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► **To cite this version:**

D. Urch. Soft X-ray spectroscopy. Journal de Physique III, 1994, 4 (9), pp.1613-1623.
10.1051/jp3:1994228 . jpa-00249211

HAL Id: jpa-00249211

<https://hal.science/jpa-00249211>

Submitted on 4 Feb 2008

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Classification
Physics Abstracts
61.10

Soft X-ray spectroscopy

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(Received 19 November 1993, revised and accepted 12 April 1994)

Abstract. — X-ray spectrometry at low energies ($< 1\,000\text{ eV}$), long wavelengths ($> 12\text{ \AA}$) presents special problems due to the inefficiency with which such X-rays are generated, the ease with which they are absorbed, and the difficulty of finding suitable dispersing elements. Advantage can, however, be taken of the ready absorption of these « soft » X-rays since their escape depth from most materials rarely exceeds one micron. Soft X-ray spectroscopy is therefore nanometer spectroscopy. Furthermore soft X-rays show large « chemical effects » which can be used to infer the chemical state of the emitting atom. The special problems associated with the production and dispersion of soft X-rays are considered in this paper together with methods for calculating the depth of X-ray production from surface layers. Examples are also given of the changes in peak shape, position and profile which can be used to assess the valency and ligand environment of the emitting atom.

1. Introduction.

X-ray emission takes place when a core vacancy is filled by the relaxation of a less tightly bound electron. The energy released in this process is emitted directly as a photon. There is, however, an alternative way in which the excited ion can relax and that is by the ejection of another electron, an Auger electron. If the relaxation energy is large, X-ray emission predominates — the fluorescent yield is high, but if the available energy is less than about 5 keV then the Auger process will be the more important and becomes increasingly so as the energy diminishes. In the case of carbon, for example, more than 99 % of the ions produced by the loss of a 1s electron relax by Auger electron emission. This is one of the reasons why X-ray fluorescence spectroscopy is only routinely used for the analysis of elements heavier than sodium. Other problems that make X-ray spectroscopy of the lighter elements difficult are the ease with which the low energy photons emitted by those elements are absorbed by the air and the lack of suitable crystals for the dispersion of long wavelength X-rays.

Faced with these difficulties one might well ask whether there is any point in seeking to experiment such perverse and awkward creatures as low energy X-rays. A positive answer results from appreciating that at least one of the « problems » is an advantage in disguise. The ready absorption of « soft » X-rays means that they will only be detected when they have

emerged from the very surface of a sample, the top micron or less. Soft X-ray spectroscopy is automatically nanometer spectroscopy. Since low energy X-rays will come from such a shallow depth it makes sense to concentrate the excitation process to a comparable depth. Low energy electron bombardment [1, 2] will therefore result in a much greater efficiency in the production of soft X-rays than X-irradiation. It is for this reason that the element range of X-ray attachments to electron microscopes is extended to include light elements, as far as boron and even beryllium. Conventional X-ray fluorescence spectrometers can also be used in the soft X-ray region, either by the use of X-ray tubes that emit a high flux of low energy X-rays (e.g. Rh L) or by the use of open window gas-discharge tubes [3] from which both low energy electrons and low energy X-rays emerge to bombard the sample.

The problems associated with the dispersion of long wavelength X-rays have, nowadays, been largely overcome [4] by the use of multilayers. These devices are characterized by very high reflectivity and may be thought of as « synthetic crystals » which can be tailor made to any desired 2d spacing. Of course this is not quite true, the production of multilayers with 2d spacings of less than 4 nm seems to be much more difficult than the manufacture of those with 2d spacings of 40 nm. Even so the wavelength range that can now be contemplated for X-ray spectroscopy without recourse to grating technology has been dramatically extended. The price to be paid is lack of resolution. The resolving power ($E/\Delta E$) of most multilayers that are currently available rarely exceeds 50. If higher resolution is required then crystals with large 2d spacings must be specially grown [5]. They are usually organic esters or salts of long chain fatty acids and typically have 2d spacings in the range 5-10 nm.

