

Photoemission studies of crystalline palladium and the metallic alloy $\text{Pd}_{0.775}\text{Cu}_{0.06}\text{Si}_{0.165}$ in its glassy and crystalline forms*

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We report x-ray and ultraviolet photoemission measurements of the core levels and valence bands of palladium and of the metallic alloy $\text{Pd}_{0.775}\text{Cu}_{0.06}\text{Si}_{0.165}$ in both its glassy and crystalline forms. The x-ray photoemission measurements show that there is little significant difference between the relative peak positions of the various core levels, and that only the copper core level widths in the glass alloy are broader than those in the crystal. The anomalously large width of the 4*p* levels, which is often more sensitive to the chemical environment than the chemical shifts, is also the same for all three samples. A large variation with angle was observed in the peak positions of the 3*d* core levels of the crystalline palladium sample. In the valence band the ultraviolet photoemission spectra of both forms of the alloy are quite similar. However, the valence band for the alloy is narrower than that for the pure palladium, and the density of states at the Fermi level is smaller. The results of these measurements are compared with the various theories of metallic glass stability, and it is suggested that chemical bonds do not contribute to the enhanced glass-forming tendency or stability against crystallization of this alloy. The results are consistent with the nearly-free-electron model of metallic-glass stability.

I. INTRODUCTION

There are certain classes of metal alloys which are surprisingly good glass¹ formers. These compositions are unique since it has generally proven impossible to bring most other metals into this amorphous solid form.² In addition, these metallic glasses have many interesting and potentially useful properties including good corrosion resistance and high mechanical strength combined with ductility.³ One class of glass-forming alloys has received the most attention, both experimentally and theoretically. These are of the form $M_{1-x}X_x$, where *M* is a noble or transition metal with a nearly-filled *d* band and *X* is an element from group IVA or VA. The concentration *x* is generally in the range 20%–25% which is near the eutectic of the binary system.⁴ Closely related ternary alloys can be made where the metal content is now made up of two different elements of the same type *M*, but where the relative concentration *x* of the non-metal *X* is still the same as for the binary system. Some of these ternary systems have been shown to have an even greater stability against crystallization than their binary counterparts.⁵ That the glass forming tendency is increased near the eutectic has been regarded^{6,7} as a consequence of a high reduced glass temperature, $T_{rg} = T_g/T_m$ (where T_g and T_m are the glass and melting temperatures, respectively). Turnbull and Cohen⁸ and Turnbull⁹ have shown that the frequency of nucleation is a sensitive function of this parameter—decreasing rapidly as T_{rg} becomes large (as it does near a eutectic) and thus impeding crystal-

lization. There are several theories which attempt to explain the underlying reasons for this deep eutectic. Our aim, in this paper, is to try to distinguish between these competing approaches by means of a series of photoemission studies on the glass and crystal alloy and on the pure metal which is the major component of the alloy.

The first theory treats the glass as a Bernal structure made up of a random matrix of close-packed hard-sphere metal atoms, *M*, with the smaller atoms, *X*, filling in the larger voids inherent in such a structure.^{4,9} It is estimated⁴ that 13–20 at. % of the *X* atoms can fit into such vacancies and that these occupied voids will act to stabilize this amorphous structure. The second alternative is that the amorphous structure is stabilized by strong interactions between the dissimilar atoms, i. e., chemical bonds. In fact, based on detailed studies of what the effects are of alloying with elements of differing atomic radii, Chen and Park conclude that¹⁰ “the properties of glassy alloys are apparently dominated by chemical bonding among the constituent atoms rather than their relative atomic sizes.” If such bonds exist, they may produce a “chemical shift” of the core levels of the atoms involved.¹¹ These shifts would then be observable by a comparison of x-ray photoemission (XPS) measurements between the glass and crystal or between the alloy and the pure metal.

Finally, a recent proposal¹² treats the glass as a nearly-free-electron metal. It is found that for such a system there will be an increased stability against crystallization when the Fermi level E_F is located at a minimum in the density-of-states

curve $D(E)$. The size and location of this minimum is in turn determined by the structure factor of the system and for an amorphous system, with a spherically symmetric structure factor, the system will be in a metastable state. Ultraviolet photoemission (UPS) should give relevant information about the Fermi-level density of states in the glass.

