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# X-RAY SYNCHROTRON WHITE BEAM EXCITATION OF AUGER ELECTRONS

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## Abstract

Auger electron spectra have been measured at the Cornell High Energy Synchrotron Source (CHESS), using the full white beam x-ray spectrum as the excitation source. Ordinary Auger spectra obtained in the laboratory with an electron beam source must employ derivative techniques to distinguish the Auger structures from the large background due to the excitation beam. The synchrotron white beam eliminates this source of background and produces signal rates as high as $10^7$ cps. Superior signal-to-background ratios are found for Auger peaks above a few hundred eV, and count rates are large enough to suggest microprobe applications. X-ray induced Auger satellite peaks were observed with intensities much greater than the electron-induced counterpart; this anomaly is not completely understood.

KEY WORDS: Auger electron spectroscopy, synchrotron radiation, Au on silicon, ionization cross-sections, x-ray white-beam Auger excitation, microprobe analysis, shake-up, shake-off, plasmon gain, Auger satellites.

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## Introduction

The intense monochromatic photon beams available at synchrotron sources have made possible many different types of electron spectroscopies. At the lower energy synchrotron sources with photon spectra centered in the vacuum ultra-violet, for example, photoemission investigations now routinely derive occupied valence band structures. At the higher energy x-ray sources, electron detection combined with x-ray absorption studies has resulted in surface-sensitive Extended X-ray Absorption Fine Structure (SEXAFS) measurements. The resonant interaction of photons near an absorption threshold in either energy range can be investigated by monitoring the emission of Auger and photoelectrons. In each of these spectroscopies the interaction of photons with atoms is observed as a function of photon energy.

## Discussion

In this paper we report on a new type of synchrotron electron spectroscopy, which results from using the entire spectral output of an x-ray synchrotron to excite Auger electrons (Matthew and El Gomati, 1979). In experiments conducted at the Cornell High Energy Synchrotron Source (CHESS), the Auger electron spectra of clean Si and small coverages of Au on Si (to be described below) showed striking qualitative and quantitative differences when compared to Auger spectra obtained with the usual electron beam excitation.

The Auger process (Auger, 1925; Alford et al, 1979) is initiated by the ejection of an electron from a tightly bound core level, which can result from the interaction with energetic electrons, photons, or ions. When the core hole is filled by an electron from a less tightly bound level, the amount of energy released can be carried by a photon, i. e. fluorescence, or by the ejection of another loosely bound electron, the Auger electron. Because the energy of this Auger electron is determined by the energy levels of the core electron and the two less-tightly bound electrons, its value is characteristic of the atom involved and, to a

lesser extent, its chemical state. It is this feature which makes Auger electron spectroscopy so useful for chemical analysis.

For the same reason, it is clear that the Auger energy will not depend on whether a photon or an electron created the initial core hole. The cross-sections for electron-ionization and photo-ionization, however, are quite different. As illustrated in Fig. 1a, the photo-ionization cross-section has a resonant peak at a core-electron binding energy BE, and then falls off rapidly. The electron-ionization cross-section, on the other hand, turns on gradually at E=BE and goes through a very mild maximum at about E=4B. As a result, using the CHESS white beam with a median energy of about 10 keV to excite the Auger spectrum of Si, with K electrons bound by less than 2 keV, will result in a much weaker Auger signal than that obtained from a 10 keV electron beam of comparable intensity. Note that although the CHESS spectrum (shown in Fig. 1b) has a significant intensity near 2 keV, the white beam had to pass through several Be windows and a 1 meter air path before reaching the sample. This absorption path essentially removes the low-energy end of the white beam spectrum, which makes resonant absorption below 2 keV entirely negligible.

Although an electron beam can excite a larger Auger signal, the incident electron beam itself is the source of a background signal which can make the signal-to-background ratio S/B quite small for all but the lowest energy Auger transitions, which is why the derivative of the Auger electron spectrum is most commonly measured in electron-excited systems. The large background is due to the partial back-reflection of the incident electron beam, which is at least several orders of magnitude larger than any Auger signal, after having suffered multiple inelastic collisions. For an incident electron energy in the 3-5 keV range, this large inelastic tail of the primary beam will dominate the electron spectrum for energies above 300 eV.

