

ON THE IMPORTANCE OF PHOTOCONDUCTION IN ESCA EXPERIMENTS

H GONSKA, H J FREUND and G HOHLNEICHER

Lehrstuhl für Theoretische Chemie der Universität zu Köln, Köln (W Germany)

(Received 25 April 1977)

ABSTRACT

With a specially designed experiment it is shown that the absence of charging often observed with materials of low specific conductivity is due to photoconduction. These results lead to a preparation technique which reduces charging to an almost negligible extent.

INTRODUCTION

In a preceding paper¹ we discussed a method which is of great help if one wants to detect whether or not a solid sample in an XPS experiment is charged. This method is based on the measurement of line positions as a function of the angle θ , defined as the angle between the normal to the sample surface and the direction of the analyser (Fig. 1). While practising this method, which we call RDOLP (rotational dependence of line position), we found that most organic and even many inorganic materials are

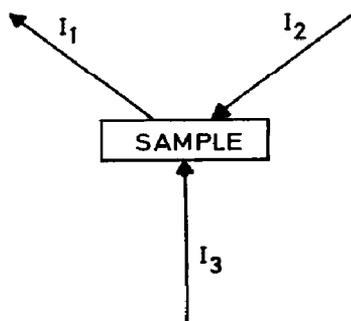
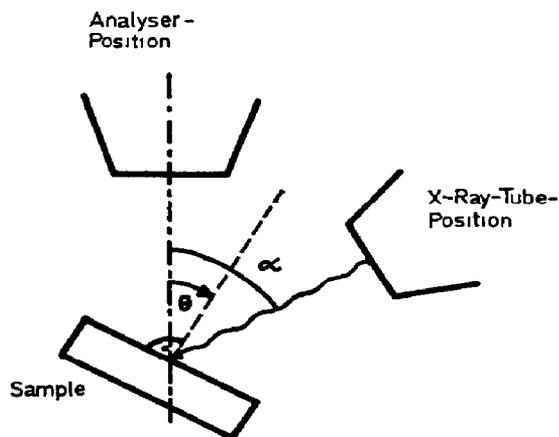


Figure 1 Schematic drawing of the experimental set-up and definition of the rotation angle θ

Figure 2 Definition of the currents I_1 , I_2 , I_3

charged less than 0.1 V if the sample is prepared as follows. A metallic sample holder with a circular cavity of 8 mm diameter and 1 mm depth is used. The powdered sample is filled into the cavity and slightly pressed down. If necessary, a small amount of solvent is used to obtain sufficient solidification. The metallic surface of the sample holder outside the cavity is kept thoroughly clean. When such a sample is located at the measuring position the whole sample surface and also some part of the surrounding metal is illuminated by the X-ray beam (illuminated area about 12 mm diameter in the Leybold-Heraeus LHS 10 instrument).

In this paper we shall show that the absence of charging widely observed for this type of sample is mainly the result of photoconduction. Photoconduction has always been considered as one of the most important discharging mechanisms²⁻¹⁰ but until now only a few papers have dealt with this subject in detail^{2, 3} and the results obtained are contradictory. We shall also discuss some further well known aspects of charging in connection with photoconduction.

BASIC CONSIDERATIONS

Today it is generally accepted that the surface potential of a non-conducting sample in an ESCA experiment is determined by three different currents¹¹ (Fig. 2), I_1 arising from photoelectrons leaving the sample, I_2 resulting mainly from secondary electrons coming to the sample surface from different sources, and I_3 representing a possible flow of charge between the sample surface and sample holder. If I_3 is too small to compensate any deficiency of charge at the sample surface, the potential of the surface may be different from the potential of the sample holder.

Following the work of Ascarelli and Missoni², we know that for isolated metallic samples a current I_3 of ca. 10^{-7} A is necessary to establish the equilibrium between sample surface and sample holder. Taking into account the lower emission rate of non-metallic samples, we come to the following estimation. For a sample thicker than 0.1 mm and a charging potential of less than 10 V, the contribution of bulk conductivity to I_3 is not sufficient to establish the equilibrium between sample surface and sample holder if the specific conductivity of the sample material is smaller than 10^{-12} cm⁻¹ Ω⁻¹. Such values are, however, not unusual. Most of the organic and inorganic materials we usually call "insulators" have specific conductivities lower than 10^{-12} cm⁻¹ Ω⁻¹.