Other points that need attention in soft X-ray spectrometry are the need for a modest vacuum within the spectrometer — a few Pascals is more than adequate, and a thin window on the proportional counter used to detect the X-rays. Commercially produced windows with a thickness of one micron have been shown [3] to transmit soft X-rays with wavelengths of nearly 20 nm (Al L) !

Whilst most « hard » X-rays are generated by the relaxation of a core electron to a more tightly bound core hole many soft X-rays arise from transitions that involve valence electrons. Thus it is more usual for soft X-rays to exhibit « chemical effects ». This is because the particular atomic orbital involved in the X-ray process may be found participating in many molecular orbitals or bands with different energies. Relaxation can take place from each orbital or band giving rise to many possible X-rays of similar but distinct energies. Considerable fine structure can therefore be anticipated in the peaks of such valence-band X-rays (VXR). Fine structure which is a reflection of electronic structure and which, when measured as a soft X-ray spectrum, can be used to determine the nature of the electronic structure in a molecule or to investigate the band structure of metals, alloys and other solids. At a slightly more mundane level VXR spectra can often be used to determine valency, to indicate coordination number or to infer the presence of a particular type of ligand. By a happy coincidence these « chemical effects » will be more easily perceived in soft X-ray spectra. The energy range of the perturbations in VXR spectra will be the same as the energy range of molecular orbitals, a few tens of electron volts. It is of course very much easier to measure changes of this magnitude when they are superimposed on X-rays of a hundred volts rather than ten thousand. This then is another reason for studying « soft » X-ray spectra. Such spectra provide unique insight into the electronic structure of the chemical bond.

The presence of large easily observable chemical effects in soft X-ray spectra means that such spectra can be used [6] in chemical speciation and because of their nanometer range, soft X-ray spectra can be used in the chemical speciation of elements in surface layers. There is one further advantage that can be wrested from soft X-ray spectra which arises when they are excited by electron beam bombardment. If the energy of this beam is varied then the excitation

depth is also varied. This provides a simple qualitative method of depth profile analysis coupled with the possibility of being able to determine the chemical state of each element as a function of depth. The purpose of this paper is to discuss these aspects of soft X-ray spectroscopy in some detail and to indicate its application to nanometer problems.

2. Soft X-ray spectroscopy techniques.

2.1 DISPERSION. — The method whereby the greatest resolution may be achieved in the wavelength dispersion of soft X-rays is by means of a grating [7], but this requires an expensive and specialized spectrometer. Cheaper but less effective is the use of a real crystal or a Langmuir-Blodgett film with a large 2d spacing in a conventional X-ray fluorescence spectrometer. Of the two the crystal is to be preferred as it is more robust and usually has better resolution. Esters of long chain carboxylic acids have proved [5] the most effective ; tetradecyl hydrogen maleate (THM - 2d, 5.25 nm), octadecyl hydrogen maleate (OHM - 2d, 6.38 nm) and dioctadecyl adipate (OAO - 2d, 9.18 nm). Although these crystals have a long thin habit it is possible to assemble a mosaic of them which still has a tolerable resolution.

For very much better reflectivity than can be achieved with the organic crystals multilayers may be used. These devices are available commercially with nominal 2d spacings of between 4 and 30 nm. And whilst they have very high reflectivity they have poor resolution. With a resolving power of only 40 or 50 most of the fine structure that would convey chemical information is lost in VXR spectra of elements such as carbon and nitrogen, where the K_{α} emission energies are roughly 280 and 390 eV. The picture is somewhat better for boron (K_{α} , 182 eV) and chemical shifts can easily be seen [8] in the long wavelength X-rays, Be K_{α} , Si, P and S $L_{2,3}M$.

Multilayers, although they dramatically extend the wavelength range of X-ray spectroscopy, cannot simply be treated as replacement crystals. This is because they exhibit large refraction effects [9], which cause an apparent change in the 2d spacing of the device. This change varies with wavelength of the incident X-ray and with the order of diffraction. In order to cope with this wayward behaviour it is necessary to use a form of the Bragg equation which takes explicit account of refraction,

$$n\lambda \sim 2 d_{\infty} \cdot \sin \theta (1 - \delta_{\lambda}/\sin^2 \theta) \quad [\text{provided } \delta_{\lambda}/\sin^2 \theta \ll 1].$$

n is the order of reflection, λ X-ray wavelength, θ observed angle of reflection, $2 d_{\infty}$ the limiting value of 2d in the absence of refraction, δ_{λ} refraction constant at wavelength λ .

