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ELECTRON CORRELATION EFFECTS
IN THE UPS VALENCE BAND SPECTRA OF Au AND Ag

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Electron Correlation Effects in the UPS Valence Band Spectra of Au and Ag

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Modulations of the relative peak heights of the d band maxima previously observed in UPS spectra of Au and Ag are shown to correspond to the thresholds of excitations from inner levels with equal principal quantum number. Contrary to earlier proposed interpretations the correspondence leads to an explanation of the modulations as an effect of atomic electron correlation interaction.

In a previous publication from 1976 Lindau et al. reported on their photoemission measurements on polycrystalline gold films in the energy range 30 - 300 eV[1]. As one result they showed that an unexpected modulation of the relative amplitudes of the two maxima in the valence band occurs for photon energies between 100 eV and 200 eV. The authors had no really satisfactory explanation for this effect[1]. It was held most likely that differences in the energy dependence of the photoionization cross-sections for the two spin orbit components, $5d_{5/2}$ and $5d_{3/2}$, are responsible for the observed modulation. In a later publication Stöhr et al. took up this discussion on the basis of their angle resolved photoemission measurements of the Au valence band[2]. Since they found a similar effect only for the $[111]$ surface but not for the $[001]$ surface, they excluded the explanation of Lindau et al. concluding that band structure induced cross-section effects in connection with a preferential orientation of the crystallites in evaporated Au films might have been responsible for the above mentioned effect[2].

It is the objective of this paper to show that a by far more satisfactory interpretation of the observed amplitude modulation is achieved, if it is considered in connection with older measurements of Freeouf et al. in the energy range below 100 eV[3]. The result is that the modulation is caused by electron correlations in the different O-subshells (i.e. 5s, 5p and 5d) of the atom. This is supported by a reinterpretation of a similar effect observed for Ag[4] leading to a corresponding result.

Freeouf et al. published in 1973 a set of energy distribution curves (EDC's) from the Au valence band for excitation energies below 100 eV[3]. The comparison with an X-ray photoemission spectrum led the authors to the conclusion that the "X-ray limit" from which on the spectra resemble the density of initial states, is reached at around 30 eV for Au. However, small changes in the spectra with photon energy have also been noted[3]. Their experimental results have been confirmed by Lindau et al.[1]. Nevertheless, no attempt has been made to analyze the relative peak heights of the valence band maxima from the EDC's presented by Freeouf et al. and to connect them to the above mentioned results for photon energies above 100 eV. This is done in Fig. 1 showing rich structure over the entire energy range. Three pronounced modulations are to be seen and they all set in at the thresholds of the 5p and 5s excitations. While the intensity ratio in Fig. 1 increases at the two 5p thresholds, it decreases at the 5s threshold. It should be mentioned that the onset of 4f excitations at 84 eV[1] has no influence on the relative peak heights. This striking result points out the role of correlation interaction between electrons belonging to shells with equal principal quantum number even in a closed shell system.

The explanation is in direct contradiction to the one of Stöhr et al. based on a solid state effect[2]. Such an effect should also show up in the subshell cross-section of the valence band. In fact, this cross-section measured by Stöhr et al. in the angular integrated mode[2] is in excellent agreement with theoretical predictions for the Au 5d cross-section based on purely atomic calculations[6,7].

An assignment of the valence band maxima to the atomic spin orbit components is implicitly involved in the interpretation of Lindau et al.[1] as it is in the one presented here. It has been shown that calculated densities of states only agree with the XPS valence band spectrum if spin orbit coupling is included[8]. However, the energy separation of the d band maxima is about 3 eV[1] while the atomic spin orbit splitting is only 1.5 eV[9].

In order to clarify the relation between the atomic spin orbit components and the d band of solid Au, many attempts have been made to measure the atom-to-solid transition by alloying Au in different concentrations to other metals[10-14]. As a consistent result of all of these experiments it was shown that the d band maxima in the solid continually develop out of the spin orbit components when the interaction between the Au atoms increases. Furthermore, McAlister et al. have been able to explain their $N_{6,7}$ X-ray emission spectrum of solid Au in terms of atomic-like 5d levels[15]. These results demonstrate a very close relationship between the $5d_{5/2}$ and $5d_{3/2}$ levels and the d band maxima in solid Au. It is therefore not surprising that the relative intensity of the two valence band maxima is sensitive to inner atomic correlation effects.