In this paper we report XPS and UPS studies on $\text{Pd}_{0.775}\text{Cu}_{0.08}\text{Si}_{0.165}$ which has been shown⁵ to form a particularly stable glass. Both the glass and the crystal forms of the alloy were studied as well as pure palladium. Because of its particularly enhanced stability against crystallization this ternary alloy is preferable to binary Pd-Si alloys as a material on which to perform the photoemission measurements. Measurements on the binary alloy¹³ should reveal less about the glass formation since whatever interaction leads to stability is apparently less important in that case.

In Sec. II the experimental details will be given, including the sample preparation techniques. In Sec. III the XPS and UPS results will be presented. Finally in Sec. IV these results will be discussed in terms of the various theories of glass stability outlined above.

II. EXPERIMENTAL

The preparation of the samples followed the same procedures that have been used in the specific-heat¹⁴ and the magnetic-susceptibility¹⁵ measurements on the same alloy composition. The melt was prepared from elements with purity greater than 99.999%. The evacuated quartz capillary containing the melt at 1373 K was rapidly quenched into ice water. The glass produced in this way was in the form of a 1-mm rod. Subsequently this rod was cold rolled into a flat sample suitable for the photoemission measurements. X-ray-diffraction studies of this sample showed that it was still amorphous after this treatment. The sample was also annealed at 525 K for 3 min which has been shown¹⁶ to relieve cold working. No detectable effect was found in the photoemission spectra due to this annealing. Crystalline samples were prepared by heating the glass to 673 K for 16 min. X-ray-diffraction measurements showed that the sample had indeed crystallized. The resulting crystal is in its first metastable crystalline state.^{15,17} The pure palladium used for comparison with the alloy was a polycrystalline sample with a purity of 99.99%.

The system on which the photoemission measurements were made was an AEI 200B ESCA spectrometer equipped with both an x-ray source ($\text{Al } K\alpha$, $\hbar\omega = 1486.6$ eV; or $\text{Mg } K\alpha$, $\hbar\omega = 1253.6$ eV) and a differentially pumped He lamp ($\hbar\omega = 21.2$ eV) for the ultraviolet work. The resolution using the x-rays (XPS) and the ultraviolet (UPS) was 1.0

eV (x-ray linewidth limited) and 0.1 eV (as determined by the sharpness of the Fermi energy cut-off in various samples), respectively, although with XPS the peak positions of the core levels could be obtained with much better accuracy (0.1 eV). During the measurement the pressure in the sample chamber was in the 10^{-9} Torr (10^{-7} Pa) range. The samples could be cleaned *in situ* by sputtering with a beam of 900-eV argon ions, typically 3 min at $5 \mu\text{A}$, at an argon pressure of 2×10^{-5} Torr, until the impurity spectra (mostly carbon and oxygen) were small. The ratio of the concentration of Pd to that of Si, as determined by core level intensity ratios, was the same for both alloys. The sample could be heated *in situ*. This enabled annealing of the crystal alloy after sputtering to ensure crystallinity. One additional feature of this machine is that, although the source and analyzer are fixed, the orientation of the sample can be varied so that one can observe electrons leaving the sample either normal or parallel to the surface. Since the electrons escaping parallel to the surface are more sensitive to the surface conditions than those leaving at a steeper angle,¹⁸ a comparison of the spectra for the two orientations can yield additional information about the surface, in particular the effect that the argon sputtering may have had on the crystallinity.

III. RESULTS

A. X-ray spectra of core levels

In Fig. 1 the Pd-3d core levels are shown for the three samples: the glass and crystal alloy and

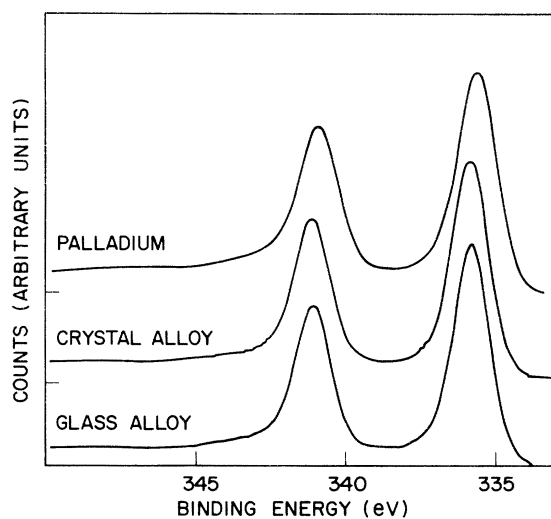


FIG. 1. XPS spectra of the Pd-3d levels for the three samples: (a) polycrystalline palladium, (b) crystal Pd-Cu-Si alloy, and (c) glass alloy. Binding energies are measured relative to the Fermi level. Note that the alloy levels are at the same binding energy in both forms and are only slightly higher than for pure Pd.

