mains. These results may have significant implications for understanding the particle-size dependence of demanding reactions in heterogeneous catalysis. In such systems involving transition-metal clusters we may reasonably expect that electronic configurations will change in the same size region as observed here for Sm.

This work was supported in part by the Director, Office of Energy Research, Office of Basic Sciences, Chemical Sciences Division of the U. S. Department of Energy under Contract No. W-7405-ENG-48, and by the National Science Foundation under Grants. No. DMR-7821080 and No. DMR-7821888. The authors are grateful for the cooperation of the staff of the University of Wisconsin Synchrotron Radiation Center.

---

[1] R. C. Baetzold, in *Catalysis in Chemistry and Biochemistry. Theory and Equipment*, edited by B. Pullman (D. Reidel, Boston, Mass., 1979), p. 191–206, and references therein.

[2] M. G. Mason, L. J. Gerenser, and S. T. Lee, Phys. Rev. Lett. 39, 288 (1977).

[3] W. F. Egelhoff and G. G. Tibbetts, Solid State Commun. 29, 53 (1979); W. F. Egelhoff and G. G. Tibbets, Phys. Rev. B 19, 5028 (1979).

[4] G. K. Wertheim and G. Crecelius, Phys. Rev. Lett. 40, 813 (1978).

[5] G. K. Wertheim and M. Campagna, Chem. Phys. Lett. 47, 182 (1977).

[6] J. W. Allen, L. I. Johansson, R. S. Bauer, I. Lindau, and S. B. M. Hagstrom, Phys. Rev. Lett. 41, 1499 (1978); J. W. Allen, L. I. Johansson, I. Lindau, and S. B. Hagstrom, Phys. Rev. B 21, 1335 (1980).

[7] J. K. Lang and Y. Baer, Solid State Commun. 31, 945 (1979).

[8] J. K. Lang, Y. Baer, and P. A. Cox, Phys. Rev. Lett. 42, 74 (1979).

[9] J. F. Herbst, R. E. Watson, and J. W. Wilkins, Phys. Rev. B 17, 3089 (1978), and references therein.

[10] J. N. Chazalviel, M. Campagna, G. K. Wertheim, and P. H. Schmidt, Phys. Rev. B 14, 4586 (1976).

[11] R. Rosei, J. H. Weaver, M. Campagna, W. Gudat, F. Hulliger, and H. Bach, Bull. Am. Phys. Soc. 25, 237 (1980).

[12] J. C. Fuggle, M. Campagna, Z. Zolnierek, R. Lässer, and A. Platau, Phys. Rev. Lett. 45, 1597 (1980).

[13] G. K. Wertheim and M. Campagna, Solid State Commun. 26, 553 (1978); J. F. Herbst, J. M. Burkstrand, and J. W. Wilkins, Phys. Rev. B 22, 531 (1980).

[14] S. P. Kowalczyk, N. Edelstein, F. R. McFeely, L. Ley, and D. A. Shirley, Chem. Phys. Lett. 29, 491 (1974).

[15] J. M. Haschke and T. A. Deline, Inorg. Chem. 19, 527 (1980).

[16] R. C. Baetzold, private communication.

[17] Because of the reactivity of samarium and its tendency to aggregate, evaporated overlayers were made to inhibit such effects.

[18] S.-T. Lee, G. Apai, M. G. Mason, R. Benbow, and Z. Hurych, Phys. Rev. B 23, 505 (1981); G. Apai, S.-T. Lee, and M. G. Mason, Solid State Commun. 37, 213 (1981).

[19] C. Bonnelle and F. Vergand, J. Phys. Chem. Solids 36, 575 (1975), and references therein.

Probing the Electronic Structure of Metallic Glasses using Auger *XVV* Transitions

A. J. Bevolo, C. S. Severin, and C. W. Chen
Ames Laboratory and Departments of Physics and Materials Science and Engineering,
Iowa State University, Ames Iowa 50011

(Received 26 March 1981; revised manuscript 27 July 1981)

The bandlike *XVV* Auger transitions of glass-forming elements are shown to provide a sensitive method for investigating the electronic properties of metallic glasses. For amorphous $Fe_{82}B_{18-x}Be_x$, not only do the Auger results correlate remarkably well with the magnetic data, but more importantly, a 14-eV shift was detected in the Be *KVV* Auger spectra between $x = 4$ and $x = 5$. This large shift reflects a pronounced change in the short-range order of this metallic glass system.