Fig. 2 shows the electron spectra recorded with a PHI double-pass cylindrical mirror analyzer operated in the pulse-counting mode

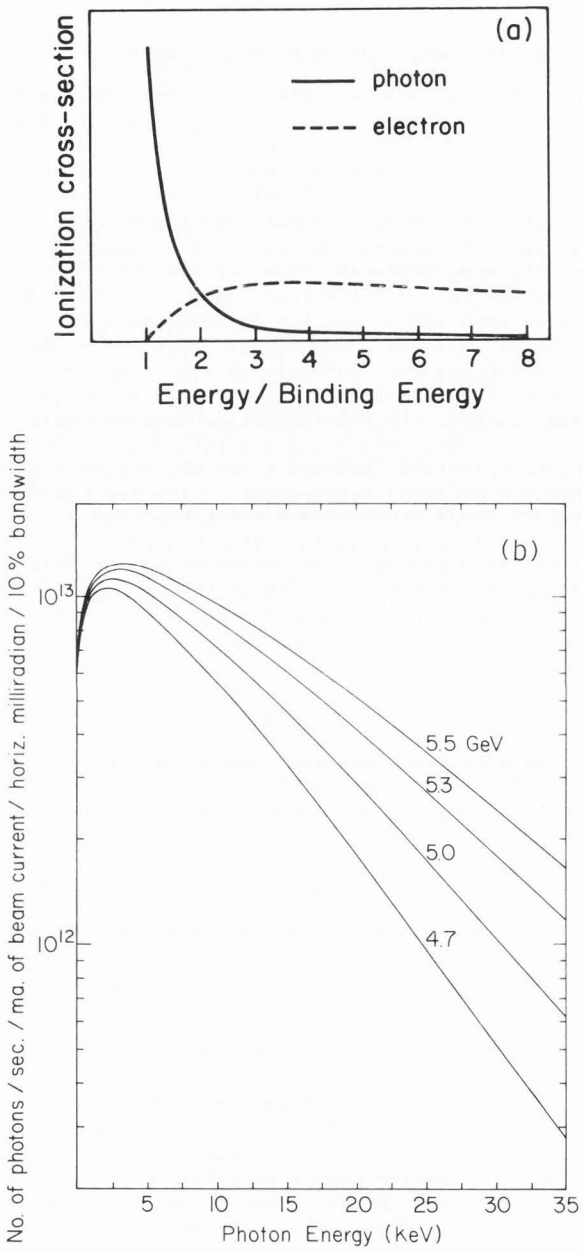


Figure 1: a) Schematic of the ionization cross-sections for electron and photon excitations, from Alford (1979); b) the calculated energy spectrum of the CHESS white beam for various stored electron energies.

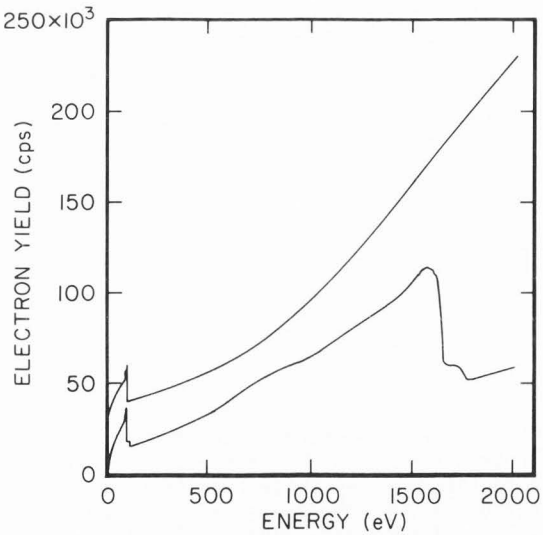


Figure 2: The upper curve is the measured CMA yield for an Auger electron scan from 0 to 2000 eV, using electron excitation at 3 keV and 0.01 microamps; the lower curve was measured using the synchrotron white beam as the excitation source.

