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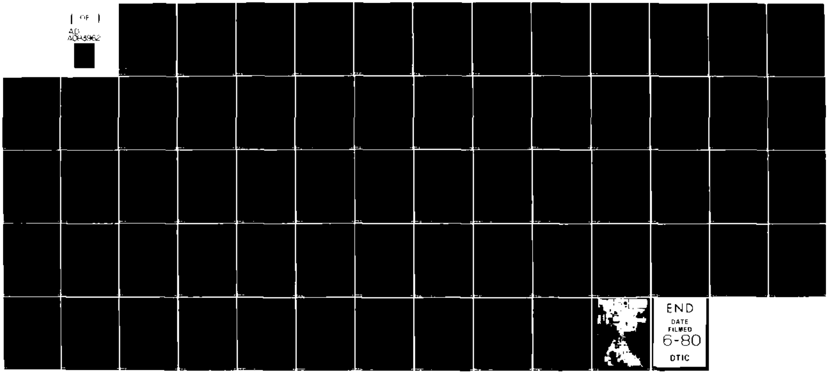

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LOW ENERGY X-RAY AND ELECTRON INTERACTIONS WITHIN MATTER

Burton L. Henke

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March 1980

Interim Scientific Report

01 October 1978 through 30 September 1979

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This research program is concerned with ~~the continued development of~~ the physics and the application of low energy x-ray and associated electron interactions. It has been concentrated upon the sub-kilovolt energy region where the need has been greatest for the development of efficient and precise spectroscopic methods, for the measurement of fundamental interaction cross sections, and for the basic theoretical modeling of certain important x-ray and electron interaction processes as, for example, x-ray induced photoemission and fluorescence. This work is applied, independently (cont.)

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and collaboratively, to two areas of considerable present importance and need:

1. The development of high efficiency spectroscopic methods that can be effectively applied to the diagnostics of high temperature plasmas--particularly as generated by high power pulsed lasers, electron or ion beams and by exploding wires, for which high temporal resolution as well as high spectral resolution is needed. These developments include continued studies on the optimization and precise photon-energy calibration of x-ray photocathode systems ~~as may~~ be applied in x-ray detectors, streak and framing cameras.

2. The testing and application of high-efficiency low-energy fluorescent spectroscopic measurement and analysis for valence and molecular orbital electron energy state studies, for the solid state characterization of surfaces, and for studies of the effects of radiation damage. The molecular orbital and valence band spectra can provide much needed complementary information to that as obtained by x-ray and UV excitation photoelectron spectroscopy, and can also provide an important basis for testing and guiding the new, large-computer theoretical calculations for the electronic structure of matter.

Presented here is a brief description of these research schedules. The Appendices include a listing of research accomplishments as reported to date, along with abstracts of this project's more recent research publications.

Interim Scientific Report
Grant AFOSR 79-0027

LOW ENERGY X-RAY AND ELECTRON INTERACTIONS WITHIN MATTER

01 October 1978 through 30 September 1979

This 1978-79 Interim Scientific Report includes the following sections:

1. A preprint of a paper presented for an international seminar at the University of Hawaii, November 5-9, 1979. This review paper by the principal investigator discusses the current research in low energy x-ray and electron physics of this AFOSR program.

2. A brief, general description of this program as to its background, its continuing objectives, and its accomplishments.

Appendix I:	Some first-page abstracts of recent publications.
Appendix II:	A listing of principal publications of this program to the present date.
Appendix III:	A listing of persons acquainted with this research program.
Appendix IV:	A listing of papers presented by the principal investigator from 1970 to the present date.

Invited Paper Presented at an International Seminar on
Synchrotron Radiation Facilities
University of Hawaii, November 5-9, 1979

To be Published in Nuclear Instruments and Methods

X-RAY SPECTROSCOPY IN THE 100-1000 eV REGION

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ABSTRACT

Some current methods for achieving low-energy x-ray spectroscopy in the 10-100 A region are reviewed. Gratings, crystals and multilayers can be used as monochromators or dispersive analyzers. Some of the important characteristics are noted here which can help to determine their applicability to a given spectroscopic analysis need. The "trade-off" between resolution and spectrographic speed (gratings vs multilayers) may be an important consideration when the number of photons available for measurement is limited, as, for example, by the excitation dosage allowed for a given sample. For pulsed x-ray

sources and for time-resolved spectroscopy, special fixed-crystal spectrographs have been developed. These may be applied with x-ray diodes and fast oscilloscopes or with x-ray streak cameras for detection. The optimum design and characterization of the photocathode systems for such detection have been studied in detail and some of the results of this work are briefly reviewed.

I. INTRODUCTION

The new synchrotron radiation and laser-produced plasma sources can provide pulsed, broad-band radiation in the uv and x-ray region of such high intensity as to present a new dimension for spectroscopic analysis. This may be of particular importance for low energy x-ray spectroscopy in the 10-100 A region for which high intensity, selective excitation has generally not been available.

X-ray absorption and emission spectroscopy in this low energy region is of considerable interest for the measurement of the spectra that originate from transitions between the outermost electronic levels and the relatively sharp, first core levels. Such valence band spectroscopy can sensitively reflect the chemical, optical and electronic properties of matter.

The importance of having continuous selectivity of the excitation for absorption spectrometry is well known, particularly for the extended absorption fine structure measurements. Selective, narrow-band excitation can also be of critical advantage in emission spectrometry in order to provide "clean" meaningful spectra with a minimum of background radiations, and to minimize possible effects of radiation-induced changes in the sample.

An illustration of the critical role of radiation damage in molecular orbital spectroscopy is presented in Fig. 1. The Chlorine-$L_{II,III}$ spectra in the 150-250 eV region were measured in order to determine the relative molecular orbital strengths of s and d symmetries for various oxidation states in chlorine compounds.[1] In the design of such measurements it is necessary to know how much radiation dosage can be tolerated without significantly affecting the spectrum characteristic of the system under study. Shown here are "fast" spectral scans that were taken as a polycrystalline sample of $NaClO_4$ was irradiated under a typical excitation line source of C-$K\alpha$ (277 eV) of 1.75×10^{13} photons/cm^2-sec intensity at the sample surface. Demonstrated here upon an analysis of the successive spectra is a radiation-induced reduction of the $NaClO_4$ through the various oxidation states to finally that for the NaCl state. The allowable radiation exposure for a proposed spectral analysis measurement can be determined from such data and the required "speed" for an appropriate spectrograph is fixed as is usually the spectral resolution that may be expected. For high resolution spectroscopy of many materials, it is very important to selectively excite the spectra with only those photons of such energy as to be most efficient in creating the desired "hole" states. Then a minimum of excitation energy is deposited for the given measurement and the radiation damage is correspondingly minimized.

An example is shown in Fig. 2 that illustrates the importance of narrow-band selective excitation in emission spectroscopy. Argon-$L_{II,III}$ spectra were studied in order to determine the possible differences in the outer electronic level structure for the gas and solid states.[2] Shown here is the Ar-$L_{II,III}$ spectrum of solid argon selectively excited by a C-Kα (277 eV) line source and resulting from predominantly single ionizations of either the $2p_{1/2}$ or $2p_{3/2}$ levels. The allowed transition from the M_I level results in the expected doublet with the statistical weights of 2:1 in the spin-orbit splitting of 2.2 eV. Also shown here is the spectrum measured under similar conditions but with Cu-Lα (932 eV) line source excitation. This excitation results in the obliteration of the single-electron transition spectrum by the superposition of slightly higher energy satellite, multiple ionization structure. The ionization energies of the L_I and the $L_{II,III}$ levels are 320 and 250 eV, respectively. With the Cu-Lα (932 eV) excitation the L_I level is also ionized. The L_I hole decays by a Coster-Kronig process, for example as $L_IL_{II,III}M_I$, resulting in a double vacancy and consequently the high energy satellite of the $L_{II,III}$ spectrum. The selective excitation of only the $L_{II,III}$ levels results primarily in a single electron transition spectrum that is immediately amenable to relatively simple theoretical modeling. A nonselective excitation typically results in multiple ionization structure (and often high-order dispersed background) that seriously compromises the spectral analysis.

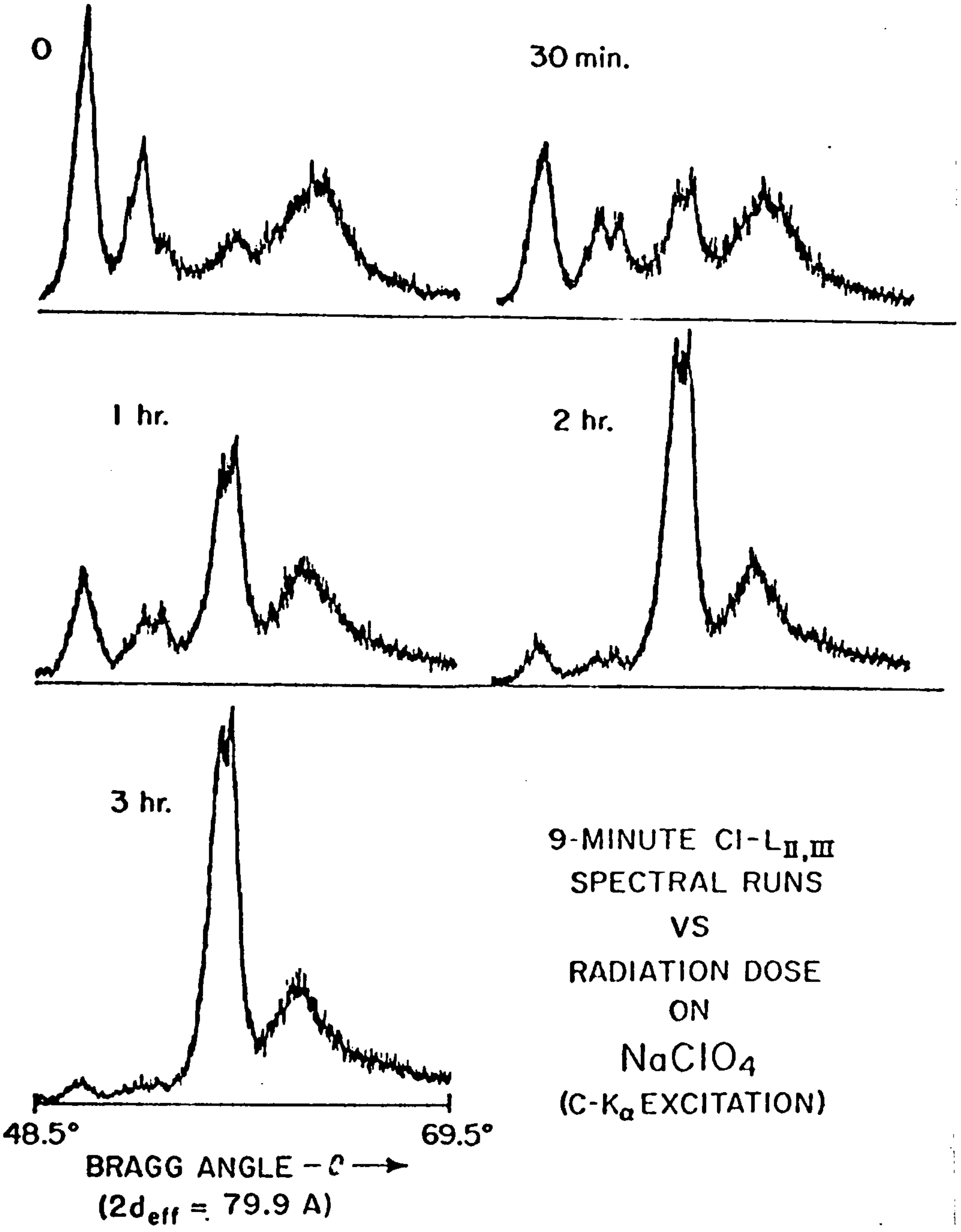


Figure 1. Radiation-induced decomposition of polycrystalline NaClO$_4$. Excitation intensity was similar to that employed for the Cl-L$_{II,III}$ spectroscopy (1.75 x 10^{13} C-Kα (277 eV) photons per sec-cm^2 at sample surface). The quick scans reveal spectral changes corresponding to the appearance of reduction products such as NaClO$_3$ and NaClO$_2$. After three hours, the spectra corresponds to that for NaCl.

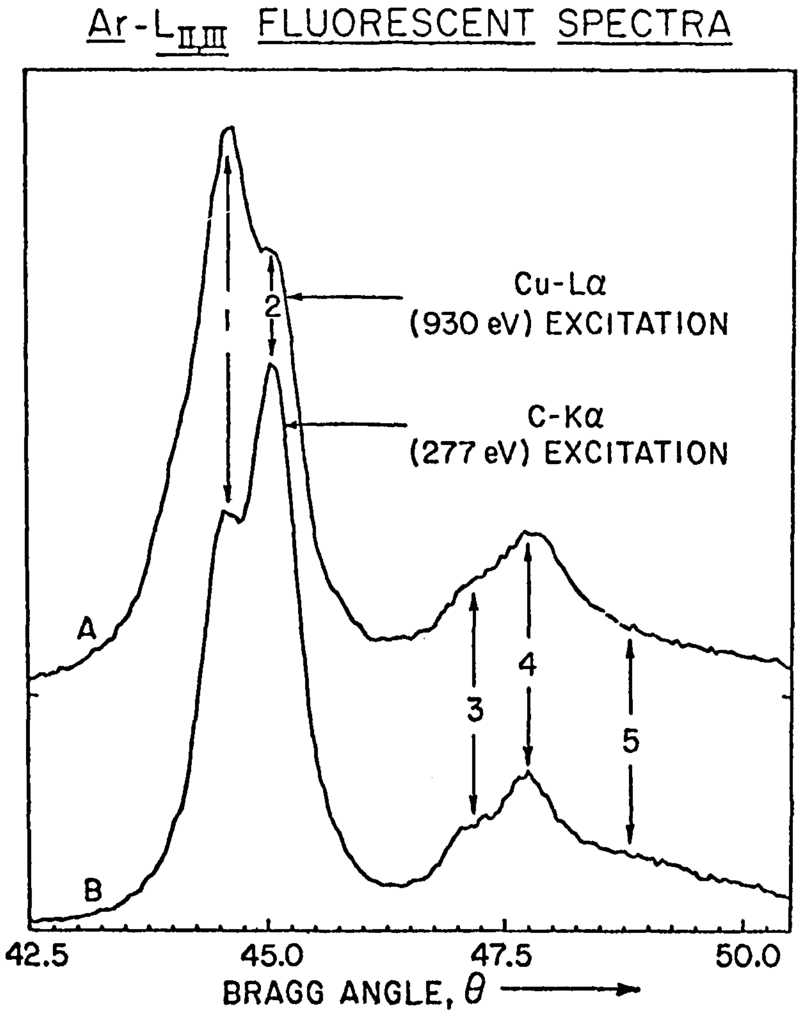


Figure 2. An example of selective excitation. The $L_{II,III}$ spectra for solid argon as excited by C-Kα (277 eV) and Cu-Lα (932 eV) line sources. With the C-Kα excitation, predominantly L_{II} and L_{III} levels are excited (∿250 eV ionization energy) and the single electron transition, $L_{II,III}-M_I$, results, revealing the spin-orbit splitting of 2.2 eV of the $2p_{1/2}$ and $2p_{3/2}$ states (peaks 1 and 2). The Cu-Lα excitation can also excite the L_I level (∿320 eV ionization energy) which decays through a Coster-Kronig process to create, for example, the double vacancy in $L_{II,III}$ and in M_I. As illustrated here, this multiple ionization obliterates the single electron transition spectrum by a superposition of higher energy satellite. (The molecular multilayer, lead myristate, was the analyzer for this study.)

With synchrotron radiation sources, the excitation line source is replaced very effectively by a narrow band selected by a suitable primary monochromator. Such a monochromator for the low energy region is described in Sec. II on multilayer analyzers.

Another important capability of the new synchrotron and laser-produced plasma sources is that the high intensity radiation can be presented in pulses of duration in the sub-nanosecond region. With a proper choice of the photocathode, x-ray streak cameras can be used to characterize the structure of these pulses in the picosecond resolution range and to apply them for time-resolved spectroscopy. The characterization of x-ray photocathodes for photoelectric detection systems is described in Sec. III. In Sec. IV a fixed-analyzer crystal spectrometer for pulsed x-ray spectroscopy and for time-resolved spectroscopy is briefly described.

II. LOW ENERGY X-RAY ANALYZERS

A. Diffraction Gratings

The advantage of the grating over of crystal spectrograph in the low energy x-ray region of 10-100 A is its higher resolution capability.[3] Typically one can obtain about 0.1 eV resolution with gratings and about 1 eV resolution with appropriate crystals. The disadvantage of grating systems is that the grazing incidence geometry that is required is more tedious and the "speed" or effective aperture is usually considerably smaller than that of the crystal spectrograph.