PACS numbers: 75.50.Kj, 71.25.Mg, 79.20.Fv

Attempts to understand the magnetic behavior of iron-base metallic glasses in terms of saturation magnetization (M_s), the average magnetic moment per Fe atom ($\bar{\mu}_{Fe}$), and the Curie temperature have been limited to magnetization measurements supplemented by such experiments as Mössbauer and NMR spectroscopies for indirect information on related electronic properties. We demonstrate in this Letter that the energy and line shape of the Auger *XVV* (*V* is the valence level) transitions of glass-forming elements in metallic glasses provide a new probe of their electronic structure.

There are two basic types of Auger transitions depending on the interaction strength of the final two holes.[1] If the hole-hole interaction is strong, the Auger spectrum is derived from multiplet states of the two interacting holes. These quasiatomic spectra do not reflect the electronic environment of the atom. If the hole-hole interaction is weak, then the XVV Auger line shape represents the self-fold of the valence band density of states and large line-shape changes are observed when such an element is placed into a different chemical environment. The hole-hole delocalization essential to bandlike Auger spectra is commonly found for broadband sp elements such as aluminum rather than for narrow-band transition metals. A method[2] for distinguishing bandlike and quasiatomic XVV Auger transitions is based on the effective hole-hole interaction energy given by

$$U_{\text{eff}} = E(X) - E(V) - E(V) - E(XVV), \qquad (1)$$

where $E(XVV)$ is the energy of the Auger line, and $E(X)$ and $E(V)$ are the energies of the core and valence bands, respectively, measured by a one-electron hole spectroscopy such as x-ray photoemission (XPS), x-ray emission (XES), or ionization loss (ILS). The Auger spectrum is either bandlike or quasiatomic, depending on whether the value of U_{eff} is nearly zero or large, say 5 eV. If $E(V)$ is at the Fermi level, then $E(XVV)$ will attain its maximum value, $E_{\max}(XVV)$, and Eq. (1) becomes

$$U_{\text{eff}} = E(X) - E_{\max}(XVV), \qquad (2)$$

which does not involve the valence state energies.

Many metallic glasses consist of a transition metal and one or more glass-forming metalloids such as B, P, and Si. These elements are precisely those that form *sp* valence bands in their elemental solids. Therefore, they should exhibit bandlike XVV Auger spectra that should be a sensitive probe of the electronic structure of metallic glasses. In particular, the effects of a changed local chemical environment of the glass-forming elements on the magnetic and electronic properties of the alloys can be directly studied as a function of composition and temperature.

The amorphous ternary system $\text{Fe}_{82}\text{B}_{18-x}\text{Be}_x$ was chosen for study because the alloys with x up to six, i.e., 6 at.% Be, exhibited an anomalous peak in $\bar{\mu}_{\text{Fe}}$ between 4 and 5 at.% Be.[3] Our application of AES to the amorphous Fe-B-Be alloys thus had the additional incentive to confirm this puzzling magnetic behavior besides the purpose aforementioned.

Random sections of each alloy in ribbon form were analyzed in a PHI TFA Auger spectrometer with use of a 3-keV, 2-μA electron beam with a 100-μm spot size. Intensive Ar^+ ion bombardment was required to prevent reabsorption of carbon- and oxygen-bearing gases onto the sample surface. From their relative sensitivity factors,[4] the surface concentration of either element was estimated to be less than 0.1 at.% which was too low to affect the KVV spectra of B or Be.

In Figs. 1(a) and 1(b), the Auger spectra from $\text{Fe}_{82}\text{B}_{13}\text{Be}_5$ and $\text{Fe}_{82}\text{B}_{14}\text{Be}_4$, respectively, show that the Be KVV transition for $x = 5$ appears at 106.2 eV but for $x = 4$ it occurs at 92.3 eV. Such a large shift of 13.9 eV for such a small change in composition is very unusual. Spectra taken but not shown for $x = 2$ show the same low-energy Be KVV line as for $x = 4$ while that for $x = 6$ has the same energy as $x = 5$. No line near 106 eV was observed at the five percent level for $x \leqslant 4$ and none near 92 eV at the ten percent level for $x \geqslant 5$. No changes were observed in the B or Fe Auger transitions.

Before discussing the implication of the Be KVV energy shift in the $\text{Fe}_{82}\text{B}_{18-x}\text{Be}_x$ alloys it is necessary to consider the Be KVV Auger spectrum in other Be alloys and compounds. In agreement with previous workers[5] we find that the Be

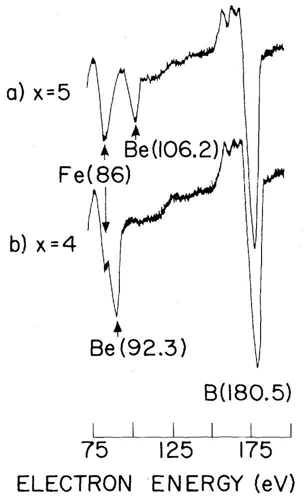

FIG. 1. Auger spectra of sputter-cleaned amorphous $\text{Fe}_{82}\text{B}_{18-x}\text{Be}_x$ showing the 13.9-eV shift of the Be KVV transition when x goes from 5 to 4 at.% Be.

