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# Investigation of the extended x-ray absorption finestructure (EXAFS) at L-edges of heavy elements

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## Abstract

Using the synchrotron radiation of the Deutsches Elektronen-Synchrotron DESY the extended X-ray absorption finestructure at the L-edges of Au have been investigated. The magnitudes of the Fourier transforms of the $L_I$ and the $L_{III}$ finestructures yield maxima in real space showing a splitting which is the same for both edges. This splitting is attributed to the oscillatory behaviour of the backscattering amplitude of the photoelectron wave which is characteristic for heavy scattering atoms. Only transitions to d-symmetric final states contribute significantly to the $L_{II}$ and $L_{III}$ absorption.

## 1. Introduction

The investigation of the extended X-ray absorption finestructure (EXAFS) has been proven to be a powerful method for the determination of parameters of the local ordering in polyatomic systems (Sayers et al 1971, Lytle et al 1975, Stern et al 1975, Martens et al 1978). Most results up to now have been extracted from K-absorption spectra. At K-edges transitions to only one final state symmetry contribute to the absorption coefficient so that EXAFS can be described by a simple formalism.
On the other hand the application of this method to K-absorption spectra of heavy elements is hindered by several problems:

i) The reflectivity of crystals as well as the intensities of x-ray sources decrease at high photon energies.

ii) With increasing atomic number the lifetime broadening becomes appreciable. For gold e.g. a width of the K-edge of 54 eV is reported (Parratt 1959). By this effect the finestructure is smeared out and an analysis of EXAFS is impossible.

The investigation of EXAFS above L-edges offers a way out of this dilemma. In these cases the lifetime broadening amounts to only several electronvolts even for the heaviest elements (Parratt 1959). Consequently the geometrical structure should be determined from $L_I$-absorption spectra where only transitions to p-symmetric final states are allowed. The theoretical description of the finestructure is identical to that of the K-shell EXAFS. Unfortunately the $L_{II}$ finestructure in many cases extends beyond the $L_I$-edge and a separation of these components is difficult. Furthermore the $L_I$-edge jump is considerably smaller

than the $L_{III}$-edge and superimposed on the high monotonous background of $L_{II}$- and $L_{III}$ -shell absorption. In case of $L_{III}$-EXAFS complications for the interpretation due to contributions of transitons to s and d symmetric final states are expected. In fact a splitting of structures in the Fourier transform of $L_{III}$-EXAFS of Au has been interpreted in this way (Lytle et al 1977). We shall show that this splitting is due to the shape of the backscattering amplitude of the photoelectron waves for heavy elements and that also at $L_{II}$ and $L_{III}$-edges only transitions to one final state symmetry contribute significantly to EXAFS.

## 2. Results and discussion

The finestructure above the absorption edges in the x-ray region is due to an interference of the outgoing photoelectron wave with parts of this wave backscattered from the neighbouring atoms (Stern 1974, Lee and Pendry 1975). In the case of K-shell EXAFS only transitions to p-symmetric (l=1) final states are allowed and the finestructure can be described by

$$(1)\quad \chi_K(k) = -\frac{1}{k}\sum_i A_i(k)\sin(2kR_i+\emptyset_i(k))$$

with

$$(2)\quad \emptyset_i(k) = 2\,\delta_1(k) + \arg\{f_i(\pi,k)\}$$

Here k means the wave number of the photoelectrons. The scattering phase $\phi_i(k)$ is composed of $\delta_1(k)$ determined by the absorbing atom and arg $(f_i(\pi,k))$ determined by the scattering atoms. $A_i(k)$ describes the k-dependence of the amplitudes of the oscillations contributed to $\chi(k)$ from a single scattering shell i.e. $N_i$ identical atoms at a distance $R_i$. Apart from monotonous damping due to thermal disorder this k-dependence is mainly determined by the backscattering amplitude $|f(\pi,k)|$

$$(3) \qquad A_i(k) = |f_i(\pi,k)| \frac{N_i}{R_i^2} \exp(-2\sigma_i^2 k^2) \exp(-\gamma R_i)$$

The two exponentials consider the displacements $(\sigma_i)$ of the atoms around their average positions and the damping of the electron wave due to inelastic scattering $(\gamma)$.