For the case of Ag a similar amplitude modulation of the two valence band maxima as observed for Au has been reported by Wehner et al.[4]. They explained their result as due to the strong decrease of the 4d subshell cross-section between 100 eV and 130 eV leading to an enhancement of the valence band peak at higher binding energy by a maximum value of 17%[4]. A quantitative analysis of the 4d peak heights ratio is presented in Fig. 2. The ratio increases above 60 eV to a maximum of 1.67 at 80 eV and then decreases to a minimum of 0.94 at 120 eV followed by an increase again. This gives a modulation of ± 28% relative to the mean value. Although the mechanism discussed in Ref. 4 must be considered for the valence band peak height modulation in Ag, it fails to explain the increase of the intensity ratio below 100 eV and it does not give the full magnitude of the modulation above 100 eV. On the contrary, the correlation between the modulations and the thresholds of the 4s and 4p core level excitations is obvious again (see Fig. 2). In fact, the same arguments as above can be applied for Ag. The atomic spin orbit splitting of the 4d level is 0.6 eV[8] and the comparison between the XPS valence band spectrum and calculated density of states revealed the importance of spin orbit coupling also in the solid[16]. Again, photoemission measurements of alloys with different concentrations of Ag demonstrate a similar relation between the atomic spin orbit components and the d band maxima of the solid[17, 18]. Furthermore, a comparison of the 4d photoemission from Pd to Xe shows that for the case of Ag band effects and the spin orbit coupling appear to be equally important[19].

In conclusion, it can be stated that the intensity modulations of the photoemission from the d bands of Au and Ag both find an explanation as due to an atomic correlation interaction between electrons belonging to subshells with equal principal quantum number. This was demonstrated by the correspondence between the modulation onsets and the thresholds of inner level excitations. Recent measurements on Pt[20], Ni[21] and Cr[22] show that the 5d (3d) subshell cross-section is coupled to excitations from inner shells into the empty d states. While these results point out the

importance of the interaction of an incompletely filled outer d shell with inner core level excitations, correlation effects have also been found in gaseous Xe[23]. In this case oscillator strength of the huge 4d absorption maximum is given to the 5s and 5p excitations. For Au and Ag the situation is rather different because the inner shell excitations do not lead to spectacular features in the absorption spectrum. In this respect, Au and Ag turn out to be unexpected examples for intershell correlations. This result stresses the importance of correlation interaction for photoemission spectra introduced by inner level excitations even if the corresponding photoionization cross-section is very low.