As suggested above, it is not necessarily the intensity of the excitation source that determines the requirement for spectrographic speed but rather, very often, it is the excitation radiation dose permitted by the sample to be analyzed. It is of considerable importance that the design of grating spectrographic measurements be optimized as to geometry, excitation and detection in order to achieve maximum speed without a loss of the high resolution capability. In the past two decades, there has been a large improvement in the overall efficiency of x-ray grating spectrographs.[4] Nevertheless, high resolution grating spectroscopy is not practicable or even possible for a large number of materials analysis applications because of insufficient speed and/or flexibility. For such applications, one must consider the possible advantages of low energy x-ray crystal or multilayer spectroscopy.

B. Crystal Analyzers

For an optimization of a crystal spectrographic measurement, it is usually important to choose a crystal of 2d-value that approaches that of the wavelengths to be measured in order to have large Bragg angle diffractions.[5,6] Although the integrated reflectivity of the crystal analyzer is usually maximized for both small and large Bragg angles, the large angle operation allows the very crucial maximization of resolution. The higher angular dispersion for the large Bragg angles allow a more efficient utilization of collimation or, alternatively, of focussing geometry for high resolution and thus a minimum loss of aperture or speed. At the small Bragg angle operation for the low energy x-rays, the tail of the specular reflection distribution from the crystal may contribute an appreciable background relative to the Bragg reflected spectrum.[7]

For spectroscopy in the 10-20 A range, the most effective analyzers that are available at this time are the organic acid phthalates of 2d-values of 25-27 A.[8] These include potassium acid phthalate (KAP), rubidium acid phthalate (RAP) and thallium acid phthalate (TAP). These crystals have rocking curve widths (FWHM) of about 1 eV and relatively high, monotonic integrated reflection coefficients for the 10-20 A band as shown in Figs. 3 and 4. Generally these analyzers cannot be used for analysis above 20 A because of the marked reflectivity changes near the Oxygen-K absorption edge.[9] It is also important to note the existence of a very sharp and large enhancement of reflectivity at 23.3 A. The KAP analyzer can be cleaved to sufficiently thin (~200 microns) and flexible, large area sections which allows it to be bent to curvatures suitable for focussing crystal optics.

C. Sputtered and Evaporated Multilayers

There are, at present, no naturally grown crystals of 2d-values in the 40-50 A range that are suitable as analyzers for the 20-50 A wavelength region spectroscopy. However, it has been recently demonstrated that relatively high quality multilayer analyzers with these 2d values can be constructed by the successive vacuum deposition (sputtering or evaporation) of heavy and light element of alloy layers.[10,11] Preliminary evaluations of such multilayer systems for low energy x-ray spectroscopy have recently been made at this laboratory and at others.[12,13] Shown here in Figs. 5 and 6 are the reflection characteristics of a sputtered multilayer constructed with 62 d-spacings of 11 A tungsten and 11 A or carbon. The multilayer was mounted in a flat-crystal vacuum spectrograph and a series of profiles of characteristic line sources in the low energy region were recorded using a collimator of 0.34° Gaussian full width. Upon deconvoluting the collimation broadening and that caused by the respective emission line widths, the intrinsic reflectivity curves for the multilayer were determined and found to be essentially Lorentzian. Shown here are the areas under the I/I_0-vs-θ deconvoluted curves (the integrated reflectivity, R, in milliradians), the FWHM, W, in equivalent eV units, and the peak value of I/I_0, P (%).

As noted in Fig. 6, this multilayer had no measurable even or odd high order reflections, indicating that the layered structure must consist of a graded tungsten carbide. By modeling this structure with sinusoidally varying optical constants, δ and β, as shown, a theoretical expression for R was derived and plotted here for first-order reflection and which becomes equal to zero for all high order order reflections.[14]

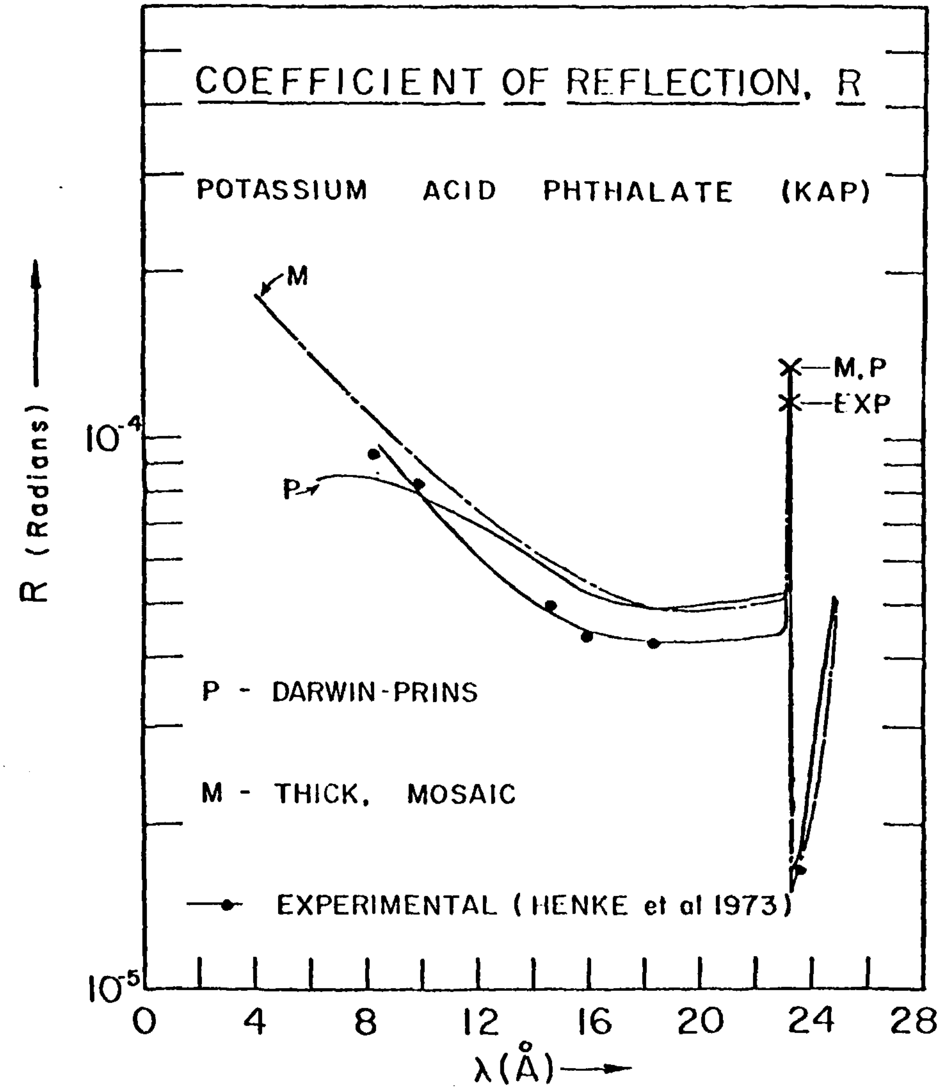


Figure 3. The measured integrated reflectivity, R, for the KAP analyzer and compared with that calculated using the Darwin-Prins perfect crystal theory and the thick mosaic crystal theory. The Oxygen-K absorption edge structure and the strong, resonance reflection at 23.3 A limits its application for spectral analysis to wavelengths below 20 A. It is an outstanding analyzer for the 10-20 A region.

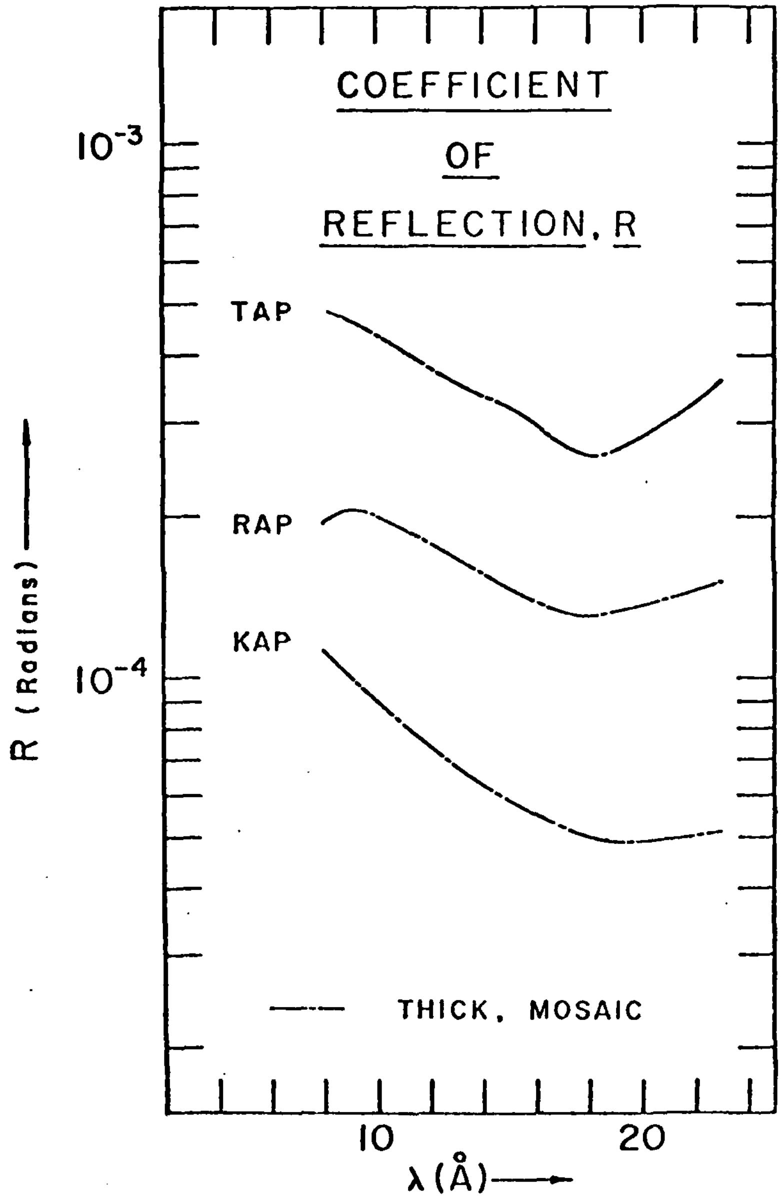
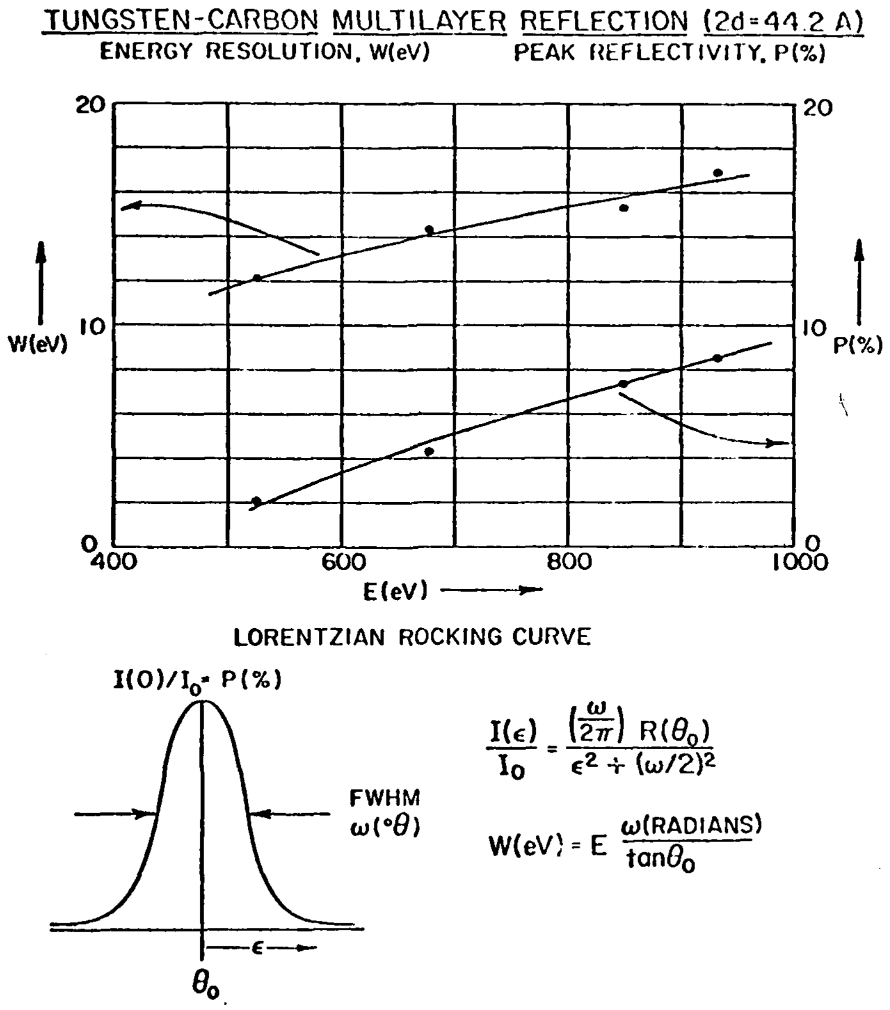


Figure 4. The relative integrated reflectivities for thallium acid phthalate, rubidium acid phthalate and potassium acid phthalate are presented here. (The rocking-curve width also increases, however, with the atomic number of the cation.)

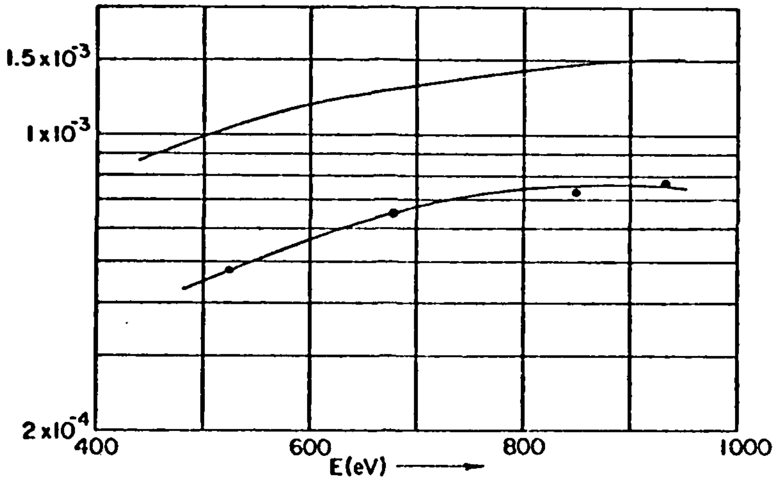


$$\frac{I(\epsilon)}{I_0} = \frac{\left(\frac{\omega}{2\pi}\right) R(\theta_0)}{\epsilon^2 + (\omega/2)^2}$$

$$W(eV) = E \frac{\omega(\text{RADIANS})}{\tan\theta_0}$$

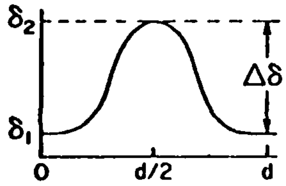
Figure 5. Reflection characteristics of a tungsten-carbon, sputtered multilayer of 62 d-spacings (11 A of W and 11 A of C) and an effective 2d-value of 44.2 A. Reflectivity curves were obtained by the deconvolution of a series of low energy x-ray line spectra and found to be essentially Lorentzian. Presented here are the peak reflectivities and the FWHM equivalent energy widths.

TUNGSTEN-CARBON MULTILAYER REFLECTION (400-1000 eV REGION)

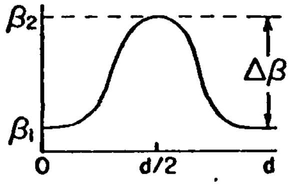


EQUAL-THICKNESS TUNGSTEN-CARBON MULTILAYER (2d=44.2 A)
(NO MEASURABLE HIGH-ORDER REFLECTION FOR Mg-Kα (1254 eV))

INTEGRATED REFLECTIVITY, R, MODELED BY
SINUSOIDAL-GRADED TUNGSTEN CARBIDE



REFRACTIVE
INDEX
$n=1-\delta-i\beta$



FIRST ORDER:

$$R = \frac{\pi}{32}\,\frac{(\Delta\delta)^2+(\Delta\beta)^2}{\beta_1+\beta_2}\,\frac{1+\cos^2 2\theta_0}{\sin 2\theta_0}$$

ALL HIGHER ORDERS:

$R = 0$ $\qquad$ θ_0— BRAGG ANGLE

Figure 6. The measured integrated reflectivities for the W/C multilayer described for Fig. 5. This multilayer has no high order reflectivity indicating that the structure is probably a graded tungsten carbide with an effectively sinusoidal variation in the optical constants δ and β. A theoretical expression derived for the integrated reflectivity for this multilayer with such a variation in the refractive index is also presented here.