EXAFS at $L_I$-edges is equivalent to K-shell EXAFS. Again only transitions to p-symmetric final states are allowed so that the finestructure can be described by equ.1. In the case of $L_{II}$- and $L_{III}$-EXAFS transitions to s- and d-symmetric final states have to be considered. Therefore for each scattering shell two different contributions to the finestructure are expected. In these cases EXAFS has to be described by

$$(4) \quad \chi_{L_{II,III}}(k) = \left(\mu_o(k)\chi_o(k)+\mu_2(k)\chi_2(k)\right) / \left(\mu_o(k)+\mu_2(k)\right)$$

with

$$(5) \qquad \chi_l(k) = \frac{1}{k} \sum_i A_i(k) \sin\left(2kR_i + 2\delta_l(k) + \arg\left(f_i(\pi,k)\right)\right)$$

$$l = o,2$$

The two contributions are weighted with the partial cross-sections $\mu_o(k)$ and $\mu_2(k)$. $\chi_o(k)$ and $\chi_2(k)$ differ from $\chi_K(k)$ only by the sign of the amplitude function and by the phase $\delta_1(k)$ contributed from the absorbing atom.

We have compared these theoretical predictions with experimental absorption spectra at the L-edges of Au and at the K-edge of Cu in the metal and in CuJ. The data have been taken at the Deutsches Elektronensynchrotron in Hamburg. The synchrotron radiation is monochromatized with a channelcut Si(220) crystal. The monochromatic radiation is monitored by airfilled ionization chambers. The samples have been cooled to liquid nitrogen temperature. Details about the experimental setup are published elsewhere (Rabe et al 1978).

The absorption coefficient of Au in the range of the L-edges is shown in Fig. 1. The separation of the $L_I$, $L_{II}$, and $L_{III}$ levels amounts to about 800 eV and 1600 eV and the different EXAFS contributions $\chi_{L_I}$, $\chi_{L_{II}}$, and $\chi_{L_{III}}$ can be treated individually. The EXAFS above the three edges are shown in Fig. 2. The monotonous background due to excitations of weaker bound electrons has been removed with a procedure desbribed elsewhere (Martens et al 1978). As expected theoretically the $L_{II}$- and $L_{III}$- finestructures are identical in the measured k-region.

A comparison of $L_I$-EXAFS with $L_{II}$-and $L_{III}$-EXAFS again shows a close similarity. Note that $\chi_{L_I}(k)$ is shown with the reverse sign as compared to $\chi_{L_{II}}$ and $\chi_{L_{III}}$. This similarity points to the fact that only **one final state symmetry** contributes to EXAFS at $L_{II}$-and $L_{III}$-edges.

A more quantitative analysis of the data is obtained from a Fourier transform of the EXAFS to real space. To compare the results with K-shell EXAFS we have used Cu as a reference material which as well as Au crystallizes in a fcc-lattice. The magnitude of the Fourier transform of Cu K-shell EXAFS shows five well separated maxima (Fig. 3c). They are assigned to the five shells of nearest neighbours surrounding the absorbing atom. The arrows point to the true distances. They are labeled with the number of atoms in each shell. The shift between arrows and maxima is caused by the k-dependent parts of the scattering phase $\emptyset_i(k)$.

For the Fourier transform of $L_I$-EXAFS of Au we expect structures in real space similar to that of Cu. These structures should split in the case of $L_{II}$- and $L_{III}$ EXAFS due to differences in the k-dependent parts of $\delta_o$ and $\delta_2$ (Lee and Beni 1977). For $L_{III}$-EXAFS a splitting is observed (Fig. 3). However $L_I$-EXAFS shows the same splitting of all structures (Fig. 3 a,b) above $r = 0.2$nm. This means that the origin of this splitting cannot be attributed to different final state symmetries. This result is supported by theoretical considerations (Manson and Cooper 1968) which estimate $\mu_o$ to be an order of magnitude smaller than $\mu_2$. Investigations of EXAFS at the $L_{III}$-edge in WSe yield a ratio $\mu_o/\mu_2 \leq 1/50$ (Heald and Stern 1977). Therefore the contribution of $\mu_o$ to $\mu$ is too weak to be observed in the absorption spectra.