KVV spectrum of elemental Be consists of a single asymmetric line with an energy of 105 ±1 eV. The energy of the Be 1s core level is 111 eV,[6] and the peak in the valence band density of states,[7] as determined by XES, lies 3 eV below the Fermi level. Using Eq. (1) we find $U_{\mathrm{eff}} = 0$ eV suggesting the bandlike nature for the Be KVV transition in Be metal. We have measured $E_{\max}(KVV)$ at 110.0 ±0.5 eV so that Eq. (2) gives U_{eff} of about 1 eV. The latter result thus provides conclusive evidence for the bandlike nature of this transition since it avoids the question of the different matrix element effects across the valence band that might occur when comparing XES and AES spectra. Jennison, Madden, and Zehner[8] have shown that the major component of the Be KVV line shape in Be metal is the $1s2p2p$ transition with a smaller $1s2s2p$ component as a low-energy shoulder.

The Be KVV spectrum from $Fe_{97}Be_3$, $Fe_{93}Be_7$, and $Fe_{70}Be_{30}$ alloys was found to be a single asymmetric line at 106.0 ±0.3 eV. From ILS the binding energy of the Be 1s state was within 0.6 eV of that measured for elemental Be, while $E_{\max}(KVV)$ was 110 ±1 eV for all three alloys. With Eq. (2) these results conclusively demonstrate the bandlike nature of the Be KVV spectra for these alloys, independent of any assumptions concerning the unmeasured values for $E(V)$. From Eq. (1), $E(V) \simeq 3$ eV as was the case for elemental Be. Thus the 2p states of Be are essentially unaffected when Be is placed in the iron-rich Fe-Be alloys.

The Be KVV Auger spectra for the Fe-Be alloys and elemental Be are in sharp contrast to that of BeO.[9] The most intense line for BeO occurs at 94 eV, whereas the 105-eV line is absent because the Be 2p orbital has been significantly depopulated by an ionic charge transfer. The Auger final states are primarily composed of O 2p states some 7 eV below the Be 2p state in Be metal. This type of Auger transition, involving orbitals not on the same atom as the initial core hole, is often called interatomic. The Be 1s state binding energy in BeO is 3 eV higher than it is in Be.[10] In the absence of any change in $E(V)$ this would produce an Auger line 3 eV higher for BeO when compared with that from Be metal, instead of the nearly 10-eV lower energy actually observed. The Be KVV Auger spectrum of BeO illustrates a case where a large energy shift can be interpreted in the bandlike picutre.

The Be KVV Auger spectra from the $x = 5$ and $x = 6$ $Fe_{82}B_{18-x}Be_x$ alloys have the same $E_{\max}(KVV)$ as Be metal and the Fe-Be alloys, thereby confirming that the Be 2p states are essentially unchanged in energy. Since similar Be KVV spectra were observed in elemental Be with exclusively Be-Be bonding and in Fe-rich Fe-Be alloys with predominantly Fe-Be bonding, it was difficult to determine from either our Auger results or other techniques whether or not clustering or segregation of Be had occurred in the $x = 5$ and $x = 6$ ternary alloys, which would result in prominently Be-Be bonding. But because our amorphous alloys were prepared by induction melting and rapid quenching and because segregation of minor elements in these alloys has not been reported as a common phenomenon, we did not favor this possibility.

The Be KVV spectra from the $x = 2$ and $x = 4$ alloys, with energies near 92 eV and no 105-eV component, represent a drastic change from those measured for elemental Be, the iron-rich Fe-Be alloys, and the $Fe_{82}B_{18-x}Be_x$ alloys with $x = 5$ and $x = 6$. The 92-eV Be KVV spectra for $x = 2$ and $x = 4$ alloys must be considered anomalous. From ILS the binding energy of the Be 1s state in the $x = 4$ and $x = 5$ alloys was 112.2 ±0.5 eV and 111.9 ±0.5 eV, respectively. Thus, the energy shift of the Be KVV Auger transition on going from $x = 4$ to $x = 5$ must be due to a change in the valence local density of states of Be. Because of the highly local nature of the Auger process the large 14-eV energy shift could only occur if the nearest-neighbor environment of all of the Be atoms had been drastically altered when x goes from 4 to 5. It is this conclusion from the Auger experiments and its correlation with the magnetic properties of this amorphous alloy system that is the main result of this investigation.