The actual value of the refraction constant at any given wavelength can be calculated [10] from tabulated values [11] of f_1 and f_2 provided the composition and thicknesses of layers that make up the multilayer are known. In practice it is often easier to calibrate a multilayer by measuring the angles at which a particular X-ray is reflected in many orders. A plot of $(n\lambda/\sin \theta)$ versus $\sin^{-2} \theta$ has a slope $(2 d_{\infty} \cdot \delta_{\lambda})$ and an intercept, $2 d_{\infty}$. It is therefore possible to determine these two parameters independently. This procedure may be repeated at other wavelengths generating a family of lines of different slopes but with a common intercept. The different slopes enable the changes in the refraction constant as a function of wavelength to be determined. Only when a multilayer has been calibrated in this way can it be used for spectroscopy. A further consequence of refraction in multilayers is that « high-order » peaks will not appear at their expected positions, since the appropriate value of 2d increases with the order of diffraction.

2.2 EXCITATION AND DETECTION. — Once the characteristic X-rays of the sample have been dispersed by the crystal or multilayer they can be detected in a normal proportional counter

fitted with a standard one micron window. Improvements in counting efficiency for soft X-rays can be made by operating the counter at low pressure and using pure methane as the counting gas, but the gain achieved is usually neither necessary nor worth the effort. Changes are necessary however in excitation procedures if an adequate flux of soft X-rays is to be generated. Recent developments in sealed tube design based on a rhodium anode have meant that conventional, sealed X-ray tubes can now be used to excite soft X-rays. Other methods involve the use of open window gas-discharge tubes and direct electron beam bombardment. Both of these methods are very effective but the latter can often cause sample decomposition (reduction).

2.3 COLLIMATION. — One further factor needs to be taken into account if well resolved soft VXR spectra are to be measured and that is the control of « horizontal divergence ». The conventional diagram for the passage of X-rays through a spectrometer is a vertical cross section, with the X-rays lying in this plane. But by no means all the X-rays follow this path in that plane. There will be some that start from one side of the sample, are reflected from near the middle of the crystal and are detected at the other side of the proportional counter. If the « vertical cross-section » X-rays are reflected at an angle θ then the out-of-plane X-rays, of the same wavelength, will be reflected at a somewhat larger angle. This gives rise to peak distortion in the form of tailing to higher angles. This effect is greatest at high angles, precisely where resolution is best, and is most apparent when fine collimation is used, again the conditions for high resolution. The problem may be overcome [12] by the simple expedient of the insertion of a new small collimator with blades at right angles to the main collimator. Some intensity is lost but symmetric peak shape is restored.

3. Low energy electron induced X-ray spectroscopy - LEEIXS.

In this application of soft X-ray spectroscopy excitation is by means of direct electron beam bombardment, but the energy of the electron beam can be varied, usually in the range 1-15 kV. This enables the penetration depth of the electrons to be varied, and as the escape depths of photons are about three orders of magnitude greater than electrons of the same energy, the X-rays that are generated will escape.

The quantification of this process is quite difficult [2] for the following reasons.

i) The electrons will rapidly lose energy within the surface layers of the solid, some even being back-scattered out of the sample completely. A satisfactory empirical relationship to describe electron range (R_e , nm) as a function of the initial electron beam energy (E , keV) is that of Feldman [13],

$$R_e \propto (E^n - E_c^n) \cdot \rho^{-1} \cdot A \cdot Z^{-n/2}$$

E_c , ionisation energy threshold, $n = 1.2 (1 - 0.29 \log Z)^{-1}$, ρ , sample density, A mean relative atomic mass of sample, Z mean atomic number of sample.

ii) As the electrons lose energy so the photo-electron cross section (σ) for the production of core hole states will change. This can be reasonably well estimated [14] by the use of a « universal curve » for σ as a function of E/E_c (E = electron energy and E_c = ionisation threshold).

iii) The X-rays that are produced will, on their way out of the solid be subject to some degree of absorption, which will diminish the yield. This absorption can be estimated from known mass absorption coefficients, distance travelled and angle of emergence from the sample. A proper consideration of these processes gives rise to complex equations [2] from which quantitative results can be obtained.