The structure below $r = 0.2$nm in Fig. 3a is caused by the $L_{II}$-EXAFS which extends into the region where $L_I$-EXAFS shows up. The $L_{III}$ finestructure which is observed up to 1600 eV beyond the edge can be used to reduce at least part of these distortions. To simulate the influence of $L_{II}$-EXAFS on the Fourier transform of $L_I$-EXAFS we have subtracted the $L_{III}$-EXAFS from the finestructure above the $L_I$-edge. A Fourier transform of the resulting finestructure shows an effective reduction of contributions to $|F(r)|$ in the region below 0.2nm. The doubling of the peaks above 0.2nm is not affected by this procedure.

From our results the splitting of the peaks in $|F(r)|$ for Au can only be attributed to the shape of the envelope function $A_i(k)$ which is independent on the initial and final state symmetry of the photoelectrons. The k-dependence of $A_i(k)$ is determined from $|f(\pi,k)|$ which is specific for the atomic number Z of the scattering atom. Calculations show that up to $Z = 36$ the theoretical backscattering amplitude can be approximated by a Lorentzian in k-space (Teo et al 1977). This function is not the adequate description of $|f(\pi,k)|$ for heavier elements. For the three scattering atoms Cu, J, and Au we have summarized the envelope functions in Fig. 4. We have extracted the $A_i(k)$ for the single scattering shells from backtransforms of limited ranges of $|F(r)|$ to k-space. For Cu and Au we have indicated these ranges in Fig. 3. All A(k) have been normalized to $R = 0.1$nm and $N = 1$. With increasing atomic number of the scattering atoms a systematic change of the envelope function is observed. Whereas for the lightest scatterer the backscattering amplitude decreases monotonously with k (Martens et al 1978) A(k) of Cu shows a maximum at 69nm$^{-1}$. In going to J an additional minimum appears at $k = 69$nm$^{-1}$. The maximum of A(k) decreases and moves to higher k-values. A(k) of Au shows a complete oscillation over the whole k-range and the maximum values are further reduced. Similar changes are observed in the scattering phases $\phi(k)$. In Fig. 5 we show $\phi(k)$ for Cu and Au calculated from the backtransform. Like other light elements the scattering phase of Cu deviates only slightly from a straight line. In contrast the scattering phase of Au shows a significant nonlinear k-dependence.

From the systematic change of the amplitude functions and the scattering phases with the atomic number a systematic change of structures in real space is expected. For the three scattering atoms Cu, J,and Au we show the magnitude of the Fourier transform in Fig. 6. In all these cases we have used the same Gaussian transformation window. In the case of Cu we observe a slight asymmetry in $|F(r)|$ which grows stronger to a shoulder at the small distance side of the peak of J. This additional structure results from the beginning oscillation in A(k). In the case of gold a small structure is completely separated from the main peak. One has to be aware that this structure has to be included in the data processing (e.g. back-transform to k-space) when bond lengths and coordination numbers for a single scattering shell are extracted from EXAFS.

The oscillatory behaviour of $|f(\pi,k)|$ and the nonlinear k-dependence of $\phi(k)$ for Au affect the structures in real space in the same way as a beating due to a superposition of transitions to s- and d-symmetric final states with different k-dependent parts of $\delta_l(k)$ $(l = 0,2)$ or due to superpositions of contributions from close lying shells (Martens et al 1977): The structures in the magnitude of the Fourier transform split.