This W/C multilayer analyzer as compared with KAP has an order of magnitude larger integrated reflectivity, but also an order of magnitude larger energy width (pass band). In the 20-50 A region with a 2d-value of 44.2 A, it has very similar reflection properties as that of the molecular multilayer, lead myristate, of 80 A 2d-value. At this point in the development of the sputtered, evaporated and molecular multilayers, none have achieved the energy resolution of 1 eV for the 20-50 A wavelength region.

It is important to note, however, that unlike the organic analyzers, this W/C sputtered multilayer can be operated under high total radiation intensities and at relatively high temperatures and therefore can be applied at this time as a very efficient primary monochromator for narrow-band, selective excitation with a complete rejection of high order reflected components.

D. Molecular Multilayers

Molecular multilayers have been developed with 2d-values in the 70-160 A range. For the 50-100 A wavelength region, these multilayers have high reflection efficiency and an energy resolution of about 1 eV. They may be constructed on relatively large areas and upon surfaces of any curvature. As depicted in Fig. 7, the molecular multilayer is built up by the successive dipping of a substrate into a water surface on which is deposited an insoluble monomolecular layer (usually a lead salt of a straight-chain fatty acid--the length of the

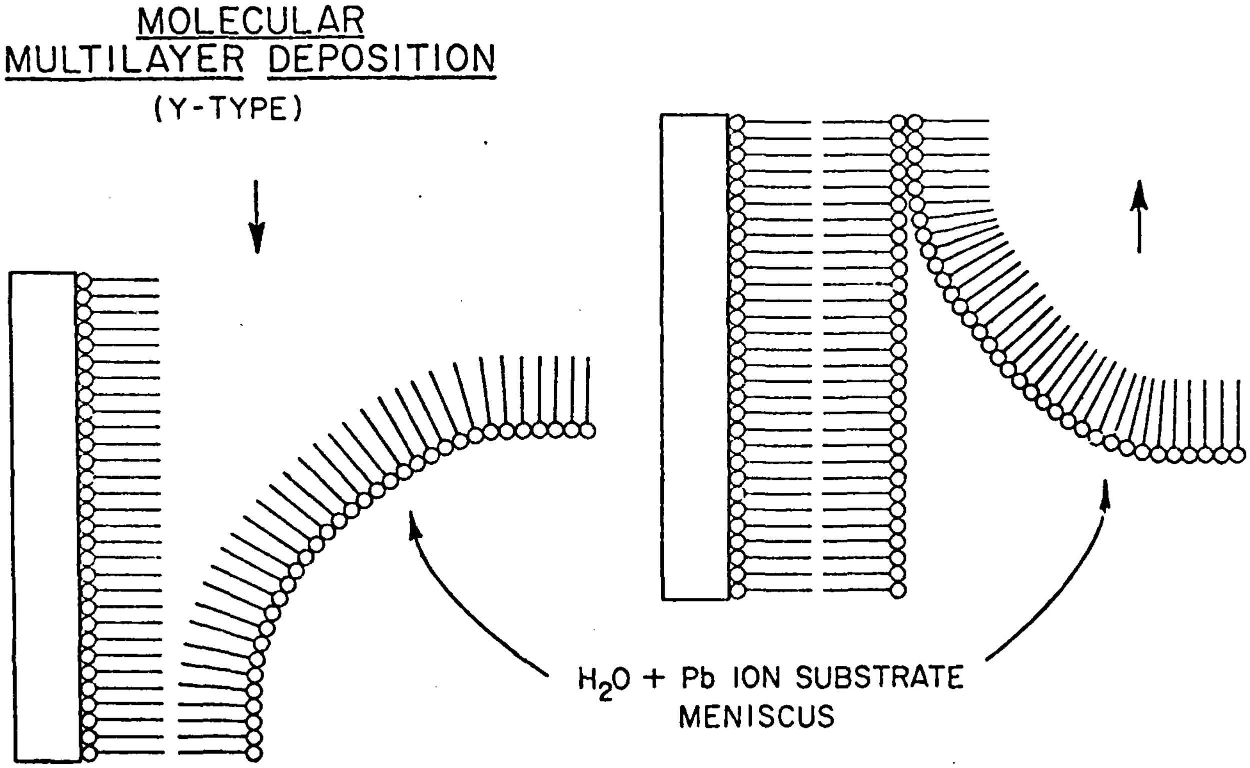


Figure 7. Illustrated here is the deposition of a Langmuir-Blodgett, Y-type monomolecular layer system of a salt of a straight-chain fatty acid. For the construction of molecular multilayers for x-ray analysis, the cations are usually heavy metal atoms such as lead (circles).

chain determines the d-spacing of the multilayer). The multilayers that have been developed in this laboratory for application as analyzers for the low energy x-ray region have been lead laurate, lead myristate, lead stearate, lead lignocerate and lead melissate of 2d-values equal to about 70, 80, 100, 130 and 160 A, respectively. Their construction and reflection characteristics have been reported elsewhere[5,6,7,15] and, as an example, the characteristics of the lead myristate multilayer are presented here. In Fig. 8 are shown the theoretical and the experimental integrated reflectivity curves. Illustrated is that for the long wavelength region of 50-100 A (at the large Bragg angles and high dispersion), the integrated reflectivity, R, is maximized. However, below the carbon absorption edge, in the 20-50 A region, these multilayers have relatively low reflection efficiency. The monotonic region of high integrated reflection above 50 A is associated with high percent reflectivity and good energy resolution as described in Figs. 9 and 10. As may be noted from the semi-empirical relation presented in Fig. 9 which has been derived for the FWHM energy width, W, of these multilayers,[5,6] highest resolution is obtained by choosing a multilayer of 2d-value that is close to that of the wavelengths that are to be measured. In Fig. 11, the effect of the 2d-value upon the integrated reflectivity is predicted by the mosaic crystal model. Also presented here is the specific dependence, according to the mosaic crystal model, of the integrated

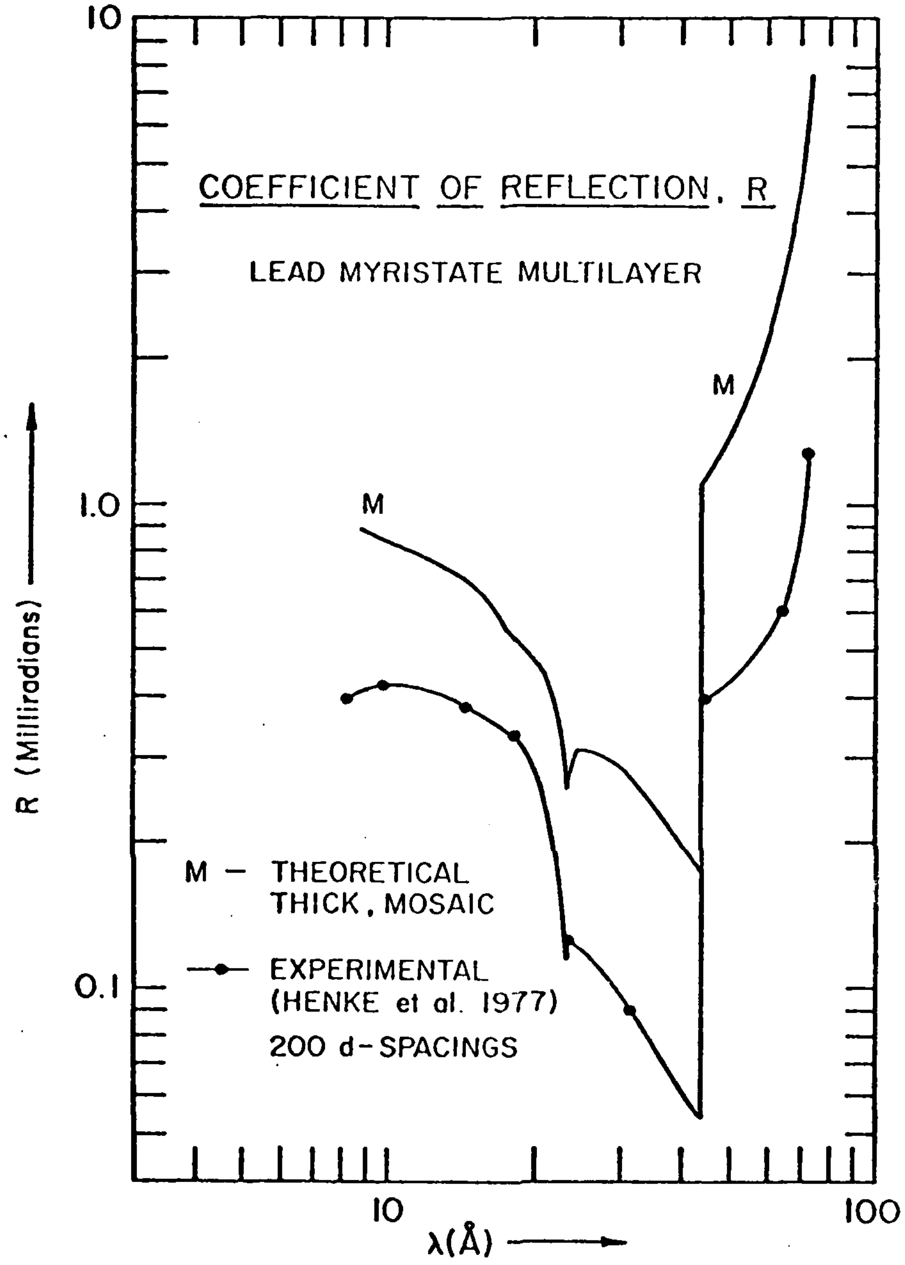


Figure 8. The measured reflectivity for the lead myristate, molecular multilayer and compared with that calculated according to the mosaic crystal theory. The 2d-value is 80 A. The reflection characteristics for this type of molecular multilayer analyzer is outstanding for wavelengths above the Carbon-K edge of 44 A.

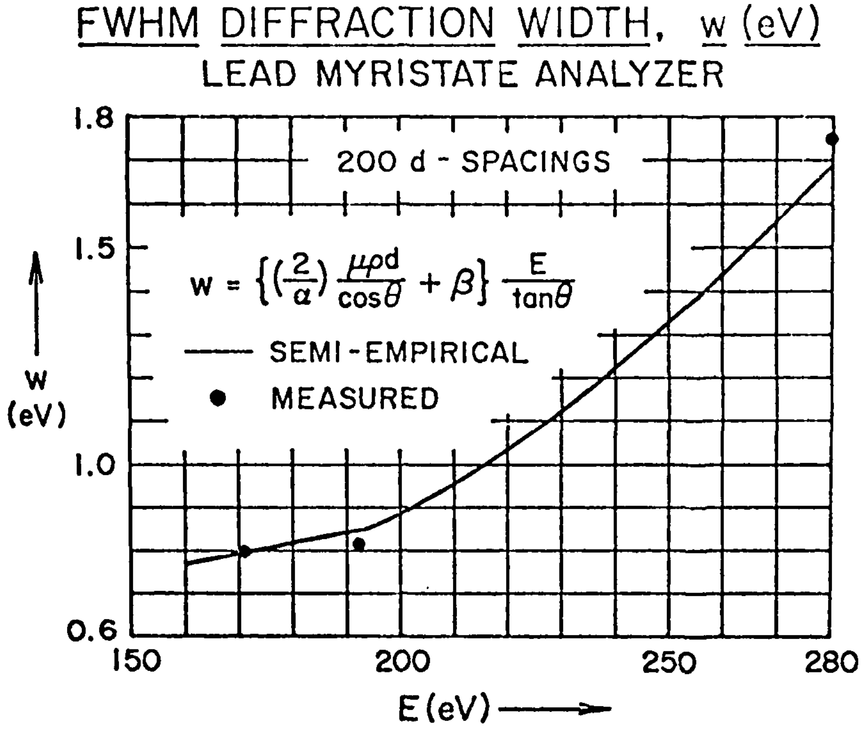


Figure 9. The measured FWHM-energy widths for a lead myristate analyzer of several d-spacings at several line source wavelengths and compared with an energy resolution curve predicted by a semiempirical expression derived for the molecular multilayer energy resolution.

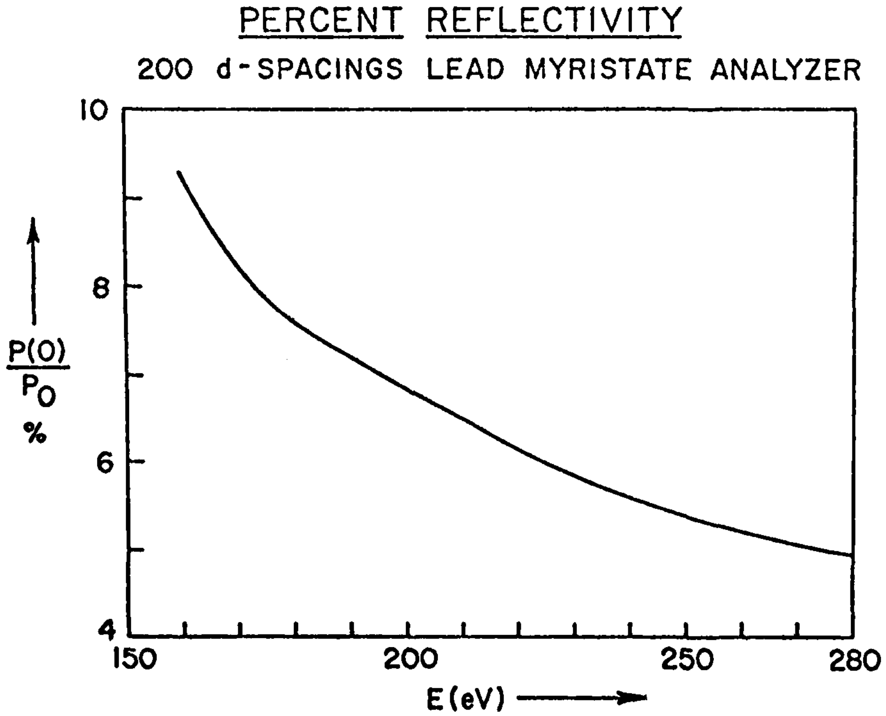
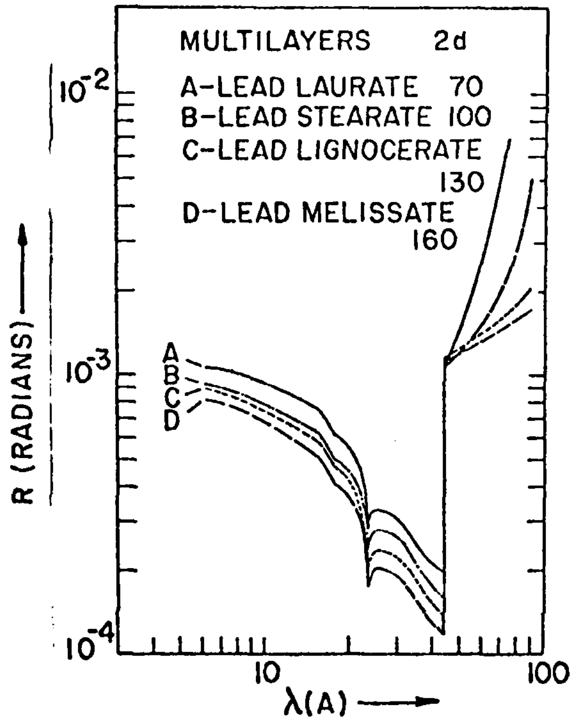


Figure 10. The peak reflectivity (percent) corresponding to the area, R, and the FWHM values for the lead myristate analyzer described in Figs. 8 and 9.



COEFFICIENT OF REFLECTION, R

(THICK, MOSAIC CRYSTAL MODEL)

$$R = \frac{r_0^2 \phi^2 \lambda^3 (F_1^2 + F_2^2)}{4\mu\rho} \left(\frac{1+\cos^2 2\theta_0}{\sin 2\theta_0} \right) \text{radian}$$

Figure 11. The relative values of the integrated reflectivity, R, according to the mosaic crystal theory for molecular multilayers of several 2d-values. Also expressed here is the dependence of R upon the molecular number density, ϕ, the real and imaginary components of the molecular structure factor, F_1 and F_2, the multilayer mass absorption coefficient, μ, its mass density, ρ, and the Bragg angle, θ_0.

reflectivity, R, upon the molecular density, ϕ, the real and imaginary components of the molecular structure factor, F_1 and F_2, the mass absorption coefficient, μ, the mass density, ρ, and the Bragg angle, θ_0.

It has been noted earlier that the energy resolution of typical grating spectrographic measurements is about 0.1 eV and that of crystal or molecular multilayer measurements at large Bragg angles is about 1 eV. It should be noted here, however, that it has been demonstrated that for the crystal and multilayer spectrographic measurements in the low energy x-ray region, a very simple and efficient deconvolution procedure can be applied to bring this energy resolution into the sub-electron-volt region.[6] This is because it is possible to determine precisely by direct measurement the two broadening functions, that for the collimation and other spectrographic geometric effects and that for the diffraction broadening of the analyzer. (The corresponding instrument functions are not so easily determined for the grating incidence grating spectrographs.)