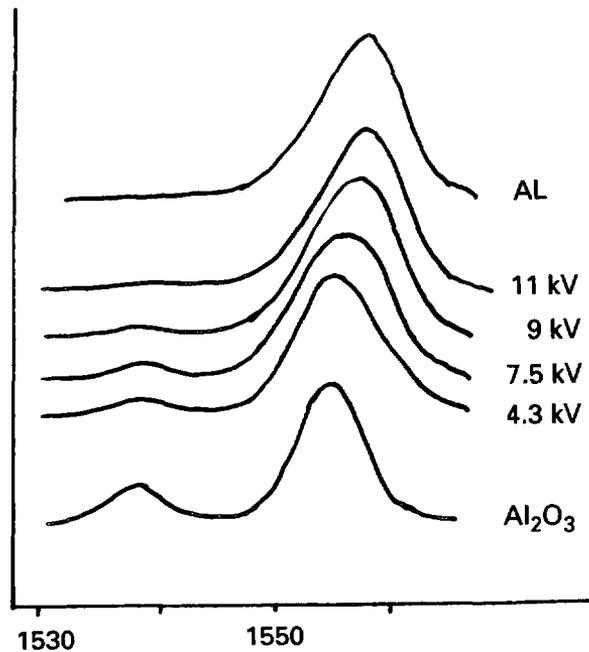


Fig. 1. — Aluminium $K_{\beta} - K_{\beta}$ spectra from aluminium metal (top), alumina (bottom) and anodised aluminium (150 nm layer of oxide). The intermediate spectra were obtained by bombardment with electron beams from 11 to 4.3 kV.

But, to demonstrate the power of the method, it will suffice here to consider a simple, if qualitative, example. Figure 1 shows a series of AlK_{β} spectra from a sample of aluminium upon which a 150 μm layer of alumina had been grown electrolytically, together with spectra for aluminium metal and aluminium oxide. The advantage of this spectral line is that it changes extensively upon oxidation. Not only is the main peak sharper and more symmetrical from the oxide than from the metal, there is also a distinct change in peak energy and, for the oxide, a new peak (K_{β}') is observed on the low energy side of the main peak and separated by about 15 eV from it. This demonstrates the power of VXR spectroscopy in chemical speciation [15] and enables the spectra shown in figure 1 to be interpreted as follows. At high electron beam energy (11 kV), only a relatively small energy loss takes place in the oxide layer and so the spectrum is that of the metal. As the electron beam energy is progressively reduced so the presence of K_{β}' becomes more apparent and the main K_{β} peak becomes broader. This is due to a larger fraction of the electrons' energy being lost in the oxide layer. At the lowest beam energy (4.3 kV) the spectrum is approximately 40 % oxide.

4. « Chemical effects » in soft X-ray spectra.

4.1 THEORETICAL INTRODUCTION. — Many low energy X-rays are generated by electron transitions between valence band orbitals and core vacancies, and so give rise to VXR spectra. Such X-rays will therefore originate from molecular orbitals in the valence band. The simplest representation of a molecular orbital (ψ) is as a linear combination of atomic orbitals,

$$\psi_i = \sum a_{ri} \varphi_i$$

where ψ_i is the i -th molecular orbital, φ_r is the r -th atomic orbital, and a_{ri} is a coefficient which describes the contribution of φ_r to ψ_i .

