Electronic Structure Studies of Ca_xAl_{1-x} Metallic Glasses

Sidney R. Nagel
The James Franck Institute and the Department of Physics, The University of Chicago, Chicago, Illinois 60637

and

U. M. Gubler, C. F. Hague,[a] J. Krieg, R. Lapka, P. Oelhafen,[b] and H.-J. Güntherodt
The Institute of Physics, Universität Basel, CH-4056 Basel, Switzerland

and

J. Evers and A. Weiss
The Institute of Inorganic Chemistry, Universität München, D-8000 München, Germany

and

V. L. Moruzzi and A. R. Williams
IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598

(Received 17 May 1982)

The first photoemission spectra are reported for the valence bands of two metallic glasses, $Ca_{0.70}Al_{0.30}$ and $Ca_{0.50}Al_{0.50}$, containing only normal metals. It is found that the valence bands dramatically change and split into two parts. Significant structure is observed near the Fermi levels as well. Confirmation comes from soft-x-ray spectroscopy data and band-structure calculations for hypothetical crystalline alloys of similar compositions.

PACS numbers: 71.25.Mg, 71.20.+c, 78.70.En, 79.60.-i

Metallic glasses can often be made in composition ranges where crystalline compounds cannot be formed. This provides the opportunity of studying the alloying behavior of elements which cannot otherwise be found in a homogeneous compound. Considerable attention has been focused on several glass formers,[1] all containing transition metals. In particular there have been studies of glasses of the form[2-6] T_xN_{1-x} (where T is a transition metal, N a polyvalent normal metal) and of the form[7-11] $T_x{}^E T_{1-x}{}^L$ (where T^E is an "early" transition metal with a less than half-filled d band and T^L is a "late" transition or noble metal with a more than half-filled d band). Systematic photoemission studies[10] of this latter class of glasses demonstrated interesting d-band splittings and binding-energy shifts.

No comparable studies have as yet been made on the class of glass formers that contain only normal metals. These alloys are important because d bands do not play an important role in the valence-band density of states and therefore their electronic structure should be more easily understood from a theoretical standpoint. Usually, however, normal metals are expected to have a valence band which is featureless and seemingly uninteresting. In this paper we report photoemission and soft-x-ray emission measurements on glass-forming alloys[12] containing only normal metals. However, these alloys do show remarkable structure in their valence-band density of states: Not only is there obvious structure but the valence band actually splits into two parts! This is an unexpected result which not only indicates the richness that may appear in the electronic structure of alloys of simple metals but also should have profound implications for the properties of these glasses and even perhaps for why these alloys can be formed into glasses in the first place.

For the purpose of the ultraviolet photoemission spectroscopy (UPS) experiments, two glasses of quite different composition were prepared: $Ca_{0.70}Al_{0.30}$ and $Ca_{0.50}Al_{0.50}$. Considerable precautions had to be taken to obtain oxygen-free samples but full details will be given elsewhere.[13] In brief, polycrystalline ingots were first prepared from vacuum-distilled calcium and high-purity aluminum. With use of levitation melting the $Ca_{0.70}Al_{0.30}$ sample was splat cooled between a hammer and anvil device. The $Ca_{0.50}Al_{0.50}$ glass, which was very difficult to make, was obtained in ribbon form by melt spinning. X-ray diffraction verified that the samples were indeed amorphous as has been reported elsewhere.[12]

Immediately after preparation the samples were transferred under argon atmosphere to the photoemission spectrometer (base pressure

10^{-10} mbar) and cleaned by Ar-ion etching. Repeated monitoring of the core-level peaks by x-ray photoemission spectroscopy (XPS) showed that etching had no detectable effect on surface composition. A scraper was not used to remove surface contamination because of the brittleness of the samples. The soft-x-ray spectroscopy (SXS) measurement was performed on the $Ca_{0.70}Al_{0.30}$ glass under a residual pressure of 10^{-7} mbar. The other experimental details are similar to those reported recently for pure Al.[14]

In Fig. 1 we present the UPS data using He I radiation for the valence bands in $Ca_{0.70}Al_{0.30}$ and $Ca_{0.50}Al_{0.50}$ metallic glasses. Spectra were also obtained with He II and Ne I radiation. The bandwidths of the pure crystalline elements Ca and Al are 4 and 11 eV, respectively[14] and the densities of states increase monotonically as the binding energy decreases. The valence bands for the glasses, however, instead of having a single monotonically increasing density of states, have marked shoulders located about 5 eV below the Fermi level. This is especially apparent for $Ca_{0.70}Al_{0.30}$. Such a strong feature was surprising as the mixing of two simple metals is expected to give a single valence band instead of the splitting apparent from this experiment. The structure is also observed with the other incident photon energies ($h\nu = 16.8$ and 40.8 eV).