III. X-RAY PHOTOCATHODES

Typically, for synchrotron radiation and laser-produced plasma sources, x-ray sensitive photomultipliers, x-ray diodes and x-ray streak cameras are used for detection depending upon the time resolution that is needed. The application of these detectors for quantitative spectroscopy requires that the photocathodes which convert the photon flux to electron current be well characterized. The electronic signal consists of a spectrum of primary electrons (photoelectrons and Auger electrons) along with a considerably larger number of secondary electrons of energies below 30 eV. In Fig. 12 is depicted such an electron energy spectrum from a photocathode. When the photocathode is excited by photons in the 0.1 to 10 keV region, the fraction of the number of electrons of energy above 30 eV increases from about 1 to 20 percent as the photon energy increases for relatively insensitive photocathodes as gold and aluminum. This fraction is typically less than 1 percent for photocathodes of relatively high yield as cesium iodide.[16]

In the x-ray streak camera, only the secondary electrons are utilized and the energy width of their distribution ultimately determines the spread in arrival time at the image intensifier end of the tube and hence the temporal resolution.[17] This dependence upon the width of the secondary distribution, Δ, is described in Fig. 13. For an energy distribution width of 2 eV and an extraction field at the photocathode of 5000 volts/mm, the leading term in the expression for the time resolution, τ, becomes equal to 1 picosecond. It is therefore feasible that a streak camera can resolve the shapes of the subnanosecond pulses characteristic of the new storage rings and of the laser-produced plasma sources for their diagnostics, calibration and application to time-resolved spectroscopy.

Shown in Fig. 14 are the measured secondary electron distributions for the photocathodes consisting of thick films

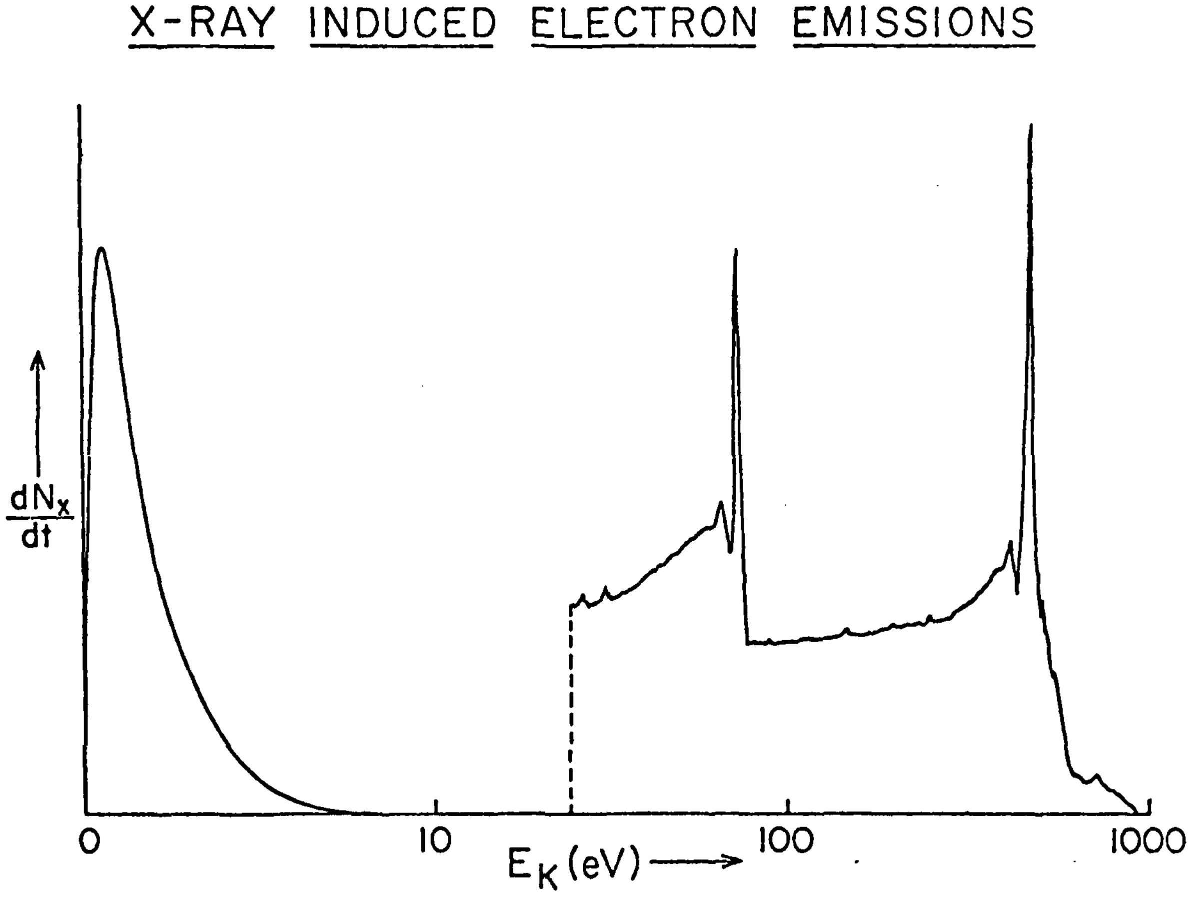
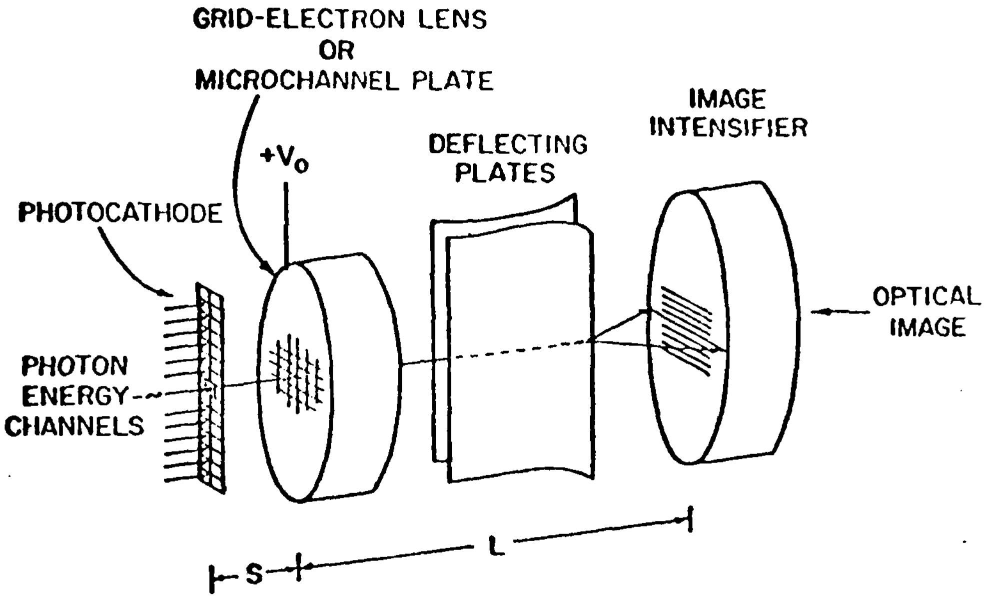


Figure 12. Depicting the electron emission spectrum as excited by x-rays. Most of the electron current is in secondary emission, usually below 10 eV electron energy. The remaining primary electron emission is associated with that of the photoelectrons and Auger electrons excited by the initial photon absorption.



TEMPORAL RESOLUTION LIMIT, τ

$$\tau = 3.37\ \frac{(\Delta)^{1/2}}{\epsilon_0}\left\{1 + \frac{1}{4}\left(\frac{L}{S} - 2\right)\left(\frac{\Delta}{eV_0}\right)^{1/2} \ldots\right\}\ \text{PICOSECONDS}$$

Δ = SECONDARY ELECTRON ENERGY SPREAD IN eV

ϵ_0 = EXTRACTION FIELD, V_0/S IN kV/mm

Figure 13. For fast, time-resolved x-ray spectroscopy, the electron image of the spectrum that excites the slit transmission photocathode is deflected across an image intensifier section presenting a time base in the subnanosecond range. The quantum yield of the photocathode must be high and the energy width, Δ, of its secondary electron distribution must be small. The spread in the arrival time at the image intensifier, τ, is given here as a function of Δ and of the extraction field at the photocathode surface, ϵ_0.

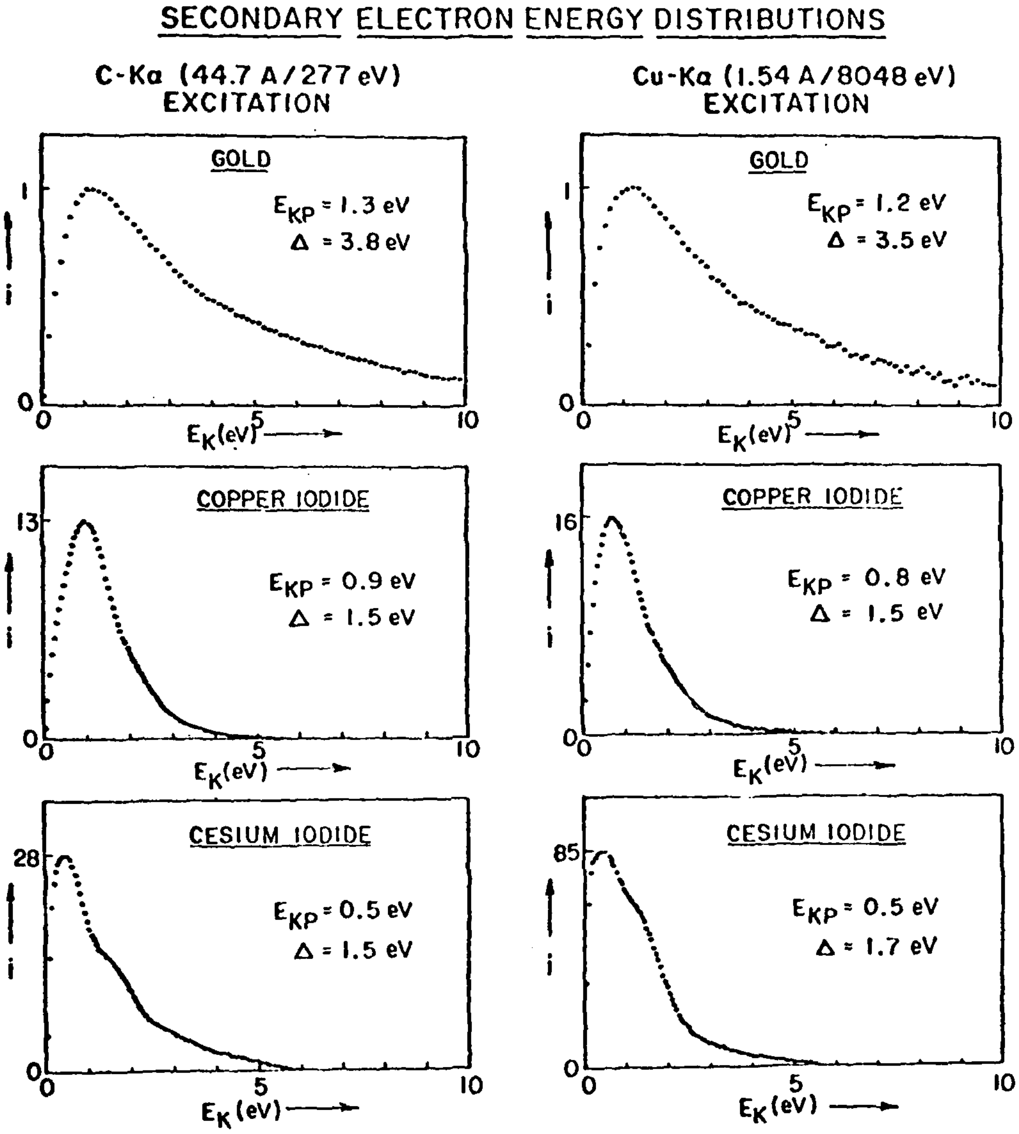


Figure 14. The measured secondary electron energy distributions for the photocathode layers of gold, copper iodide and cesium iodide, as excited by C-Kα (277 eV) and Cu-Kα (8050 eV) photons. p and y are the peak currents and the secondary electron yield relative to these values for gold under identical excitation and measurement conditions. The shapes of the electron energy distribution curves are essentially invariant for photon energies in the 0.1 to 10 keV region.

of gold, of the semiconductor, copper iodide, and of the insulator, cesium iodide, as excited by Carbon-Kα (277 eV) and Cu-Kα (8050 eV) photons.[18,19] The distribution peak height, p, and the area under the distribution or yield, y, are given here relative to the corresponding values for the gold photocathode. It is important to note that the CuI and the CsI photocathodes have appreciably smaller distribution widths and higher quantum yields than does the gold photocathode. It has also been recently determined that the time response of these nonmetal, thin film photocathodes is essentially the same as that for gold in the subnanosecond region.[20]

Based upon such as these measurements which indicate that the shape of the secondary electron distribution in the 0.1 to 10 keV photon energy region is essentially invariant, a relatively simple theoretical model for x-ray photoemission has been derived which predicts that the total yield (electrons per normally incident photon) should follow approximately as the product of the photon energy and the photocathode mass absorption coefficient, $E\mu(E)$.[18,19] This prediction is borne out as illustrated in the log-log plots of the measured total quantum yields alongside the $E\mu(E)$ curves for the gold and cesium iodide photocathodes in Figs. 15 and 16. This relationship seems also to obtain for the euv photon energy region as shown in Fig. 17.[21] Methods for precisely measuring such photocathode response curves have been recently developed at this and other laboratories in order to support the quantitative application of low energy

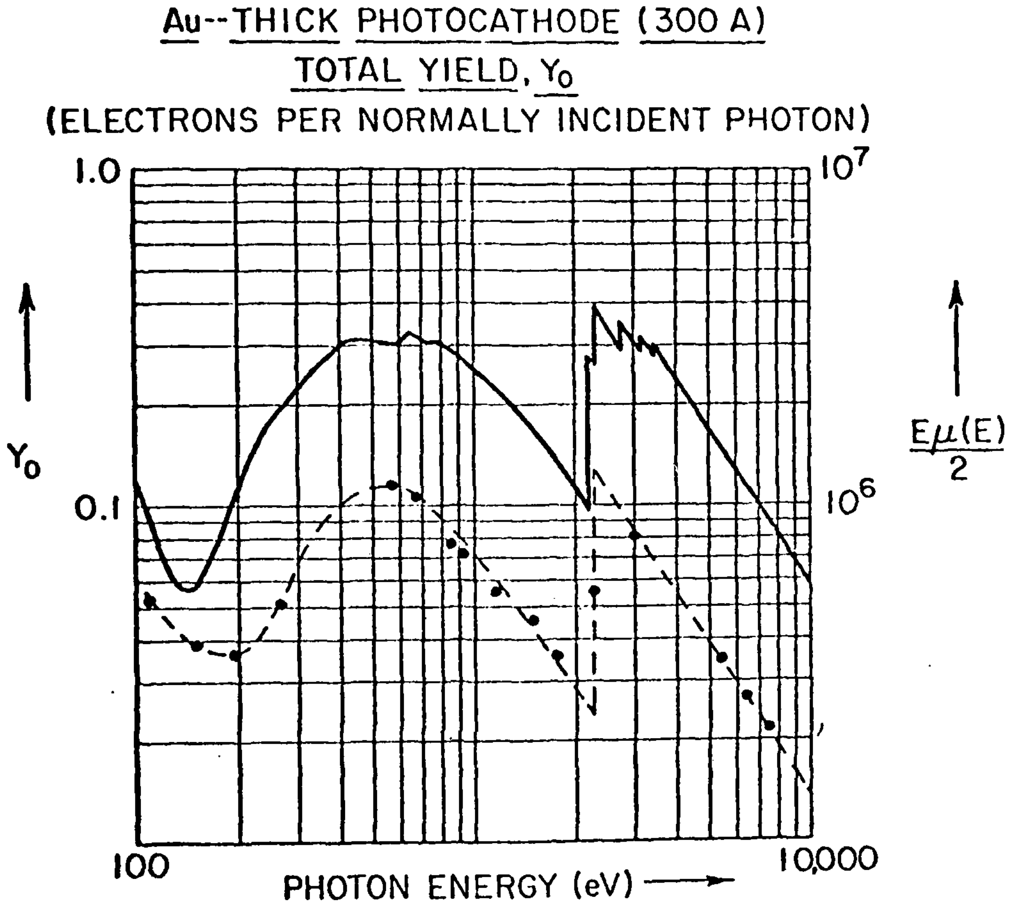


Figure 15. The total yield from the surface of 300 A vacuum evaporated film of gold on a chromium substrate. As predicted, the response in this 0.1 to 10 keV region follows approximately as the product of the photon energy and the photocathode mass absorption coefficient, Eμ(E).