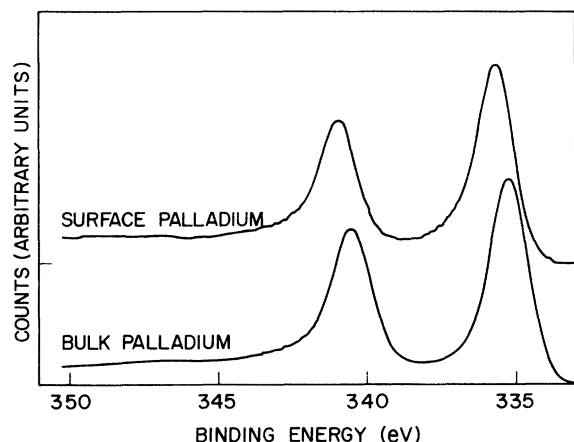


FIG. 2. XPS spectra of the Pd-3*d* levels of the polycrystalline palladium for two orientations of the sample. The sample used for the top curve is oriented so that the detected electrons were emitted almost parallel to the surface ($\sim 10^\circ$) and therefore were more surface sensitive. The sample used for the lower curve was oriented so that the detected electrons were emitted more normal to the surface ($\sim 80^\circ$) and therefore probed the bulk to a greater depth. The core level for the more surface-related palladium appears at 0.35 eV lower binding energy than for the more bulk-related measurements.

the pure palladium. The x-ray source for this measurement was the Mg $K\alpha$ line. These levels give the strongest signals, as viewed by XPS, in our spectra. As such they are the most suitable for use in comparing the different samples because the time taken to measure each sample was small. All the other levels in each spectra were then measured relative to these. Because the Pd-3*d* spectra gave such a large signal, two samples could be cleaned, by sputtering, and both measured before significant oxygen or carbon impurities could build up upon their surfaces. The two samples to be compared were held on opposite sides of a probe which could be rotated to bring either into the correct position for measurement. By working in this way we minimized any change that might take place in the analyzer either over a period of time or any change that might take place if the argon sputtering was performed between two measurements. There is no discernible difference between the spectra for the glass and crystal alloy. The peak positions occur at the same energies in each case to within 0.1 eV, and the half-widths also are equal. The measured width is 1.7 eV. There is a difference however between the alloy and the pure Pd. The Pd spectra are slight shifted to lower binding energy by 0.25 eV. This shift, although small, is nevertheless clearly resolvable in our system.

One significant fact was found by comparing the spectra for the pure-palladium 3*d* levels for two

orientations of the samples. When the observed electrons were escaping at a steep angle to the surface ($\sim 80^\circ$), the signal was as shown in Fig. 1. However, when the sample was turned so that the detected electrons were escaping parallel to the surface ($\sim 10^\circ$) the 3*d* peaks shifted by over 0.35 eV to higher binding energy as shown in Fig. 2. This effect may be due to damaging of the surface caused by argon pattering. Earlier studies on palladium films¹⁹ showed a similar difference between those evaporated *in situ* and those that were subsequently argon sputtered. Our spectra, for electrons escaping at a steep angle to the surface, are similar to those of the earlier study for evaporated Pd, and our spectra, for electrons escaping parallel to the surface, are similar to those reported for sputtered Pd. The interpretation of this earlier observation was that the sputtering made the surface of the film amorphous and that this caused the change in the position of the 3*d* levels—the levels in the amorphous film having a higher binding energy than those in the freshly evaporated sample. Our results are consistent with this interpretation since the orientation in which the sample displayed the higher binding energy was presumably more surface sensitive than the other and is as such more affected by surface damage. The angular dependence of the core levels for both alloys was about 0.1 eV (or at least 0.25 eV smaller than for the pure Pd) indicating much less surface damage in these samples.