Another important aspect of these measurements is that there is a drop in the density of states at the Fermi energy in $Ca_{0.50}Al_{0.50}$ as compared to $Ca_{0.70}Al_{0.30}$ where the density of states is already beginning to decrease from its maximum value. The main feature in the density of states, i.e., the structure 1 eV below the Fermi energy, narrows in $Ca_{0.50}Al_{0.50}$ whereas according to a rigid-band approach one could expect the bandwidth to increase as the Al content increases.

Figure 2 shows the Al $K\beta$ emission band from the $Ca_{0.70}Al_{0.30}$ metallic glass along with that of pure aluminum and the UPS measurement of the same alloy. Subject to corrections for transition matrix elements and broadening effects due to initial- and final-state lifetimes, the Al $K\beta$ emission band represents the partial $3p$ density-of-states contribution from Al sites. The dramatic change we observe between the pure element and the alloy corresponds to a narrowing of the Al $3p$ bandwidth from 11 eV[14] (i.e., a value close to that predicted by Moruzzi, Janak, and Williams[15]) to an estimated 3.5 eV. The Al $3p$ density of states is clearly pushed to lower binding energy and peaks just below E_F. The Al s, Ca s, and Ca p states must therefore contribute to the peak at 5 eV. Because the cutoff at the Fermi level is more affected by lifetime broadening in the SXS experiment than with UPS, the density of states at the Fermi level is difficult to assess. However, it is clear that there is a very significant drop relative to pure Al.

Despite the sensitivity of the method, UPS has not been able to reveal any gross differences between the electronic structure of several metallic glasses and the recrystallized alloys of the same composition.[1,2,10] Thus a band-structure calcula-

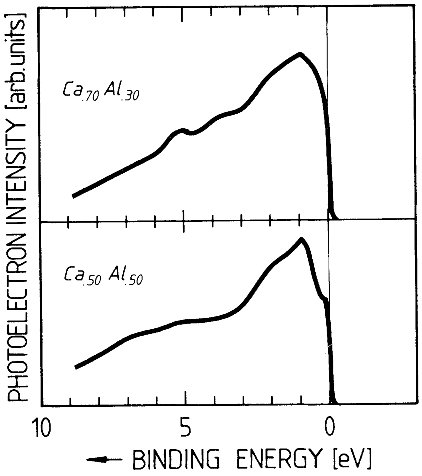

FIG. 1. The photoemission spectra of $Ca_{0.70}Al_{0.30}$ and $Ca_{0.50}Al_{0.50}$ metallic glasses obtained with He I($h\nu = 21.2$ eV) radiation.

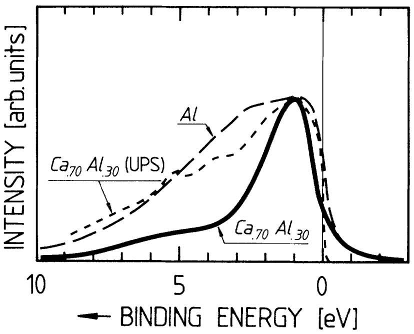

FIG. 2. The soft-x-ray $K\beta$ emission band ($3p \rightarrow 1s$ transition) for aluminum in the pure metal and in the metallic glass $Ca_{0.70}Al_{0.30}$. The spectra are compared to the UPS valence-band determination. The x-ray spectra were situated relative to the Fermi energy by means of core-level binding-energy measurements (Ref. 14).

tion of the crystal has, in the past, given a great deal of insight into the electronic structure of glasses. In the present case there is no crystalline alloy with which to compare our data on the glass since the equilibrium phase is separated. Nevertheless such a calculation can still help one qualitatively understand the glassy electronic structure, especially, as we shall see is the case here, if one can associate each feature found in the calculation with one seen in the UPS experiment. We have done augmented-spherical-wave[16] band-structure calculations for $Ca_{0.75}Al_{0.25}$ and $Ca_{0.5}Al_{0.5}$ crystals in various crystal structures. In each calculation the lattice parameter has been relaxed to give total energy minimization.

