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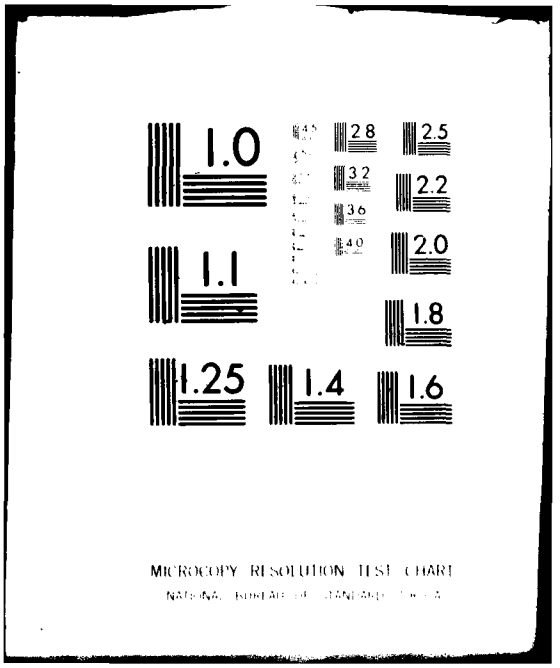
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The findings in this report are not to be construed as an official Department of the Army position, unless so designated by other authorized documents.

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

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

The work was concentrated on deepening our understanding of the properties of electrons in metallic glasses and amorphous thin silms and their role in determining the atomic arrangement in these materials. It includes a photoemission study of Nb-Ni glasses, an analysis of an electronic contribution to the free energy of a binary liquid that determines the atomic correlations, EXAFS studies of the structure of Pb-Ge quenched glasses and amorphous thin films, optical studies of amorphous Au-Si system, and a study of the magneto-optic effect in $Fe_{80}B_{20}$ metallic glass.

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INTRODUCTION

Metallic glasses prepared by the fast quenching of some alloys have many valuable properties and are likely to become materials of considerable technological importance. The work [1-8] done under this grant was concentrated on deepening our understanding of the electronic properties of these materials.

It is well-known that many properties of crystalline metals are related to the properties of the electron gas in these materials. Experimental data and a theoretical understanding of the electon gas in metallic glasses is very limited. Our interest in their properties was stimulated by the idea [9] that the electron gas may play an important role in determining the stability of certain metallic alloys in the liquid state against crystallization, and therefore is a factor figuring in the glass-formation ability of metallic alloys. We proposed [9] that in the transition or noble metal-metalloid system (M_xX_{1-x} such as $Pd_{80}Si_{20}$) at the glass forming composition relation $2k_F = q_p$ holds where k_F the Fermi vector and q_p is the wave-vector at the peak of the structure factor that corresponds to the distance of metal atoms. Experimental data show that the criterion $2k_F = q_p$ is valid with a surprising generality in many metallic glasses, even those for which our arguments do not seem to be applicable [10]. Other justifications of this relation were proposed which, however, are based on the same basic idea [11]. A fundamental difficulty in the theoretical work has been the inability of quantitatively estimating the actual contribution of the proposed interaction to the energy of the system to see whether it can be significant. This difficulty is partly related to a rather poor knowledge of the electronic structure of metallic glasses.

In the work supported by the grant, we first studied [1] the photoemission spectra of Nb-Ni glasses as a metallic glass system different from the M_xX_{1-x} system. It is an early transition metal-noble or transition metal system

(N_xM_{1-x}) in which glasses are formed in a broad compositional range. Our data indicates a low density of states at the Fermi level in agreement with the assumption about the relevance of the electronic structure for the glass forming ability.

In a theoretical study on correlations in binary liquid and glassy metals [2] we discuss how electronic interactions favor certain atomic correlation in a M_xX_{1-x} amorphous system (in particular, the absence of metalloid-metalloid nearest neighbors).

From our EXAFS studies [3] of the structure of a few typical metalic glasses we drew a convincing conclusion that the geometrical structural models are not adequate and the role of chemical forces (that is electronic interactions) is essential.