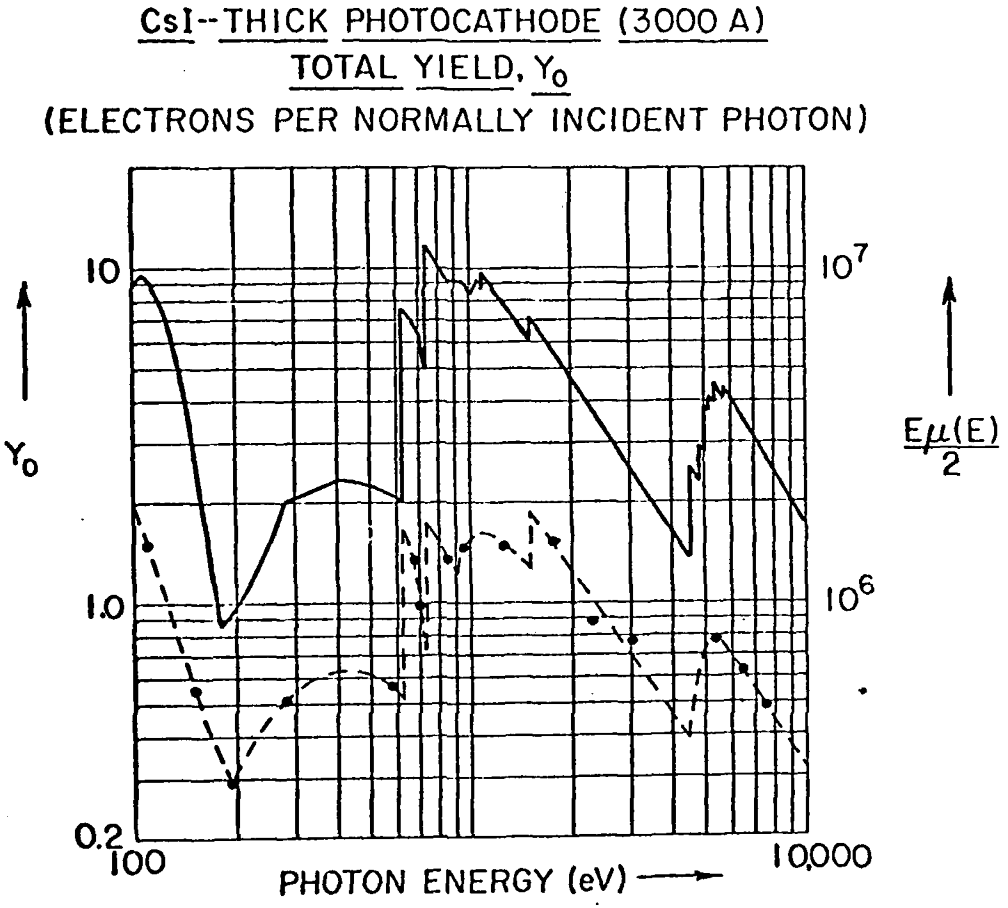


Figure 16. The total yield from the surface of a 3000 A vacuum-evaporated cesium iodide film on a chromium substrate. As indicated also in Fig. 5, the yield is approximately proportional to $E\mu(E)$ in its photon energy dependence.

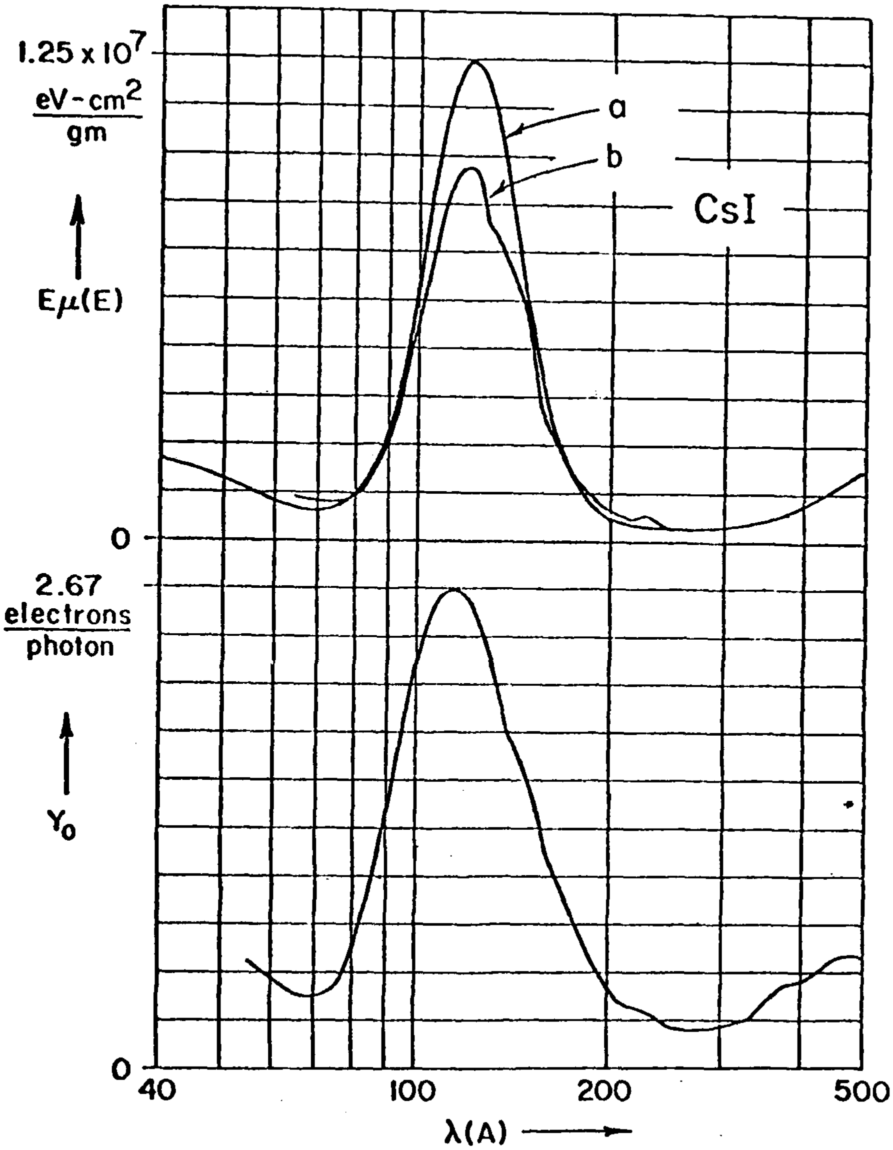


Figure 17. The total yield of the cesium iodide photocathode in the euv region. (Measurements were made using the SURF II Facility at the National Bureau of Standards--Saloman, et al. 1979.) Shown here for comparison are the Eμ(E) plots, (a) using data for Xenon (Cs and I in the ionic crystal CsI are Xenon-like) and (b) using directly measured absorption data for CsI films. The strong resonance absorption and yield at about 100 eV is the result of the atomic-like 4d-4f transitions in both cesium and iodine ions.

x-ray spectroscopy with pulsed x-ray excitation sources.[16,22,23,24]

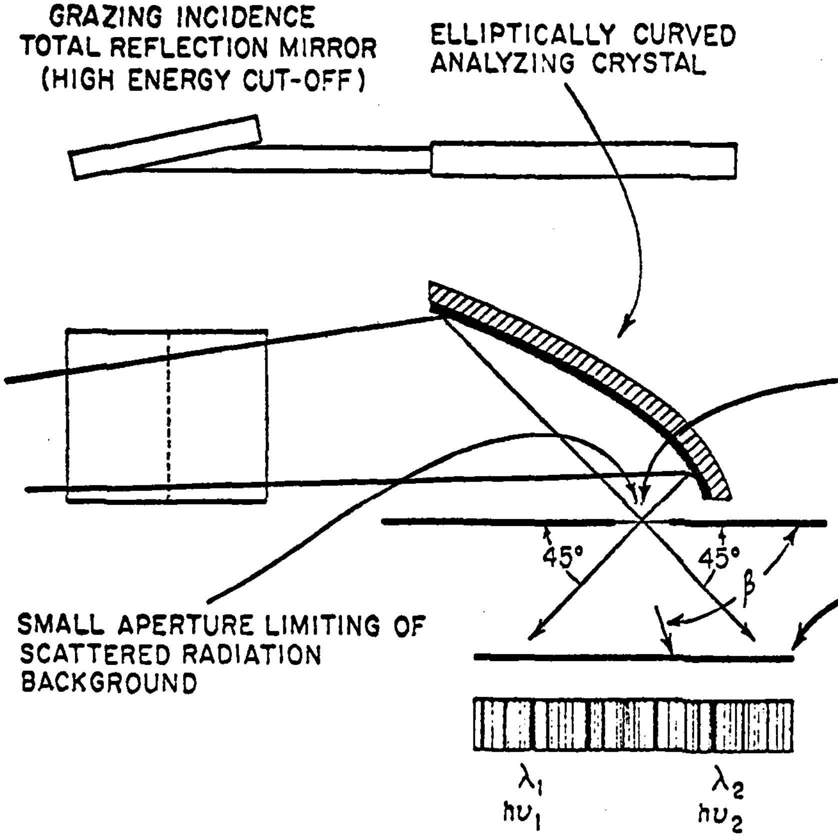
IV. SINGLE PULSE AND TIME-RESOLVED SPECTROSCOPY

The high intensity and short duration pulse characteristics of the synchrotron radiation and laser-produced plasma sources allow fixed-analyzer, single-pulse spectroscopy with time resolutions in the subnanosecond and picosecond range. Focussing grating spectrometers can be most efficient for pulsed, low energy x-ray spectroscopy provided that the constraints of grazing incidence optics do not seriously limit the application of appropriate detection and recording systems. Fixed crystal or multilayer analyzers may also be used and usually with a considerably simpler and more flexible geometry. Such a spectrometer is described in Fig. 18.[25] For this spectrometer, an ellipsoidal or a cylindrically elliptical analyzer is utilized. Molecular multilayers are easily constructed upon doubly curved surfaces. Thin cleaved crystals and sputtered or evaporated multilayers on thin flexible substrates can be pressed into cylindrical curvatures. All wavelengths from a point source at one of the foci of the elliptical arc will reflect and focus through the other focal point at which is located a small scatter aperture at the entrance of a detector module. For synchrotron radiation sources, the incoming radiation in this plane is essentially parallel and the focussing surface becomes effectively parabolic. For this case, the exit angle, β, is simply equal to twice the Bragg reflection angle off the analyzer and the associated wavelength for a first-order diffraction is 2d sin (β/2). Examples of wavelength bands that are accomodated for β-values between 45° and 135° for nearly parallel source radiation and for several analyzer d-spacings are indicated here. Such spectrometer systems are of thin geometry and may be "stacked" for multiple-band coverage. A grazing incidence mirror reflection is applied to the incident beam as shown in order to effect a high energy cut-off, and appropriate low energy cut-off filters can be applied at the scatter aperture and as selected filter segments along the detection plane. Detection may be photographic, by microchannel, charge collecting arrays or the spectrum can be placed upon the entrance slit of an x-ray streak camera for time resolved spectroscopy.

ACKNOWLEDGEMENTS

The author gratefully acknowledges the invaluable assistance of the students and staff of the Low Energy X-Ray Physics Group, University of Hawaii. This program is supported by a grant from the Air Force Office of Scientific Research, Grant No. 79-0027B, and by a supplemental contract from the Department of Energy, DOE DE-AS03-76SF00235.

PULSED X-RAY SOURCE SPECTROSCOPY



SPECTRAL RANGE

CRYSTAL-2d (A)	λ_1 (A)	$h\nu_1$ (eV)	λ_2 (A)	$h\nu_2$ (eV)
KAP--26.6	25.6	505	10.2	1220
LAURATE--70	64.7	192	26.8	463
MELISSATE--160	148	83.9	61.2	203

Figure 18. A spectrograph for pulsed x-ray spectroscopy utilizing a fixed crystal or multilayer analyzer. All wavelengths from a point source at one of the foci of an elliptically curved analyzer will focus at the other focal point and through a small scatter aperture into the detector module. For nearly parallel incident radiation, the analyzer is parabolic and the wavelength for first-order diffraction is given by 2d sin ($\beta/2$). A grazing incidence mirror reflection of the incident beam provides a high-energy cut-off. A low-energy cut-off is effected by an appropriate filter at the scatter entrance aperture.

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detail for the 2-25 A region (to be published). It is experimentally verified that for the cations thallium, rubidium, potassium, sodium and ammonium (NH_4), the integrated reflectivity, R, and the energy resolution, W, decrease with the atomic number of the cation.

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[11] Evaporated multilayers have been constructed at the IBM T. J. Watson Research Center, Yorktown Heights, New York, and the Deutsches Elektronen - Synchrotron DESY, Institut fur Experimentalphysik, Universitat Hamburg, Hamburg, West Germany. We have recently measured the reflection characteristics of their Re-W/B analyzers and found them to be of comparable reflectivity as the sputtered W/C multilayer described here but with normally strong high-order reflections present.

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HISTORY AND OBJECTIVES

This research program in Low Energy X-Ray and Electron Physics was initially set up by the principal investigator at Pomona College in 1954 with the support of the Air Force Office of Scientific Research. It has continued to have the support of the AFOSR to this date. With the encouragement of the late Kenichi Watanabe, this program was brought to the University of Hawaii in 1967. Its principal objectives have been:

1. To participate in the development of the physics and the applications of what was initially a neglected region of the electromagnetic spectrum between the ultraviolet and the conventional x-ray regions (10-100 angstroms), and of the associated low energy electrons (100-1000 eV). Because these low energy radiations interact strongly with the outermost and least bound electrons within matter, they have become the basis of important new techniques for the analysis of the chemical, optical and electronic properties of matter. And when matter is raised to the high temperature plasma state of one to ten million degrees, it radiates most strongly in this low energy x-ray region. Low energy x-ray spectroscopy of such plasmas has become invaluable in x-ray astronomy and in the diagnostics of plasmas in the controlled nuclear fusion energy research.

2. To develop a research program that can provide a meaningful and motivating basis for the training of a significant number of undergraduate and graduate students in the methods of professional scientific research. And,

3. To extend this University research program by active, collaborative efforts with groups at other major universities and at government and industrial laboratories. Such collaborations are considered essential in maintaining good scientific breadth and depth in a particular research program and also in providing broad and helpful contacts with scientists outside the University for our students.

WORK ACCOMPLISHED TO DATE

The work of this program has been reported in about seventy scientific publications. Most of these have been published in the major U.S. and international journals, some are as technical reports which are available through the U.S. Document Service. In order to indicate the type of research studies that have been completed, a selected set of first-page abstracts of papers published in the past ten years have been assembled in Appendix I. In Appendix II is a complete publication list for this project.

COLLABORATIVE PROGRAMS

The principal investigator has been appointed as a scientific consultant for the University of California's Lawrence Livermore and Los Alamos Research Laboratories. Each summer he spends about one week at these laboratories presenting seminars on the x-ray and electron physics research of this University of Hawaii program and setting up joint research programs. Many such laboratories send members of their groups to this UH laboratory to work with this staff. A list of some persons who have been closely acquainted with this program is attached as Appendix III. Invited papers which have been presented in recent years by the principal investigator at other laboratories and at major scientific meetings are noted in Appendix IV.

STUDENT PARTICIPATION

Working with the principal investigator on this research program are the following: two research associates (APT), an electronics engineer, Murray Tester, and an administrative assistant, Priscilla Piano. For the past four years, the Department of Energy has provided the supplemental support for one year appointments of young post-doctoral scientists to train and participate in this program. Eight to ten undergraduate and graduate students are employed as research assistants. These students work on this project typically for two or more years, and do most of the measurement and data analysis work and often co-author the scientific reports. The undergraduate participants who are usually from Hawaii are encouraged to proceed from this program as graduates to summer employment at mainland laboratories and for advanced degree work at the major mainland universities.

Two recent post-doctoral participants have been University of Hawaii graduates Dr. Jerel A. Smith (PhD-Solid State Physics) and Dr. James P. Knauer (PhD-High Energy Physics). They have proceeded on to positions in x-ray physics research at ARACOR, Sunnyvale, California, and at Lockheed, Palo Alto Research Laboratories, respectively. At the present time, Premaratne Kandatege (A.B. University of Sri Lanka) and Tina Tanaka (A.B. Pomona College) are completing their PhD programs in experimental x-ray and electron physics. Our current group of graduating physics majors, Robert Hockaday, Mary Pottenger and Bruce Young, will be working in x-ray physics at the Los Alamos and the Lawrence Livermore Laboratories this summer and will then go on to mainland universities for their advanced degrees. Recent "graduates" of this research program who are currently completing their PhD programs in physics are Ronald Ono at the New York State University at Stony Brook; Chris Berg and Mark Schattenburg at the Massachusetts Institute of Technology; and Eric Gullikson at the University of California at San Diego.

