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Absorption Measurements of $AuAl_2$ in the Region of the Al $L_{2,3}$ Transitions

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$AuAl_2$ alloy samples were prepared as thin films both by simultaneous evaporation and by diffusion from sandwich films. Absorption spectra in the Al $L_{2,3}$ region were obtained using synchrotron radiation from the 7.5 GeV electron accelerator DESY. The onset of the Al $L_{2,3}$ transitions is shifted upward in energy by about 0.3 eV. In addition, a very steep and prominent edge with the characteristic Al $L_{2,3}$ splitting occurs 1.6 eV above the edge of pure Al. This structure constitutes a puzzle since it implies an abrupt increase in the density of unoccupied states occuring within an energy range of less than 0.2 eV. This does not have any precedent in any other metal or alloy observed so far. A calculation of Switendick yields an edge in the spectrum at approximately this energy, but the experimental edge is considerably steeper than that of the calculation. Since one could argue that other phases in the sample are responsible for the structure at the low energy side of this edge we have checked the samples by electron diffraction. These tests support the assumption that we deal with a homogeneous $AuAl_2$ alloy.

Recently there has been considerable interest in the electronic structure of the intermetallic alloy $AuAl_2$[1-4]. Earlier studies showed that this material is a good metallic conductor and behaves to some extent like a free electron metal[2-4]. Its conspicuous purple colour has raised the question as to the positions of the Au d-bands. Recent x-ray emission measurements[5-8] of the $L_{2,3}$ bands of Al in $AuAl_2$ agree in part with a theoretical calculation by Switendick[9] based on an augmented plane wave calculation. But among other differences, between the experiments and between experiment and theory, there are discrepancies in the position of the high energy edge (Fig. 1). This edge should coincide with the onset of transitions in the absorption spectrum. The desire to resolve these discrepancies together with the possibility of learning something about the electron states in the region above the Fermi energy led us to an investigation of the Al $L_{2,3}$ absorption structure in $AuAl_2$.

Sample preparation

In preparing alloy samples as thin films of thicknesses of the order of 500 Å, it is impossible to duplicate the refined heat treatment usually used for the preparation of bulk samples. We have used simultaneous evaporation from two sources and subsequent annealing at about 300° for 1 h in a vacuum of about 2×10^{-6} Torr. The evaporation rate and the total amount was controled by an oscillating quartz crystal monitor. The samples were investigated by electron diffraction with 75 keV electrons and the diffraction pattern (CaF_2 structure[10]) showed only slight contributions of either Au or Al. This point will be discussed in detail below. The samples were covered on both sides with thin layers of carbon of the order of 50 Å in order to reduce oxidation. Collodion served as a substrate which was dissolved before annealing.

It proved to be very helpful for interpretation to measure also a sandwich film with the same relative amounts of Al and Au where the two layers were prevented from diffusing into each other by a thin layer of carbon. If no carbon barrier is used significant diffusion occurs already at room temperature as was reported by Weaver and Parkinson[11]. Thus it is also possible to obtain alloy films by annealing sandwich films which contain no carbon barrier. With alloy films prepared in this manner, we obtained essentially the same results as with those prepared by simultaneous evaporation.

Measuring technique

The measurements were performed using synchrotron radiation emitted by the 7.5 GeV electron accelerator DESY. The continuum was monochromatized by a special spectrometer[12] giving a spatially fixed photon beam with a resolution of the order of 0.2 eV in the energy region of interest. Figure 2 shows the arrangement behind the exit slit. A gold coated mirror was mounted as the cathode of an open magnetic photomultiplier (Bendix). The signal of which served as a reference for monitoring the fluctuations of the source. The beam, after passing the sample, was detected by an open Cu:Be photomultiplier (Johnston). The spectrum of an alloy sample and a carbon film of thickness equal to that of the protective layers on the sample give the absorption coefficient to an accuracy of the order of ±15 %. The uncertainty results principally from the uncertainty in the determination of the film thickness. Occasionally a two-beam technique[13] was utilized which permitted a direct comparison of an alloy and a sandwich sample. Especially, energy shifts of structures in the spectra are accurately obtained with this arrangement.