## 3. Conclusions

Our comparision of $L_I$ and $L_{III}$ spectra of Au and of absorption spectra at the Cu K-edge show that the observed splitting in the magnitude of the Fourier transform of Au $L_{III}$-EXAFS is due to the shape in k-space of the backscattering amplitudes and scattering phases of heavy elements. For transitions of electrons from $L_{II}$ and $L_{III}$ shells only d-symmetric final states contribute considerably to the absorption coefficient. This fact facilitates the analysis of these spectra. Including the $L_{III}$-edges the investigation of EXAFS for structural analysis can be extended to elements with atomic numbers greater than 60 which means a substantial expansion for the application of this method.

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## Figure captions

Fig. 1 : L-absorption spectra of Au

Fig. 2 : EXAFS at the L-edges of Au

Fig. 3 : Magnitude of the Fourier transforms of EXAFS at $L_I$-and $L_{III}$-edges of Au and at the K edge of Cu

Fig. 4 : Envelope function of EXAFS for the scattering atoms Cu, J and Au

Fig. 5 : Scattering phases $\phi(k)$ for Cu and Au

Fig. 6 : Magnitude of the Fourier transforms of single scattering shells of Cu, J and Au

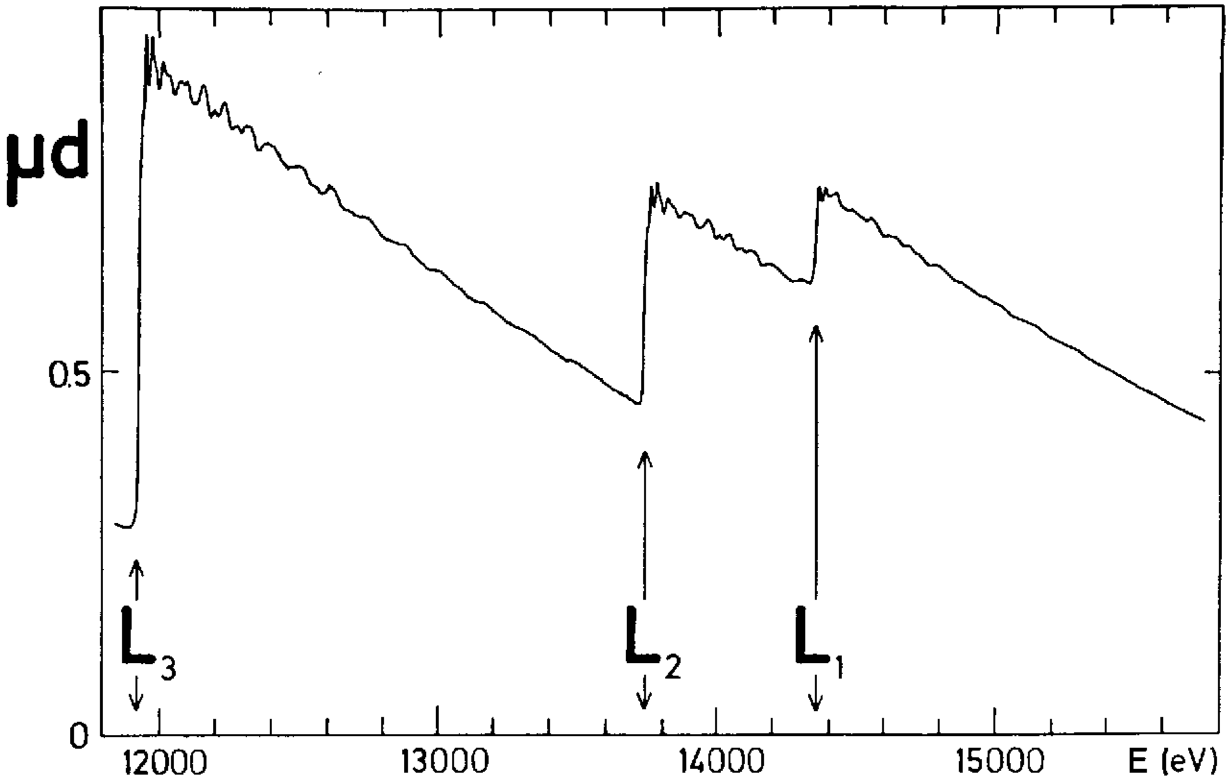

μd
0.5
0
L3
L2
L1
12000
13000
14000
15000
E (eV)

