FINAL REPORT

on the IUVSTA Workshop on

X-Ray Photoelectron Spectroscopy: from Physics to Data

Organized under the auspeces of IUVSTA Surface Science Division on 26-30 April, 1999 Hortobágy, Hungary

Rapporteur: J.E. Castle

The workshop, similarly to the very successful previous IUVSTA Workshop on Auger Spectroscopy (Saint Pierre de Chartreuse, 1995) brought together experts in the field of X-Ray Photoelectron Spectroscopy (XPS) with the aim of reviewing and discussing recent developments and trends as well as perspectives for the future concerning the fundamentals and applications of the XPS method, from the point of view of the analytical use and reliability of the data obtained by surface analysis using XPS. The scientific field and scope of the Workshop falls within the area of activity of the Applied Surface Science Division of the IUVSTA. Attendance of the Workshop was ensured in the first instance by invitation and many of the best and most active scientists of the field participated in the meeting. The 45 participants of the Workshop were drawn from 16 countries (including 15 member countries of IUVSTA) of Europe, North-America, Asia and Australia.

The scientific programme of the meeting was developed by the Scientific and Program Committee, chaired by J.E. Castle and L. Kövér and including M.-G. Barthés, J.T. Grant, C.J. Powell, M.P. Seah, J. Végh and K. Yoshihara as members, while the Local Organizing Committee, with L. Kövér (Chairman), E. Bene, I. Cserny and J. Végh as members, was responsible for most local matters of organization and for ensuring appropriate conditions for the meeting. Registration, contracts for accommodation, meals and transportation were organized by the Roland Eötvös Physical Society.

The main objectives of the participants-scientists and analysis with interests ranging from the basic theory to practical applications of XPS-were to:

- improve the quality and accuracy of XPS analysis through utilization of available fundamental knowledge in physics
- identify inadequacies in present knowledge of phenomena or procedures that limit the accuracy of XPS analyses
- stimulate research to address present inadequacies

The structure of the scientific program based on sessions of 1,5h each including 17 invited reviews on special topics as well as extended and intense scientific debate and discussion in each session between the experts present. The sessions were moderated by selected experts of the particular topics. In addition to these sessions, two after dinner meeting were organized, a panel discussion on the impact of XPS on solving practical problems of industry, and a software demonstration. At the end of the meeting the closing summary of the technical content of the meeting was provided by Professor J.E. Castle acting as rapporteur (please, find the written version of the summary enclosed). Attached please find a copy of the scientific program of the Workshop and the list of participants. Although no proceedings of the Workshop will be published, a detailed Summary of the contributions and discussions is planned to be submitted for publication in the journal Surface and Interface Analysis, similarly to the previous AES Workshop.

The venue of the meeting was the Hotel Epona lying in the heart of the Hortobágy National Park (close to Debrecen), a boundless plain ("puszta") rich in natural resources, historical and etnographic traditions. A unique resort of Eastern Hungary, the four star hotel in the Epona Riding Village provided full comfort accommodating the delegates and ensuring a quiet place for the conference. A social occasion was also organized for the participants including a visit to the famous Rákóczi wine-cellar in Tokaj.

Debrecen, 24. 06. 1999.

Dr. László Kövér
Co-Chairman, Scientific and Program Committee
Chairman, Local Organizing Committee

Prof. James Castle
Co-Chairman, Scientific and Program Committee

Report of Workshop on XPS

Rapporteur: J.E.Castle

INTRODUCTION

In making this report the impressions and notes made of a very full week of discussion have been extensively abridged and suitably grouped with the intention of giving an overall impression of a week long activity. The report was timed to be given in a 30minute presentation immediately following the final scheduled talk and has not been modified in this written version which is a summary of the viewgraphs used in making the presentation. This report will be fully augmented in good time by the author's abridged versions of the papers delivered at the meeting.

PROGRESS IN RECOGNITION OF CHEMICAL STATE

a. a priori calculation of BE

Weightman first gave a review of the frozen orbital method. He showed that many approximations are now replaced by full calculation of e.g. the Dirac-Fock code. Calculations use determinants, instead of products, to mix the wave functions of appropriate orbitals, correlation effects are included by including the core hole in differing orbitals. Typical calculation for Ar gives BEs correct to 1% on ls, 4% on 2s, 25% on 3s. The differences arise from static relaxation effects, and correlation associated with dynamic relaxation – mobile holes. The error in calculation of BE is mirrored in calculation of transaction rates and hence intensities.

b. Density Functional Theory

Charlier showed exciting results for Cls calculation using the Density Functional Theory of Chong – a development of the unrestricted generalized transition state theory. This theory enables relaxation in free organic molecules to be introduced into the calculation by use of partial charge (2/3e) in ionised bonds. Free molecules give spectacular agreement with experimental values. Absolute average deviations between measured and calculated 0.11 eV are found for a set of 20 molecules. The method extended to adsorbed molecules (g aminotriethoxysilane) and to their reaction with H_2CO_3.

c. By use of valence band

Sherwood showed how X-ray excited valence band spectra gave unique finger print identification and that these could be supported by calculations. Monochromatic sources were of value to remove confusing influence of the a $_{34}$ peak.