In Fig. 3 we show the total as well as the partial site-decomposed densities of states calculated for $Ca_{0.75}Al_{0.25}$ in the Cu_3Au structure. The Fermi level lies slightly above a peak in the density of states and we see that there is a pronounced minimum in the density of states just above the Fermi level. We also observe that the valence band is split into two parts. In the Al portion of the site-decomposed densities of states the high binding-energy peak at 5 eV is formed entirely of Al s states and the low binding-energy peak consists almost completely of p states. This split in the Al partial densities of states is due to reduced overlap of orbitals from nearest-neighbor like atoms. The Ca orbitals are then subject to strong hybridization leading to a split band also, but this time the s- and p-like states contribute equally to both peaks. In addition Ca d states occur which give a large contribution to states at E_F.

Agreement with the UPS measurements is excellent as concerns the binding energies of the two main features. The density of states at the Fermi level seems higher than in the experiments. However, the exact position of the Fermi energy relative to the sharp peak in the p states is likely to be highly sensitive to composition. An increase in the Al content to bring the calculated Al concentration up to 30% would have the effect of dropping the Al $3p$ density of states at the Fermi level very considerably. The predicted Al $3p$ bandwidth and position agree well with the SXS measurement, giving additional confidence of the relevance to glass samples of this band-structure calculation for a hypothetical crystal.

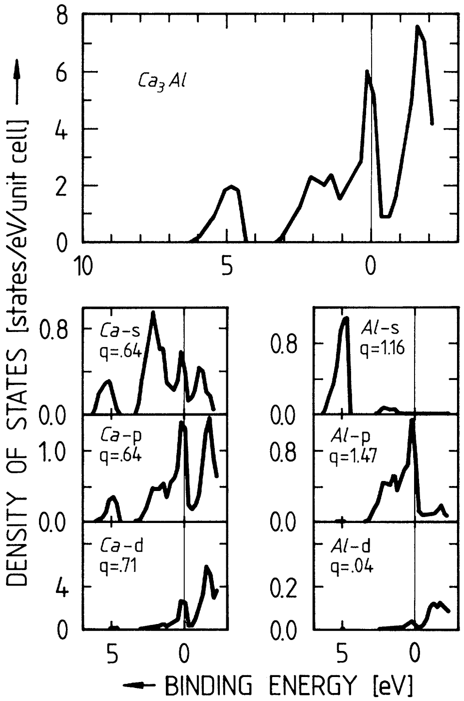

FIG. 3. Band-structure caloulation using the augmented-spherical-wave method for Ca_3Al in the Cu_3Au crystal structure. The total density of states is represented at the top of the figure; the other curves represent the partial site-decomposed state densities which contribute to the total density of states. q is angular momentum and site-decomposed charge.

A calculation for CaAl in the CsCl structure shows that the gap between the Al s and p states has begun to fill in as the number of Al-Al nearest neighbors increases, but the two-peak structure is still the main feature. The Ca s, p, and d states are distributed very much as in Ca_3Al. Now the Fermi level lies close to the minimum in the density of states. This minimum in the density of states at the Fermi energy is reminiscent of the nearly-free-electron model for glass formation,[17-19] but we note that $Ca_{0.50}Al_{0.50}$ does not correspond to the most favorable glass-forming concentration.

It is interesting to speculate on how the electronic structure we have found affects the various properties of these alloys. The presence of significant Ca d states at the Fermi level may account for the very large resistivity values found for these alloys[12] due to d-resonance scattering. Also the fact that the Al s states split off from the bottom of the valence band may account for why no stable crystalline compounds occur in the Ca-rich region of the phase diagram and why there is a deep eutectic at 35 at.% Al.

In conclusion we have found that even these simple metals display very complex behavior when alloyed together. Care must obviously be taken to understand the electronic structure in detail before predictions for either the transport or glass-forming properties can be made in even a glass free of transition metals.

We would like to thank T. Gabriel for help in making the metallic glasses. Several of us (C.F.H., V.L.M., and S.R.N.) would like to thank the University of Basel for making their stay there possible during part of this work. One of us (S.R.N.) was the recipient of an Alfred P. Sloan Foundation Fellowship. This work was supported in part by National Science Foundation Grant No. DMR 8201182. Thanks are due to the Swiss National Science Foundation for financial support.