From the fact that many of these materials remain uncharged under the experimental conditions described above, we have to conclude that other contributions to I_3 must be important. As mentioned above photoconduction has often been considered as a possible contribution to I_3 , but experimental results concerning this subject are very few and also contradictory. Ebel and Ebel³, for example, state that they have directly measured the current between two electrodes mounted on a glass surface under X-ray irradiation as a function of X-ray intensity. They quote a value which is of the order of 10^{-9} A under the X-ray conditions usual for an ESCA experi-

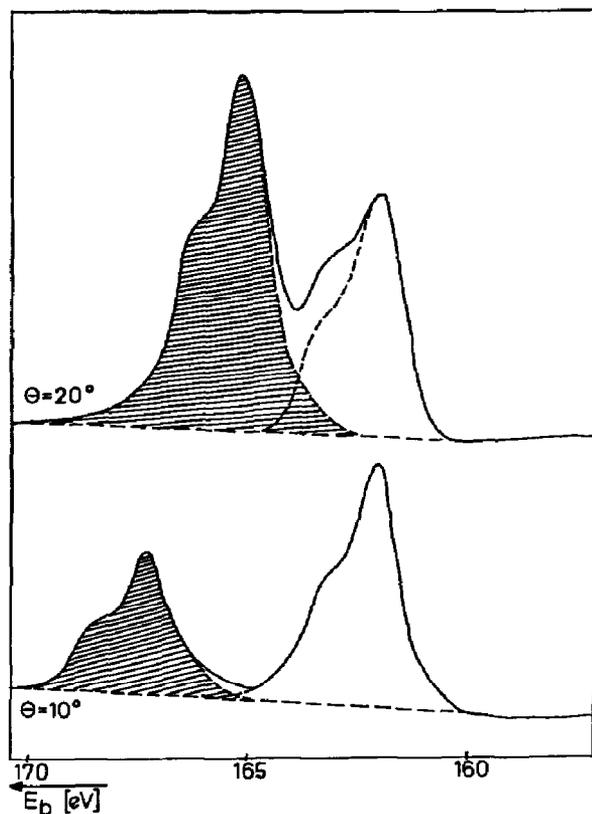
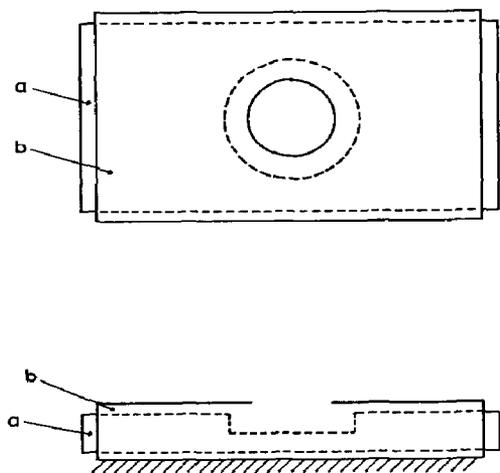


Figure 3 Sample holder with cavity and shielding (a) Sample holder, (b) copper foil

Figure 4 Spectra obtained from a shielded (o d 4.4 mm) S_8 sample. Shaded area S_8 $S2p_{3/2, 1/2}$ lines. Unshaded area CuS $S2p_{3/2, 1/2}$ lines.

ment. In contrast to this, Ascarelli and Missoni² have reported results gained with a special experimental set-up, in which a symmetrical potential of ± 20 V is applied parallel to the surface. Owing to the fact that in this experiment the applied potential had hardly any effect on the observed PE lines, Ascarelli and Missoni concluded that photoconduction does not make a significant contribution to the setting of the surface potential.

To obtain a better insight of the importance of photoconduction, we designed the experiment described in the next section.

EXPERIMENTAL SET-UP AND RESULTS

If photoconduction is responsible for the discharging of a given sample, charging should be observed only if the inner area of the sample surface is illuminated—and not the sample-metal interface. We therefore investigated samples of the following type (Fig. 3). A shield made from copper foil was mounted about 1 mm above the sample holder. Two shields with holes of 6 mm and 4.4 mm diameter,

respectively, were used. With this set-up, only the inner part of the sample surface was irradiated by X-rays.

As a testing material we used sulphur (S_8) for two reasons: firstly sulphur is known to be a very good insulator ($\sigma = 10^{-18} \text{ cm}^{-1} \Omega^{-1}$) for which bulk conductivity can be neglected without doubt. Secondly, sulphur slowly evaporates in the high vacuum of the sample chamber forming thin layers of sulphide on the surrounding metal surfaces, especially on the copper shield. As the copper shield was in electrical contact with the sample rod to avoid disturbance of outgoing electrons the $S2p$ signal of CuS provided us with a non-rotational dependent standard.