From another point of view this result is also of importance in that it displays such a large angular dependence of the core levels. This angular dependence may be a useful tool for checking the surface conditions of other samples. If such a

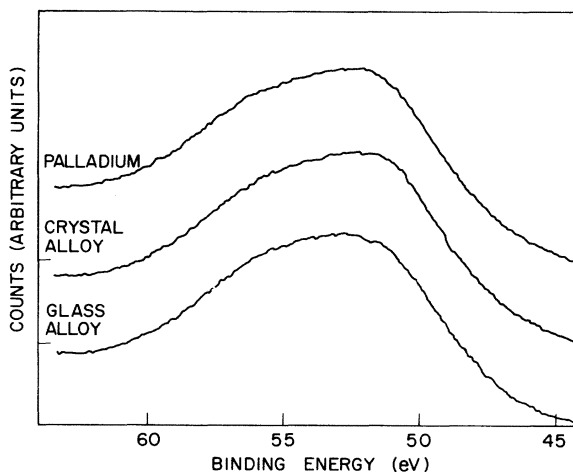


FIG. 3. XPS spectra of the Pd-4*p* levels for the three samples, (a) polycrystalline palladium, (b) crystal alloy, and (c) glass alloy. The curves are nearly indistinguishable in energy and shape.

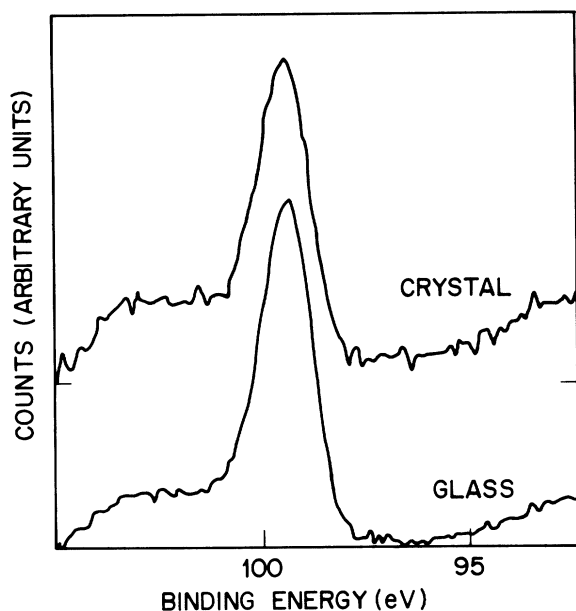


FIG. 4. XPS spectra of the Si-2*p* levels for the crystal and glass alloy. The curves are nearly identical in energy and shape.

shift of the core levels with angle is present it indicates that the conditions of photoexcitation at the surface are not the same as those in the bulk. Of course it will also complicate the interpretation of the spectra since it is now no longer clear that any orientation will exactly correspond to the bulk properties.

Photoelectron spectra depend on both a system's initial and final states. One is usually able to interpret spectra in terms of only the initial states. However, an example of dependence on the final states is the palladium 4*p* level seen in Fig. 3. There is no sign of the initial state's spin-orbit splitting. Also immediately evident is that this level is unusually wide—the full width at half-maximum being over 9 eV. To digress briefly, we are aware that XPS measurements of the 4*p* levels have shown²⁰ that this anomalous behavior occurs in a growing trend through the fifth period of which Pd is a member. For example, the generally single-peaked, but structured 4*p* levels grow from a width of 5 eV in Mo to about 40 eV in Te. They return to normal in the sixth period.²¹ For the fifth period elements this effect was first related²⁰ to super Coster-Kronig Auger transitions ($N_{2,3}N_{4,5}N_{4,5}$) which depend strongly on the relative energy separation of the filled 4*p* ($N_{2,3}$) and 4*p* ($N_{4,5}$) levels and the unfilled 4*f* ($N_{6,7}$) level. Related final-state effects are seen in many solids.^{21,22} Of more significance for our present work is that the appearance of the 4*p* level (e. g., its width) is extremely sensitive to the environ-

ment of the atom, much more sensitive than the chemical shifts which are normally used to indicate changes in the chemical bonding.²⁰ This is presumably because of the greater dependence of the unfilled 4*f* level on the bonding. To return to our data, we see from Fig. 3 that the 4*p* levels in all three of our samples are similar. The full widths at half-maximum are 9.5 ± 0.1 eV for each sample and their shape is the same, which may show, with more precision than can be obtained from Fig. 1, that there is little difference between the chemical bonding in these three cases. In addition, there are no indications of any other differences in relaxation or other final-state effects between the three cases.