Examples were:-

MnO_2 – strong '3d' contribution
MnO_3 – zero '3d' contribution
Water of crystallisation in sulphate and other similar compounds was recognisable
Differentiation of bicarbonate and carbonate
Differentiation of AlOOH and Al_2O_3

An example was given in which spectrum subtraction enabled Ti alcoxide to be observed at a buried interface.

d. By use of Auger Parameter

Moretti - reviewed the history and use of the Auger parameter and especially of the chemical state diagrams. This can be used to obtain the extra-atomic relaxation energy - well known final state. In a new contribution to the use of such diagrams he showed that if the data were charge-referenced before plotting then lines representing initial state effects could be drawn on the chemical state diagrams. This approach was illustrated by work in zeolytes.

e. By use of data base and library spectra

Crist, Gaarenstroom, and Powell each gave presentations illustration recent developments in the use of data bases.

PROGRESS IN INTERPRETATION OF THE ELECTRON TRANSPORT STEP

a. Powell reminded us that overlayer methods:-

1. give the EAL. (EAL $\simeq$ 30% < IMFP)
2. that IMFP can be obtained (Gergely) by reflection of primary beam.
3. by calculation from a combination of optical and momentum transfer properties: currently, calculated against measured, deviated by @ 15%.
4. By use of TPP2M. Comparisons suggest that calculation matched data well if valence electrons plus core electrons excluding all 4f electrons and those with energy less than 14eV are assumed to contribute to N_v

a. Jablonski considered that uncertainties in IMFP are less than uncertainties in EAL. Discussed the introduction of elastic scattering effects into XPS formation v DDF. In principle rather large corrections should be made to observed intensity at high angles (to surface normal). In practice the attenuation of intensity at these angles is so high that they are not used.

SIMULATION OF SPECTRUM BACKGROUND

a. Tougaard showed how surface morphology could be deduced from a fitting match which included both peak area and background shape. This was now available in QUASES.
A 3-parameter universal curve was now used for Al Si and C-polymer cases. He showed that background shape was primarily established over 0-5 IMFP ranges (3 parameters) and complete over 0-8.

A comparison of calculation with known structure of Au/Ni sandwiches showed that determination of thickness of a buried layer to within a 15% error.

b. Werner described background functions generated by 'in'fold scattering. The PIA model generated required input of a set of material parameters but then gave a good agreement to background and peak structure – this gives a good understanding of emission processes – thermal to relativistic. The method warrants acquisition of data from routine samples and is in support of the Tougaard background shape.

STRUCTURAL INFORMATION

a. Cumpson – described a new spreadsheet approach to obtaining information from a range of algorithms. In particular he emphasised how the lack of phase information in XPS spectra minimised the amount of real information on structure that was actually available from ARPES. Structure models were therefore limited to 3 parameters with any precision. It followed that it was important to:

- use additional information
- use background as well as peak
- be wary of sharp interfaces

a. Bonzel discussed the current state of XP Diffraction. The strong point was that atom specific intensities are available and this differentiated the technique from conventional diffraction. Molecular orientation, bond angles, local order, site occupancy were all available and long-range order was not required.
b. Fadley - then dealt with Fourier transformation of diffracted intensity. 3D models almost available from this work and the advent of still more intensity from new beam lines will increase the practicality of this holographic method. Sample damage is likely to become the limiting factor.

It was noted that these two methodologies included the phase information that Cumpson had indicated to be absent from conventional XPS.

INSTRUMENTAL DEVELOPMENTS

a. Gelius gave a historic review - current imaging techniques compared, using Scienta, Ultra, and ESCASCOPE as examples. Energy resolution improved from 5eV (1960) to 9 meV (1998). (150 meV/ year). This represented a 10^5 improvement of current instruments against that described in the 1st ESCA book.
b. Kawai described the new technique of Total Reflection XPS
c. Cumpson introduced the new IS0 Calibration Standard (Draft) on energy calibration of spectrometer to 0.1 eV and recommended that a control chart should be maintained.

Cu Ag Au C can all be used as standards.
Standardised instruments should feature:

- Intensity Calibration
- Traceable response function
- Estimate of reproducibility
- Diagnosis of internal scattering
- Correct peak ratios

ELECTROSTATIC CHARGING

Pireaux introduced a paper by Cazaux

Key recommendation:
Flood gun defocussed and in the range 0.1-2.0 keV and 0.1-10 m A
Good compensation when potential overlaps secondary electron cascade of 'Auger' flood gun.
Surface charge is trapped at defects. De-trap with heat on UV lamp.
Thin samples have high field and hole current compensates surface charge.
Negative charging can occur in this samples by photoemission from sample holder.
ARPES and rough surfaces may give inhomogenous charging.
The flood gun can have an influence on peak ratios.

THE FUTURE

a. Margaritondo described work now commencing at ELETTRA

   This facility gives 20 nm resolution and XPS (!) examination of:
   nanophases; m m cross sections; band-bending; and inhomogenities in junctions
   is now possible. Many examples were given, especially dealing with human cell biochemistry.
   XPD from 1 m m objects and diffraction rings from nano objects were shown.

b. Fadley described work on the advanced Light Source (ALS)

   The Future developments could be summarised by the slogan:
   "100x faster at 20x smaller"