---

[a] Permanent address: Laboratoire de Chimie Physique, Université Pierre et Marie Curie, F-75231 Paris, France.

[b] Present address: IBM Thomas J. Watson Research Center, Yorktown Heights, N.Y. 10598.

[1] See, for a review of recent work, H.-J. Güntherodt *et al.*, J. Phys. (Paris), Colloq. 41, C-8, 381 (1980).

[2] S. R. Nagel, G. B. Fisher, J. Tauc, and B. G. Bagley, Phys. Rev. B 13, 3284 (1976).

[3] P. Oelhafen, M. Liard, H.-J. Güntherodt, K. Berresheim, and H. D. Polaschegg, Solid State Commun. 30, 641 (1979).

[4] J. D. Riley, L. Ley, J. Azoulay, and K. Terakura, Phys. Rev. B 20, 776 (1976).

[5] E. Cartier, Y. Baer, M. Liard, and H.-J. Güntherodt, J. Phys. F 10, L21 (1980).

[6] M. Matsuura, T. Namoto, F. Itoh, and K. Suzuki, Solid State Commun. 33, 895 (1980).

[7] S. R. Nagel, J. Tauc, and B. C. Giessen, Solid State Commun. 22, 471 (1977).

[8] A. Amamou and G. Krill, Solid State Commun. 28, 957 (1978).

[9] P. Oelhafen, E. Hauser, H.-J. Güntherodt, and K. H. Bennemann, Phys. Rev. Lett. 43, 1134 (1979).

[10] P. Oelhafen, E. Hauser, and H.-J. Güntherodt, Solid State Commun. 35, 1017 (1980).

[11] C. F. Hague, R. H. Fairlie, W. M. Temmerman, B. L. Gyorffy, P. Oelhafen, and H.-J. Güntherodt, J. Phys. F 11, L95 (1981).

[12] J. Hong, Ph.D. thesis, Northeastern University, unpublished.

[13] U. M. Gubler *et al.*, to be published.

[14] C. F. Hague, Phys. Rev. B 25, 3529 (1982).

[15] V. L. Moruzzi, J. F. Janak, and A. R. Williams, *Calculated Electronic Properties of Metals* (Pergamon, New York, 1978).

[16] A. R. Williams, J. Kübler, and C. D. Gelatt, Jr., Phys. Rev. B 19, 6094 (1979).

[17] S. R. Nagel and J. Tauc, Phys. Rev. Lett. 35, 380 (1975).

[18] H. Beck and R. Oberle, in *Proceedings of the International Conference on Rapidly Quenched Metals, III, Brighton, 1978*, edited by B. Cantor (The Metals Society, London, 1978), Vol. I, p. 416.

[19] J. Hafner and L. von Heimendahl, Phys. Rev. Lett. 42, 386 (1979).

Scattering Cross Section of Low-Coverage CO on Pt(111) for Thermal He and H_2 Beams

Bene Poelsema, Siebe T. de Zwart, and George Comsa
Institut für Grenzflächenforschung und Vakuumphysik, Kernforschungsanlage Jülich, D-5170 Jülich, Germany

(Received 12 May 1982)

The scattering cross section of an adsorbed CO molecule is about 1 order of magnitude larger than expected from the van der Waals radius. The dependences on the He and H_2 incident velocities reveal glory structures similar to those in corresponding gas-phase experiments. Accordingly the long-standing puzzle of the extreme sensitivity of molecular beams to adsorbates is explained by inhomogeneities of the attractive potential.

PACS numbers: 79.20.Rf, 34.20.-b, 34.40.+h, 68.20.+t

The diffraction of thermal atoms has become an increasingly important tool for investigation of the structures of clean and adsorbate-covered metal surfaces.[1-4] The diffraction patterns have been satisfactorily compared with calculations based on the assumption that the scattering is dominated by the repulsive potential. The various models consider the repulsive potential to be a hard corrugated wall (HCW—see, e.g., Ref. 1 and references therein) or to have a shape permitting some penetration of the wave function into the metal.[5] Except for describing the selective adsorption phenomenon, the attractive potential played only the role of a correction accounting