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by

W. Eberhardt, G. Kalkoffen and C. Kunz
II. Institut für Experimentalphysik der Universität Hamburg
and
Deutsches Elektronen-Synchrotron DESY, Hamburg

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W. Eberhardt[+], G. Kalkoffen and C. Kunz

II. Institut für Experimentalphysik, Universität Hamburg
D-2000 Hamburg 50, Germany

and

Deutsches Elektronen-Synchrotron DESY, D-2000 Hamburg 52,
Germany

We observe a drastic broadening of the photoemission lines of the 2p core levels of Al when the surface sensitivity of the measurement is enhanced by an appropriate choice of the photon energy using synchrotron radiation. This surface broadening appears to be quite universal and occurs also for other substance like e.g. Au. Its possible origin is discussed. There is no surface induced shift of the Al 2p binding energy within ± 40 meV.

The electronic properties of solid surfaces are of considerable current interest. Research is not only concerned with the changes of the electronic states upon adsorption and during catalytic reactions but it is also concerned with the properties of clean surfaces. Surface states have been observed for many materials, but until today there are open questions concerning the changes of the bulk electronic states at the surface[1-3].

For semiconductors, as for example Si, several theoretical calculations are concerned with the electronic structure at the surface[4-6] and especially with surface states. All these calculations, however, deal with the valence band region and give no information about the core levels of an atom at the surface. For metals there is only scarce theoretical information available[7-9].

We have obtained photoemission spectra of the 2p core levels of Al and Si and the 4f levels of Au with a previously not yet reached overall resolution showing differences in the emission from bulk and surface atoms. The investigations were carried out using the synchrotron radiation of the storage ring DORIS monochromatized by the FLIPPER monochromator[10]. The electron analyzer, a double pass CMA, was operated at a pass energy of 3.5 eV thus having a resolution of 70 meV as verified by photoemission spectra of gases.

When atoms are put together to form a solid the wavefunctions of the outermost, namely the valence electrons, are more or less drastically changed. The tightly bound core electrons are atomic-like but nevertheless they are affected by these changes. These changes show up clearly in the different absorption spectra of gaseous and solid samples. While in the $L_{2,3}$ absorption spectrum of Al vapour a line width of 50 meV is observed[11] the $L_{2,3}$ edge measured at 4 K in transmission with films evaporated in UHV has a width of about 100 meV[10].

Transmission measurements give bulk properties whereas photoemission is a surface sensitive technique. In photoemission in general the information is restricted to the outermost layers of the solid due to the small escape depth of the unscattered photoelectrons. This surface sensitivity of the signal can be enhanced by varying the selected kinetic energy of the photoelectrons. An electron with an energy of 5 eV (40 eV) with respect to the Fermi level has an escape depth L of about 25 Å (4 Å) (see also Fig. 2). Thus the surface atoms contribute up to 50 % to the observed signal if photoelectrons around 40 eV are selected. Figure 1 shows in an energy distribution curve (EDC) the Al 2p levels taken at a photon energy of 78.7 eV (resolution: $\Delta h\nu$ = 32 meV) yielding a kinetic energy of about 1.5 eV relative to the vacuum level. The sample was an Al-single crystal with a (100) surface cleaned by ion-bombardment and subsequent annealing. The main contribution in this spectrum originates from bulk Al atoms. The two lines are superimposed on the background of the secondaries but are clearly resolved and separated.

Figure 1 also shows an EDC from the same sample with the photon energy changed to 117.5 eV (resolution: Δh = 64 meV) yielding a kinetic energy of about 40 eV relative to the vacuum level. Here the signal has a very high contribution (about 50 %) from atoms immediately at the surface and the two lines are significantly broadened. This broadening is much larger than the slight increase in the band pass of the monochromator. Figure 2 shows the measured full width at half maximum (FWHM) of the Al 2p 3/2 level taken with evaporated samples which give the same result as obtained from a single crystal surface. The quadratically resolution corrected value of Citrin et al.[12] obtained with Al K_α radiation is included. For our own results the corrections are small and do not affect the general behaviour of the data. The escape depth of the photoelectron is shown in Fig. 2. From the correlation between the escape depth and the width of the peaks we conclude that the broadening is a surface effect.

How can this effect be understood? From a simple argument rather a smaller width of the core levels at surface atoms would be expected since the coordination number at the

surface is lower than in the volume. For the Cu d-bands such a behaviour was observed[1]. In the following we shall discuss possible explanations for this broadening of the lines with increasing kinetic energy and surface sensitivity.