The absence of the 105-eV Auger line in the $x = 2$ and $x = 4$ alloys and its association with an occupied 2p orbital indicates that for these alloys the Be 2p orbital may have become depopulated. A reduction in the intensity of an Auger transition due to a reduced occupancy of the final state has been reported[11] for the oxygen $1s2p2p$ line in a series of oxides. In our case, the reduction is nearly complete and comparable to that observed for BeO. On the basis of a charge transfer of the Be 2p electrons, which accounts for the absence of the 105-eV line, several alternative sources remain for the final Auger states, notably a $1s2s2s$ transition and an interatomic-type transition. Both could produce the 92-eV line. In the interatomic case, the nature of the final state is not known except that it cannot be the O 2p state since the oxygen concentration in the sputtered alloys is too low to have a significant effect. Another possibility is the $1s2p2p$ transition with the $2p$ state still occupied but shifted 7 eV below the energy it has in every other metallic Be alloy. Since Be segregation would produce primarily Be-Be bonding and a prominent 105-eV transition, Be segregation can be ruled out for the $x \leq 4$ alloys. The unusual 14-eV shift of the Be KVV Auger line in the ternary Fe-B-Be alloys requires further data on the valence band from either XPS or XES before various possibilities can be critically examined.

There are two major shortcomings in the analysis of XVV Auger line shapes. One is the use of ion beam sputtering which can produce compositional or structural changes in alloys.[12] Another is the low energy of an XVV Auger transition, typically less than 200 eV. Since this limits the escape depth of the Auger electrons to about 5 Å,[13] the technique is highly surface sensitive. However, the observed Auger changes with alloying in the sputter-cleaned $Fe_{82}B_{18-x}Be_x$ system and the high degree of correlation with the *bulk* magnetic properties suggest that Auger analysis of XVV transitions may be widely applicable.

In common with Auger spectroscopy, XES and core level shifts in XPS can also be used to probe the chemical changes of individual elements. We expect that they, along with Auger analysis of XVV spectra, will complement the widely used techniques of NMR and Mössbauer spectroscopy in the study of the electronic properties of metallic glasses. In conclusion, our Auger results (a) establish in metallic glasses a discontinuous change in atomic bonding with alloy composition, possibly involving a charge transfer of the type usually found only in ionic compounds, and (b) correlate very well with the unusual bulk magnetic properties of the amorphous $Fe_{82}B_{18-x}Be_x$ alloys system.

This work was supported by the Director of Energy Research, Office of Basic Energy Science, U. S. Department of Energy, Contract No. WPAS-KC-02-01-03, and by the U. S. Department of Energy under Contract No. W-7405-Eng.-82.

---

[1] See Dwight R. Jennison, J. Vac. Sci. Technol. 17, 172 (1980) for a recent review of this topic.

[2] C. J. Powell, Solid State Commun. 26, 557 (1978).

[3] C. S. Severin, C. W. Chen, A. J. Bevolo, and M. C. Lin, J. Appl. Phys. 52, 1850 (1981).

[4] L. E. Davis, N. C. McDonald, P. W. Palmberg, G. E. Riach, and R. E. Weber, *Handbook of Auger Electron Spectroscopy* (Physical Electronics Industries, Eden Prairie, Minnesota, 1976).

[5] M. Suleman and E. B. Pattinson, J. Phys. F. 3, L53 (1973).

[6] J. A. Bearden and A. F. Burr, Rev. Mod. Phys. 39, 125 (1967).

[7] T. Sagawa, in *Soft X-Ray Band Spectra and the Electronic Structure of Metals and Materials*, edited by D. J. Fabian (Academic, London, 1968), p. 29.

[8] Dwight R. Jennison, H. H. Madden, and D. M. Zehner, Phys. Rev. B 21, 430 (1980).

[9] E. J. LeJune, Jr., and R. D. Dixon, Phys. Rev. Lett. 43, 1998 (1972).

[10] K. Harmin, G. Johansson, U. Gelius, C. Nordling, and K. Siegbahn, Phys. Scr. 1, 277 (1970).

[11] R. Weissmann, Solid State Commun. 31, 347 (1979).

[12] R. Behrisch, *Sputtering by Ion Bombardment* (Springer, Berlin, to be published).

[13] M. P. Seah and W. A. Dench, Surf. and Interface Anal. 1, 2 (1979).