Fig. 1

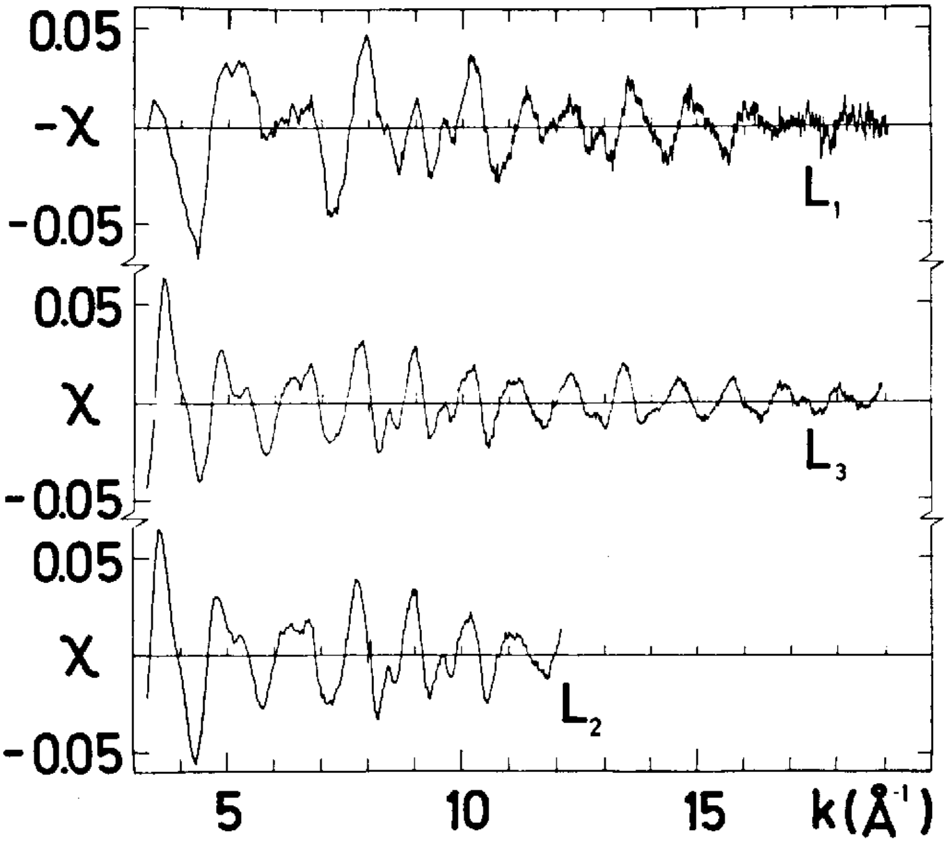

0.05
-X
-0.05
L1
0.05
X
-0.05
L3
0.05
X
-0.05
L2
5
10
15
k(Å-1)