It therefore follows that, in principle at least, each molecular orbital may have contributions from any of the valence shell atomic orbitals from each constituent atom of the molecule. An exactly analogous expression could be written to describe the composition of the orbitals that make the bands of a solid. Although molecular orbitals, or bands, are necessarily delocalised, the atomic core hole to which an electron will transfer in order to produce an X-ray will be both localised and have a very small physical volume. Furthermore the intensity of X-ray emission is largely determined by the overlap of the wavefunctions that describe the initial and final states. It therefore follows that the probability of X-ray emission will be determined by the nature of the molecular orbitals at the site of the emitting atom. It can be shown [16] that, except for some cases involving first row elements, « cross-over » transitions, that is to say electron transfers from one atom to a core vacancy on a neighbouring atom, are of negligible importance.

X-ray emission is subject to the electric dipole selection rule which requires that the orbital angular momentum quantum number should change by unity if the transition is to be allowed. Thus s vacancies will attract transitions only from p orbitals, p vacancies only from s and d orbitals etc. Herein lies the great attraction and unique advantage of VXR spectroscopy that it enables the bonding role of a particular type of orbital on a specific atom to be investigated in isolation [17]. Or each VXR spectrum probes a partial density of states in the vicinity of one type of atom. If many such VXR spectra are collected together they can be arranged on a common energy scale, provided that the energy of each initial state can be found. This can readily be done using X-ray photoelectron spectroscopy. The value of the initial state ionisation energy on the X-ray emission energy scale corresponds to a molecular orbital ionisation energy of 0 eV. Once this zero has been established for each VXR spectrum, their alignment is straightforward.

4.2 SILICATE. — Such a diagramme of aligned spectra provides an immediate picture of the composition of each molecular orbital, and thus the electronic structure of the molecule. An example of the procedure [18] is shown in figure 2 for the silicate anion (in Mg_2SiO_4). The peak intensities in each spectrum can be related to the amount of the appropriate atomic orbital present in the molecular orbitals of the silicate anion. The high symmetry of this anion (point group T_d) enables these molecular orbitals to be classified, in order of increasing ionisation energy, as follows,

| | | | |
|--------|------------------------|---|-----------------------|
| $1t_1$ | $0\ 2p$ | } | oxygen « lone pairs » |
| $5t_2$ | $0\ 2p, \text{Si } 3d$ | | |
| $1e$ | $0\ 2p, \text{Si } 3d$ | } | silicon-oxygen |
| $4t_2$ | $0\ 2p, \text{Si } 3p$ | | |
| $5a_1$ | $0\ 2p, \text{Si } 3s$ | } | σ bonds |
| $3t_2$ | $0\ 2s, \text{Si } 3p$ | | |
| $4a_1$ | $0\ 2s, \text{Si } 3s$ | | |

The least tightly bound electrons are in the oxygen lone-pair orbitals and it is their relaxation to an $0\ 1s$ core vacancy that gives rise to the main peak in the oxygen K_α spectrum (523-526 eV). The structure that is observed in this peak is due to the mutual interaction of the $1t_1$, $5t_2$ and $1e$ orbitals. It is also due to interaction between $\text{Si } 3d$ and $0\ 2p$ orbitals with the same irreducible representations. Experimental evidence that such interaction occurs is provided by the alignment of the peak at 94 eV in the $\text{Si } L$ spectrum with the $0\ K_\alpha$ shoulder at