We performed optical studies [4-6] of the amorphous gold-silicon ($a\text{-}Au_{1-x}Si_x$) system in a broad compositional range from small values of x (metallic state) to large values of x (semiconducting state) and combined them with studies of electrical conductivity [7,12]. We obtained information about the electron gas in the metallic state with extremely short relaxation times and its transition into the amorphous semiconducting state.

Finally, we did some exploratory magneto-optical studies of $Fe_{80}B_{20}$ glass [8].

MAIN RESULTS

Photoemission Study of Nb-Ni Glasses

Amorphous Nb-Ni alloys are representative of $N_{1-x}M_x$ alloys where N is an "early" transition metal with a less than half filled d-band and M is a noble metal or a "late" transition metal with a nearly full d-band. The glass forming region is broad, between 40 and 66 at % of Ni. This is in contrast to another major class of melt-quenched amorphous metals, noble or transition metal-metalloid $M_{1-x}X_x$ which form glasses only in a restricted compositional range at about 20% metalloid in the narrow region of a sharp minimum in the liquidus temperature at the eutectic (Turnbull-Cohen criterion). In Nb-Ni glasses the liquidus temperatures are relatively low as compared to the average melting temperatures of the components in the range of glass formation, suggesting a generalized Turnbull-Cohen criterion for glass formation may be applicable also for these glasses. The photoemission work was done to test the possibility that the low liquidus values are due to a favorable electronic structure. In particular, the reasoning based on our previously mentioned ideas [9] can be generalized [13]. It leads to an expectation that the density of states at the Fermi level would be relatively low for glass forming compositions.

To test this assumption the energy of the core levels and the density of states of valence bands can be probed by photoemission spectroscopy. X-ray and u.v. photoemission spectra (XPS and UPS) were measured for two Nb-Ni glasses and compared to those for elemental Nb andd Ni. The broad composition range of the glass accessible in the Nb-Ni system afforded the possibility of studying the electronic structure of a binary amorphous metal as a function of the component ratio. Nb-Ni alloys also pose an interesting theoretical problem: the width of the nickel d-band is much narrower than that of niobium, and it is not clear how the two d-bands will interact on alloying. The study is the first experimental investigation of this problem.

The data show a decrease of the density of states at the Fermi level in the glasses compared with that of either pure elements, in agreement with the prediction. Two possible models were tentatively proposed for explaining this experimental fact.

Correlations in Binary Liquid and Glassy Metals

In this work [2] the contribution of electronic energy to the cohesion energy of $M_{1-x}X_x$ glasses is considered as a function of the structure of the liquid. It is shown, starting from a nearly-free electron approximation, that the electron contribution favors certain correlations in the atomic positions. In particular, the metalloid-metalloid nearest neighbors should be absent in the glass and the the metal-metalloid distance should be shorter than the sum of the atomic radii.

These conclusions are in agreement with experiment (see next section), however, they do not constitute a convincing theoretical argument for the presence of these correlations. The reason is that only electron energy was considered; the total free energy contains also energy of the ions and entropy.

EXAFS Studies of the Structures

Before our work, the structural data on $M_{1-x}X_x$ glasses were obtianed from diffraction experiments. From them one obtains metal-metal correlations, but it is difficult to get reliable information concerning the metalloid. In our work [3], we applied the EXAFS method and chose the metalloid as the atom whose surroundings were investigated. In this way we obtained new and reliable data on metalloid-metal and metalloid-metalloid correlations.

The work was done at the Stanford Linear Accelator Center at Stanford University during the principal investigator's leave at Stanford University. The material chosen was Pd-Ge (arc-quenched and sputtered) and the main conclusions about the structure were:

(a) The environments of Ge in the arc-quenched glassy $Pd_{78}Ge_{22}$ and in sputtered amorphous $Pd_{80}Ge_{20}$ are essentially identical.

(b) Ge atom has 8.6 ± 0.5 Pd neighbors.

(c) The spread of the Ge-Pd distances is very small (< 0.1Å) .

(d) The Ge-Pd distance (2.49Å) is smaller than the sum of the atomic radii of Pd (1.38Å) and Ge (covalent radius is 1.22Å, metallic radius 1.37Å).

(e) Ge has no Ge nearest neighbors (taking the accuracy of the method into consideration the conclusion is that Ge has less than 0.5 Ge atoms as nearest neighbors, considerably less that two Ge atoms expected from a random arrangement of atoms).