In Fig. 4 the silicon 2*p* level is shown for the crystal and glass alloy. The radiation used was from the Al $K\alpha$ line. Here, once again, we see no observable difference in either position or width. However, in the spectra for the copper 3*p* level (using Al $K\alpha$ radiation) shown in Fig. 5, we do see a difference in the width and shape. The level in the glass has a width that is 0.8 eV broader than the one in the crystal. The spin-orbit splitting is not observed. The Cu spectra, we should emphasize, show the only difference, as seen by XPS, observed between the glass and crystalline forms of the alloy. It is not clear how this change should be interpreted or how important it is, especially since Cu is only a small component of this alloy and is not a necessary component for glass formation.⁵

B. Ultraviolet photoemission of the valence band

The valence bands for the three samples studied are shown in Fig. 6. These spectra were taken with the helium light source ($\hbar\omega = 21.2$ eV). The

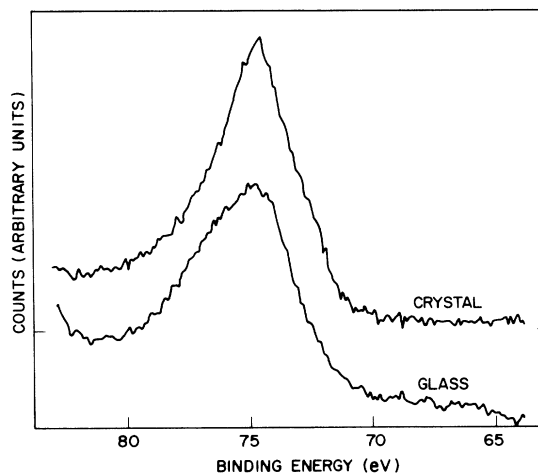


FIG. 5. XPS spectra of the Cu-3*p* levels for the crystal and glass alloy. The width of the level is 0.8 eV greater in the glass. Cu makes up 6% of each alloy.

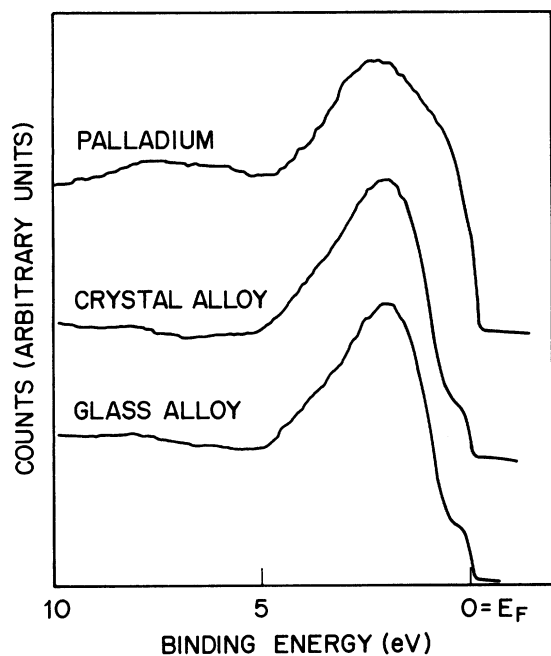


FIG. 6. The UPS spectrum ($\hbar\omega = 21.2$ eV) of the valence band for the three samples, (a) polycrystalline palladium, (b) crystal alloy, and (c) glass alloy. The alloy samples are quite similar with a noticeably lower emission at E_F relative to pure Pd.

spectrum for pure palladium is similar to that of Eastman²³ on evaporated Pd. Our curve is somewhat more smeared out near the Fermi level presumably due to argon sputtering.¹⁹ The other features are similar. For the crystal alloy, the sample was annealed after the sputtering (at 625 K for 5 min) in order to relieve any damage at the surface due to the cleaning procedure. This produced no change in the spectrum. In comparing the three curves, one again sees little difference between the crystal and the glass alloys. However, there are significant differences between the energy distribution curve (EDC) for pure palladium and those of the two alloys: both the width and the peak position of the band have changed. In pure palladium the peak of the EDC lies at 2.4 eV below the Fermi level and the band is approximately 4.1 eV wide. For the alloy the peak of the valence band has shifted to lower binding energy, 2.0 eV below E_F , and has become narrower as well (full width at half-maximum is 3.0 eV). Of particular interest is that the EDC for the alloy is small at the Fermi level whereas for pure palladium it is large. This implies that there is a smaller density of states at the Fermi level in the alloy than in the element. In making this statement we have neglected the possible effect that the matrix elements are changing between samples. Such an effect could prevent the EDC from reflecting the

