

## Soft-X-Ray Appearance Potential Spectroscopy of Metallic Glasses

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Soft-x-ray appearance-potential spectroscopy has been applied to the metallic glass  $\text{Co}_{58}\text{Ni}_{10}\text{Fe}_5\text{B}_{16}\text{Si}_{11}$ . The  $L_{\text{III}}$  spectra of the transition metals resemble closely those of pure samples in the region determined by the  $d$  partial density of states. Distinct differences occur in the region characteristic of the  $s$  partial density of states. This part of the signal is also clearly affected by crystallization for Co and Fe, Ni remaining unchanged. A dramatic change upon crystallization is exhibited by the boron  $K$  spectrum.

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In this Letter, we report the first successful attempt to observe band-structure changes of a metallic glass upon crystallization. Electron spectroscopic investigations of metallic glasses are particularly attractive since our current understanding of electronic properties of solids is so far based on crystal periodicity. Several experiments employing Auger-electron spectroscopy (AES), x-ray photoelectron spectroscopy (XPS), and ultraviolet photoelectron spectroscopy (UPS) have been reported. However, since alterations of the observed spectra due to crystallization either escaped detection<sup>1</sup> or remained within the limits of experimental uncertainty,<sup>2</sup> the main emphasis in this work was on the change of electronic properties of the alloy constituents upon alloying. Moreover, in the course of this work, it turned out that application of XPS valence-band spectroscopy is practically limited to binary alloys because progressive interpretation difficulties are encountered as the number of alloy constituents rises.

Soft-x-ray appearance-potential spectroscopy (SXAPS)<sup>3</sup> differs from the above-mentioned methods in two respects. In contrast to AES and XPS which probe occupied electronic states of the sample, SXAPS measures the density of empty electronic states. Further, SXAPS is a local probe because it measures the density of empty states in the environment of a particular alloy constituent. Since spectra of different constituents are well separated in energy, the application of SXAPS is by no means limited to binary alloys.

In the present work, we report SXAPS measurements on the commercially available metallic glass  $\text{Co}_{58}\text{Ni}_{10}\text{Fe}_5\text{B}_{16}\text{Si}_{11}$  (Vitrovac 6010). All of its constituents are known to produce easily detectable appearance-potential spectra. The experiment was carried out in a small ultrahigh vacuum (UHV) system at pressures below  $5 \times 10^{-10}$  Torr

during data acquisition. In order to avoid changes of chemical composition in the surface layer due to selective sputtering, the sample was cleaned *in situ* mechanically with the help of a tungsten brush. Most of the carbon contamination and all the oxygen could be removed. Residual carbon as monitored by SXAPS may well be a trace bulk impurity.<sup>4</sup>

The  $L_{\text{III}}$  spectra of the pure elements Ni, Co, and Fe are shown as solid dots in Figs. 1 to 3. Energy scales are not corrected for cathode bias and cathode work function. The prominent first maximum is due to the  $3d$  partial density of empty states. The amplitude of the subsequent minimum indicates the importance of the  $s$  partial density of states as compared to the  $d$  density of states (DOS). The lower the  $s$  DOS, the deeper this minimum.<sup>5</sup> The structures at 866, 790, and 720 eV in the respective spectra of Ni, Co, and Fe are most probably satellites since they correlate well with corresponding structures in XPS.<sup>6</sup>

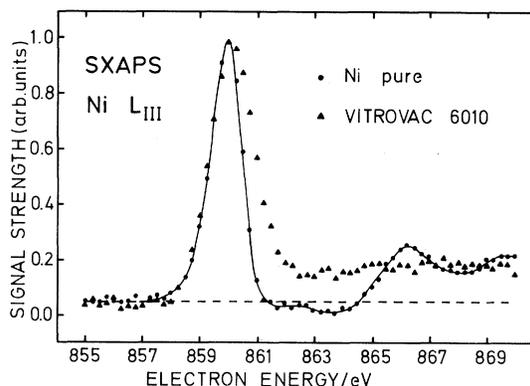


FIG. 1. Solid dots are the nickel  $L_{\text{III}}$  appearance-potential spectrum obtained from a pure nickel sample. Triangles are the  $L_{\text{III}}$  spectrum in Vitrovac 6010. Note the considerable broadening in the alloy. This spectrum remains unchanged upon crystallization.