Fig. 2

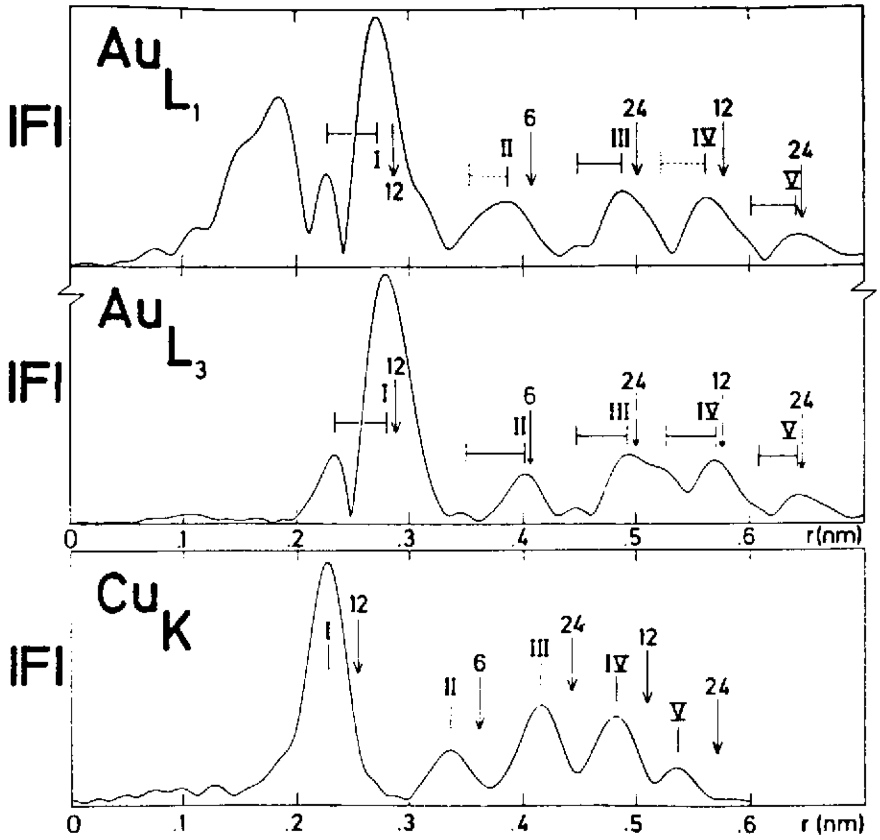
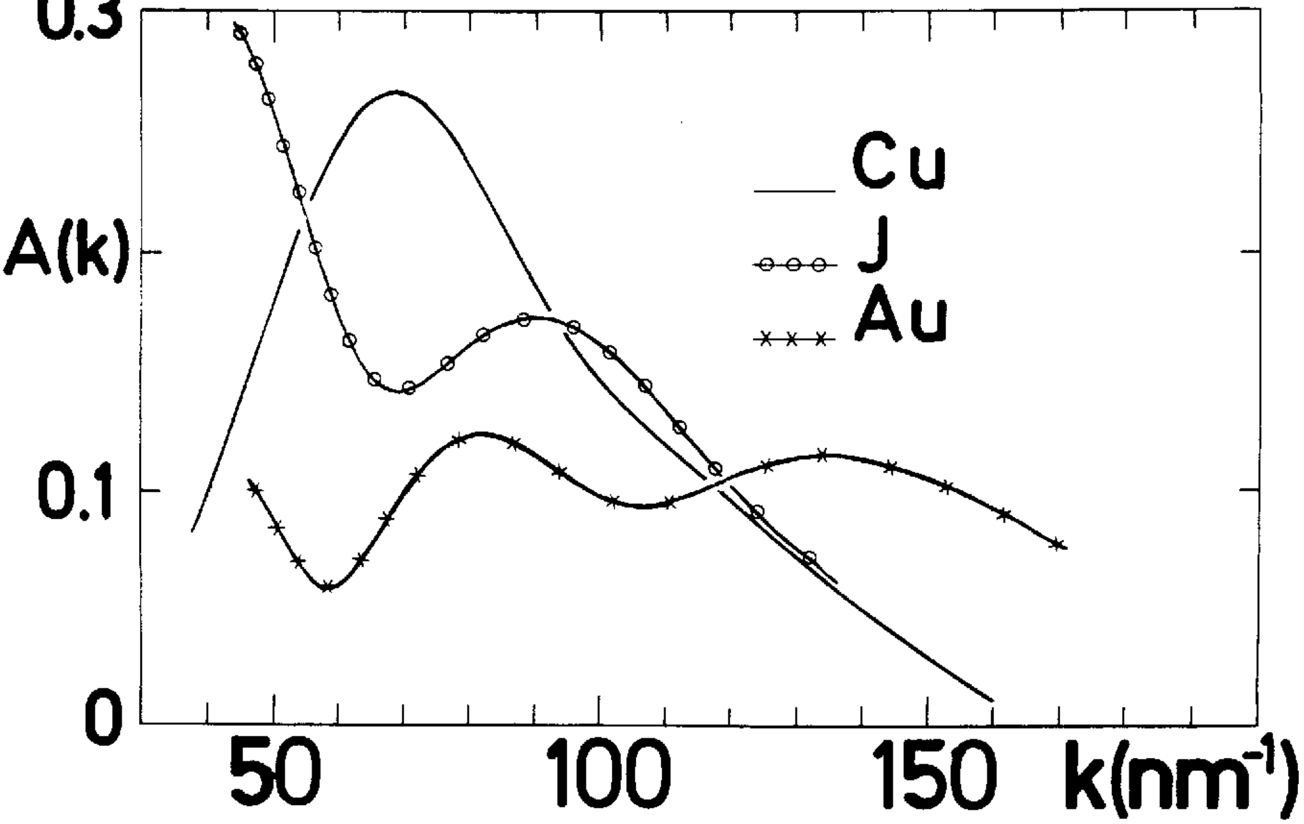

