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X-Ray Analysis by Photoelectron Spectrometry*

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Abstract

Electron spectrometry is shown to be an excellent method for determining relative and absolute intensities of x-ray emission lines owing to the simple and well-defined relationship between the photoelectron spectrum and the corresponding x-ray spectrum. Energies and widths of lines can also be measured. An appropriate converter, such as the neon atom, acts as intermediary between the two types of spectra; and electrons are dispersed in an electrostatic energy analyzer of well known characteristics. This type of apparatus has a resolution $\Delta E/E$ of typically 0.1% and covers a photon energy range from about 20 eV to 3000 eV. The new instrument compares favorably with grating and crystal spectrometers in energy resolution and is superior for intensity determinations. It has greater resolution than solid state detectors and proportional counters but lower detection efficiency.

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The method is illustrated by a measurement of the ZrL x-ray emission spectrum.

While the grating and crystal spectrometer, standard instruments of x-ray spectroscopy, are the preferred instruments for determining line widths, line shapes, and energies of x rays, the solid state detector and proportional counter are the preferred devices for determining intensities of x-rays. However, the excellent intensity characteristics of the nondispersive devices are counter-balanced by poor energy resolution and a low-energy limit which lies at several hundred eV for proportional counters and about 1 keV for present-day solid state detectors. As we shall show, photoelectron spectrometry offers a number of advantages when studying x rays in the energy range from about 20 to 3000 eV. The new method combines the virtues of the conventional methods: relative intensities can be measured accurately and as readily as with solid state or gaseous counters, and energies can be measured with a resolution comparable to that of grating and crystal spectrometers. In addition, x-ray intensities can be determined on an absolute scale. Another advantage inherent in the method is the capability of comparing intensities of x rays that are separated in energy by two orders of magnitude. Perhaps the major weakness of the new approach lies in the low detection efficiency, which, however, is competitive with other dispersive apparatus and is subject to much improvement.

In recent studies,^{1,2} we have demonstrated the potential of the method by investigating the various properties of ultrasoft character-

istic x rays between 130 and 190 eV.

In this paper, we give a brief description of apparatus and method, and present for illustration the ZrL x-ray spectrum which lies between 1700 and 2500 eV. A detailed analysis and interpretation of the spectrum is given elsewhere.³

Basis and characteristics of method

The principle of the method is simple and consists of converting the x-rays under study into photoelectrons which are then analyzed in a suitable instrument according to energies and flux.

Given a known energy level E_B of some converter atom, free or bound, the energy $h\nu$ of the photon is obtained from the kinetic energy $E_{e,kin}$ of the photoelectron according to

$$h\nu = E_B + E_{e,kin} \quad (1)$$

If $E_{e,kin}$ were proportional to a quantity which can be monitored, such as a voltage V , $h\nu$ could be displayed on a linear scale. This is, indeed, true in the case of an electrostatic electron energy analyzer to which we shall restrict our discussion in the following.

The number of photons in a given energy interval, $N_{h\nu} dE$, which enter the converter volume is related to the number of photoelectrons, $N_e dE$, which enter the analyzer by the formula:

$$N_e dE = f(E_e) E_e \frac{d\sigma_{nl}}{d\Omega} \Big|_{\phi} N_{h\nu} dE \quad (2)$$

where E_e is the photoelectron energy and $\frac{d\sigma_{nl}}{d\Omega} \Big|_{\phi}$ represents the differential photoionization cross section for subshell nl of the converter atom at angle ϕ between photon and electron. The factor $f(E_e)$ depends

on the apparatus and is given by

$$f(E_e) = GN_A T \eta \quad (3)$$

where

G is a geometry factor (essentially the conversion volume),

N_A the number of converter atoms,

$T = T(h\nu)$ the transmission of the window, if any, between photon source and converter, and

$\eta = \eta(E_e)$ the response of the electron detector.