In Fig. 4 spectra obtained from one of the shielded samples are shown as an example. The line positions have been evaluated from the measured spectra using either a DuPont curve resolver or a numerical deconvolution programme¹². In Fig. 5 the line positions are plotted as a function of the rotation angle θ . If the whole sample surface and the metallic surrounding is illuminated by the X-ray beam as in the unshielded sample, the line positions are completely independent of θ , showing that the sample surface is uncharged, within the limits of experimental error. In the same way the $S2p$ lines of the copper sulphide formed on the surface of the shield do not show any θ dependence. However, for the shielded samples the $2p$ lines of the sulphur itself show well resolved RDOLPs. Contrary to the fact that charging has been found¹ to be always positive for unshielded samples in the region $-20^\circ \leq \theta \leq 50^\circ$ the shielded samples show negative charging for $\theta \geq 15^\circ$ and $\theta \geq 25^\circ$, respectively. The maximum shift to higher binding energies is larger for the sample with the small hole (4 mm o.d.) than for the sample with the larger hole. For $\theta = -10^\circ$ the electrons emitted from the sample with the larger hole show the same kinetic energy as those emitted from the unshielded sample. At about this angle the inclined incidence of the beam leads to an illumination of the metal-sample interface.

DISCUSSION

The experiment described here clearly shows the importance of photoconduction as a decharging mechanism. If the illuminated part of the sample surface is completely separated from the sample-metal interface by an unilluminated zone, charging is observed for a sample like sulphur. Only if at least parts of the sample metal interface are illuminated does charging diminish.

The experimental results also show that, even under irradiation, there is no conduction through the bulk for a sample of such a low conductivity if the thickness of the sample is of the order of 1 mm. This is to be expected since it is known that the penetration depth is only a few μm for Al or Mg $K\alpha$ radiation. The unimportance of bulk conductivity and also of normal surface conductivity, which might have been considered as another possible contribution to I_3 , is confirmed by the influence of the different shieldings.

As has been seen, the amplitude of the RDOLP curve, which is a rough

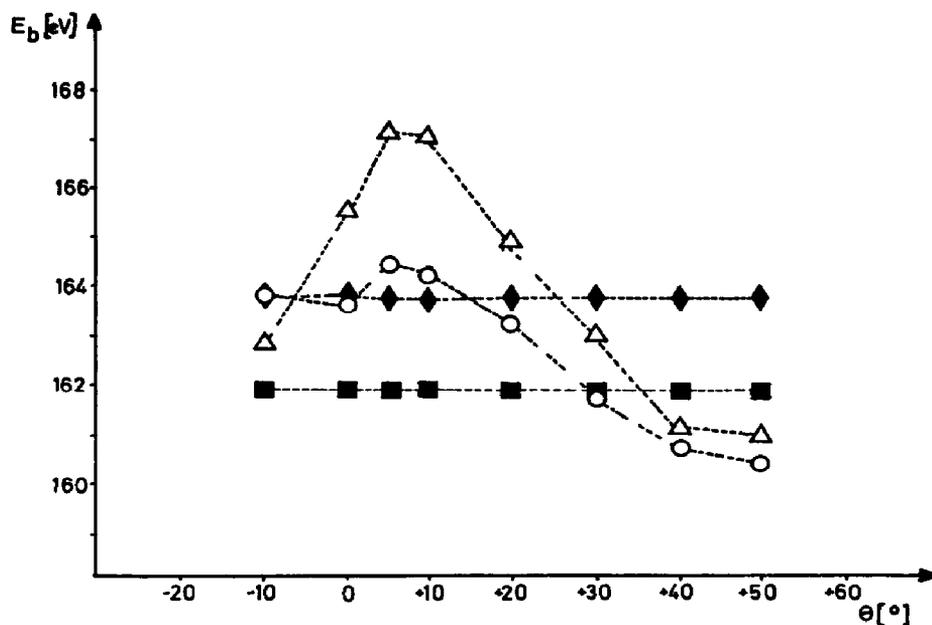


Figure 5 Dependence of line position on the rotation angle θ (■) CuS $S2p_{3/2}$, (◆) S_8 $S2p_{3/2}$, (△) S_8 with Cu shielding (o d 4.4 mm) $2p_{3/2}$, (○) S_8 with Cu shielding (o d 6 mm) $2p_{3/2}$

measure for the absolute amount of positive charging¹, is larger the smaller the hole in the shielding is. This is due to the interference of I_1 and I_2 . For the shielded samples the main source of secondary electrons is the metallic shielding itself which is partly irradiated by the X-rays. If for a fixed angle θ the hole gets smaller, the penetration of the charging potential to the space outside the shielding where the secondary electrons are created becomes smaller and, therefore, I_2 becomes smaller as well. If the other possible sources of charge flow to the surface, like bulk conductivity or surface conductivity, through the unilluminated surface are negligible, a smaller I_2 must lead to larger positive charging. This is in accordance with the fact that the RDOLP curve of the shielded sample with the smaller hole lies at higher binding energies than the curve of the sample with the larger hole in the shielding (see Fig. 5). This is true for all angles θ except $\theta = -10^\circ$ when the metal-sample interface is illuminated.