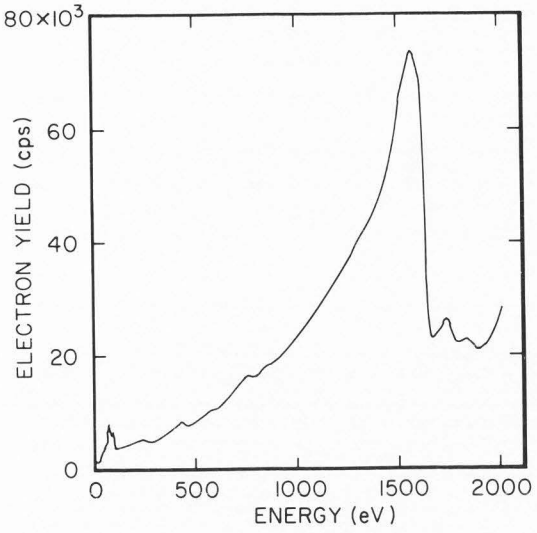


Figure 3: The Auger electron spectrum of 0.3 monolayers of Au on Si (111), using white beam excitation.

with a fixed bandwidth dE/E =1.2%, using a clean Si (111) crystal as the target sample. The upper curve was obtained with an incident electron beam energy of 3 keV and a current I=0.01 microamps; the lower curve shows the response to the CHESS white beam with the synchrotron operating at 4.7 GeV and 20 milliamps stored current. There are two striking features evident in this comparison:

1) The most prominent feature in the photon-induced curve, the Si KLL transitions near 1600 eV, is barely perceptible in the electron-induced curve; even for derivative measurements made with large electron currents the KLL feature is very small, because S/B is very small. This difference makes white-beam excitation of Auger electrons the preferred method for studying transitions to the most tightly bound core levels.

2) The actual photon-induced Auger count rates are enormous. After making detector dead-time corrections, the peak Si KLL count rate exceeded $10^7$ cps.

The magnitude of this signal suggests that white beam Auger excitation may be applicable to microprobe analysis. If the synchrotron were operated at 5.5 GeV, its most common beam energy, and if the stored current were increased to 50 milliamps, which should be routinely available in the near future, we estimate that the Auger signals would increase by more than a factor of 5. Taking the data on the CHESS wiggler beamline would provide another factor of 6. The use of a wide-bandpass monochromator to focus the most intense part of the white beam should result in another factor of 10. These improvements would increase the Si KLL signal to more than $3x10^9$ cps. Scaling down from the 4 mm spot size used in our studies, we conclude that a 1 micron spot size would yield over 1000 cps. Finally, if these measurements could be made in a chamber continuous with an evacuated beamline, eliminating the Be windows and air absorption paths, resonant photoabsorption at lower photon energies could increase the yield by orders of magnitude.

As another example of the sensitivity of this technique, we show in Fig. 3 the Auger electron yield from the same Si (111) crystal with a Au coverage of 0.3 monolayers. The illuminated area of the sample was intentionally reduced so that the Si KLL peak intensity would not require any dead-time corrections, which allows the true signal-to-background ratio to be seen. After scaling up these intensities to correspond to the full beam size, several of the Au Auger peaks which would not be easily discernible in an electron-excited Auger spectrum have intensities which exceed $10^5$ cps with good signal-to-background ratios.

Up until now we have considered the absence of a backscattered primary electron beam and the energy dependence of the cross-sections to be the only differences between white-beam-excited and electron-excited Auger spectra. A fundamental difference in the excitation processes is revealed in Fig. 4, which is essentially a blow-up of Fig. 2 in the energy region near 100 eV. The peak near 90 eV is the Si LVV transition, where the initial core hole is in an L level, and the other two electrons originate in the valence band. Note that the broad satellite peak occurring near 106 eV is quite prominent in the white beam spectrum and almost non-existent in the electron spectrum. Because the LVV peak heights have been set equal and have about the same background level, this large difference between satellite intensities cannot be explained in terms of simple cross-section or background differences. In other words, it seems as if these Auger