(a) The binding energy as measured in photoemission may change for the 2p levels of a surface atom with respect to the bulk atom value. Such a behaviour has been reported for the 2p levels of Ni, Ti and Cr[2]. Such a change, if it is small enough so that it is not resolved, would cause the linewidth to increase when the surface atom contribution to the signal is increased. But simultaneously the center of gravity of the line must shift. In our experiment we did not observe a shift of the binding energy with increasing photon energy (within an error of ± 40 meV for the (100) and (110) surfaces).

(b) The lifetime of the 2p hole at the surface may be shorter than in the volume and thus increase the width of the core levels. The lifetime is mainly determined by the LVV Auger process which is calculated[13] to contribute 20 meV to the observed bulk level width. This value is at least not in contradiction with experimental results but it is too small to explain the increase of roughly 100 meV to 200 meV at the surface. We mention however, that recently Hertel and Pfuff[14] have calculated a considerable increase of the Auger width at the surface of Al.

(c) The relaxation of the electron gas may change at the surface. Simultaneously with the excitation of the photoelectron many electron hole pairs with infinitesimally small excitation energies are created[15]. This many-body effect causes the photoemission lines to have an asymmetric tail at the high binding energy side. The theoretical line shape profile of such a distorted line is given by Doniach and Sunjic[16], but until today no theoretical predictions for surface atoms are available. The changes observed here, however, manifest themselves mainly in the linewidth and not so much in the asymmetry. Further, we have observed[3] a similar broadening for the Si 2p emission where such a manybody mechanism is not possible.

(d) The just mentioned many-body effects are influenced by the switch-on time of the hole potential[17]. When the photoelectron is excited with high energy photons the hole potential is switched on suddenly and the many-body effects are very pronounced. Whereas, at threshold the potential is switched on rather adiabatically and much less electron hole pairs are created at the Fermi level causing the asymmetry of the lines to be smaller. This effect is valid for bulk atoms as well as for atoms at the surface and is predicted by theory[17] but has not yet been observed in experiments. A detailed analysis of the Al data with a computer fit program decomposing the increase in level width and asymmetry of the lines[18] revealed an only small increase of the asymmetry parameter with excitation energy whose significance appears to be marginal. The whole effect would be in contradiction with the back bending of the curve in Fig. 2 for high kinetic energies.

(e) A broadening of the Al 2p photoemission lines after oxidation[19] has been reported. We have investigated the oxidation of Al single crystals with (100) and (110) surfaces with a much better resolution and did not observed such a broadening of the original Al 2p lines[20].

(f) Phonon coupling may change for a surface atom. The phonon contribution to the linewidth has been calculated by Flynn[21] including the recoil due to the outgoing photoelectron. The recoil effect is neglegible at least for the energies in our experiment. The phonon broadening depends on the sample temperature and some averaged phonon energy which has a value of 20 meV to 30 meV for the bulk[22]. The surface phonons should have smaller energies as can be derived from a simple force constants model and therefore should give a smaller contribution to the observed linewidth. We have measured the temperature dependence of the linewidth[18] and can show that the increase in linewidth indeed is smaller with higher surface sensitivity. Thus we rule out that the surface induced broadening is due to a different phonon contribution.

(g) Finally we want discuss crystal field splitting of the 2p levels of a surface atom. We have calculated the shift and splitting of the 2p levels on an Al atom in a homogeneous electric field (Stark-effect) by applying second order perturbation theory. The polarization of the 2p levels in the field is described by an admixture mainly of the localized 2s states. Thus the atomic picture ought to be a fairly good approximation for an atom at the crystal surface. All other contributions are at least one order of magnitude smaller. In order to get an idea about the electric field at the position of a surface atom we have taken the geometry of the (100) surface and calculated the normal component which is due to the 4 nearest neighbours of the surface atom in the plane below the surface and due to the electrons outside the surface plane. These calculations are described in detail elsewhere[13]. Here we give only the result that the 2p 3/2 level has a splitting of 65 meV in this field. This value is of the right order of magnitude to explain the observed broadening. There are, however, open questions with respect to the effective charges which we used in order to calculate the field.

The change of the level width at the surface is also detectable by measuring the partial yield in the region of the $L_{2,3}$ absorption edge of the samples. The total yield of electrons is proportional to the absorption[23] of the samples. The Al 2p holes decay via an LVV Auger transition producing electrons with a kinetic energy around 65 eV. By collecting only these energetic primary Auger electrons the absorption near the surface is obtained (see the mean free path curve Fig. 2). On the other hand, the slow secondaries give the absorption of the bulk atoms. These partial yield spectra are shown in Fig. 3. At 77 K the width of the L_2 (L_3) edges changes from 120 meV (115 meV) to 200 meV (190 meV) which is comparabel to the values from the EDC's.