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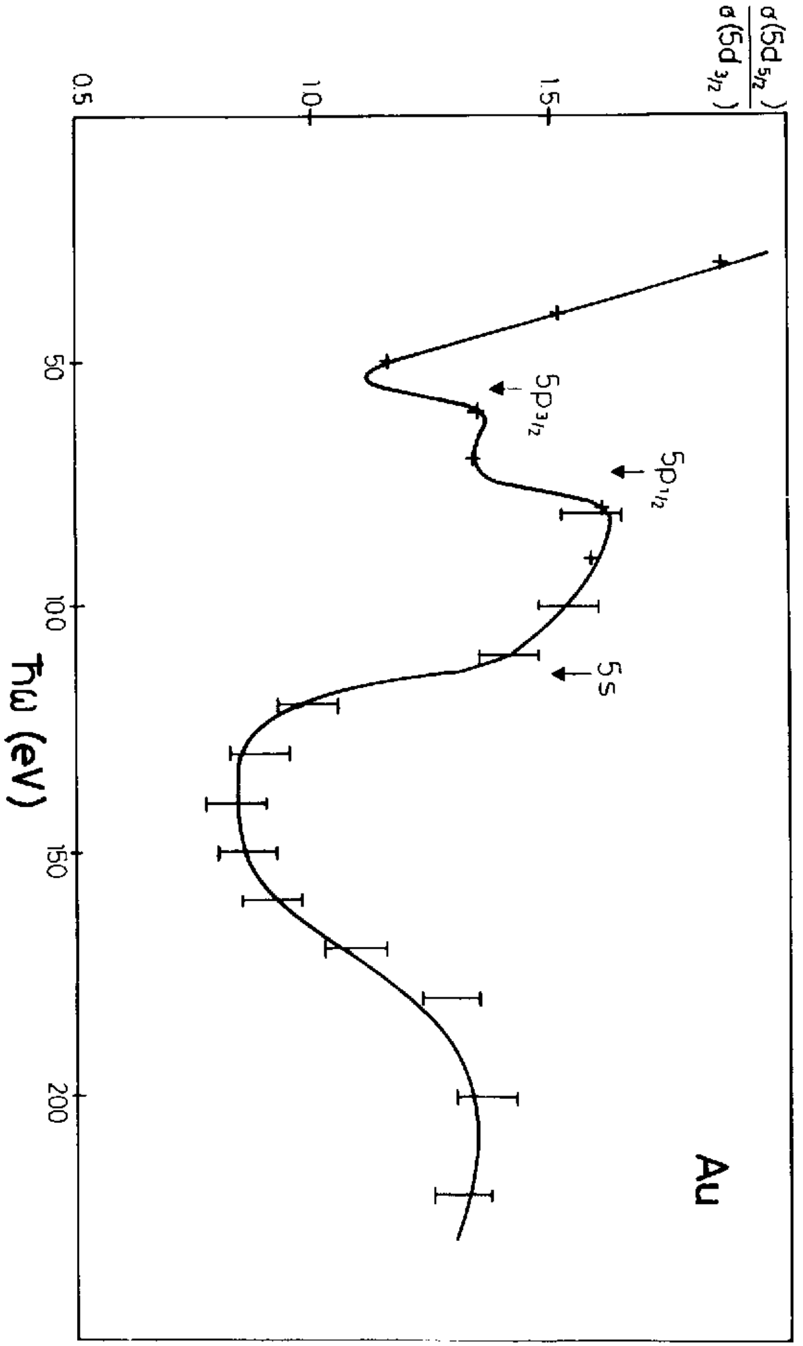
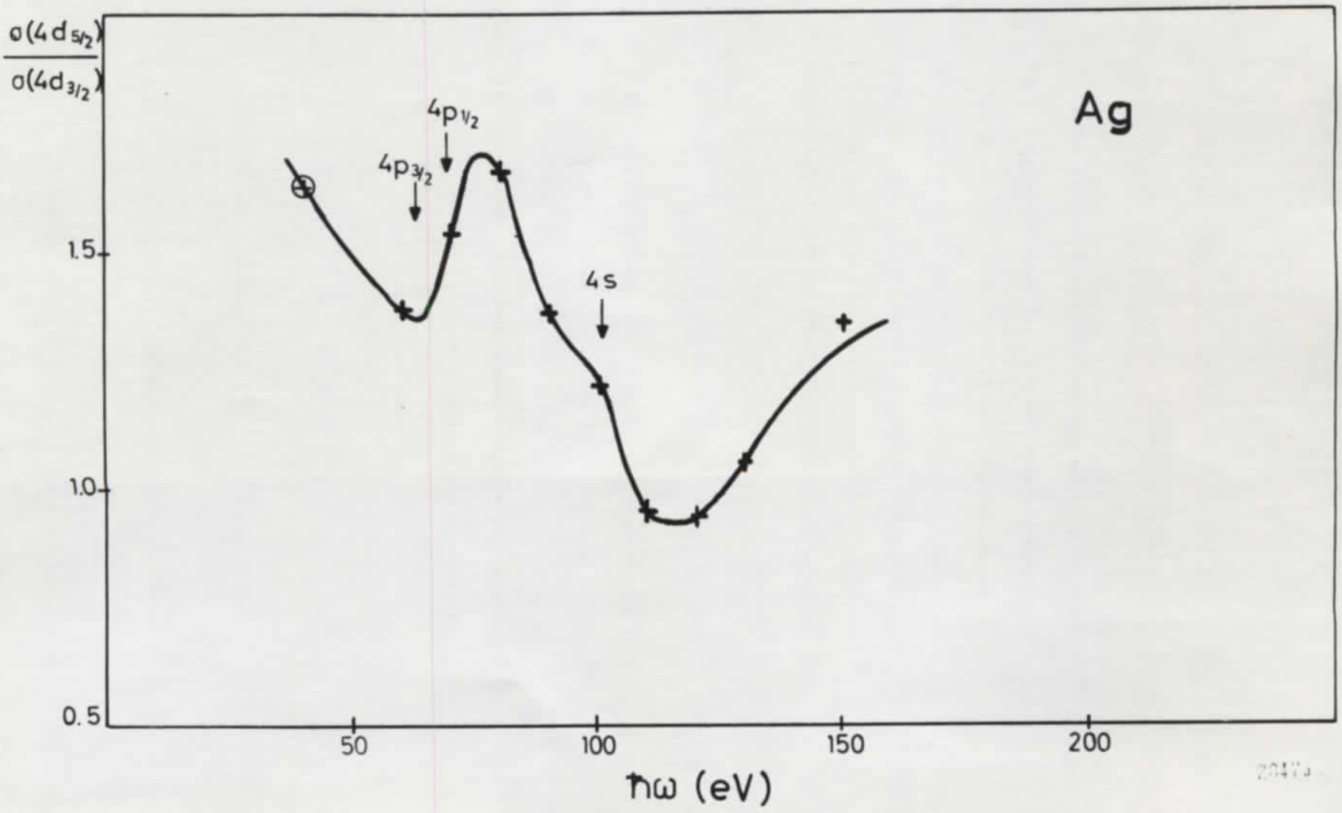
Figure Captions

Fig. 1 Ratio between the photoemission peak heights of the low binding energy and the high binding energy maximum in the Au valence band (after subtraction of linear background) as a function of photon energy. The values are obtained from Ref. 3 (+) and Ref. 1 (I). The arrows indicate the thresholds of 5p and 5s excitations as given by the binding energies from Ref. 1 (5p) and Ref. 5 (5s).

Fig. 2 Ratio between the photoemission peak heights of the two d band maxima in Ag. The values are obtained in the same way as for Au after Ref. 4 (+) and Ref. 18 (⊕). The arrows indicate the thresholds of the 4p and 4s excitations as given by the binding energies from Ref. 5.




σ(4d$_{5/2}$)
σ(4d$_{3/2}$)
Ag
4p$_{1/2}$
4p$_{3/2}$
4s
1.5
1.0
0.5
50
100
150
200
ħω (eV)
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