Results

The upper part of Fig. 3 shows the spectra of the individual Au and Al components. Agreement with previous measurements[14,15] is generally good, but in addition we were able to resolve the Au $N_{6,7}$ edges (N_7 at 84.0±0.2 eV, N_6 at 87.6±0.2 eV). These values should be compared with the XPS values[16] of N_7 at 83 eV and N_6 at 87 eV. The Al spectrum is in good agreement with previous measurements[15]; the most remarkable features are the small peaks right at the edges, the so-called "spikes", a many-body phenomenon[17]. Further, the prominent maximum at 97 eV (F) has attracted considerable attention. Attempts have been made to correlate it with the plasma-like oscillations[18] refered to as "plasmarons", but agreement at present seems not to be satisfactory. In the lower part of Fig. 3 we show the alloy spectrum together with the spectrum of a sandwich film. The latter is a 1:2 superposition of the two upper curves within the experimental accuracy. The alloy spectrum shows a fairly broad edge with an onset A' at 72.9 eV. Thus the onset is shifted to higher energy by about 0.2 eV as compared to the pure Al $L_{2,3}$ edge. We prefer to mark the onset rather than the steepest point of the edge in the alloy.

The onset A' is followed by two steep edges B' at 1.4 eV and C' at 1.9 eV above the onset. The separation of B' and C' is obviously that of the Al L_3 and L_2 levels. In the region of peak E' a correction was made for two small oxide structures at 77.3 eV and 79.9 eV which could be identified from a separate measurement of Al_2O_3. It is possible that faint structures in the region of this peak originating from the alloy have not been detected. There follow several smaller structures and finally a steep decrease to higher energies. The edge at 85.0 eV could in principle be the Au N_7 edge with a shift of about 1 eV to higher energy as compared with pure Au. If this assignment is correct, the position would be in good agreement with the XPS measurements of Chan and Shirley[19]. But it is also possible that one of the other structures should be identified with N_7 (the more prominent of the two) or that N_7 is hidden in an increase of absorption as is the case with the sandwich spectrum. Samples which were not annealed showed somewhat broadened structures B' and C' but no other significant difference. The positions of the structures are given in Table 1.

Discussion

We shall confine our discussions mainly to the energy region near the onset. The sharpness of the edge at 74.3 eV, with its characteristic spin orbit partner, together with the edge near that of pure Al constitute a puzzle. We are led along two different paths in interpreting these results depending on which of these features we associate with the onset of Al $L_{2,3}$ transitions:

1. If we take the onset A' to lie at 72.9 eV, we are in agreement with the soft x-ray emission measurements of Kapoor et al.[8] (Fig. 1). The result is also in agreement with Al K x-ray emission measurements of Källne[20] who found a shift of 0.33±0.17 eV to higher energy compared to pure Al.

Then we are confronted, however, with a sharp edge having a width of less than 0.2 eV which we have to place at an energy about 1.3 eV above the Fermi level. This could only be understood as a sudden increase in the density of states and has no precedent with any other metal observed so far. One of the narrowest edge-like structures above the Fermi edge would be the structure at about 34 eV in Na metal[15], 3 eV above the onset, with a width of about 0.6 eV.

2. In taking the Al L_3 edge to be at 74.3 eV, we are in complete disagreement with all the soft x-ray emission results which were obtained with bulk samples. However, we would agree with XPS data of Chan and Shirley[19] who found the unresolved $L_{2,3}$ levels at 75 eV. Watson _et al._[21] have recently performed improved XPS measurements under UHV conditions and they did observe another peak at 0.3 eV above the position which occurs in pure Al. They ascribe the other peak at around 75 eV to oxide. (Note that the oxide structures in XPS and in absorption will not be observed at the same energy). In order to explain the onset at 72.9 eV, we would need to assume a considerable amount of another phase in the alloy, say pure Al (of the order of 30 %).