Additionally we show spectra of the Au 4f levels taken at different photon energies at SSRP[24] and DESY with the same resolution in both cases (Fig.4). The Au 4f lines show again the same broadening effect as the Al 2p lines. Moreover, these spectra confirm the back-bending of the curve in Fig. 2 at higher photon energies. The Au 4f level emission has a low cross section near its onset and therefore we were not able to follow these peaks down to threshold as with Al. Baer et al.[25] recently also found a broadened surface contribution to the Au 4f lines with XPS.

We here have demonstrated that the 2p core levels of Al and the 4f levels of Au are broadening when they are localized at surface atoms. Model calculations indicate that this effect could well be ascribed to a crystal field splitting of the hole states in the strong fields near the metal surfaces. Therefore it should be observable also for other metals. We note however that quite unexpectedly no shift in the core hole binding energy within ± 40 meV is observed when the 2p holes are located at the surface atoms in Al.

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[+] Now at Dept. of Physics, University of Pennsylvania, Philadelphia, PA 19104, USA

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Figure Captions

Fig. 1: Photoemission spectra of the Al 2p 1/2, 3/2 core levels taken at two different photon energies: at 78.7 eV (excitation from bulk atoms) the spin orbit splitted lines are clearly resolved, at 117.5eV (excitation from atoms near the surface) the lines show a broadening. Each curve is superimposed on a background of secondaries.

Fig. 2: FWHM of the Al $2p_{3/2}$ level from evaporated samples for different excitation energies. The values corrected for the resolution of the monochromator and the analyzer show the same behaviour. The high energy value is taken from Citrin et al.[12]. The dashed line indicates the mean free path curve of the photoelectrons.

Fig. 3: Partial yield spectra of the $L_{2,3}$ edges at 77K for different surface sensitivities obtained by selecting different kinetic energies E_f relative to the vacuum level.

Fig. 4: Au 4f core level spectra at different photon energies at SSRP[24] and DESY.