APPENDIX I

FIRST-PAGE ABSTRACTS OF SOME RECENT PUBLICATIONS

ADVANCES IN X-RAY ANALYSIS

681-page text

Volume 13 (1970)

Edited by Burton L. Henke
Department of Physics and Astronomy
University of Hawaii
and John B. Newkirk
and Gavin R. Mallett
Denver Research Institute
The University of Denver
Denver, Colorado

FOREWORD

This conference has attempted to achieve a balance in the presentation of papers on the application of current methods to established problem areas and on the introduction of new methods and applications. It has recognized the relevance of papers on basic physics and chemistry and on the total interaction of x-rays with matter. In order to achieve sufficient depth, a topic is chosen each year for special emphasis. This conference had as its central theme, "The Interactions and Applications of Low Energy X-Rays."

Those who were invited as speakers and as contributors to this volume are among the outstanding workers in the application of low energy x-ray and the associated photo-Auger electron interactions. These include A. K. Baird and W. L. Baun on Light Element Analysis and Long Wavelength Instrumentation; J. E. Holliday, D. W. Fischer, R. J. Liefeld and D. J. Nagel on Bonding and Valence State; H. Friedman and W. P. Reidy on X-Ray Astronomy; and R. Nordberg on Photo-Auger Electron Spectroscopy.

Upon reading over the papers as presented here, one cannot help but be impressed by the steady, dynamic growth and expansion of the field of applied x-ray analysis, beginning about thirty years ago with quantitative elementary analysis and extending to the present time with dramatic and exciting applications to x-ray astronomy.

It has been most appropriate and indeed a privilege to have Dr. Herbert Friedman as a speaker and contributor to this volume. He was among the few who pioneered the application of x-ray spectroscopy as an analytical technique and now he is noted as one of the first to open the new field of x-ray astronomy.

Burton L. Henke
Invited Co-Chairman

JOURNAL DE PHYSIQUE *Colloque C4, supplément au n° 10, Tome 32, Octobre 1971, page* C4-115 - 123

MEASUREMENT OF PRIMARY ELECTRON INTERACTION COEFFICIENTS (500 TO 1 500 eV REGION)

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Résumé. — Etant donné que les électrons d'énergie incidente comprise entre 500 et 1 500 eV n'ont d'interaction appréciable qu'avec peu de couches atomiques dans les solides, des mesures précises et l'application de leurs coefficients d'interaction sont difficiles. La statistique des interactions et la sensibilité à la disposition géométrique de la cible nécessitent une attention particulière. Nous présentons ici une méthode pour l'étude de telles interactions, basée sur la déposition contrôlée d'une couche monoatomique de cations métalliques bivalents comme cible, sur un support formé d'une double couche de stéarate du type de Langmuir-Blodgett. Pour vérifier la méthode, nous avons mesuré les sections efficaces des cations de barium à 466 eV, 706 eV et 1 349 eV, et celles du zinc et du plomb à 706 eV. Les valeurs mesurées sont en accord avec des mesures récentes de faisceau atomique sur le barium et avec un modèle théorique simple. Nous considérons que des mesures de ce type sont d'une grande importance dans le développement de l'analyse chimique quantitative de surface par spectroscopie d'électrons et de rayons X de basse énergie.

Abstract. — Because electrons of incident energy in the 500-1 500 eV range interact appreciably within only a few atomic layers in solids, precisely measuring and applying their interaction coefficients becomes difficult. The statistics of the interactions and the sensitivity to the geometric arrangement of the target atoms require special attention. A method for the study of such interactions is presented here that is based upon the controlled deposition of monatomic layers of bivalent metal cations as targets within the framework of stearate double layers of the Langmuir-Blodgett type. To demonstrate the method, cross sections of the barium cation have been measured at 466 eV, 706 eV and 1 349 eV, and those of zinc and lead at 706 eV. The measured values are shown to be consistent with recent atomic beam measurements on barium and with simple theoretical models. Measurements of this type are considered to be of great importance in the development of quantitative surface chemical analysis by low energy X-ray and electron spectroscopy.

1. Introduction. — *This work is concerned with* the measurement of primary electron interactions in solids for incident electron energies in the 500-to-1 500 eV region. Such electrons have an associated wavelength of about 0.5 Å. Their mean free paths within condensed matter are generally less than 100 Å.

Although a considerable amount of theoretical work on the passage of electrons through matter has been presented and from a variety of approaches, very few experimental measurements have been reported for kilovolt-electron interactions in solids [1]. Interesting questions remain to be answered as to the relative roles of elastic and inelastic scattering, and of collective and individual electron energy loss mechanisms.

The ionization of matter by keV electrons should be similar in both mechanism and magnitude to that by MeV protons, for example [2]. Important new insights might be gained by comparing measurements with electrons in this region to the relatively large amount of data reported in recent years on heavy particle cross sections in the MeV region.

Finally, important analytical techniques based upon chemical and structural analysis by electron and X-ray spectroscopy demand a precise knowledge of X-ray and electron cross sections. Although many important applications involve radiations in the 100-to-1 000 eV region, it has been only relatively recently that low energy X-ray cross sections have become available to any extent [3, 4]. There remains an appreciable need for further work on low energy X-ray interaction coefficients and an even greater need for work on the low energy electron cross sections.

2. Electron spectroscopy of thin films. — The electron spectrograph which is used for the present work is shown in figure 1 and has been described previously [5]. It employs hemispherical plates as the electrostatic analyzer. These have inner and outer diameters of 18.5 and 21 inches. For this work the slits were set at 0.3 % energy resolution and to receive only photoelectrons which leave nearly normally from the surface of the sample (maximum angles off normal are plus-minus 3°). Al-K_α photons (1 487 eV) were used to excite the samples as generated by an

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Ultrasoft-X-Ray Reflection, Refraction, and Production of Photoelectrons (100–1000-eV Region)*

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(Received 14 February 1972)

The reflection, refraction, and associated production of photoelectrons by ultrasoft x rays (10–100 Å) can be important bases for the determination of material constants such as the linear x-ray absorption coefficients and the electron mean free paths. These may then be used to establish directly the photoionization cross sections and the electron-collision cross sections which account for the dominant energy-absorbing processes within solids for this energy region. Because the effective sample depths for these interactions are typically less than 100 Å, they constitute an important practical basis for surface characterization. By applying the exact theory for the reflection-refraction of a plane electromagnetic wave at an absorbing dielectric interface to the shorter-wavelength region (< 10 Å), it can be shown that the conventional approximate theory of x-ray reflection is adequate. However, the more exact theory must be applied in the region of longer x-ray wavelengths (> 50 Å). Although the derivations of the exact theory are tedious, the results can be expressed in relatively simple form as functions of two material constants α and γ, which are identifiable as the unit decrements to a complex dielectric constant, of the grazing-incidence angle, and of a parameter which is a function of this grazing angle and which becomes the angle of refraction for small angles of incidence. X-ray absorption coefficients and electron mean-free-path values have been determined from x-ray reflection and refraction and photoelectron excitation data. These values have been shown to agree reasonably well with such material constants as determined by transmission measurements through thin samples.

I. INTRODUCTION

It is well known that x rays do reflect from surfaces with high efficiency in the grazing-incidence region. The characteristic reflectance curve, which falls off to zero value with increasing angle, is the basis for an important method for determining the optical constants of the reflecting medium and its surface structure.[1,2] Also, a precise knowledge of this "total-reflection" characteristic curve is important in the design of mirror monochromators,[3] of optimized diffraction gratings, and of astronomical telescope systems for the x-ray region.

As will be described below, the refracted x-ray beam, when used to produce photoelectrons, can also be an important basis for the determination of certain constants of the medium and of its surface structure.[4]

In order to relate experimental reflection, refraction, and associated photoelectron excitation data to the optical constants, one may apply a relatively simple electromagnetic model based upon approximations permitted by the small values of the grazing-incidence angles and of complex refractive-index unit decrements which obtain for the

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University of Tokyo Press, 1972

pp. 367-384

Surface Characterization by Low Energy Photo-Auger Electron Spectroscopy

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Low energy photoelectron spectroscopy (100 to 1000 eV region) has shown considerable promise as an effective method for the microanalysis of sample surface layers no thicker than 100 Å. Quantitative information can be obtained about the elementary chemistry, chemical bonding, and structure within the surface. Essentially, all elements throughout the periodic table can yield photoelectron lines within this low energy region which are suitable for such analysis.

A relatively simple electron spectrograph system has been developed. Its sensitivity is sufficiently high to permit the measurement of photoelectron lines from single atomic layer thicknesses at better than 0.5% energy resolution.

In order to develop methods for correlating photoelectron spectral information with surface characteristics, electron interaction cross sections are being measured, and simple models for predicting line intensities are being evaluated.

I. INTRODUCTION

Photo-Auger electron spectra in the 100–1000 eV region are relatively easy to obtain and are rich in information that is characteristic of the chemistry, density, and structure of the first 100 Å or less of the sample surface. The quantitative analysis of such spectra can constitute an effective technique for solving problems in the difficult areas of surface characterization. Examples of two such areas, noted for their extreme importance, are catalysis and biological membranes.

In order to develop practical methods for quantitative photo-Auger electron analysis, certain steps are necessary: A choice must be made for an optimum set of parameters that are amenable to measurement and can precisely define the electron signal generation within the sample. Correspondingly, photo-electron-sample interaction models that directly relate measured intensities to sample chemistry and structure must be developed and tested. Finally, from theory and measurement, the necessary tables for the appropriate fundamental interaction cross sections must be established.

The objective of this paper is to describe some current work in this laboratory that is addressed to the development of methods for photo-Auger electron analysis of surfaces. A proposal for an interaction model, an experimental test of its validity, and descriptions of new methods for the measurement of basic interaction coefficients are presented.

II. A MODEL FOR PHOTOELECTRON INTENSITY ANALYSIS

Figure 1 shows the essential geometry of the model adopted here for the generation of the unscattered, no-loss photoelectron signal. Monoenergetic, parallel X-radiation of wavelength λ is incident upon a plane surface at an angle, ϕ, refracting into an amorphous sample with angle ϕ'. The linear absorption coefficient for this radiation within the sample is equal to μ. In a sample layer at depth x and thickness dx, photoelectrons are generated in an effective sample area which is the projection of the limiting slit area, A_0. The atomic cross section for the crea-

J. Appl. Phys,
page 1027-1037

Quantitative low-energy x-ray spectroscopy (50–100-Å region)*

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(Received 27 August 1975)

The quantitative analyis of emission spectra in the 10–100-Å region has become of considerable importance for high-temperature plasma diagnostics (10^6–10^7 °K region) and for molecular orbital and solid-state-band analysis. Because measurement intensities are typically low in these applications, achieving an optimum spectrographic measurement is essential. In order to present specific procedures and methods for optimizing and calibrating a low-energy spectrographic measurement, a molecular orbital analysis in the 70–90-Å region (S-$L_{II,III}$ emission spectra) has been carried out quantitatively in energy and intensity using a recently described single-crystal (lead stearate) spectrographic approach with about 1 eV resolution. Radiative yields, Y, for the radiation process being investigated are determined by the relation, $Y = Z/(X_0 RSTQ)$, where Z is the area (intensity x angle) under the spectrographic line, X_0 the excitation function, $R(\lambda)$ the coefficient of reflection of the analyzer, $S(\lambda)$ the effective source thickness, $T(\lambda)$ the window transmission, and $Q(\lambda)$ the quantum counting efficiency of the detector. The determination of each of these parameters has been considered in detail.

PACS numbers: 32.10.F, 32.10.Q, 52.70., 07.85.

I. INTRODUCTION

Low-energy x-ray spectroscopy in the 10–100-Å wavelength region (100–1000-eV energy region) has become of considerable interest as applied in two types of research:

(1) High-temperature plasma analysis. Ionized gases (plasmas) in the 10^6–10^7 °K temperature range radiate strongly in the 100–1000-eV x-ray region (1 eV corresponds to about 10^4 °K). Because such high-temperature plasmas are characteristic of important astrophysical sources, their analysis is a fundamental aspect of the relatively new science of x-ray astronomy. And now it has become possible to generate such plasmas in the laboratory which radiate sufficiently strongly in the x-ray region for spectroscopic analysis. These are developed magnetohydrodynamically and magnetically confined, or by pulsed laser or electron beams and inertially confined. An important application of such high-temperature plasma analysis is for controlled thermonuclear fusion research. The x-ray measurements can yield information as to the temperature, density, time history, and spatial characteristics of the plasma.[1]

(2) Molecular orbital and solid-state-band analysis. When an atom is singly ionized with a vacancy created in one of its higher inner core levels, this vacancy is then promoted to one of the outermost electronic levels and a radiative transition typically in the 100–1000-eV region may result. The electronic structure of the initial ionization state of the atom is relatively insensitive to its molecular or condensed matter environment, but that of the final ionized state is strongly affected by this atomic environment. The major features of the associated x-ray emission spectra can yield direct information as to the populations, energy levels, and widths (or band structure) of the outer electronic levels. Because the strong radiative transitions obey the dipole selection rules, information as to the symmetry character of the outer electronic states may also be gained. Finally, the degree of localization of certain outer levels relative to a particular ionized atom can often be revealed by the existence of molecular orbitals rather than band structure and by comparative analyses of such spectra originating from inner core vacancies on adjacent atoms. Such low-energy x-ray emission spectra can be directly applied, using standard sample systems, for the identification of unknown valence states. These spectra can be applied to establish and to test molecular orbital and/or band theory models for which computer analysis is rapidly becoming more practical and precise.[2,3]

Typically, low-energy x-ray emission spectra of interest are of low intensities. At these transition energies, radiative transition rates are small as compared with those for the competing Auger and Coster-Kronig processes. For this reason it is generally required that the low-energy spectroscopy be by methods of optimum efficiency. Usually, the characteristically low emission intensities will not permit the use of double crystal spectrometry or of high-resolution grating spectrographs. The basic spectrographic approach that is used in this laboratory is shown in Fig. 1. It is

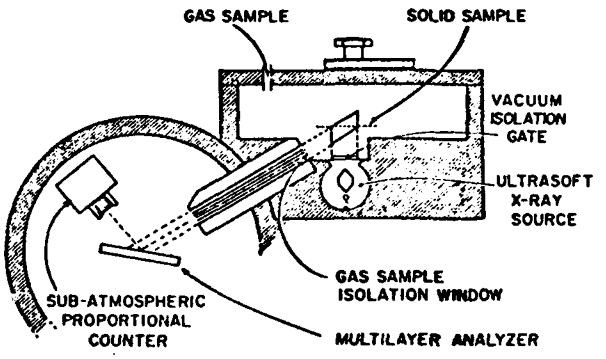

FIG. 1. A single-crystal spectrographic approach for low-energy x-ray spectroscopy applying closely coupled 2-kW demountable x-ray source, large d-spacing crystal analyzer, and tuned subatomospheric pressure proportional counter.

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0.1–10-keV x-ray-induced electron emissions from solids—Models and secondary electron measurements

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Analytical models are presented describing the x-ray-excited emission of "no-loss" photoelectrons and Auger electrons and the energy distribution of emitted secondary electrons. The secondary electron energy distribution is given in terms of the electron kinetic energy E_K, work function W, photon energy E_o, and mass photoionization coefficient $\mu(E_o)$, as proportional to $E_o\mu(E_o)E_K(E_K+W)^{-4}$. Techniques of electron spectral measurements utilizing uniform field preacceleration and limited acceptance angle spectrometers are discussed. Secondary electron energy distributions are measured at about 10^{-8} Torr from thick evaporated films of gold and aluminum at photon energies 277, 1487, and 8050 eV. The shapes of these distributions do not depend significantly upon photon energy. The full width at half-maximum (FWHM) of these distributions are 3.9, 6.7, and 4.4 eV for Au and ion-cleaned Au and Al photocathodes, respectively. The data agree well with the model predictions.

PACS numbers: 79.60.Cn, 73.30.+y, 72.10.Bg

I. INTRODUCTION

This work is in sequel to and in support of a recent presentation by the authors of some measurements on the secondary electron energy distributions from gold as excited by C-K_α (277 eV) and Al-K_α (1487 eV) x-ray photons.[1] It is an attempt to present the basic physics for the measurement and for the interpretation of the x-ray-induced electron emissions from uniform isotropic solids.