Since all the parameters in Eqs. 2 and 3 are amenable to determination on both a relative and an absolute basis, x-ray spectra in terms of particle-number distributions can be measured both relatively and absolutely. The possibility of absolute intensity measurements may prove to be a particularly attractive feature of the method. The most formidable quantity $d\sigma_{nl}/d\Omega$ has recently been determined⁴ as a function of energy for Ne2p at $\phi = 90^\circ$ and $\phi = 54^\circ 44'$. In other cases, when only σ_{total} or σ_{nl} are known, it is helpful to remember that $d\sigma_{nl}/d\Omega$ is proportional to σ_{nl} at $\phi = 54^\circ 44'$.

Neon or helium atoms are appropriate converters with few and narrow levels and differential and total subshell cross sections that are known to $\pm 5\%$ or better. With level widths of 0.1 eV for the Ne2p doublet and about 0.3 eV for Nels and an instrumental energy resolution of typically 0.1%, x-rays can be analyzed with an energy resolution of 0.1 to 0.9 eV in the range from 20 to 870 eV, and 0.3 to 2.2 eV, from 870 to 3000 eV. These widths compare favorably with those of conventional instruments, particularly below 1 keV, and in general are

smaller than the natural widths of characteristic x-ray lines in that range.

Apparatus and operating procedure

A number of different apparatus could be designed or adapted to measure soft or ultrasoft x-ray spectra of any origin. In this demonstration study we made use of the instrument shown in Fig. 1, an electrostatic double-focussing energy analyzer. X rays enter the converter cell which contains neon at a pressure of 10N/m^2 through a $12\text{ }\mu\text{m}$ thick Be window, and photoelectrons ejected at right angles to the x-ray beam are accepted by the analyzer and focused onto an electron multiplier. The signal pulses are stored in a multichannel scaler whose channel advance is synchronized with the (sawtooth) potentials V of the spherical condenser plates of the analyzer.⁵ Thus each channel corresponds to a given potential and, because of $E_{e,\text{kin}} = V$, to a given photoelectron energy or photon energy $h\nu$ according to Eq. 1. A preselected energy interval is scanned every 50 msec, resulting in 10^5 repetitive sweeps for a typical run. X-rays originating from a Zr anode, purity > 99.9%, were excited by 9 keV electrons. Takeoff angle for the x-rays was 23° and photoelectrons were analyzed with a resolution of $\Delta E/E = 0.16\%$. The anode was scraped with a fine file under argon atmosphere before use and kept at about $2 \times 10^{-4}\text{ N/m}^2$ during operation.

Analysis procedure

The entire photoelectron spectrum⁶ Nels (ZrL) was recorded in three overlapping runs over a period of 24 hours and is shown in Fig. 2. This spectrum represents the primary (raw) datum from the

standpoint of x-ray spectrometry; but as closer inspection of the conversion factors in Eqs. 2 and 3 reveals, only small adjustments are needed to convert the photoelectron spectrum into the x-ray spectrum. Detector response and window transmission vary but little over the energy range of the spectrum, and the product E_e times $d\sigma_{nl}/d\Omega$ varies slowly. Thus, the spectrum of Fig. 2 closely resembles the x-ray spectrum and we labelled abscissa and peaks correspondingly.

In Table I, intensities of the photolines are given as area values relative to the intensity of $ZrL\alpha_1$. Numerical values of the multiplier g_1 , which contains all the conversion parameters of Eqs. 2 and 3, are listed in column 3 of the Table, and the resulting x-ray intensities are tabulated in column 4 with the normalization $I(L\alpha_1) = 100$. These are the relative intensities of the x rays incident on the entrance window of the converter cell. In our example they are identical with the relative intensities of x rays escaping through the surface of the anode at a take-off angle of 23° .

We neglected two corrections to the spectrum; one for the scattering losses⁷ of photoelectrons as they traverse the converter gas, and another one for shakeoff, including shakeup, losses⁸ at the time of the photoionization act. This was justified since scattering losses were very small in this experiment and since shakeoff losses, while amounting to about 20%, are invariant with energy.⁹ In one instance shakeup losses associated with $L\beta_1$ and labelled $\epsilon, n[\beta_1]$ can be discerned in Fig. 2 between 2080 and 2090 eV.