We have performed several tests in order to clarify the constitution of the samples. The main method was an investigation of the electron diffraction pattern obtained with 75 keV electrons. The pattern was definitely that of the known structure[10] of $AuAl_2$. Only very slight indications of the presence of either pure Al or pure Au were obtained. It was not possible to determine whether these traces were pure gold, pure Al, or if both were present. If we attribute this contribution to pure Al the contribution would amount to less than 10 % in the best samples.

The relative intensities of the two structures (one being the change in absorption between the onset A' and the onset of edge B' and the other being the change at the edge B') was fairly insensitive to a slight unbalance in the two constituents. The same ratio was obtained with samples prepared in such different ways as simultaneous evaporation before and after annealing and with diffusion from sandwich films. Together with H.-J. Hagemann, the results were reproduced again recently with two samples obtained by evaporation under improved rate control in a much better vacuum.

A comparison with the spectrum calculated by Switendick[9] from a band calculation by Switendick and Narath[22] is shown in Fig. 4. This is a continuation of the valence spectrum shown in Fig. 1. We have added the contribution from transitions into s and d states, but did not take into account the $L_{2,3}$ spin orbit splitting. The peak found experimentally between 74.3 eV and 77 eV occurs also in the theoretical curve, but shifted somewhat to lower energy. It is not clear to us that absolute positions of deep levels should be taken as seriously in such calculations as Switendick does. The band calculations were intended to be best in the region of the valence band and become less accurate at higher energies. Therefore, the wiggles at energies above 78 eV could be artificial. Although the big maximum near the edge appears to be present in the theoretical calculations, it should be mentioned that it has become clear recently[17] that one-electron calculations of absorption and emission spectra of metals can change dramatically near the onset because of many-electron interactions with the core hole.

Conclusion

Although most experimental tests, including the soft x-ray emission spectra, support positioning the onset of transitions at 72.9 eV, we feel that the question is not yet completely settled. Accepting this position for the edge leaves us with the problem of finding a reasonable explanation for the remarkably small width of a structure 1.3 eV above the Fermi level. If we try, on the other hand, to identify this sharp edge at 74.3 eV as the real onset of L_3 transitions, we would need to assume a two phase constitution of our samples and our spectra would not agree with the soft x-ray emission results.

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Table 1 Energy position of structures in $AuAl_2$. The Al L_3 edge served as a calibration point

Al L_3	edge	72.7 eV
A'	onset	72.9 ± 0.1 eV
B'	edge	74.3 ± 0.1 eV
C'	edge	74.8 ± 0.1 eV
D'	min	76.8 ± 0.3 eV
E'	max	82.5 ± 0.4 eV
F'	min	84.0 ± 0.4 eV
G'	max	86.0 ± 0.4 eV
H'	max	88.7 ± 0.4 eV
I'	min	89.7 ± 0.4 eV
J'	max	92.0 ± 0.4 eV

Figure Captions

Fig. 1 Experimental L-emission spectra of $AuAl_2$ according to different authors[5-8] and a theoretical calculation[9]. The absolute energy position of spectrum c) is given according to reference 9. We have marked the position of the Al L_3 edge at 72.7 eV.

Fig. 2 Experimental arrangement behind the exit slit of the monochromator.

Fig. 3 Upper part: absorption coefficient μ of pure Au and Al versus photon energy. Lower part: absorption coefficient of the alloy $AuAl_2$ and the measured absorption spectrum of an equivalent sandwich sample.

Fig. 4 Comparison of the experimental absorption spectrum of $AuAl_2$ with a theoretical spectrum[9]. The separation of the theoretical curve into components with different final state symmetry at the Al atom is also given. The position of the Fermi level according to the theoretical calculation[9] is marked at 73.8 eV.