In Fig. 1 are shown the typical characteristics of an electron spectrum induced by an x-ray beam incident upon a solid. Illustrated here are the sharp photoelectron and Auger electron "no-loss" lines with their characteristic energy loss tail structure, along with the low-energy secondary electron distribution. In contrast to uv-excited electron spectra, here the photoelectrons and the principal sharp Auger electron emissions are well outside the low-energy secondary electron energy region. The secondary electron spectrum peaks at about 1 to 2 eV and has a full width at half-maximum (FWHM) that is usually below 10 eV. In this 0–30 eV interval are typically from 50 to 90% of the total number of electrons emitted for photon excitation in the 100–10 000-eV region.

The x-ray-excited electron spectra constitute a unique "window" into the solid and its electron excitation, transport, and escape processes. When a thorough understanding of the physics of these processes is gained, electron spectroscopy can provide an important quantitative basis for the physical and chemical analysis of solids. The electron spectroscopy for chemical analysis (referred to as ESCA or XPS) has become a well-recognized research area within the last ten years.[2]

The photoelectric conversion of x-ray intensity into electron emission can provide an important practical basis for x-ray intensity measurement. X-ray photoelectric detectors are vacuum devices and, unlike gas ionization detectors, can be windowless. A unique advantage of the photoelectric detector is that it can be applied effectively over a wide band of photon energies.[3,4]

A very recent application of secondary electron detectors has been in the development of streak and framing cameras for the diagnostics of x-ray bursts from laser-produced plasmas. The time spread in the photoconverted secondary electron emission per photon is probably of the order of 10^{-14} sec, and the energy spread is of the order of 10 eV. An x-ray source can be imaged and photoconverted to an electron source which may then be reimaged down a streak or framing camera tube with an accelerating electron lens system. The time history of an x-ray event can be obtained by a fast transverse deflection of this image, e.g., to form a "streak" pattern with a time resolution in the picosecond range.[1,5–9]

In order to support research and application in x-ray photoemission, considerably more theoretical and experimental work should be done on the development of a quantitative relationship between the electron emission spectrum, the incident photon energy, and the characteristics of the photocathode. There is no complete theory of x-ray photoemission that is available

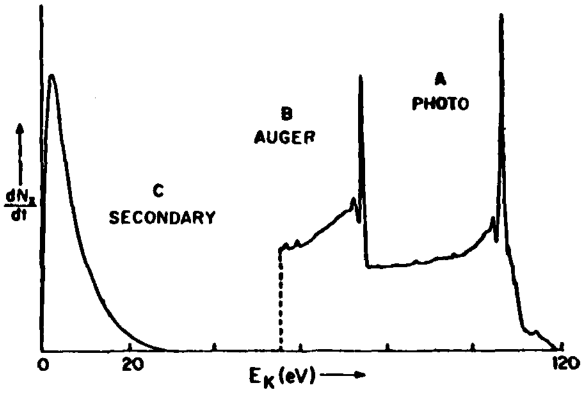

FIG. 1. A typical x-ray-excited photoemission spectrum.

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High-efficiency low-energy x-ray spectroscopy in the 100–500-eV region

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The lead myristate multilayer analyzer has provided a basis for a relatively simple and efficient spectroscopy for the low-energy x-ray emissions in the 20–80-Å region (where conventional crystal spectroscopy and grazing incidence grating spectroscopy are generally inefficient). The percent reflectivity, the integrated coefficient of reflection, and the Bragg diffraction width of the lead myristate analyzer have been measured and found to be consistent with the predictions of a simple theoretical model for multilayer diffraction. This multilayer spectroscopy at large Bragg angles has a high efficiency (high instrument transmission) as compared to grazing incidence grating spectroscopy in this 20–80-Å region. However, the resolution is limited to that set by the diffraction width of the lead myristate analyzer of about 1 eV. Because the collimator-crystal broadening function can be precisely defined, a simple and effective deconvolution procedure can be applied with this multilayer spectroscopy to bring the resolution into the sub-electron-volt region. To demonstrate the efficiency of lead myristate spectroscopy in the 20–80-Å region, spectra were measured and analyzed from x-ray excited fluorescent sources which are characteristically of low intensity. (X-ray excitation yields a minimum of background spectra and of radiation damage.) These include the $L_{2,3}$ atomic spectrum of argon and the C-K molecular spectrum of CO_2, both in the gas phase, and the Cl-$L_{2,3}$ and O-K spectra from solid lithium perchlorate. Many samples undergo appreciable radiation-induced chemical change during the exposure time that is required for measurement—even with an optimally fast spectrograph and with fluorescent excitation. A method has been developed to evaluate and to correct for radiation damage by distributing the exposure over an effectively large sample volume either by gas flow or by rotating through multiple samples during measurement. Several spectral scans were made on the $LiClO_4$ using six samples. The total exposure time for each data point in each scan was recorded which permitted an extrapolation into a "zero" exposure spectrum. Finally, Fe-$L_{2,3}$/O-K spectrum (from Fe_2O_3) in the 17–25-Å region is presented to illustrate the effectiveness of the lead myristate analyzer in third-order diffraction. For this multilayer, the third-order diffraction efficiency is one-third that of the first order and is nearly twice that of the second order for this wavelength region.

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I. INTRODUCTION

There are two areas in which low-energy x-ray spectroscopy is of particular importance at this time—the diagnostics of high-temperature plasmas[1] and the determination of the chemical and solid-state electronic structure of atomic systems.[2]

In the controlled thermonuclear fusion research, a critical temperature region of current interest is in the (1–10) × 10^6 °C range. The plasmas involved emit radiations most characteristically in the low-energy x-ray region (100–1000 eV/10–100 Å). The detailed spectroscopy of these plasma radiations can yield information as to the plasma density, temperature, and the identity and amount of contaminating elements. The low-energy x radiation from pulsed plasma sources (as produced by lasers or exploding wires) can be very efficiently converted to relatively sharp distributions in energy of secondary electrons[3] that are amenable, with streak camera techniques, to time-history measurements approaching psec resolutions.

Often, the energy and the symmetry of the outer electronic states of atomic systems can be sensitively revealed through the spectra associated with the transitions from these states into a nearby relatively sharp core level. Such spectra can yield valuable data complementary to that which are available from photoelectron Auger electron spectroscopy on the structure of valence bands, solid-state bands, and molecular orbitals.[4] These sensitive first transitions into the core levels typically result in low-energy x-ray spectra at a few hundred eV or less.

Using, for example, the acid phthallate crystals (2d value of about 26.6 Å), the conventional x-ray crystal spectroscopy has been very effectively extended down to about 500 eV.[5] Extreme ultraviolet diffraction grating spectroscopy has been extended with high efficiency (with relatively large angles of grazing incidence) up to about 100 eV.[6] We have found that a very efficient spectroscopy in the gap region of 100–500 eV is by using the multilayer analyzers as the lead stearate and lead myristate of 2d values equal to 100 and 80 Å, respectively. We have recently presented the detailed characteristics and application of the lead stearate analyzer.[7,8] In this paper, we extend the presentation of the methods and techniques of low-energy x-ray spectroscopy as specially applied with the lead myristate analyzer.

In Secs. II–V, we present an analysis and measurements of the x-ray optical characteristics of this multilayer analyzer, an optimized spectroscopic and data analysis procedure for gaining maximum overall efficiency and resolution, and, finally, we present some examples of applications to atomic and molecular low-energy x-ray spectroscopy.

II. REFLECTION PARAMETERS FOR THE LEAD MYRISTATE MULTILAYER

Lead salts of the fatty acids deposited as Langmuir-Blodgett multilayers have been demonstrated to be highly efficient

Cl-$L_{II,III}$ fluorescent x-ray spectra measurement and analysis for the molecular orbital structure of ClO_4^-, ClO_3^-, and ClO_2^-

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The chlorine $L_{II,III}$ low energy x-ray spectra from sodium perchlorate, chlorate and chlorite have been obtained using carbon K_α (277 eV) photon excitation and a lead myristate analyzing "crystal" ($2d = 80$ A). X-ray induced decomposition was observed for each of these compounds. By taking repeated spectral scans, systematically distributed over six samples, it was possible to extrapolate to "zero-dose" Cl-$L_{II,III}$ spectra. A specially developed least-squares fitting program was applied to precisely determine the energy and strength of each spectral component which utilized the known collimation and crystal broadening functions and yielded energy resolutions of less than 1 eV. Broad low-energy satellite structures were observed for all the oxy-anions and for chloride (NaCl) and have been compared to similar satellites as measured in the Ar-$L_{II,III}$ spectrum. These structures were thus identified as resulting from multielectron processes. The other peaks in the Cl-$L_{II,III}$ spectra of the oxy-anions could be understood as corresponding to transitions from molecular orbitals with Cl 3*s* or 3*d* character. These results have demonstrated that 3*d* orbitals do play a definite role in the formation of chemical bonds in the oxy-anions of chlorine and that the importance of this role increases with the oxidation state of the chlorine. Satisfactory correlations have been obtained with the complementary K_β x-ray emission and photoelectron spectra and with molecular orbital theory for the same anions.

I. INTRODUCTION

Transitions between the molecular orbital states and the nearby and relatively sharp core level states result in low energy x-ray spectra that typically lie in the 100–300 eV (40–100Å) region. Such spectra can sensitively portray the orbital structure of the molecule (or, in many cases, of an ionic group). For the second-row elements, the nearest core levels are the $2p_{1/2}$–$2p_{3/2}$ spin-orbit split states. The atomic binding energies of these $L_{II,III}$ levels, for example, for 15 P, 16 S, 17 Cl, and 18 Ar are 136–135, 165–164, 202–200, and 247–245 electron volts, respectively. In a particular chemical environment, these core levels of a given atom may shift as much as 10 eV. Such core level chemical shifts can be measured by x-ray photoelectron spectroscopy (XPS). The molecular orbital energies are of the order of 10 eV and can also be measured directly by ultraviolet photoelectron spectroscopy (UPS). The x-ray emission spectra directly yield the difference in the energy of the molecular orbitals and the core level states. However, unlike the photoelectron spectra, the x-ray emission spectra reveal appreciable information about the symmetries of the molecular orbital states. The $L_{II,III}$ spectral intensities are determined mostly by the *s* and *d* character of the orbitals and the K_β spectral intensities are determined mostly by the *p* character of the orbitals. If the $L_{II,III}$ or K_β spectrum originates from an atom of a molecule or of a strongly ionic group that contains only one such atom, it is then relatively easy to approximately calculate the energy and the relative intensity of the x-ray spectral components. Such theoretical predictions can simply be based upon one-electron integrals with the molecular orbital states described as linear combinations of the *s*, *p*, and *d* atomic orbital functions (LCAO approximation). The calculated eigenvectors are used to obtain the dipole transition probabilities. From such MO calculations the relative amounts of *s*, *p*, and *d* contribution can readily be estimated.

In an earlier work, Henke and Smith[1] were able to demonstrate the feasibility of obtaining the $L_{II,III}$ spectra of phosphorous, sulfur, and chlorine in different chemical states by applying spectrographic techniques of such efficiency as to minimize the effects of radiation decomposition. Recently, the S-$L_{II,III}$ spectra have been more precisely measured and analyzed by Henke and Taniguchi[2,3] for the SO_3^{-2} and SO_4^{-2} ions for polycrystalline samples and for the molecules containing single sulfur atoms and in the gas or vapor states—H_2S, SO_2, SF_6, C_4H_4S. The molecular orbital information derived from these spectra were compared to that obtained from the complementary photoelectron and K_β spectroscopy and to the predictions of molecular orbital theory. In this present work, the Cl-$L_{II,III}$ spectra for the ClO_2^-, ClO_3^-, and ClO_4^- ions for polycrystalline samples are measured, analyzed and compared to the photoelectron, K_β and MO calculated[4] data for the same ionic systems. Also, important comparisons with the measured atomic $L_{II,III}$ spectra for Ar and NaCl are presented.

A striking difference in the experimental determinations of the $L_{II,III}$ spectra of the sulfur and the chlorine compounds has been that the latter undergo considerably greater chemical change as induced by the excitation radiation that is required for the spectral measurement. That radiation decomposition might be important in the soft x-ray spectra of chloro-anions had been discussed by Best[5] in the electron excitation of Cl K_β spectra and had also been suggested by Urch[6] in attempting to interpret the early spectra of Henke and Smith.[1] Subsequently, both Prins[7] in x-ray photoelectron experiments and Sadovskii *et al.*[8] in measuring Cl-$L_{II,III}$ emission

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The Secondary Electron Emission Photocathode Characteristics for Time Resolved X-Ray Spectroscopy

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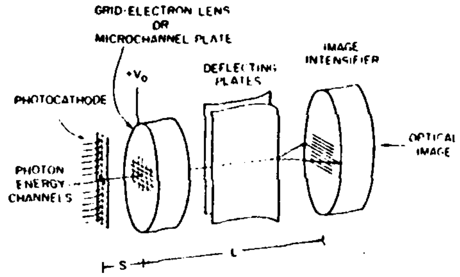
Recently the secondary electron energy distributions and the relative secondary electron yields for the 0.1 to 10 keV photon excitation region have been measured for gold, aluminum and for sixteen representative semiconductors and insulators (alkali halides), and a simple phenomenological model for X-ray photoemission has been developed. This work is discussed here as it might be applied to the application of streak cameras for time resolved X-ray spectroscopy.

§1. Introduction

Time resolved X-ray spectroscopy has recently become of considerable value in studies of high temperature plasmas in the one second range (magnetically confined fusion) to the picosecond range (laser produced fusion). Mode-locked laser systems are available that can generate high intensity pulses of X-radiation from matter in the picosecond region. Ultra-fast spectroscopy is needed for the characterization of such X-ray sources and of the effects of their radiation bursts upon materials. Pico second X-ray spectroscopy may be a valuable tool for the measurement of the lifetimes of metastable atomic and molecular states and of certain photochemical processes.[1–3)]

A proven method for accomplishing time resolved X-ray spectroscopy is that with the X-ray streak tube.[4–6)] An X-ray beam is dispersed according to its photon energy along a slit-defined photocathode using a non-focusing crystal or a diffraction grating (or by a series of absorption filter and/or total-reflection monochromator channels). The secondary electrons from this slit source are used to form a line image at an image intensifier (needed particularly for ultra-fast spectroscopy). This line image is "streaked" to establish a time base using a pair of deflecting plates. The optical output of the image intensifier is recorded photographically. A schematic of such an X-ray streak tube is shown in Fig. 1. As indicated here, two types of imaging can be used, either an electron lens system[7,8)] or a simple, proximity-focusing microchannel plate system.[9,10)]



TEMPORAL RESOLUTION LIMIT, τ

$$\tau = 3.37\,\frac{(\Delta)^{1/2}}{\epsilon_0}\left\{1+\frac{1}{4}\left(\frac{L}{S}-2\right)\left(\frac{\Delta}{eV_0}\right)^{1/2}\ldots\right\}\ \text{PICOSECONDS}$$

Δ = SECONDARY ELECTRON ENERGY SPREAD IN eV

ϵ_0 = EXTRACTION FIELD, V_0/S IN kV/mm

Fig. 1. Schematic of an X-ray streak tube as applied for time resolved X-ray spectroscopy. The temporal resolution limit, τ, is the difference in arrival time at the image intensifier for axially emitted electrons from the photocathode of initial velocities equal to zero and to v_0. The corresponding energy spread, Δ, of the secondary electron emission is $1/2 \cdot mv_0^2$.

The intensity-and-photon-energy response and the temporal resolution of the streak camera are ultimately determined by the characteristics of the photocathode. In the sections that follow, we have attempted to review (1) the basic relationship between the photoemission and the electron-optical characteristics of the X-ray streak tube, and (2) the experimental and theoretical determination of the relevant photoemission properties of metal and dielectric X-ray photocathodes as have been recently investigated in this laboratory.[11–13)]

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Soft-x-ray-induced secondary-electron emission from semiconductors and insulators: Models and measurements

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Secondary-electron energy distribution curves (EDC's) and the total secondary-electron yields relative to such for gold have been measured for seven semiconductors for which electron-electron scattering losses within the emitter were considered dominant and for nine insulators (alkali halides) for which electron-phonon scattering losses were expected to be dominant in the transport process. The secondary-electron spectra were excited by Al-$K\alpha$ (1487 eV) photons and were measured from evaporated dielectric films (of about 0.3 μ thickness) on conducting substrates with an electrostatic hemispherical analyzer of about 0.05-eV resolution. Some of the dielectric photoemitters have appreciably narrower energy distributions and higher yields than has gold; CuI and CsI have EDC widths at half-maximum of about one-third of that for gold, and yield values of 11 and 30 times greater. The FWHM and secondary-electron yield for gold were measured to be about 4 eV and 0.50 electrons per normally incident photon, respectively. The shapes of the EDC's were found to be essentially unchanged for photon excitation in the 0.1–10-keV region. Strong structural features appear only in the alkali halide EDC's, and it is proposed that these are mainly the result of single-electron promotion of secondaries from the valence band by plasmon deexcitation. A relatively simple model for x-ray photoemission has been developed which assumes that direct excitation of secondaries by photoelectron and Auger-electron "primaries" is the dominant excitation mechanism, and accounts for both electron-electron and electron-phonon scattering in the transport process. Free-electron conduction-band descriptions are assumed. The theoretical and experimental curves are in satisfactory agreement.