The results clearly show that geometrical models based on considering metallic atoms only are inadequate to account for the actual structure of this metallic glass and that it is necessary to take into account chemical ordering. The metalloids have a substantial influence on the structure of the metallic glass.

Optical Studies of the Amorphous $Au_{1-x}Si_x$ System

The aim of this work [4,5] was to obtain information about electron gas in amorphous metals from measuring the optical constants in a broad frequency range (0.01 to 6.2eV) and combining them with the measurement of the dc conductivity. The system chosen was sputtered thin films of $Au_{1-x}Si_x$ which can be prepared in the amorphous state for $x \geq 0.13$. The films are metallic for $x \leq 0.7$; above that value, they become semiconducting.

In the metallic region, the optical constants could be described as a superposition of intraband and interband transitions. The contribution due to the intraband transitions described by the Drude formula extends to much higher frequencies than in crystalline metals because the electron relaxation time is extremely short. It is somewhat frequency dependent; the extrapolated value for zero frequency decreased from about 4×10^{-16} sec for $x = 0.13$ to 0.7×10^{-16} sec for $x = 0.5$. From the Drude fit we also obtained effective electron concentrations as a function of composition. Their values increased faster with x than expected from a simple assumption that Si contributes four electrons per atom while Au only one.

On the other hand, the onset of the interband transitions changed with composition in accordance with this assumption. The picture is that the interband contribution starts with transitions from the top of the d-band to the Fermi level; the electrons from Si move the Fermi level up relative to the d-band and, therefore, the onset of the interband transitions moves to higher frequencies with increasing silicon content, as observed. When we compare the oscillator strength of the interband transitions in this system with their strength in crystalline metals or molten gold we see that it is reduced while the strengths of the intraband transitions is enhanced in the studied frequency range. We propose that this is associated with the very short lifetimes and the associated uncertainty in the electron momentum. A theory dealing with interband transitions under conditions of very strong electron scattering is not available.

From the extrapolation of the optical data one can obtain a value for the zero freqency electrical conductivity and compare it with the measured dc conductivity. The dc conductivity of amorphous $Au_{1-x}Si_x$ films prepared under the same conditions is reported in Ref. 12; we measured the dc conductivity of liquid $Au_{1-x}Si_x$ alloys [7]. Within the accuracy of the measurement, the conductivities

of the thin films and liquids agree for $x \leq 0.31$. For higher x the films have increasingly smaller conductivities indicating a transition to the semiconducting state while the liquids are metallic in the whole range (amorphous silicon thin films are semiconducting, liquid silicon is metallic). The zero-frequency optical conductivities are somewhat lower than the dc conductivities (as is usually the case); they both decrease with x indicating that the decrease of the scattering time prevails over the increase of electron concentration.

We studied [6] the optical properties of amorphous semiconducting thin films $Au_{1-x}Si_x$ with $x \geq 0.7$. We found that gold produces an absorption band in the infrared region whose shape, strength and temperature dependence can be described by photon-assisted hopping of electrons from one Au atom to another. In these samples the electrons are localized on the Au atoms in the ground state; in the samples with $x \leq 0.5$ they are delocalized (but strongly scattered). It is an interesting problem to study in detail the metal to semiconductor transition. For this study, however, one would need more homogeneous samples than we had because even small fluctuations of composition near the transition compositions are likely to make the data meaningless.

Magneto-Optic Effect in Metallic Glasses

A magneto-optic Kerr effect study has performed [8] to test the possibility of using this effect as another tool for probing the properties of electrons in metallic glasses. Since there have been no previous studies of this effect in metallic glasses, we tested its existence in $Fe_{80}B_{20}$ metallic glas. We found that the effect is easily observable although it is about five times weaker than in crystalline Fe; the shape of the magneto-optic absorption band is similar to that in Fe. The complexity of the band structure of Fe makes the interpretation

of this effect difficult in this metal and $Fe_{80}B_{20}$ glass. A study based on this effect will give more useful information when the electronic structure at the Fermi level is simpler. A possible group of materials appears to be metallic glasses or amorphous metallic films based on Ni which, however, are experimentally much more difficult to handle.

Publications resulting from the work supported by the grant

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