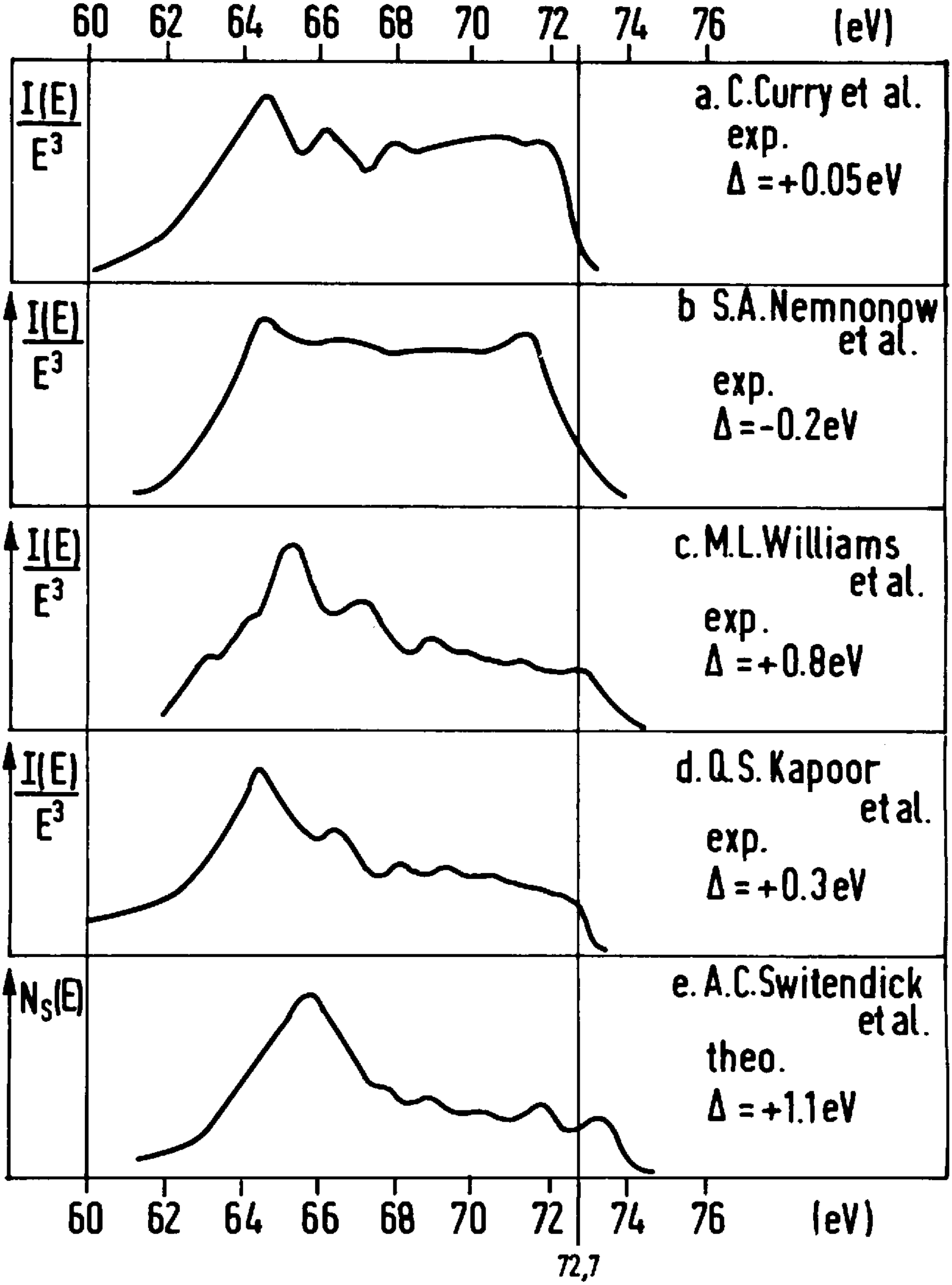
