in space and aid differentiation of the local structure of each metal type in the glass. Results of the experiments are summarized as follows:

1. By Fourier filtering the EXAFS spectra taken in the region $1-3\text{\AA}$ about the Fe atoms in the glass and crystal, the local environment of Fe in glassy $\text{Fe}_{75}\text{B}_{25}$ is shown to be quite different from that in the crystallized phase (tetragonal Fe_3B),
2. In the $(\text{FeNi})_{1-x}\text{B}_x$ glasses, the high intensity low-k oscillation (due to the B as backscatterer) in the Fe EXAFS is not recoverable from the first shell transform, suggesting low probability of B as Fe nearest neighbor. However, the same low-k oscillation in the Ni EXAFS in the same Fe-Ni-B glasses is normal, implying B is present in the first coordination shell of Ni. This preferential Ni-B interaction in Fe-Ni-B glasses is in accordance with theoretical findings,
3. In metal-metal glasses denoted by $\text{M}'\text{-M}''$, Fourier transforms of the EXAFS spectra show that there exist like as well as unlike atom pairs in the "first coordination sphere" of both constituent metals. The ratio of like to unlike pairs is found to be proportional to composition suggesting random mixing of M'' and M' in the glass structure. Furthermore for all cases studied, the $\text{M}'\text{-M}''$ interatomic separation is less than the sum of Goldschmidt radii indicative of chemical interaction between M' and M'' ,
4. Room temperature Ni EXAFS spectrum have also been obtained for two Ni-B glasses: $\text{Ni}_{81}\text{B}_{19}$ glass which has the typical 80-20 composition of metal-metalloid glasses and $\text{Ni}_{66}\text{B}_{34}$ glass which has unusually high metalloid content. These two glasses are separated by a non-glass forming region centered around $\text{Ni}_{75}\text{B}_{25}$ which corresponds to a relatively high congruent melting compound Ni_3B in the equilibrium phase diagram. Of interest too

is the homogeneous crystallization of the $\text{Ni}_{66}\text{B}_{334}$ glass to a single Ni_2B phase, the structure of which is known from x-ray diffraction study. The Ni EXAFS has also been measured for this crystal and will be used to model the structure of the glassy phase. It should be mentioned that the Ni-B system is ideal for testing the Polk's model for the structure of metal-metalloid glass. Data reduction and analysis is now underway.

4. Proposed Work for the Period March 1, 1981 - February 28, 1982

A. Theory

Recent experimental work, together with results of computer generated model structures, indicate to us that the most likely local environments around a B or P atom in Ni-Fe-B-P glasses will consist of 6 or 9 metal atoms in the first coordination shell. Thus, after the present series of TM_6 clusters are completed, we propose to begin work on clusters such as Ni_3Fe_6 , Fe_3Ni_6 , Fe_9 and Ni_9 with/without B and P atoms.

As a consequence of the specificity of interactions found for B and P with Ni and Fe, we propose to investigate whether such specificity exists for other metalloids such as C and Si.

In a separate theoretical study, a considerable effort has been devoted to develop a computational technique and computer programs to evaluate the total energies for $X\alpha$ -SW calculations in an accurate manner employing numerical integration techniques. These programs are now being tested. If these tests are successful, we propose to use this method to calculate the energetics of bonding in some of the systems we have previously investigated. We believe this energetic information is very valuable and thus if initial test calculations for these systems are successful, we intend to make this a high priority effort for the coming year.

Thus, we propose:

1. To finish work in progress;
2. To begin calculations for 9 atom clusters such as Ni_3Fe_6 , Ni_6Fe_3 with and without B and P atoms;
3. To investigate specificity of bonding both for B and P in the clusters presently being studied (i.e. containing six metal atoms) and extend the work to other metalloids such as C and Si;
4. If present independent work on an accurate $X\alpha$ -SW total energy is successful, to apply the method to this problem to investigate preferred geometries and bonding energies; and,

5. If time allows, to perform calculations on metal-metal systems as suggested by EXAFS measurements.

B. Experiments

1. Low Temperature EXAFS Experiments - The Debye-Waller term α^2 which enters into the EXAFS effect is a sum of two contributions; structural disorder which is static and thermal disorder which is dynamic. The structural contribution, which is of prime interest in metallic glasses (and in amorphous materials in general) can be sorted out experimentally by performing EXAFS spectral measurements at low temperatures which minimize the thermal contribution appreciably since for EXAFS, α^2 is equivalent to a two-body average. We propose, therefore, to extend EXAFS measurements on the above discussed Fe-B, Ni-B and metal-metal glasses at 77K.
2. Quantitative Local Structure by Simulation - Combined with low temperature data, the EXAFS data after Fourier filtering in real space, will be used to derive structural parameters such as type of nearest neighbor, their distance of separation r , coordination number N , and fractional change in disorder α^2 using the single scattering equation for EXAFS for each coordination shell observed. Transferability of atomic parameters such as phase shift, back-scattering amplitude and mean free path from crystal analogues of known structure will be employed to determine the structural parameters for the corresponding glass systems. This phase of the data analysis is time consuming, requiring careful and concentrated work.
3. Ge Substitution for Probing Metalloid Environment in Ni-B-Ge Glasses - Large quantity of Ge may be incorporated into the Ni-B structure yet maintaining a one-phase glass (Liebermann and Wong, to be published). Since readily usable flux at the Ge absorption energy is readily available at Stanford, Ge will be used as an EXAFS probe to study the metalloid environment in metalloid-rich Ni-B-Ge glasses to check particularly for the occurrence of metalloid-metalloid contact pair and to test quantitatively the applicability or otherwise the Polk's Model for this non-conventional and metal-metalloid glass.