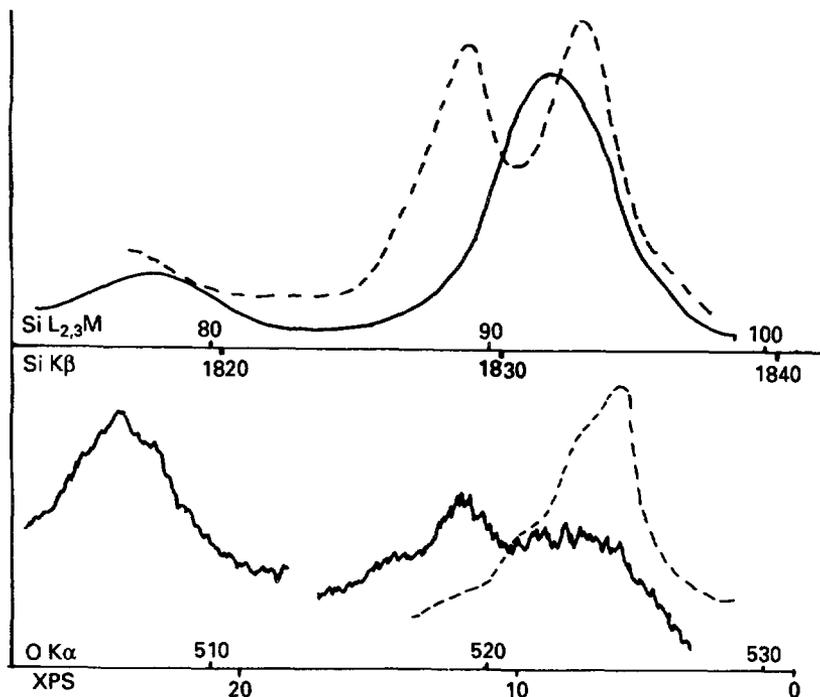


Fig. 2. — X-ray emission and X-ray photoelectron (XP) spectra for the silicate anion from magnesium silicate (forsterite). The top two spectra are Si K_{β} (solid line) and Si $L_{2,3}M$ (dashed line). The bottom spectra are the valence band XP spectrum (solid line) and the oxygen K_{α} spectrum.

523 eV. The presence of this peak in the Si L spectrum is a direct indication that silicon does use 3d orbitals in bond formation [19] in silicate. The next feature in the O K_{α} spectrum is a distinct shoulder at 521 eV which aligns with the main Si K_{β} peak at 1831 eV: both peaks correspond to a molecular orbital ionisation energy of 10 eV and thus reflect the atomic orbital composition of the $4t_2$ Si-O σ orbitals, silicon 3p and oxygen 2p (see table, above). The other Si-O σ bonding orbital is $5a_1$, generated by silicon 3s and oxygen 2p interaction. VXR evidence for this orbital is found at 12.5 eV, corresponding to an intense peak in the Si L spectrum at 89 eV (Si 3s character) and a relatively weak peak in O K_{α} at 519 eV (O 2p character).

The remaining peaks are associated with molecular orbitals that are mostly oxygen 2s in character. This is shown by the prominent peak in the XP spectrum at about 25 eV. Since this peak aligns with small peaks in both the Si K_{β} and Si L spectra, there must be some Si 3p and Si 3s character in these molecular orbitals.

4.3 LOW ENERGY SATELLITES. — The Si K_{β} and Si L peaks discussed in the last paragraph, above, that align with the ligand 2s orbitals and have an energy 14-15 eV less than the energy of the main peak are examples of a general phenomenon, that arises when covalent bonds are formed with first row elements. If the ligand atoms are fluorine then a satellite peak, of relatively low intensity, is observed with an energy about 20 eV less than that of the main peak. If the ligands are nitrogen then the satellite-main peak separation is about 12 eV and if the ligand atoms are carbon then the separation is reduced to some 8-10 eV. These separation energies are quite characteristic and can be used analytically [20] to identify ligand atoms. In

figure 1 the AlK_{β} peak is of this type and confirms that the overlayer on the aluminium sample is indeed alumina.

4.4 PEAK PROFILE - PEAK SHAPE. — Many examples have been reported in the literature of great changes in both the profile and shape of VXR peaks when the valency and/or bonding environment of the emitting atom is altered. Just two examples will be discussed here, sulphur K_{β} and silicon $L_{2,3}M$, but the conclusions are quite general.