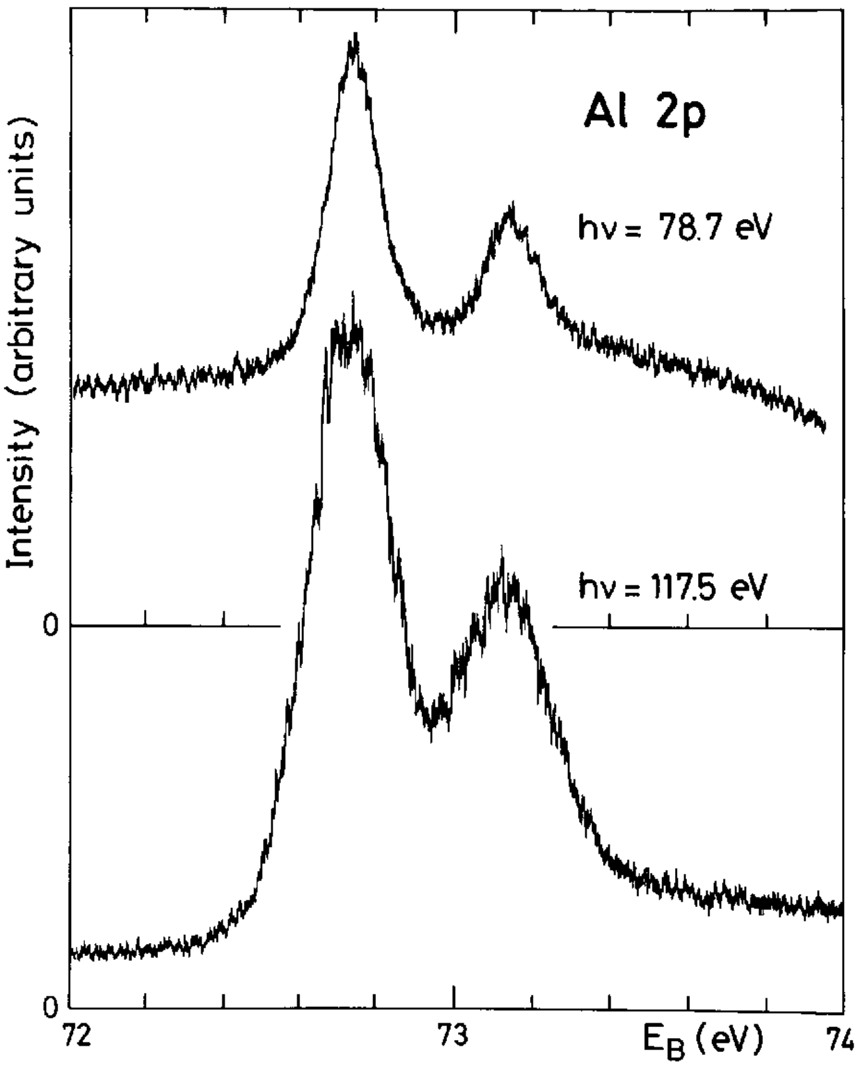

Fig. 1

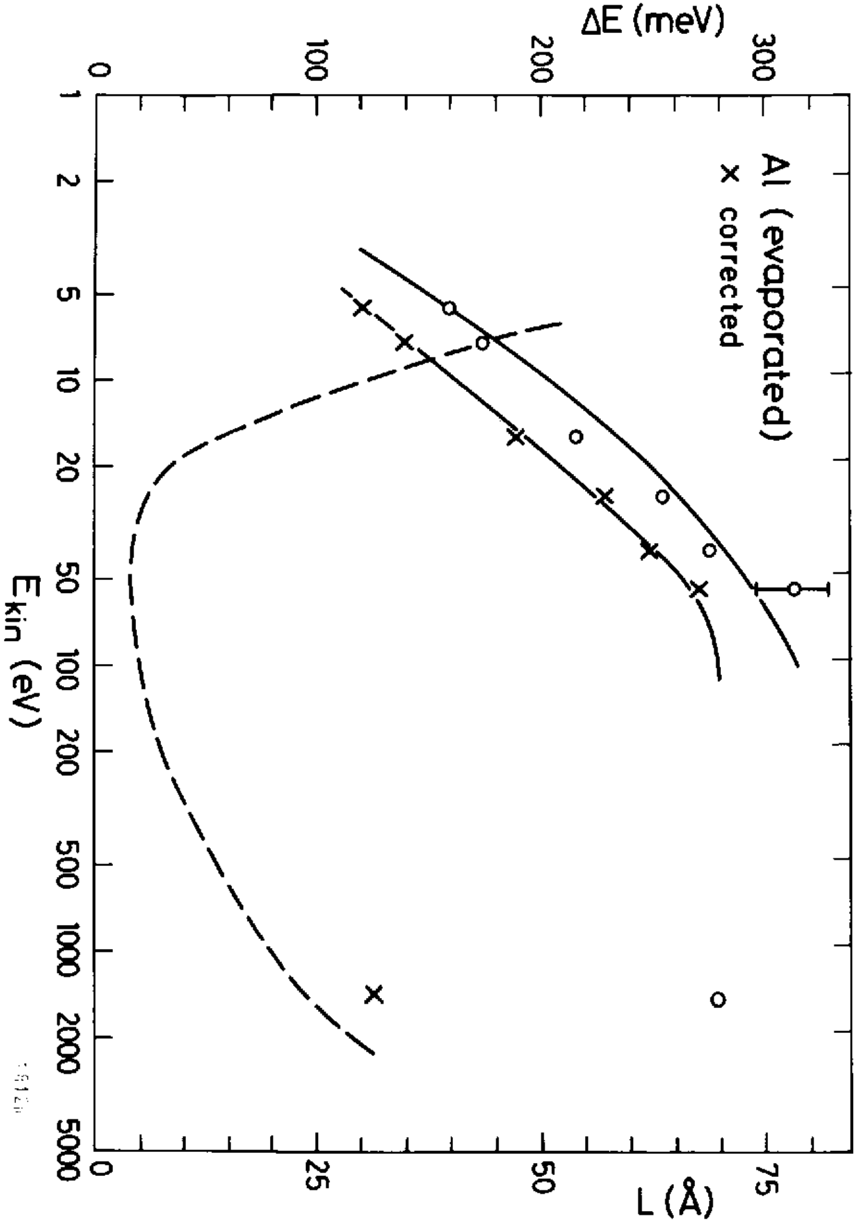
Al (evaporated)
× corrected
ΔE (meV)
0
100
200
300
L (Å)
0
25
50
75
E_kin (eV)
1
2
5
10
20
50
100
200
500
1000
2000
5000
18126