true density of states. The interpretation in terms of a decrease in the Fermi-level density of states $D(E_F)$ upon alloying is corroborated by other studies on the $\text{Pd}_{0.775}\text{Cu}_{0.08}\text{Si}_{0.165}$ glass. In particular, magnetic-susceptibility measurements¹⁵ indicate that the alloy, in both its forms, is diamagnetic whereas pure palladium is paramagnetic. Since the Pauli paramagnetism is proportional to $D(E_F)$, this result is consistent with the present study, implying that $D(E_F)$ is low in the alloy. This conclusion is also substantiated by specific-heat measurements on these glasses.¹⁴

IV. CONCLUSIONS

The results of these photoemission measurements indicate that there is little difference in the electronic structure of the glass and crystal alloy. There is no evidence that chemical bonds, which would have been expected to shift the positions of the core levels, are important for the glass-forming ability of this alloy. The small shift that is seen between the 3d core levels of pure palladium and the same level in the alloys is still smaller than the shift seen in pure palladium by merely changing the orientation of the sample. If the interpretation of Hufner *et al.*¹⁹ is correct, that argon sputtering makes the palladium surface amorphous, then the fact that the shift in the level on changing orientation is larger than that seen upon alloying in any of the spectra strongly indicates that there is no strong chemical interaction in the alloy. The small change that is seen may be due to the filling of the Pd valence band by the four free electrons in silicon. As has been pointed out²⁴ the transition metals behave on alloying as if they had one free electron. Thus on alloying with silicon the Fermi level is raised with respect to the bottom of the conduction band. This will be reflected in two ways: (i) the core levels will appear to be at a slightly higher binding energy (with respect to the Fermi level) and (ii) the Fermi level will move across the density-of-states curve to higher energy. The first effect is indeed what we observe, the core level in the alloy has a higher binding energy than in the element. The second effect we feel is at least partially what causes the decrease in $D(E_F)$ on alloying. In palladium the d band is almost filled. By adding extra electrons the Fermi level is raised above the d bands (as it is in the noble metals) and the density of states is decreased. This is consistent with what we observe. This is also consistent with the results of positron-annihilation experiments on these same alloys.²⁵

The conclusion that the chemical bonds are not important in the glass is in agreement with the observation by Gilman³ that the bonding character is mostly metallic with little directionality. He

based his conclusions on the ratio of the bulk modulus B to the shear modulus G being large. For the glass $B/G=5.3$ whereas for a Cauchy solid bound by centrally directed interatomic forces the ratio is 1.7.

The approach¹² based on the nearly-free-electron model appears so far to be consistent with the photoemission results. The main prediction of this model is that there will be a minimum in $D(E)$ at the Fermi level for good glass formers. The alloy measured here certainly has a smaller $D(E_F)$ than pure palladium, but as we mentioned above, this is due largely to the fact that the Fermi level has risen above the d bands in the alloy, although there might be some effect due to the structure factor as well. In order to establish this model, measurements for many compositions of the binary alloy around the glass-forming region are needed in order to determine if $D(E_F)$ is really at a *local* minimum for the glass. In the Pd-Si system there will be such a large background due to the d bands of Pd that the effect may be hard to see. However, the measurements made so far do not contradict the hypothesis of a nearly-free-electron system.

The electronic structure for the Pd-Si alloy might be thought to be similar to the Pd-H system which has recently been studied.^{23,26} In these studies an extra band was found below the d band of palladium. This occurred at 5.4 eV below the Fermi level. In our study of the palladium-silicon

alloy no such extra levels were seen in this region of the valence band. However, the similarity between the valence-band spectra for the two forms of alloy indicate that the long-range atomic configuration of the alloy is of little importance in determining most of the main features in the density of states. This observation should be of importance for theoretical calculations of this quantity.

The metallic glass which we have studied is one of the most stable against crystallization. As such it represents one of the most favorable places to search for chemical bonds in the glass. No evidence for a significant effect due to chemical bonding was observed with photoemission. This strongly suggests that some other theory, such as the nearly-free-electron model, must be introduced in order to explain the relatively high glass-forming tendency of these alloys. However, we also recognize the possibility that there may be bonding effects which do not appreciably affect the core levels and thus would have gone undetected by our photoemission experiments.

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¹We use the definition of a glass as an amorphous solid obtained by quenching the melt.

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