Figure 3 shows a collection of sulphur VXR spectra [21, 22], in which the formal valency ranges from -2 to $+6$, and in which different ligand types are present. The simplest spectrum that of S^{2-} shows a single, if rather broad peak but when sulphur is bound to sulphur, as in S_2^{2-} in pyrite, a more complex peak profile is observed. This structure can be rationalized [23] as due to S 3p participation in S-S σ , π and π^* molecular orbitals. Even when bound in simple organic molecules there is quite a variation in peak shape. If sulphur is bound to two aliphatic groups then a main peak at 2467 eV and a prominent shoulder at 2464 eV can be clearly seen (Fig. 3c, cysteine). When bound to aromatic groups, however, as in dibenzothiophene (Fig. 3d) then the peak at 2467 eV is almost halved in intensity. Since the highest energy

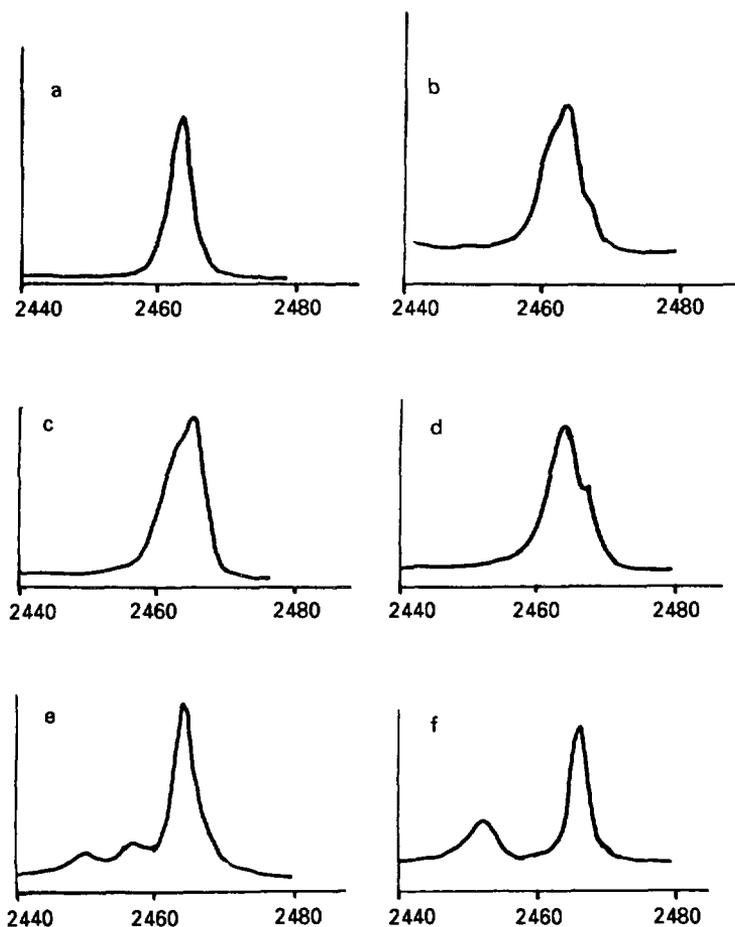


Fig. 3. — Sulphur K_{β} spectra from the following compounds: (a) lithium sulphide, (b) iron pyrite (FeS_2), (c) cysteine, (d) dibenzothiophene, (e) dimethyl sulphone, (f) sodium sulphate.

feature in an X-ray spectrum corresponds to the least tightly bound molecular orbital the 2 467 eV peak can be associated with the S 3p lone pair. When sulphur is bound to an aromatic system, delocalization of the lone pair becomes possible so that the intensity of the « lone pair » peak is reduced. The S K_{β} spectrum of sulphate (Fig. 3f) shows that the main peak is displaced to higher energies upon oxidation. The main peak shows no structure because of the highly symmetric shape of the anion. S 3p character is only present in degenerate t_2 orbitals (c.f. silicate above). A low energy satellite peak, S K_{β}' , can be seen at 2 452 eV, evidence of S 3p character in orbitals that are mostly 0 2s. A more complex spectrum is observed for dimethyl sulphone (Fig. 3e), not only is the main peak broader with evidence of some structure at 2 470 eV, but two low energy satellite peaks are present. This is because sulphur is forming covalent bonds to both carbon and oxygen.