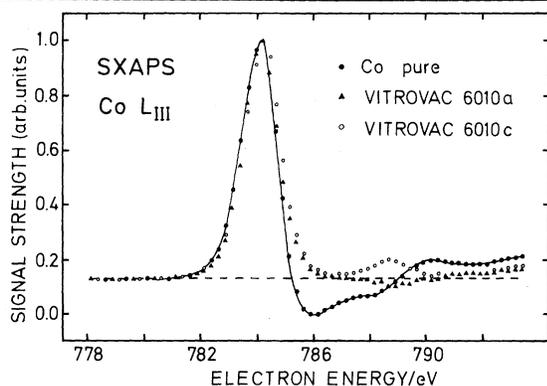


FIG. 2. Solid dots are the cobalt  $L_{III}$  appearance-potential spectrum obtained from a pure cobalt sample. Triangles and open circles represent the cobalt  $L_{III}$  spectrum in the amorphous and crystallized state of the alloy, respectively.

These satellites are almost certainly characteristic for long-range order since they do not show up in either the amorphous or the crystalline state of the alloy.

Solid triangles in Figs. 1 to 3 indicate appearance-potential spectra of the same  $3d$  elements in the amorphous state of the alloy. They have been adjusted to equal height of the first peak. Nickel shows a considerable broadening of the  $d$ -band peak while this part of the spectrum remains practically unchanged for cobalt and iron. Prominent differences occur in all three spectra in those regions where the SXAPS signal is determined by the  $s$  partial density of states. The ratio of  $s$  to  $d$  partial DOS is in all three cases considerably higher in the alloy than in the pure samples. We cannot decide presently whether this means a decrease of the  $d$  partial DOS or an enhancement of the  $s$  partial DOS. An answer to this question would be important in view of current models for glass forming tendency.<sup>7</sup>

After the sample had been crystallized by keeping it about  $200^\circ\text{C}$  above the crystallization temperature for fourteen hours, the spectra shown as open circles in Figs. 2 and 3 were obtained. No change in the nickel spectrum could be detected. We believe that this points to an unchanged random distribution of nickel in the alloy after crystallization. However, small but distinct and energetically well-localized changes show up in the cobalt and iron spectra indicating a rearrangement of the  $s$  partial density of states on the Co and Fe sites. This observation correlates nicely with the sensitivity of Mössbauer Fe spectra in

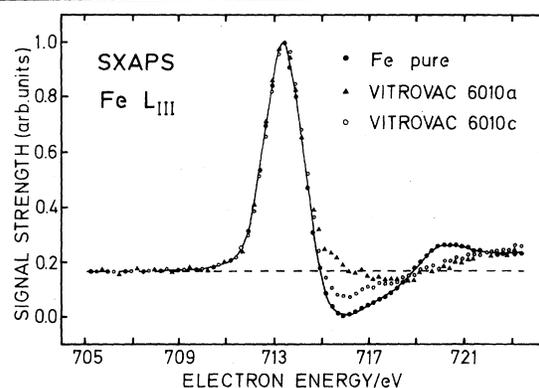


FIG. 3. Solid dots are the iron  $L_{III}$  appearance-potential spectrum obtained from a pure iron sample. Triangles and open circles represent the iron signal in the amorphous and crystallized state of the alloy, respectively.

metallic glasses to crystallization<sup>8</sup> since the Fe  $4s$  electrons contribute significantly to the magnetic field at the nucleus.

We finally discuss the spectra of the metaloids. The spectrum of silicon is not shown. It did not change upon crystallization and was in excellent agreement with that obtained previously by Park and Houston<sup>9</sup> from a pure silicon sample. The boron spectrum is shown in Fig. 4. Solid dots represent the amorphous and open circles the crystallized state of the sample. The difference is dramatic. The spectrum in the amorphous state is characteristic of a pure  $s$  band. It may well indicate that boron contributes significantly to the elevated local  $s$  partial density of states at