The change from positive to negative charging already mentioned can also be explained by taking into account the θ dependence of the ratio I_2/I_1 . θ angles of 40° and 50° lead to an increasing illuminated area of the shielding and simultaneously to a decreasing illumination of the sample itself. This is due to the geometrical conditions of the spectrometer. As a consequence, the ratio I_2/I_1 becomes greater with increasing θ and at an angle θ' , determined by the geometry of the sample, charging becomes negative. These results also throw some light on problems which may occur in connection with flood-guns. The metallic shielding with its high emission rate for secondary electrons may be compared to the effect of a flood-gun. Under such conditions,

negative charging may be observed and hence it is not always possible to correlate the lowest binding energy obtained with the uncharged sample, as it is sometimes done while using a flood-gun

The results of our experiment which prove the importance of photoconduction for discharging also lead to a better understanding of some other observations made in connection with charging

(i) It is well known that charging mainly depends on sample preparation and, especially, on the size of the sample. This is not surprising if conduction is restricted to the illuminated region of the surface

(ii) Little line-broadening arising from differential charging is usually observed with charged samples. Differential charging is important only for very particular sample materials, where the sample is prepared in a special way^{1,3}. From this, one can deduce that in most cases the potential is quite homogeneous within the illuminated surface area*. However, with the Hewlett-Packard instrument, insulators can hardly be measured without the use of a flood-gun. In this instrument a monochromator is used and the integrated X-ray flux is strongly reduced owing to the elimination of bremsstrahlung^{1,4}.

(iii) Some authors have reported that charging can be reduced or avoided if the sample is illuminated by visible or near-UV light^{8-10, 15}. This is an additional hint to the importance of photoconduction. However, from our experience we would expect that the influence of a second light source should only be observed if the interface between sample surface and grounded metallic sample holder is not illuminated by the X-ray beam

(iv) It is well known that thin films prepared on a metallic sample holder by evaporation or from solution show less charging than thicker samples. In most cases such a method of preparation leads to small islands and we believe that it is mainly the good contact between the surface of these islands and the metal of the sample holder which is responsible for the reduction of charging

CONCLUSIONS

For sulphur and many other materials photoconduction is strong enough under X-ray irradiation to prevent samples from being charged. In order to apply these results to the measurement of insulating samples by XPS one has to ensure that the surface-area of the sample from which the measured electrons are emitted and the sample-metal interface are in good mechanical contact and illuminated by the X-ray beam. From our experience only very few materials like, for example, MgO or LiF, show charging if samples are prepared in this manner

* A detailed discussion of the currents involved in the setting of the surface potential will be given in "Berichte der Bunsengesellschaft"

ACKNOWLEDGEMENTS

We thank the Deutsche Forschungsgemeinschaft for financial support. One of us (H-J F) thanks the Studienstiftung des Deutschen Volkes for a fellowship.

REFERENCES

- 1 H-J Freund, H Gonska, H Lohneiss and G Hohlneicher, *J Electron Spectrosc Relat Phenom*, 12 (1977) 425
- 2 P Ascarelli and G Missoni, in R Caudano and J Verbist (Eds), *Electron Spectroscopy*, Elsevier, Amsterdam, 1974
- 3 M F Ebel and H Ebel, *J Electron Spectrosc Relat Phenom*, 3 (1974) 169
- 4 J P Contour and G Mouvier, *Chem Phys Lett*, 33 (1975) 237
- 5 G Johansson et al, *J Electron Spectrosc Relat Phenom*, 2 (1973) 295
- 6 K Siegbahn et al, *Nova Acta Regiae Soc Sci Ups Ser IV*, Vol 20 (1967)
- 7 C K Jorgensen and H Berthou, *Chem Phys Lett*, 31 (1975) 416
- 8 F I Vilesov et al, *Fiz Tverd Tela*, 5 (1963) 2000, *Gov Phys Sol State*, 5 (1964) 1460
- 9 J W Amy, M Kelly, W E Baitinger and A Melera, private communication, 1972
- 10 B H Schechtman and W E Spicer, *Chem Phys Lett*, 2 (1968) 207
- 11 O Hachenberg and W Brauer, *Adv Electron Electron Phys*, 9 (1959) 413
- 12 W Frolich, Diplomarbeit, Koln, 1976
- 13 T Dickinson, A F Povey and P M A Sherwood, *J Electron Spectrosc Relat Phenom*, 2 (1973) 441
- 14 K Siegbahn et al, *ESCA, Applied to Free Molecules*, North-Holland, Amsterdam, 1969
- 15 E E Koch and W D Grobman, to be published