Au$_{L_1}$
|F|
I
12
II
6
III
24
IV
12
V
24
Au$_{L_3}$
|F|
12
I
6
II
24
III
12
IV
24
V
0
.1
.2
.3
.4
.5
.6
r(nm)
Cu$_K$
|F|
I
12
II
6
III
24
IV
12
V
24
0
.1
.2
.3
.4
.5
.6
r (nm)

Fig. 3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A(k)
0.1
0
Cu
J
Au
50
100
150
k(nm$^{-1}$)

Fig. 4

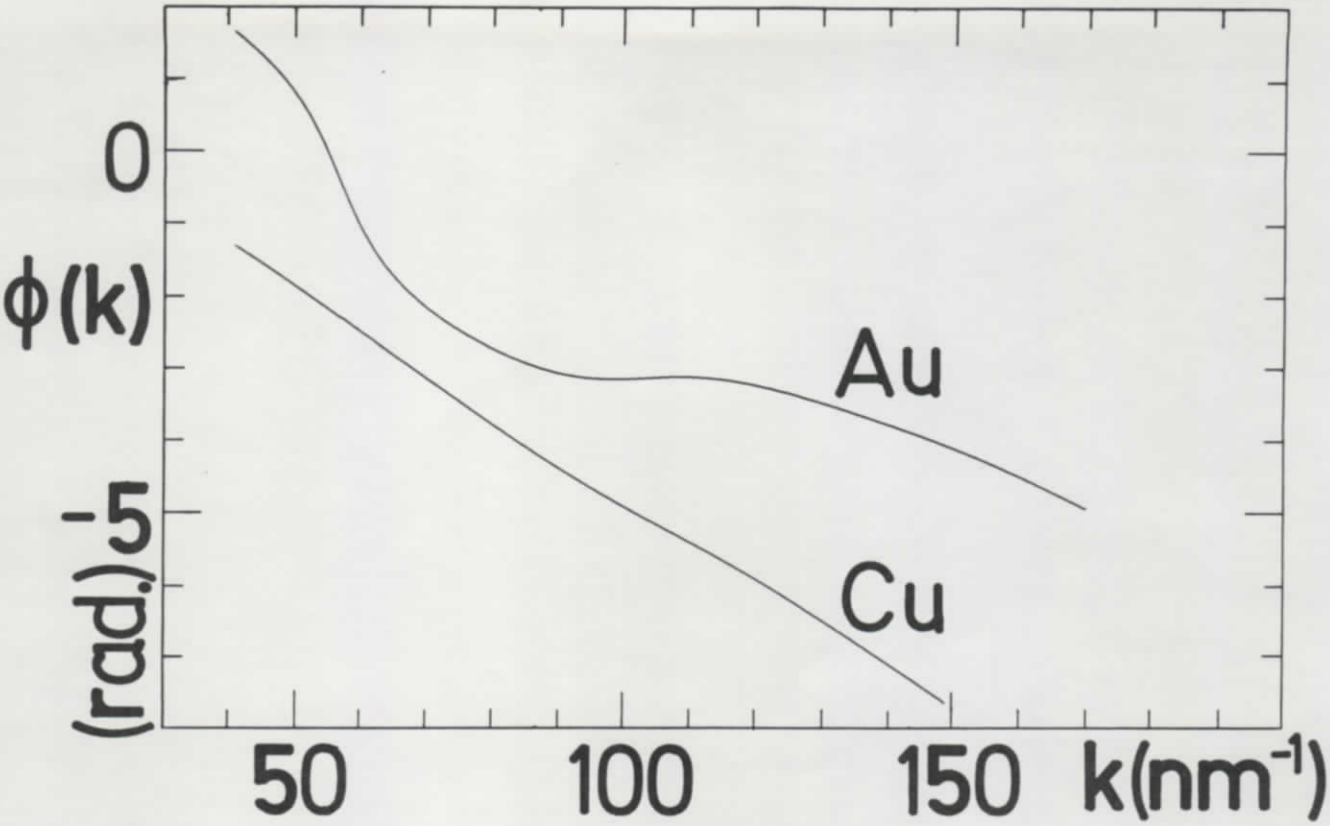

Fig. 5

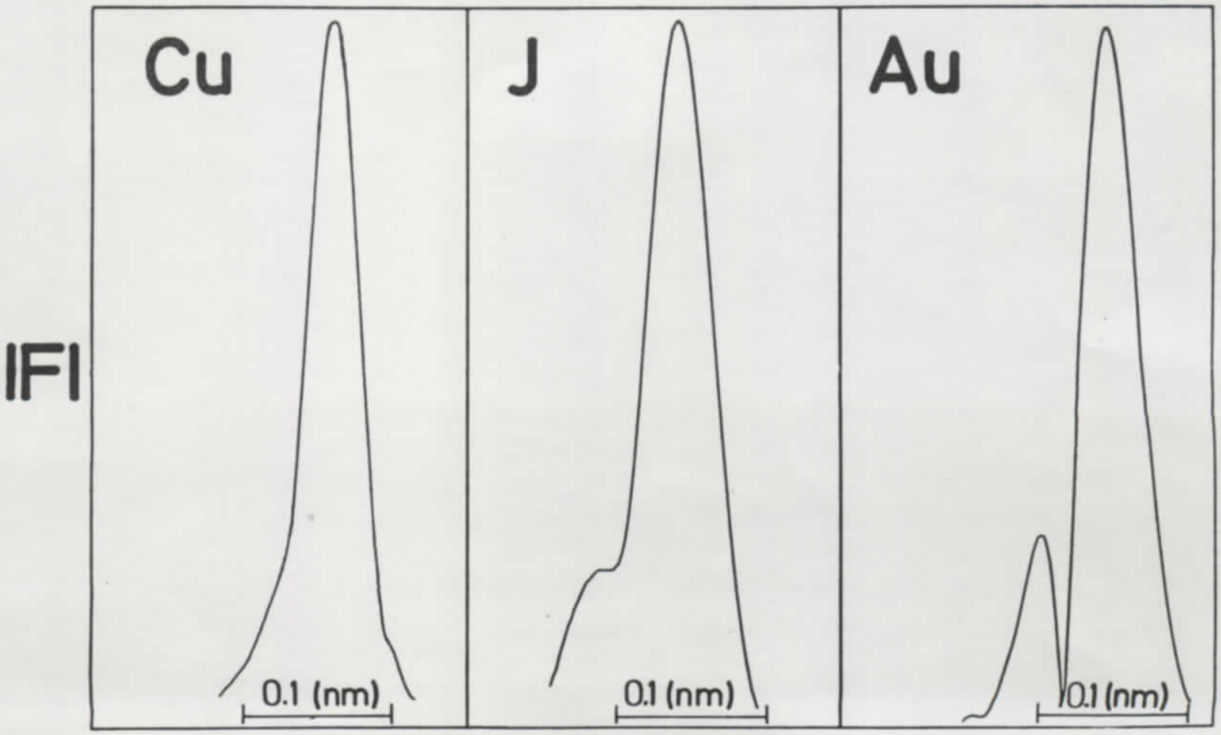

Fig. 6