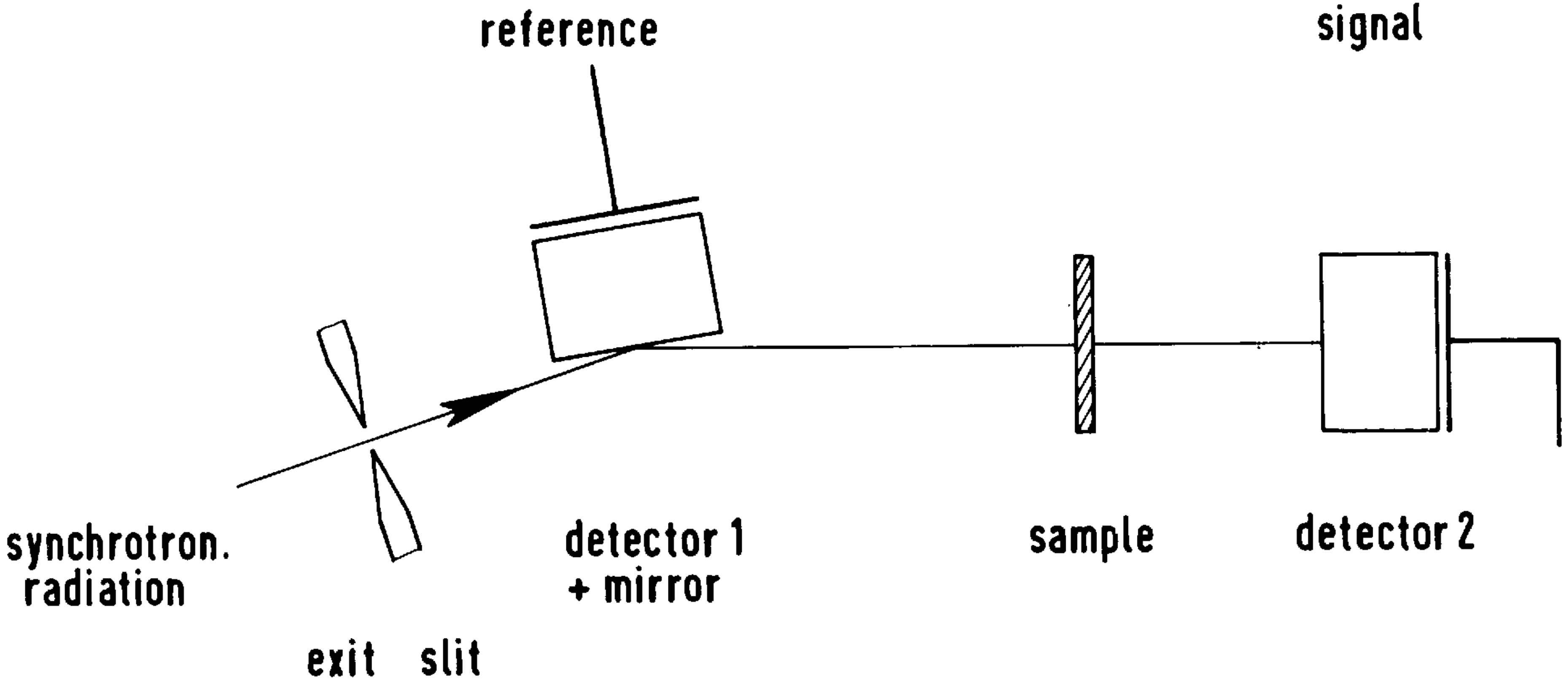