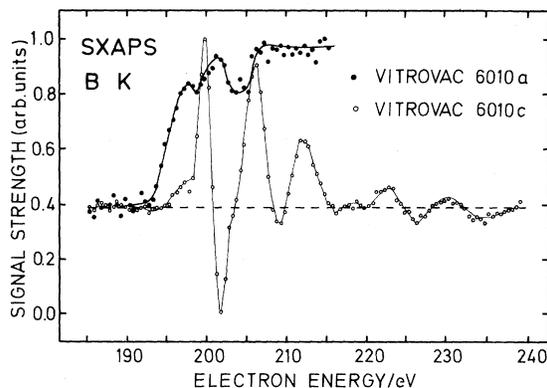


FIG. 4. The boron  $K$  spectrum shows a dramatic change upon crystallization. Solid dots correspond to the amorphous and open circles to the crystallized state of the alloy.

the cobalt and iron sites. The boron spectrum after crystallization is entirely different in nature. First of all, in contrast to  $3d$  metal spectra, it shows a large core-level shift. The shape of the spectrum resembles closely that obtained by Houston and Park<sup>10</sup> from a boron-contaminated nickel surface. The similarity of the boron spectrum after crystallization to appearance-potential spectra of graphite suggests the formation of boron islands on the surface during crystallization. If we adopt the current assumption in metallurgy that free surfaces are essentially equivalent to grain boundaries,<sup>11</sup> we conclude that boron segregation during crystallization is responsible for embrittlement of the sample.

In conclusion, we find that application of soft-x-ray appearance-potential spectroscopy to metallic glasses reveals a lot of information on their electronic structure not accessible by other spectroscopic methods.

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<sup>1</sup>S. R. Nagel, G. B. Fisher, J. Tauc, and B. G. Bagley, *Phys. Rev. B* **13**, (1976) 3284; E. Cartier, Y. Baer, M. Liard, and H. J. Güntherodt, *J. Phys. F* **10**, L21 (1980).

<sup>2</sup>A. Amamou, *Solid State Commun.* **33**, 1029 (1980).

<sup>3</sup>R. L. Park and J. E. Houston, *J. Vac. Sci. Technol.* **11**, 1 (1974).

<sup>4</sup>H. Warlimont, private communication.

<sup>5</sup>R. L. Park and J. E. Houston, *Phys. Rev. B* **6**, 1073 (1972).

<sup>6</sup>S. Hüfner, in *Photoemission in Solids II*, edited by L. Ley and M. Cardona (Springer-Verlag, Berlin, 1979), pp. 173–216.

<sup>7</sup>H. S. Chen, *Rep. Prog. Phys.* **43**, 353 (1980).

<sup>8</sup>T. Kemeňy, I. Vincze, and B. Fogarassy, *Phys. Rev. B* **20**, 476 (1979).

<sup>9</sup>R. L. Park and J. E. Houston, *J. Appl. Phys.* **44**, 3810 (1973).

<sup>10</sup>J. E. Houston and R. L. Park, *J. Vac. Sci. Technol.* **8**, 91 (1971).

<sup>11</sup>W. Losch and J. Rousselet, *Scr. Metall.* **14**, 195 (1980).

## Giant Thermoelectrically Generated Magnetic Flux in a Superconducting Bimetallic Loop and a Suggested Direct Measurement of a Normal Thermocurrent in a Superconductor

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When a counterflow supercurrent is generated in a superconducting bimetallic loop by a thermoelectric quasiparticle current, the phase difference can only be maintained constant if very large surface currents flow. We show that this implies a magnetic flux associated with the loop of order  $r/\lambda$  ( $r$  is the radius of arm perpendicular to  $\nabla T$  and  $\lambda$  is the penetration depth) greater than the simple theory suggests, and that this may be used to measure the normal current directly.

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It has been suggested that a bimetallic superconducting loop should become threaded by thermoelectrically generated magnetic flux when a temperature difference is applied between the junction.<sup>1,2</sup> The measurement of this flux would provide a unique way of studying the transport properties of the quasiparticles in a superconductor and thus the phenomenon is potentially of considerable importance. The several measurements<sup>3-6</sup> which have been made to date, however, all appear to find fluxes which are several orders

of magnitude greater than the original proposal suggests.

It is the purpose of this Letter to point out that the surface currents induced in such a loop are likely to be very large indeed and that they will provide a flux associated with the loop which is *many* orders of magnitude greater than that predicted by the simple theory.<sup>1,2</sup>

Let us first consider the usual argument for the existence of the flux linking a loop such as that shown in Fig. 1. Metal  $L$  is a superconductor just