Fig. 2

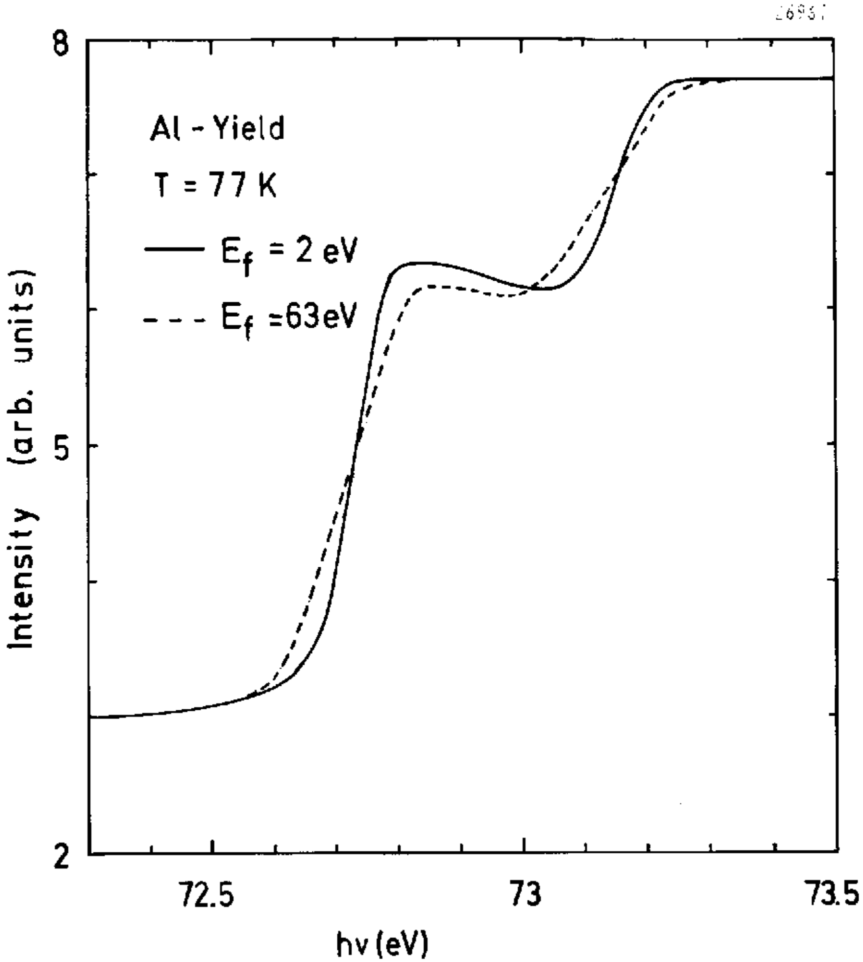
26937
Al - Yield
T = 77 K
E_f = 2 eV
E_f = 63eV
Intensity (arb. units)
2
5
8
72.5
73
73.5
hν (eV)

Fig. 3

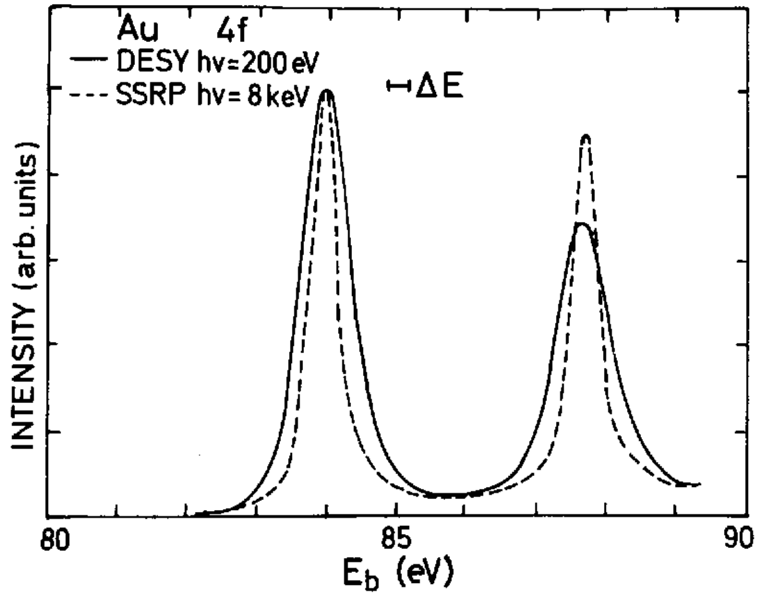
Au 4f
DESY hν=200 eV
SSRP hν=8 keV
ΔE
INTENSITY (arb. units)
80
85
90
E_b (eV)

Fig. 4