The ZrL emission spectrum

We go a step further in the analysis of the x-ray spectrum and apply a self-absorption correction to the intensities $I_{h\nu}(23^\circ)$ to arrive at the relative intensities $I'_{h\nu}$ which are commonly equated with the relative atomic emission rates for the L_1 , L_2 , and L_3 subshells respectively.

For the calculation of the range λ_0 of 9 keV electrons in Zr, we relied on the approximation given by Feldman¹⁰ and obtained a value of $\lambda_0 = 0.74 \mu\text{m}$. The self-absorption correction was then calculated from

$$F = \int_{\lambda_0 \csc \psi}^0 \exp(\mu l \csc \psi) dl \quad (4)$$

where μ is the linear absorption coefficient of Zr, taken from Heinrich's semi-empirical formula¹¹ and ψ the take-off angle. The multiplier g_2 of Table I is the correction factor of Eq. 4 normalized to that for the $L\alpha_1$ line. With two exceptions, the L_2-N_1 and L_2-N_4 lines, which lie above the L_3 absorption edge, the multiplier g_2 changes by less than 20%. Therefore, uncertainties in F arising from the limited validity of Feldman's formula and the neglect of the finite angular range ψ under which the anode is viewed, are not expected to alter the $I'_{h\nu}$ values beyond the given error margins. Assigned errors account for uncertainties of raw data and those contained in the multipliers g_1 and g_2 .

A spectrum as well resolved and clearly defined in intensity as the ZrL spectrum obtained by way of photoelectron spectrometry lends itself to a detailed analysis and interpretation. We report on this

aspect elsewhere;³ here we simply wish to point out that one can reproduce the salient features of the spectrum by a calculation which includes all physical processes that occur at the time of the initial inner shell ionization and the subsequent decay of the inner shell vacancies.

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Table I: Relative intensities (area values) of L x rays of Zr obtained by photoelectron spectrometry. Electron energy 9 keV. $I(\text{ZrLa}_1) = 100$ throughout. I_e = observed intensities Nels(ZrL); g_1 = multiplier to convert I_e to $I_{hv}(23^\circ)$. $I_{hv}(23^\circ)$ = intensities of x rays escaping from anode at take-off angle of 23° ; g_2 = self-absorption factor; I'_{hv} = atomic x-ray emission intensities uncorrected for satellite interference.

Line	I_e observed	g_1 apparatus	$I_{hv}(23^\circ)$ surface	g_2 selfabs.	I'_{hv} emission
ϵ L_3-M_1	4.2	0.865	3.6	1.17	4.2(7)
α_2 L_3-M_4					11 ^{a)}
α_1 L_3-M_5	100.0	1.000	100.0	1.000	100.0
β_6 L_3-N_1	1.1	1.022	1.1	0.814	0.9(2)
β_2 L_3-N_4	1.7	1.040	1.8	0.923	1.6(3)
η L_2-M_1	2.2	0.895	1.9	1.10	2.1(4)
β_1 L_2-M_4	48.8	1.010	49.3	0.964	47.5(3.3)
γ_3 L_2-N_1	0.4	1.052	0.4	2.08	0.8(2)
γ_1 L_2-N_4	0.9	1.068	0.9	1.99	1.8(5)
β_4 L_1-M_2	3.6	1.026	3.7	0.944	3.5(5)
β_3 L_1-M_3	5.7	1.033	5.9	0.938	5.5(5)

a) Inferred from theory, an approximate deconvolution of $\text{La}_{1,2}$ yield about 10%.

Figure Captions

Fig. 1. Schematic of 15-cm electrostatic energy analyzer used for the measurement of the ZrL x-ray emission spectrum. X rays from a variety of sources can be studied with this or similar apparatus.

Fig. 2. Photoelectron spectrum Nels (ZrL) bearing close resemblance with the ZrL x-ray spectrum.

Schematic of Apparatus.
15-cm Electrostatic Energy Analyzer
with Fixed Source Chamber.

Fig. 1

Fig. 2