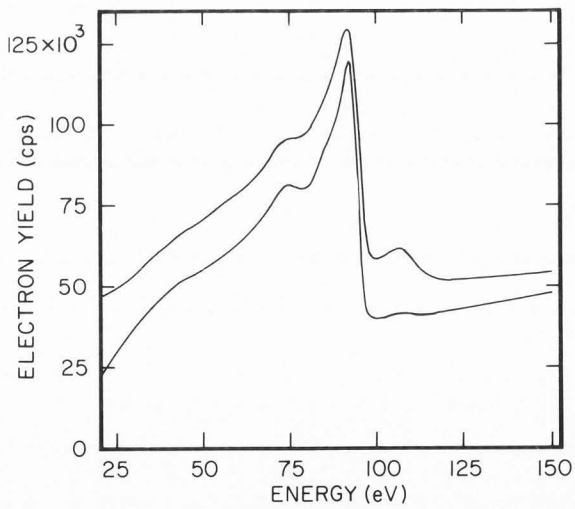


Figure 4: A detailed comparison of the electron-induced and photon-induced Auger yields near the LVV transition of Si. Note the satellite near 106 eV, which is almost completely absent in the electron induced spectrum.

electrons could tell whether the initial core hole had been created by a photon or an electron.

There are many possible causes of Auger satellites, some of which we now consider: 1) Shake-up processes. When the initial core hole is created, other electrons in the atom are forced into excited bound states. When Auger emission ensues, the energy can be shifted, but this is almost always a small effect. 2) Shake-off processes. Here a second electron is ejected from the atom at the same time the core hole is created. If this extra "spectator" hole is also from a deep level, relatively large shifts in the Auger energy are possible, which may be consistent with the observed satellites. 3) Plasmon gain. If an outgoing Auger electron absorbed a bulk plasmon before leaving the crystal, its resultant energy would be very near the observed satellite. At ordinary temperatures there are usually no plasmons existing in the crystal, but the electron ejected from initial core level can excite plasmons, which may then interact with the ensuing Auger electron. Although previous studies concluded that this satellite in the electron-excited spectrum was not due to plasmon gain (Rowe and Christman, 1973; Melles et al., 1974), the possibility of plasmon gain in the white beam spectrum cannot yet be ruled out.

Until additional measurements and more thorough analyses are made, it is not possible to determine the origin of this satellite effect. While the plasmon gain model is attractive because it gives approximately the right energy, it is hard to see how the x-ray excitations generate more plasmons than an electron beam. Similarly the "spectator" hole model will depend on establishing a greater cross-section for multiple ionization for x-rays.

## Conclusion

We have demonstrated that the Auger electron spectrum excited by an x-ray synchrotron white beam can give a much clearer picture of Auger transitions above a few hundred electron volts. In addition the Auger yields are intense enough to make microprobe analysis with a white beam appear feasible. Finally we note that photons and electrons are not equivalent excitations sources for some Auger satellite lines.

## Acknowledgements

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## Discussion with Reviewers

J. Kirschner: When using a CMA-type spectrometer the energy resolution with a 4 mm dia beam spot (photons) should be substantially worse than when using the focussed electron beam. The data in Fig. 4 seem to indicate that the resolution in the electron spectrum is indeed better than in the photon excited spectrum. Do you think that this effect might have influence on the appearance of the broad high energy satellite, especially on its relative magnitude?

Authors: We agree that the resolution should be better for the electron-excited spectrum, and that Fig. 4 bears this out. Note, however, that the high energy satellite has a magnitude very much smaller than the low energy satellite for the electron-induced spectrum, while it is distinctly larger in the photon-induced spectrum. We do not believe that this can be accounted for by the difference in resolution.

J.A.D. Matthew: 1. The most likely cause of the relatively intense Si satellite at 106 eV is double ionisation Auger emission arising from decay of 1s holes by $KL_{23}L_{23}$ emission. In electron excited spectra this is of little importance because K ionisation cross sections are much smaller than $L_{23}$. Now, with synchroton excitation, K photoionisation is dominant so that the $2p^{-2}$ yield (from $KL_{23}L_{23}$ decay) is comparable with the direct $2p^{-1}$ yield. Energy estimates confirm that 106 eV is the right energy region. To confirm such a mechanism one needs to know details like (a) the relative sensitivities of the CMA at ∿100 eV and ∿1650 eV, (b) the precise photon energy distribution incident on the sample, and (c) appropriate mean free path corrections.

If the suggestion were correct, the intensity of the satellite could be controlled by inserting appropriate absorbing filters in the white radiation path.

2. There is an interesting broad bump in the clean Si spectrum (Fig. 2) peaking at ∿900 eV. This is possibly due to photoemission from the Is level by the white radiation. This could again be checked by modifying the white radiation intensity profile.

Authors: We are grateful for your comments which will be useful areas for future work.