Publications

1. R. P. Messmer and J. Wong, "Short-Range Order in Inorganic Amorphous Solids", J. Non-Crystalline Solids, accepted for publication.
2. R. P. Messmer, "Theoretical Evidence for Specificity of Metal-Metalloid Interactions in Fe-Ni-P-B Glasses", Proceedings of "Conference on Metallic Glasses: Science and Technology, 1980", Budapest, Hungary, in press.
3. R. P. Messmer, "Local Electronic Structure of Amorphous Metal Alloys Using Cluster Models. I. Evidence for Specific Metalloid-Metal Interactions", Phys. Rev. B, in press.
4. R. P. Messmer, "Electronic Structure and Explanation of Photoemission Spectra for Fe-B Amorphous Alloys", manuscript in preparation.
5. "EXAFS Studies of the Local Atomic Environment in Metal-Metal Glasses", J. Wong, F. W. Lytle, H. H. Liebermann, and L. E. Tanner, Proceeding of Conference on "Metallic Glasses: Science and Technology", Budapest, June (1980).
6. "EXAFS Studies of Fe-Ni-B Metallic Glasses", paper presented at the 4th. International Conference on Liquid and Amorphous Metals held at Grenoble, July (1980), J. Wong, (manuscript in preparation).

Table I. Effective Magneton Numbers

<u>Theory</u>		<u>Experiment</u> ^a	
<u>Cluster</u>	<u>n_B</u>	<u>Alloy</u>	<u>n_B</u>
Ni ₂ Fe ₂	1.65	Ni ₅₀ Fe ₅₀	1.65
Ni ₂ Fe ₂ B	1.38	Ni ₄₀ Fe ₄₀ B ₂₀	1.31
	1.71 ^b		
	0.83 ^c		
Ni ₂ Fe ₂ P	0.83	Ni ₄₀ Fe ₄₀ P ₂₀	1.08

^a See refs. 12 and 13.

^b Value obtained with non-integral occupation solution.

^c Value obtained for short metal-metalloid distance (1.53 Å).

Fig. 1. Cluster geometry and coordinate system used for the $\text{Ni}_2\text{Fe}_2\text{M}$ clusters.

Fig. 2. Ni₂Fe₂ orbital energy level diagram from SCF-X α -SW spin polarized calculation. Solid lines denote occupied orbitals, dashed lines are unoccupied. Groups of levels whose corresponding molecular orbitals are largely localized on one type of metal atom are denoted. The atomic B 2p and P 3p levels are shown at the right.

Fig. 4. Orbital contour plots of the $1a_1^\uparrow$ and $5a_1^\uparrow$ orbitals of $\text{Ni}_2\text{Fe}_2\text{B}$. The $1a_1^\uparrow$ orbitals are predominantly of B 2s character. The yz-plane shows the interaction of B with the Ni atoms. The xz-plane shows the interaction of B with the Fe atoms. (See Fig. 1.) The contour values for all the orbitals shown in this paper start at 0.05 a.u. and increase in units of 0.05 a.u.

Fig. 5. Ni₂Fe₂P orbital energy level diagram analogous to Figs. 2 and 3.
The levels whose orbitals contain significant P content are labelled.

Fig. 6. Orbital contour plots of the $1a_1^\uparrow$ and $2a_1^\uparrow$ orbitals of $\text{Ni}_2\text{Fe}_2\text{P}$. The $1a_1^\uparrow$ is almost pure P 2s. The yz-plane shows the interaction of P with the Ni atoms. The xz-plane shows the interaction of P with the Fe atoms (see Fig. 1). The contour values are as in Fig. 4.

Fig. 7. Plot of difference bonding charge density, $\Delta\rho_B$, for $\text{Ni}_2\text{Fe}_2\text{B}$. See text for discussion. Positive contours about B and transition metal (TM) sites show that there is a preferential Ni-B bonding interaction. The charge density contour values start at 0.001 a.u. and double for each successive contour value.

Fig. 8. Plot of difference bonding charge density, $\Delta\rho_P$, for $\text{Ni}_2\text{Fe}_2\text{P}$. Negative contours about P suggest a preferential Fe-P interaction. See text for discussion. Contour values are the same as in Fig. 7.

Fig. 9. Plot of difference bonding charge density, $\Delta\rho_P$, obtained by subtracting bonding charge density of Fe_4P from the bonding charge density of Ni_4P . See text. The negative contours about P and the transition metal (TM) sites show a preferential Fe-P interaction. The contour values are the same as in Fig. 7.