60
62
64
66
68
70
72
74
76
(eV)
I(E)/E³
a. C.Curry et al.
exp.
Δ =+0.05eV
b S.A.Nemnonow et al.
exp.
Δ =-0.2eV
c. M.L.Williams et al.
exp.
Δ =+0.8eV
d. Q.S. Kapoor et al.
exp.
Δ = +0.3 eV
N_S(E)
e. A.C.Switendick et al.
theo.
Δ = +1.1eV
72,7

Fig. 1

Fig. 2


reference
signal
synchrotron. radiation
exit slit
detector 1 + mirror
sample
detector 2

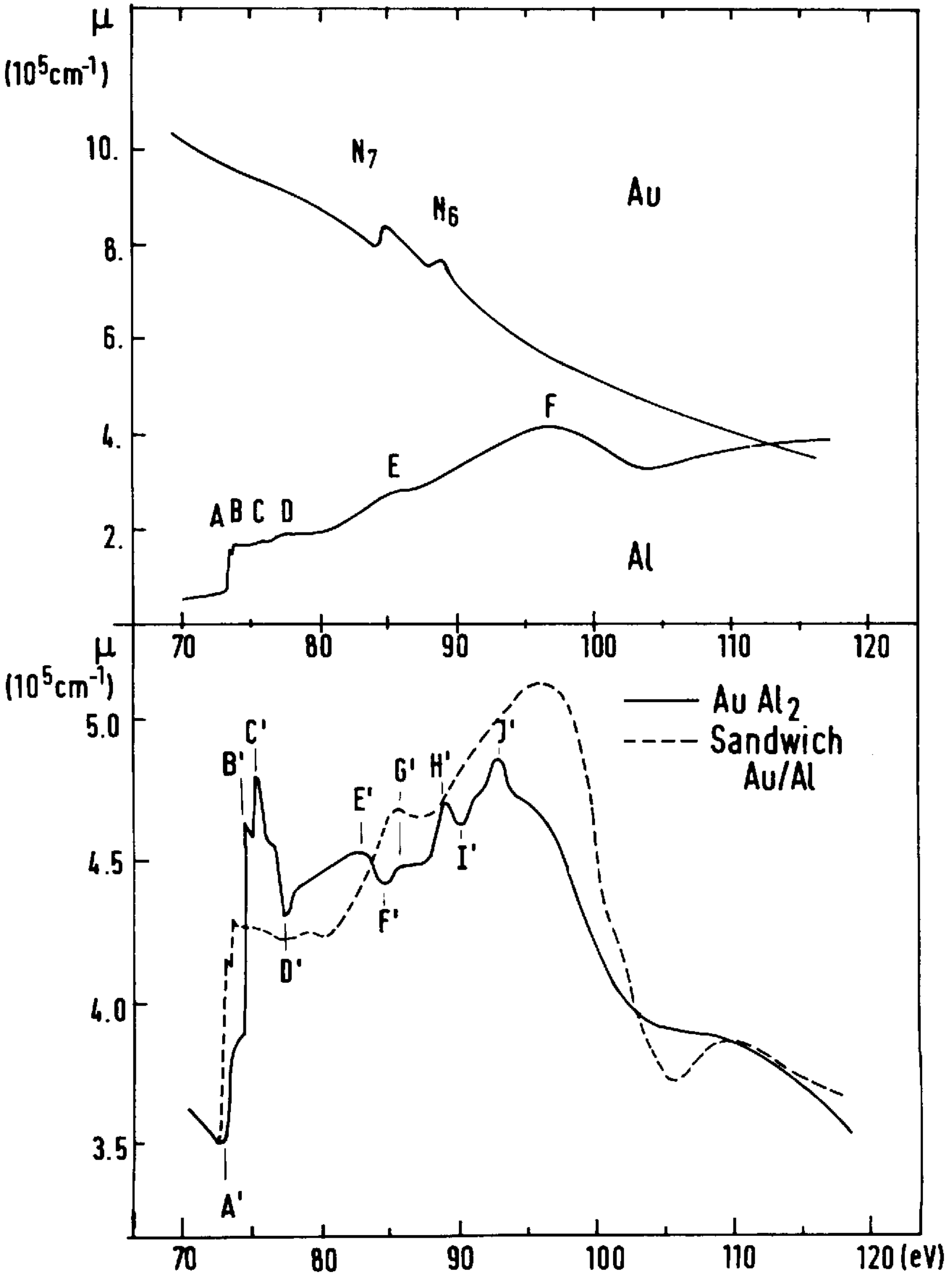

μ
(10⁵cm⁻¹)
10.
8.
6.
4.
2.
N7
N6
Au
F
E
A B C D
Al
70
80
90
100
110
120
μ
(10⁵cm⁻¹)
5.0
4.5
4.0
3.5
Au Al2
Sandwich Au/Al
A'
B'
C'
D'
E'
F'
G'
H'
I'
J'
70
80
90
100
110
120 (eV)