I. INTRODUCTION

There has been a considerable amount of effort on the theory and application of secondary-electron emissions using electron excitation in the kilovolt region (as applied, for example, in scanning microscopy) and using extreme ultraviolet excitation (as applied in band-structure analysis). There has been relatively little theoretical or experimental work reported on the generation of the secondary electrons using x-ray excitation (which is of considerable current interest as applied to the measurement of the intensity and the temporal history into the picosecond region of pulsed x-ray sources with the diode detector, the streak, and the framing cameras in high-temperature plasma diagnostics).

With electron and extreme ultraviolet generation of the secondary-electron distribution, the effective escape depths of the electrons can be very dependent upon the attenuation mechanism of the exciting radiation. With x-ray excitation of the photoelectron and subsequent emission of the associated Auger-electron "primaries" which in turn generate the internal secondary-electron distribution, the electron escape depths are usually independent of the x-ray attenuation process. This is because the x-ray penetration is very large as compared to the effective electron escape length. Thus with x-ray excitation, often a more direct and precise interpretation of the secondary-electron energy distribution can be made in terms of models for the excitation, transport, and escape processes.

In an earlier work,[1] the electron energy dependence of the secondary-electron energy distribution from metals as excited by x-rays in the 0.1–10-keV region was measured and found to be consistent and predictable by applying currently available theoretical descriptions for the excitation, mean free paths, and escape for secondaries in metals. In this present work, we have measured the energy dependence and relative yields of the secondary electrons as excited by soft x rays (principally at 1487-eV photon energy) for a representative series of semiconductors and insulators. For these systems, the secondary-electron generation processes are more complex, particularly for the insulators for which multiple scattering has an appreciable role in the transport process. In order to test available theoretical expressions for the secondary-electron excitation and for the mean free paths for pair production and for electron-phonon interactions for the energy region below 10 eV, we have used the relatively simple rate equation developed by Kane[2] for a description of the multiple scattering transport process. We believe this approach will be helpful at this time in guiding the application of more exact transport theories, analytical and numerical, in later studies.

In Sec. II, we present the "semiclassical," simple case for x-ray excited secondary- electron generation for the "no-loss" transport (no multi-

APPENDIX II

RESEARCH PUBLICATIONS BY THE PRINCIPAL INVESTIGATOR AND CO-WORKERS ON THIS RESEARCH PROGRAM

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39. "Surface Characterization by Low Energy Photoelectron Spectroscopy," *Proceedings of the 6th International Congress on X-Ray Optics and Microanalysis* (Osaka, Japan, September 1971), pp. 367-384.

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41. "Ultrasoft X-Ray Reflection, Refraction and the Production of Photoelectrons (100-1000 eV Region)," *Proceedings of Spring Meeting of the American Physical Society* (Washington, D. C., April 1972), published in *Bulleting of the American Physical Society.*

42. "The Measurement of Low Energy Electron and X-Ray Interaction Coefficients for Solids," *Proceedings of the 7th National Conference of the Electron Probe Analysis Society of America* (San Francisco, July 1972).

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    "Light Element Analysis" *Proceedings of the U.S.-Japan Seminar on Fundamentals of Scanning Electron Microscopy* (Osaka, Japan, November-December 1972).

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50. "Techniques of Low Energy X-Ray Spectroscopy (0.1 to 2 keV Region)," Interim Report, AFOSR 75-2762 (November 1974) (w/ Murray A. Tester).
51. "Valence Band Spectroscopy in the Ultrasoft X-Ray Region (50 to 100 A), *Advances in X-Ray Analysis* (Kendall/Hunt, Dubuque, 1976), Vol. 19 (w/ Kazuo Taniguchi).
52. "Parameters for the Calculation of X-Ray Absorption Coefficients for H (1) through Ge (32) in the 100-1500 eV Region," *Advances in X-Ray Analysis* (Kendall/Hunt, Dubuque, 1976), Vol. 19 (w/ Mark L. Schattenburg).
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54. "Sulfur $L_{II,III}$ Emission Spectra and Molecular Orbital Studies of Sulfur Compounds," *J. Chem. Phys. 64* (1976) (w/ Kazuo Taniguchi).
55. "X-Ray Calibration Sources for the 100-1000 eV Region," *Proceedings of the 1976 ERDA Symposium on X- and Gamma-Ray Sources and Applications* (University of Michigan, Ann Arbor, May 1976).
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57. "0.1 to 10 keV X-Ray-Induced Electron Emissions from Solids--Models and Secondary Electron Measurements," *J. Appl. Phys. 48*, 1852 (1977) (w/ J. A. Smith and D. T. Attwood).
58. "High Efficiency Low-Energy X-Ray Spectroscopy in the 100-500 eV Region," *J. Appl. Phys. 49*, 480 (1978) (w/ R. C. C. Perera, E. M. Gullikson and M. L. Schattenburg).
59. "Cl-$L_{II,III}$ Fluorescent X-Ray Spectra Measurement and Analysis for the Molecular Orbital Structure of ClO_4^-, ClO_3^- and ClO_2^-," *J. Chem. Phys. 68*, 3692 (1978) (w/ R. C. C. Perera and D. S. Urch).
60. "Some Recent Studies in Low Energy X-Ray Physics," *Proceedings of the 8th International Conference on X-Ray Optics and Microanalysis* (Boston, August 1977).
61. "Models and Measurement for the Response of Dielectric X-Ray Photocathodes," Scientific Reports, AFOSR 75-2762-F and DOE E(04-3)235-PA15, March 1978.
62. "Low Energy X-Ray Emission Spectroscopy in the 100-500 eV Region: Molecular Orbital Interpretation," (PhD Thesis by R. C. C. Perera) Special Scientific Report, AFOSR 75-2762-F, May 1978.

63. "The Secondary Electron Emission Photocathode Characteristics for Time Resolved X-Ray Spectroscopy," *Proceedings of the International Conference on X-Ray and XUV Spectroscopy* (Sendai, Japan, August 1978); *Jap. J. Appl. Phys. 17*, Suppl. 17-2, p. 23 (1978) (w/ K. Premaratne).

64. "C-K and Cl-L Emission Spectra and Molecular Orbital Analysis of CCl_4" *Proceedings of the International Conference on X-Ray and XUV Spectroscopy* (Sendai, Japan, August 1978); *Jap. J. Appl. Phys. 17*, Suppl. 17-2, p. 23 (1978) (w/ R. C. C. Perera).

65. "Soft X-Ray Induced Secondary Electron Emission from Semiconductors and Insulators: Models and Measurements," *Phys. Rev. B19*, 3004 (1979) (w/ J. Liesegang and S. D. Smith).

66. "Low Energy X-Ray Emission Spectra and Molecular Orbital Analysis of CH_4, CCl_4 and $CHCl_3$," *J. Chem. Phys. 70*, 5398 (1979) (w/ R. C. C. Perera).

67. "The Characterization of Photocathodes for Application to Time-Resolved X-Ray Spectroscopy," Technical Progress Report, AFOSR 79-0027 and DOE DE-AS03-76SF00235, April 1979.

68. "Multilayer X-Ray Spectroscopy in the 20-80 A Region: A Molecular Orbital Analysis of CO and CO_2 in the Gas and Solid States," *X-Ray Spectrometry* (1979) (w/ R. C. C. Perera).

69. "X-Ray Spectrometry in the 100-1000 eV Region," *Nucl. Instrum. Methods* (1979).

There are four papers currently to be published. One of these, entitled "The Anomolous Dispersion of X-Rays," contains the first complete compilation of atomic scattering factors and photoionization cross sections for all elements and for fifty laboratory wavelengths in the 1-to-300 angstrom region. (w/ P. Lee, T. J. Tanaka and R. Shimabukuro).

APPENDIX III

SOME PERSONS ACQUAINTED WITH THIS RESEARCH PROGRAM

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DR. RICHARD D. DESLATTES, Chief, Quantum Metrology Section, Optical Physics Division, Institute of Basic Standards, National Bureau of Standards, Washington, D. C. 20234. Ph. (301) 921-1000.

DR. MARSHALL C. HARRINGTON, Grant Administrator for this program for the Air Force Office of Scientific Research, 1967-1977. 4545 Connecticut Avenue N.W., Washington, D. C. 20008. Ph. (202) 244-3203.

DR. DAVID J. NAGEL, Chief, X-Ray Optics Branch, Naval Research Laboratory, Code 6482, Washington, D. C. 20390. Ph. (202) 767-2154.

PROFESSOR G. SHINODA, Professor Emeritus, Osaka University, Faculty of Engineering, Department of Applied Physics, Suita, Osaka 565, Japan. A senior x-ray physicist of Japan, and coordinator of several U.S.-Japan conferences co-hosted by this principal investigator at the University of Hawaii.

DR. JAMES DEGNAN, AFWL/DYP, Kirtland Air Force Base, New Mexico 87117.

DR. ROBERT DAY, Head, Diagnostics and Calibration Laboratory, Los Alamos Scientific Laboratory, J-14, Mail Stop 410, P. O. Box 1663, Los Alamos, New Mexico 87544. Ph. (505) 667-2474.

APPENDIX IV

INVITED AND CONTRIBUTED RESEARCH PAPERS PRESENTED BY THE PRINCIPAL INVESTIGATOR

1970 TO 1979

1970

- Seminar for Phillips Petroleum Corp., Tulsa, Oklahoma
- Seminar for Shell Development Company, Emeryville, California
- Seminar at Department of Physics, University of Arizona
- Colloquium on *Processus eletroniques simples et multiples du domaine X et X-UV* sponsored by the Centre National de la Recherche Scientifique and held in Paris, France, September 1970 (principal investigator participated as a guest of the French government)

1971

- Sixth International Conference on X-Ray Optics and Microanalysis, Osaka, Japan, September 5-10, 1971
- Post Conference Seminar on Scanning Electron Microanalyzers sponsored by the Japan Society of Applied Physics, Tokyo, Japan, September 14, 1971
- Seminar at Tohoku University, Sendai, Japan, September 1971

1972

- Discussion: Possibilities of low energy analysis, particularly as applied to membranes; with Dr. Poen S. Ong, M. D. Anderson Cancer Research Center X-Ray and Electron Probe Analysis Laboratory, Houston, Texas, April 1972
- International Conference on Inner Shell Ionization Phenomena, Atlanta, Georgia, April 1972
- Seminar at ORTEC, Inc., Oak Ridge, Tennessee, April 1972
- Spring Meeting of American Physical Society, Washington, D. C., April 1972
- Presentation: Slides on recent spectroscopic techniques and measurements of cross sections, Naval Research Laboratories, Washington, D. C., April 1972
- Seminar at Pomona College (and associated colleges at Claremont, California) April 1972
- Seminar at IBM Research Laboratory, San Jose, California, July 1972
- Seminar at University of California Livermore Radiation Laboratory, Livermore, California, July 1972
- U.S.-Japan Seminar on Fundamentals of Scanning Electron Microscopy, Osaka, Japan, November-December 1972
- Seminar at Rigaku Denki Co., Ltd., Osaka, Japan, December 1972

1973

- Seminar at Los Alamos Scientific Laboratory (University of California), Los Alamos, New Mexico, January 1973
- Seminar at Kirtland Air Force Base and Sandia Corp., Albuquerque, New Mexico, January 1973
- Seminar at Materials Analysis Laboratory, Wright-Patterson Air Force Base, Ohio, August 1973
- Twenty-second Annual Conference on Applications of X-Ray Analysis, Denver, Colorado, August 1973
- U.S.-Japan Seminar on Electron Probe Microanalysis (University of Hawaii), Honolulu, Hawaii, September 1973

1974

- Seminar at Lawrence Livermore Laboratory, Livermore, California, August 1974
- Twenty-third Annual Conference on Advances in X-Ray Analysis, Denver, Colorado, August 1974
- Seminar at Los Alamos Scientific Laboratory (University of California), Los Alamos, New Mexico, August 1974
- Seminar at Kirtland Air Force Base and Sandia Corp., Albuquerque, New Mexico, August 1974

1975

- A two-day symposium on *Low Energy X-Ray and Electron Spectroscopy* held at the University of Hawaii, June 12-13, 1975. This research group joined others from our Chemistry Department as host for this meeting which was also part of the 13th Northwest Regional Meeting of the American Chemical Society. Papers presented on this project's research program were:

    1. *Some Current Research in Low Energy X-Ray and Electron Physics* (B. L. Henke)
    2. *Effect of Chemical State upon Sulfur $L_{II,III}$ Fluorescence Spectra* (w/ Kazuo Taniguchi)
    3. *Effect of Chemical State upon the Characteristic Energy Loss Spectra of Molecular Gases* (w/ Taylor Norcross)

    (A total of 42 papers were presented for this symposium from U.S. and international laboratories.)

- Twenty-forth Annual Conference on Applications of X-Ray Analysis, Denver, Colorado, August 1975
- Seminar at Los Alamos Scientific Laboratory (University of California) Los Alamos, New Mexico, August 1975
- Seminar at Lawrence Livermore Laboratory, Livermore, California, August 1975
- Seminar at Kirtland Air Force Base, Albuquerque, New Mexico, and discussions with E. J. T. Burns, August 1975

1976

- American Physical Society Topical Conference on Diagnostics of High Temperature Plasmas, Knoxville, Tennessee, January 1976
- ERDA Conference on X- and Gamma-Ray Sources and Applications, University of Michigan, Ann Arbor, Michigan, May 1976
- Seminar at Lawrence Livermore Laboratory, Livermore, California, May 1976

1977

- Seminar at Lawrence Livermore Laboratory, Livermore, California, August 1977
- Seminar at Los Alamos Scientific Laboratory, Los Alamos, New Mexico, August 1977
- Eight International Conference on X-Ray Optics and Microanalysis, Boston, Massachusetts, August 1977

1978

- *A Systematic Study of the Characteristics of X-Ray Photocathodes*, Poster presentation, American Physical Society Second Topical Conference on High Temperature Plasma Diagnostics, Santa Fe, New Mexico, February 28 - March 3, 1978
- *Application of Low Energy X-Ray Spectroscopic Techniques to High Temperature Plasma Diagnostics*, Physics seminar lecture, Los Alamos Scientific Laboratory, June 1978
- *The Optimization of X-Ray Photocathodes for Time Resolved X-Ray Spectroscopy in Laser-Produced Fusion Research,* Physics colloquium lecture, University of California Lawrence Livermore Laboratory, June 1978
- Participated in a workshop on the Absolute Calibration of X-Ray Photocathodes as Applied in X-Ray Detectors (XRD's) sponsored by the National Bureau of Standards at the Lawrence Livermore Laboratory, June 1978. The results of the calibrations of two detectors that were calibrated by each of the six participating laboratories, including this one, were evaluated.
- *The Secondary Electron Emission Photocathode Characteristics for Time Resolved X-Ray Spectroscopy*, International Conference on X-Ray and XUV Spectroscopy, Sendai, Japan, August 28 - September 1, 1978
- *C-K and Cl-L Emission Spectra and Molecular Orbital Analysis of* CCl_4 International Conference on X-Ray and XUV Spectroscopy, Sendai, Japan, August 28 - September 1, 1978
- *A Review of X-Ray Photocathode Characteristics that Affect Picosecond Streak Camera Operation*, 1978 American Physical Society Annual Meeting of the Division of Plasma Physics, Colorado Springs, October 30 - November 3, 1978
- *Physics and Application of Multilayer 'Crystals' for Spectral Analysis in the 50-100 A Region,* Invited paper, American Crystallographic Assn. Meeting (Joint with Japanese Crystallographic Society), Honolulu, Hawaii, March 26-30, 1979.

1979

- Seminar at Lawrence Livermore Laboratory, June 20, 1979
- Seminar at Los Alamos Scientific Laboratory, June 26, 1979
- Seminar at Kirtland Air Force Base and Sandia Laboratories, Albuquerque, New Mexico, June 28, 1979
- Seminar at Maxwell Laboratories, Inc., San Diego, June 29, 1979
- *X-Ray Spectroscopy in the 100-1000 eV Region*, Invited review paper, Japan-U.S.A. Seminar on Synchrotron Radiation Facilities, East-West Center, University of Hawaii, November 5-9, 1979
- *The Characterization of X-Ray Photocathodes*, 21st Annual Meeting of the Division of Plasma Physics, American Physical Society, Boston, November 12-16, 1979
- Seminar at Department of Physics, Pomona College, Claremont, California, November 1979
- Seminar at Massachusetts Institute of Technology, Center for Space Research, Cambridge, Massachusetts, November 1979