A similar range of « chemical effects » can be found both in the K_{β} and $L_{2,3}M$ spectra of silicon in different chemical environments, even though there is no change in the formal valency. As the possibility of silicide formation at multilayer interfaces has been discussed extensively at this workshop, VXR Si $L_{2,3}M$ spectra from four different silicides are shown in figure 4. The differences in electronic structure are clearly reflected in the quite different spectra observed for the hemi-silicide of magnesium and the disilicides of molybdenum, titanium and barium. That the spectrum of barium disilicide is different from the others is probably due to the different physical structure, since this compound has discrete $[Si_4]^{4-}$ units rather than the layers of silicon atoms that are found in the other disilicides. In all cases it is probable that the structure observed in the spectra up to about 91 eV reflects Si 3s character and at higher energies, more Si 3d character, in the band structure of the sample.

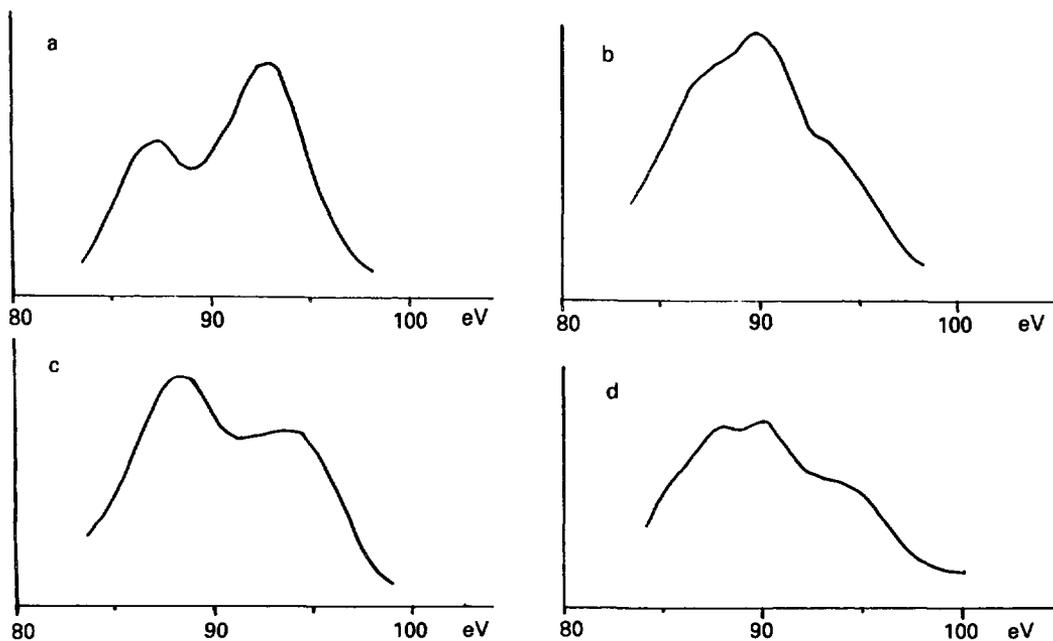


Fig. 4. — Silicon $L_{2,3}M$ spectra measured in the second order using an OVONYX 300 multilayer. (a) Mg_2Si , (b) $BaSi_2$, (c) $MoSi_2$ and (d) $TiSi_2$.

5. Conclusion.

Soft X-ray spectroscopy can now be carried out without recourse to expensive or delicate research equipment, slight modifications are all that is required. Being of low energy the

escape depths of soft X-rays are limited to a micron or less and so are ideal for nanometer analysis. If low energy electrons are used to initiate X-ray emission then it is possible to control the depth of analysis by varying the energy of the electron beam. The « chemical effects » that are so apparent in many soft X-ray spectra can be used advantageously to determine the chemical state of each element under analysis.

Acknowledgments.

The author is most grateful to his coworkers whose diligence, enthusiasm and hard work have produced many of the spectra and ideas discussed above : Bahanu Habulihaz, Sara Luck, Renate Horn, Emanuel Martins, John Purton and Phillip McClusky. Financial support, both for equipment and for bursaries, is gratefully acknowledged from : the European Commission (DG XII-BCR), the Royal Society, the Science and Engineering Research Council and the University of London Central Research Fund. It is also a pleasure to acknowledge collaboration which has assisted in this research programme from Philips Research, Nuclear & Silica Products and the Coal Board.

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