Fig. 3

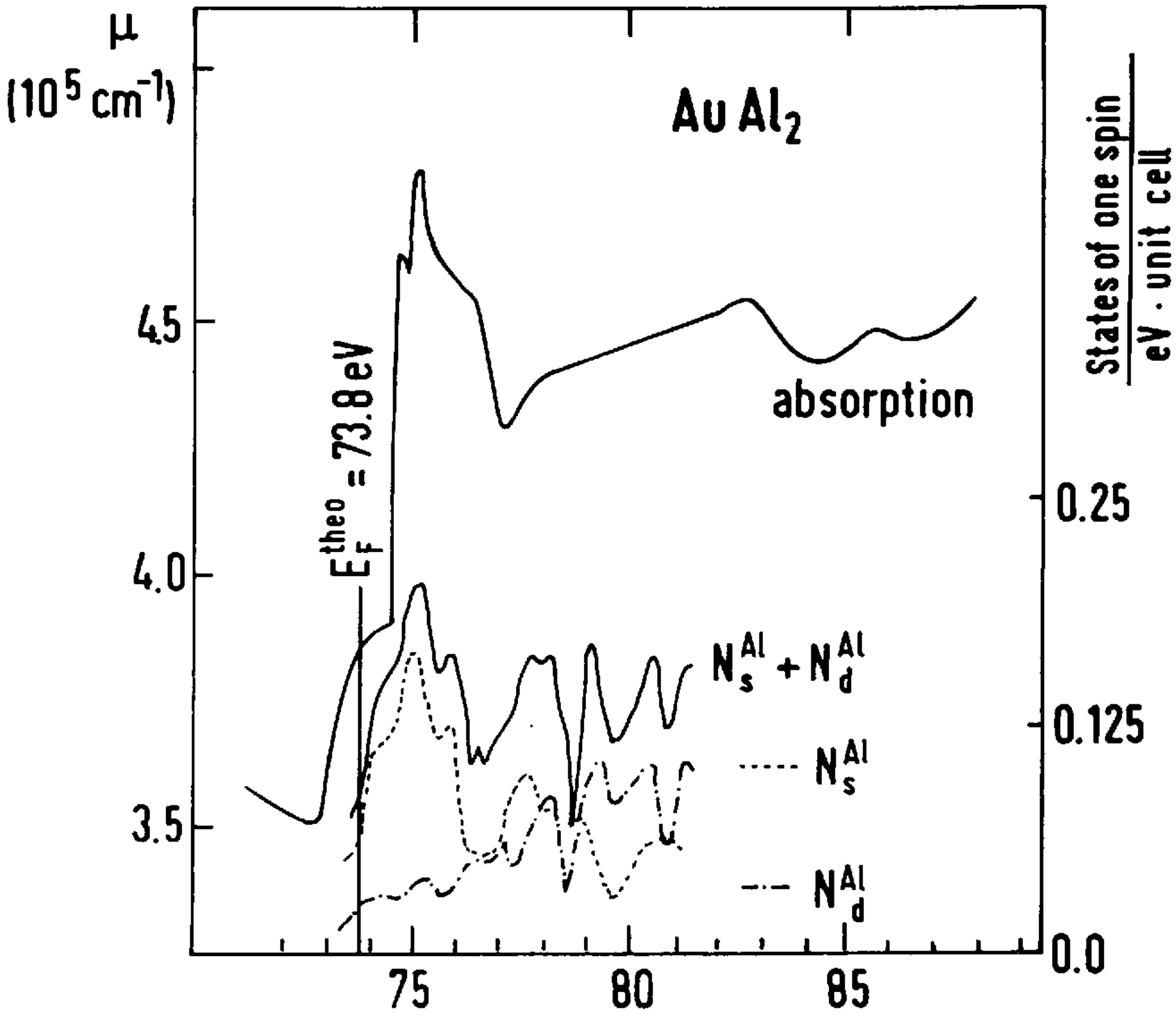

μ
(10^5 cm^{-1})
Au Al$_2$
4.5
4.0
3.5
E_F^{theo} = 73.8 eV
absorption
$N_s^{Al} + N_d^{Al}$
N_s^{Al}
N_d^{Al}
75
80
85
States of one spin / eV · unit cell
0.25
0.125
0.0

Fig. 4